ELSEVIER

Coordination Chemistry Reviews
178–180 (1998) 13–81

COORDINATION
CHEMISTRY
REVIEWS

Complexes containing bonds between group 3, lanthanide or actinide metals and non-first-row main group elements (excluding halogens)

François Nief

Laboratoire Hétéroéléments et Coordination, CNRS URA 1499, DCPH,
Ecole Polytechnique, 91128 Palaiseau, France

Contents

PII S0010-8545(98)00059-9

Abstract

A comprehensive review of coordination complexes exhibiting bonds between a group 3, lanthanide or actinide metal and a group 14, group 15 or group 16 heteroelement, excluding those of the first row of the periodic table, is presented.

Keywords: Actinide; Group 3; Group 14; Group 15; Group 16; Heteroelement; Lanthanide

Abbreviations

18-C-6-S_2	1,10-Dithia-4,7,13,16-tetraoxacyclooctadecane
18-C-6-S_4	1,4,10,13-Tetrathia-7,16-dioxacyclooctadecane
18-C-6-S_6	1,4,7,10,13,16-Hexathiacyclooctadecane
An	Any actinide element
Ar′	1-(2,6-Dimethyl)phenyl
Ar″	1-(2,6-Di*tertio*butyl-4-methyl)phenyl
Ar*	1-(2,6-Di*tertio*butyl)phenyl
Ar^{iPr}	1-(2,4,6-Tri*iso*propyl)phenyl

Ar^F	1-[2,4,6-Tris(trifiuoromethyl)]phenyl
Bdmp	Benzo-2,3-dimethylphospholyl
bipy	2,2′-Bipyridyl
bhcs	Bis(2-hydroxycyclohexyl)sulphide
BMTE	Bis(methylthio)ethane
bppmt	4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-4-yl-3-thione
Carb	*N*,*N*-di*iso*propyl-2,3-dimethylimidazolylidene
c.n.	Coordination number
COD	Cyclooctadiene
COT	Cyclooctatetraene
Cp	Cyclozpentadienyl
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
CT	Charge transfer
Cy	Cyclohexyl
Dbp	Dibenzophospholyl
DME	1,2-Dimethoxyethane
Dmp	3,4-Dimethylphospholyl
DMF	*N*,*N*-Dimethylformamide
dmpe	1,2-Bis(dimethylphosphino)ethane
DMSO	Dimethylsulphoxyde
Fc	Ferrocenyl
$HBPz_3$	Hydrotris(pyrazolyl)borate
GLC	Gas-liquid chromatography
H_2S_2TPPH	Di-2,2′thiotriphenylphosphine
$H_2S_2TPPSiMe_3$	3,3′-bis(trimethylsilyl)di-2,2′thiotriphenylphosphine
HMPA	Hexamethylphosphoric amide
Ln	Any of the following elements: yttrium, lanthanum or the lanthanides
LMCT	Ligand to metal charge transfer
Melm	*N*-methylimidazole
Mes	1-(2,4,6-Trimethyl)phenyl (mesityl)
Mes*	1-(2,4,6-Tri*tertio*butyl)phenyl
MLCT	Metal to ligand charge transfer
o.s.	Oxidation state
OPyS	2-Thiopyridyl-*N*-oxide
R-PNP	$R_2PCH_2CH_2NCH_2CH_2PR_2$
$R\text{-}P^{Si}N^{Si}P$	$R_2PCH_2SiMe_2NSiMe_2PR_2$
PPP	$Me_2PCH_2CH_2PCH_2CH_2PMe_2$
py	Pyridine
PyS (or SPy)	2-Thiopyridyl
SPNPS	Bis(diphenylthiophosphinyl)amide
SePNPSe	Bis(diphenylselenophosphinyl)amide
SPym	2-Thiopyrimidinyl
HSMePym	4-Methyl-2-thiopyrimidinyl
THF	Tetrahydrofuran

THT	Tetrahydrothiophene
Tmas	2,3,4,5-Tetramethylarsolyl
TMEDA	*N*,*N*′-Tetramethylethylenediamine
Tmp	2,3,4,5-Tetramethylphospholyl
[XR]	Referring to a compound, means “structurally analysed by X-ray diffraction”

1. Introduction, scope and limitation of the review

The coordination chemistry of group 3, lanthanide and actinide metals has begun with the study of complexes containing oxygen, nitrogen and halide ligands. This is still a very active area of research, where the use of increasingly sophisticated nitrogen and oxygen ligands has resulted in the achievement of more and more complex structures, e.g. caged, polymetallic or supramolecular. A particular aspect of this chemistry that deals with intramolecular coordination of group 3 and lanthanide metals has been recently reviewed [1], whereas a general overview on the coordination chemistry of group 3 elements, lanthanides and actinides has been presented in a well-known series [2,3].

The increasing use of inert-atmosphere techniques has led to the development of a rich organometallic chemistry of the group 3, lanthanide and actinide metals. There is no doubt that the increasing use of the X-ray diffraction technique as a powerful (maybe the ultimate) tool for structural analysis has contributed to the growing importance of this area of chemistry. A number of recent reviews on this subject have appeared, together with a chapter in the second edition of another well-known series [4–10].

Complexes of the group 3, lanthanide and actinide metals with other heteroelement-based ligands are comparatively less well known. Most of these heteroelements are soft and the ligands including them are thus well suited to bind with the typically soft middle and late transition metals in a bond that has mostly covalent character, an illustrative example being the ubiquitous transition metal phosphine complexes. The possibility for these soft ligands to bind to the hard group 3, lanthanide and actinide metals was once perceived as difficult, and a reason frequently put forward was that of a hard/soft mismatch. This concept would hold for two reasons: (a) the frontier orbitals on both fragments would not match either in radial extension or in energy, which would have for consequence a weak covalent interaction; and (b) the diffuse and polarizable charge (or partial charge) on the soft ligand would not have a strong electrostatic interaction with the much more localized charge on the hard metal, hence a weak ionic interaction. Experience alone casts some doubts on the usefulness of this concept because of the great upsurge of complexes just corresponding to this definition in the past 10 years.

As stated in the title, the scope of this review is the description of molecular complexes containing bonds between group 3, lanthanide or actinide metals and non-first-row main group elements, with literature coverage up to the date of submission. Halogen-containing lanthanide complexes are extremely common and will be excluded from this study. Concretely, the compounds described hereafter are complexes which display at least one bond between the following metals: scandium, yttrium, lanthanum and the lanthanides (cerium to lutetium) and the actinides (mostly thorium and uranium), and the following heteroelements: silicon, germanium and tin (group 14), phosphorus, arsenic, antimony and bismuth (group 15), and sulphur, selenium and tellurium (group 16); until now, no such complexes containing metal to lead or polonium bonds have been found in our literature survey. There are several examples of complexes containing group 3, lanthanide or actinide metals and group 13 elements. These are in general bridged μ-alkyl, μ-halogenido or μ-hydrido borates, aluminates and gallates with no formal heterobimetallic bond and thus they fall outside the scope of the present review. Although there are a few carborane complexes with direct boron to metal bond, they will not be considered here either, boron being a first-row element.

This review is organized according to type of ligand. Three main sections describe the complexes of, respectively, group 14, group 15 and group 16 based-ligands. These sections are in addition divided according to the nature of the formal charge that may be present on the ligand heteroatom(s): zero, single, multiple or delocalized. A further classification according to type of metal is made between the complexes of scandium, those of yttrium, lanthanum and the lanthanides, and those of actinides, with a distinction between inorganic and organometallic complexes being made whenever suitable. Some earlier reviews have addressed part of the topics analysed in this paper: phosphine complexes of group 3, lanthanide and actinides have been examined in a 1990 review by Fryzuk et al. [11]; actinide dithiocarbamates and dithiocarboxylates have been dealt with in a 1979 survey by Casellato et al. [12]; and structural aspects on some lanthanide-group 14 compounds have been examined by Zakharov and Strutchkov [13] in 1997. In addition, some chelate complexes that are of interest here have been described in the already mentioned 1996 review by Hogerheide et al. [1].

A few general principles can be given on the synthesis of the complexes that are the object of this study.

When there is no charge on the heteroatom, the ligand is a Lewis base; the metal to heteroelement bond is, thus, made by classical ligand exchange or addition in a Lewis acid–base reaction. No further comment is necessary, other than to mention that the Lewis base can be part of a multidentate ligand, so that coordination can be favoured by an entropic effect.

When the heteroatom is singly (negatively) charged (localized or delocalized), several synthetic pathways are possible for neutral complexes of general formula $[(L)_nM(ER_p)_m]$[$L=$any ligand; $M=Sc$, Ln or An; $p=3$ ($E=Si$, Ge or Sn), $p=2$ (E P, As, Sb or Bi), $p=1$ ($E=S$, Se or Te)].

(a) A metathetical pathway, also referred to as the anionic route, where a complex $[(L)_nMX_m]$, in which X is frequently a halide, reacts with a metallic derivative of the heteroelement ligand: $[M'(ER_p)]$, M′ being frequently an alkali metal:

$$[(L)_nMX_m]+m[M'(ER_p)]\rightarrow[(L)_nM(ER_p)_m]+m[M'X].$$

(b) An acid–base pathway in which a basic X ligand (amide, cyclopentadienyl, alkyl etc.) in $[(L)_nMX_m]$ is protonated by a HER_p derivative:

$$[(L)_nMX_m] + m[HER_p] \rightarrow [(L)_nM(ER_p)_m] + m[HX].$$

when the HER_p derivative is not specially acidic (e.g. E = Si and X = alkyl), then this last scheme is best called a σ-bond metathesis reaction.

(c) Oxidative pathways, in which a $[(L)_nM]$ precursor or even the zerovalent metal powder M (if necessary activated) is oxidized by a $R_pE\text{-}ER_p$ precursor:

$$[(L)_nM] + \frac{m}{2}[R_pEER_p] \rightarrow [(L)_nM(ER_p)_m].$$

$$M + nL + \frac{m}{2}[R_pEER_p] \rightarrow [(L)_nM(ER_p)_m].$$

Anionic ate-complexes of general formula $[\{(L)_nM(ER_p)_m\}^-(M')^+]$ can be also be made by analogous reactions. A few synthetic routes other than (a), (b) or (c) were also encountered.

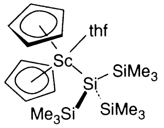
When the ligand is multiply charged, the synthetic pathways are more difficult to generalize, owing to the great variety of complexes that can be obtained. A table of metal–heteroelement bonds has been added, that supplements the one present in Ref. [11].

2. Silicon, germanium, and tin based ligands

So far, only silyl, germyl and stannyl group 3 metal type complexes, where the heteroatom is bearing a formal negative charge, have been observed, although there is a single example of a tetragermylene complex of Yb, that will be detailed in Section 2.2.1.

2.1. Scandium complexes

Silyl and germylscandocene complexes were prepared by reaction of $[(Cp_2ScCl)_2]$ with bulky $LiER_3$ in THF [14–16]. The following compounds were isolated: $[Cp_2Sc(ER_3)(thf)]$ [$ER_3 = Si(SiMe_3)_3$ [XR], $Si(SiMe_3)_2Ph$, Si^tBuPh_2, $SiPh_3$, $Ge(SiMe_3)_3$].



These compounds are extremely reactive towards a great variety of small molecules: they are active ethylene polymerization catalysts, and their reaction with phenylacetylene gave $[\{Cp_2Sc(\mu{:}\eta^1\text{-}C{\equiv}CPh)\}_2]$ [16]. The reaction of

$[Cp_2Sc\{Si(SiMe_3)_3\}(thf)]$ with CO_2 gave a silacarboxylate dimer: $[(Cp_2Sc[\mu\text{-}O_2CSi(SiMe_3)_3]\}_2]$ [15]. Up to four molecules of CO can react with 1 mol of $[(thf)Cp_2Sc(ER_3)]$, yielding a discandium enedionediolate as end product: $[Cp_2Sc\{R_3E(CO)\text{-}C(O)=C(O)\text{-}(CO)ER_3\}ScCp_2]$ via dimerization of a scandoxyketene $[Cp_2Sc\{O\text{-}C(ER_3)=C=O\}]$ (that can be trapped as a THF adduct), itself the product of CO insertion into the Sc–C bond of the postulated silaacyl complex $[Cp_2Sc(\eta^2\text{-}OCER_3)]$, the primary product of reaction of CO with $[Cp_2Sc(ER_3)]$ [16]. Likewise, xylylisonitrile inserts into the Si–Sc bond of $[Cp_2Sc\{Si(SiMe_3)_3\}(thf)]$ to give an isolable silaiminoacyl compound: $[Cp_2Sc\{\eta^2\text{-}N(xylyl)CSi(SiMe_3)_3\}]$ [14,16].

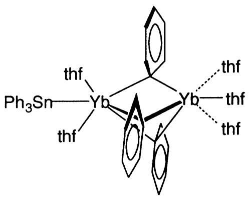
2.2. *Yttrium, lanthanum and the lanthanides*

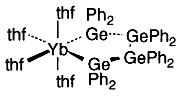
A short review of structural data on lanthanide group-14 complexes has very recently appeared [13].

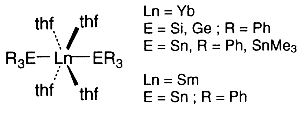
2.2.1. *Inorganic complexes*

After an early report on ill-characterized $[Bu_3SnYbI]$, obtained by insertion of Yb in the Sn–I bond of Bu_3SnI [17], several well-characterized Ln(II) (mostly Yb(II)) silyl, germyl and stannyl derivatives have been prepared. Reaction of Ph_3ECl with Yb metal in THF gave a 1:1 mixture of $[(thf)_4Yb(Ph_3E)_2]$ ([XR]: E = Si, Ge [18], Sn [19]), and $[(thf)_2YbCl_2]$ presumably via disproportionation of the initially formed $[Ph_3EYbCl]$. $[(thf)_4Yb(Ph_3Sn)_2]$ could be isolated by reaction of Yb with $Ph_3SnSnPh_3$, but also, unexpectedly, with $PhSnCl_3$ [20]. Activated ytterbium in the form of naphthaleneytterbium $[(thf)_2Yb(C_{10}H_8)]$ reacts with Ph_4Sn to give a 1:1 mixture of $[(thf)_4Yb(Ph_3Sn)_2]$ and of a new compound $[(thf)_2(Ph_3Sn)Yb(\mu\text{-}Ph)_3Yb(thf)_3]$ [XR]. Presumably the primary insertion product: $[(Ph_3Sn)Yb(Ph)]$ disproportionates into $[(thf)_4Yb(Ph_3Sn)_2]$ and $[Ph_2Yb]$, which then combines with remaining $[(Ph_3Sn)Yb(Ph)]$ to give the tris(μ-phenyl) complex [21]

Reaction of Yb with less bulky methyltin halides such as $MeSnCl_3$, Me_2SnCl_2 or Me_3SnCl gave a polynuclear Sn–Yb complex: $[(thf)_4Yb\{Sn(SnMe_3)_3\}]$ [XR], whereas reaction of Sm with Me_3SnCl afforded the analogous $[(thf)_4Sm\{Sn(SnMe_3)_3\}]$ [XR] [22].







Reaction of Yb with Ph_2GeCl_2 yielded the tetragermylene complex: $[(thf)_4\{\eta^2\text{-}GePh_2(Ph_2Ge)_2Ph_2Ge\}Yb]$ [XR]. Presumably an oligogermylene: $[(Ph_2Ge)_n]$ was formed first, followed by insertion of Yb into a Ge–Ge bond [23]. In contrast, reaction of Yb with Ph_2SnCl_2 in DME (rather than THF) gave an ionic product in which no Yb–Sn bonds are present: $[\{(Ph_3Sn)_3Sn\}_2\{(dme)_6Yb(\mu\text{-}Cl)_2]$[20].

The metathetical reaction of $[KSn(CH_2C^tBu_3)_3]$ with YbI_2 gave $[(thf)_2Yb\{Sn(CH_2C^tBu_3)_3\}_2]$ [XR]. ^{171}Yb and ^{119}Sn NMR demonstrate that its structure is similar in solution. A 1:1 mixture of $[(thf)_2Yb\{Sn(CH_2C^tBu_3)_3\}_2]$ and Ar″OH (Ar″ = $2,6\text{-}(^tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2$) yielded the mixed complex $[(thf)_xYb\{Sn(CH_2C^tBu_3)\}(OAr'')]$; although this compound was not isolated, a piece of structural evidence is provided by the absence of ^{117}Sn satellites in its ^{119}Sn NMR spectrum [24].

Unsolvated germylsamarium (II) or germylytterbium (II) were obtained when the germyl organic substituent has a pendant Lewis base (amino group) that can chelate the lanthanide element. Thus, the reaction of $[K(Ge[C_6H_4(2\text{-}CH_2NMe_2)]_3\}]$ with LnI_2 gave $[Ln\{Ge[C_6H_4(2\text{-}CH_2NMe_2)]_3\}_2]$ (Ln = Sm, Yb). NMR shows that both compounds are fluxional at room temperature (fast exchange of all pendant amino arms occur), whereas at low temperatures, this exchange is frozen. No pure product was isolated from $[K\{Ge[C_6H_3(2\text{-}OMe)(5\text{-}Me)]_3\}]$ and LnI_2 because of competing metalation of the Et_2O solvent. An original *o*-phenylenedigermane byproduct was obtained in this latter reaction [25].

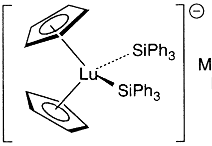
Three Er···Si···H agostic interactions are present in the homoleptic $[Er(^tBuN\text{-}SiMe_2H)_3]$, obtained by reaction of $ErCl_3$ with $[Li(^tBuNSiMe_2H)]$[26].

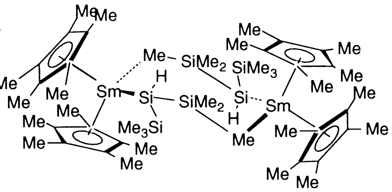
2.2.2. *Organometallic complexes*

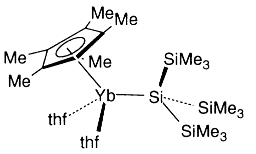
Most comppounds in this class are silyl, germyl or stannyl dicyclopentadienyllanthanide (III) neutral or anionic ate-complexes. A couple of Yb(II) complexes have been also recently prepared.

Neutral $[Cp_2Ln(EPh_3)]$ (Ln = Er, E = Ge, Sn; Ln = Yb, E = Sn) were obtained by reaction of $[Cp_2LnCl]$ with $Li(EPh_3)$. The THF adduct $[Cp_2Yb(SnPh_3)(thf)_2]$ is monomeric in benzene solution [27].

The substituted cyclopentadienyl derivatives: $[(\eta^5\text{-}L)_2LnSi(H)(SiMe_3)_2]$ (L = Cp*, Ln = Y, Nd, Sm; L = C_5Me_4Et, Ln = Sm, Nd) could be prepared by a σ-bond metathesis reaction of $[(\eta^5\text{-}L)_2LnCH(SiMe_3)_2]$ with an excess of neat $H_2Si(SiMe_3)_2$ (in order to overcome competitive decomposition of the alkyllanthanide starting material). Although the Sm complex: $[\{Cp^*_2SmSi(H)(SiMe_3)[SiMe_2(\mu\text{-}Me)]\}_2]$ [XR] is dimeric in the solid state, it is monomeric in pentane solution. The Sm and Nd compounds are active olefin polymerization catalysts; their reaction with hydrosilanes gave hydrides $[(Cp^*_2LnH)_2]$ [28–30].







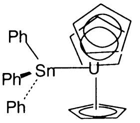
The reaction of $[Cp_2LnCl_2Na(dme)_x]$ with $LiSiMe_3$ yielded the anionic ate-complexes: [{(dme)$_3$Li}{Cp$_2$Ln(SiMe$_3$)$_2$}] (Ln = Sm, Dy, Ho, Er, Tm, Lu). The outcome of this reaction was not the same with LiGeMe$_3$: reaction of this germyllithium with [Cp$_2$SmCl$_2$Na(dme)] in 1:2 ratio gave [{Cp$_2$Sm}$_2$(μ-Cl)] and Ge$_2$Me$_6$ in a redox/redistribution reaction, whereas with the same starting materials, but in a 4:1 ratio, redistribution of Cp occurred and [(Li(dme)$_3$]{[Cp$_3$Sm]$_2$(μ-GeMe$_3$)}] was isolated [31].

The X-ray data in Ref. [32] that had been mistakenly attributed to [(dme)$_3$Li} {Cp$_2$Sm(SiMe$_3$)$_2$}] were, in fact, measured on the Lu compound. The structure of [{(dme)$_3$Li}{(Cp$_2$Lu(SiMe$_3$)$_2$}] has been subsequently corrected [33].

Displacement of a Cp* ligand of [Cp$_2^*$Yb(Et$_2$O)] by LiSi(SiMe$_3$)$_3$ resulted in the obtention of the unique monomeric Cp*Yb(II) species [Cp*Yb (Si(SiMe$_3$)$_3$}(thf)$_2$] [XR]. ^{29}Si and ^{171}Yb NMR confirm the structure in solution [34]. Finally, [Cp*Yb{SnCH$_2{}^t$Bu$_3$)$_3$}(thf)$_2$] has been detected by NMR in the reaction of [(thf)$_2$Yb{Sn(CH$_2$C^{t}Bu)$_3$}$_2$] with Cp*H [24].

2.3. Actinide complexes

Reaction of [Cp$_3$UCl] with Li(EPh$_3$) afforded the silyl and germyluranium derivatives: [Cp$_3$U(EPh$_3$)] (E = Si [35], Ge [36]), whereas [Cp$_3$U(SnPh$_3$)] [XR] was best made from [Cp$_3$U(NEt$_2$)] and HSnPh$_3$. This stannyl compound is also accessible via a transmetalation reaction of [Cp$_3$U(SiPh$_3$)] or [Cp$_3$U(GePh$_3$)] with HSnPh$_3$ [37]. The silyl compound is very reactive: [Cp$_3$U(OSiPh$_3$)] is a frequent by-product. Insertion of xylylisonitrile into the U–Si or U–Ge bonds afforded the η^2-xylyliminoacyl complexes: [Cp$_3$U{μ^2-N(xylyl)C(EPh$_3$)}] (E = Si, Ge) [35,36].



Reaction of [Cp$_2^*$ThCl$_2$] with bulky [LiSi(SiMe$_3$)$_3$] gave unstable [Cp$_2^*$Th (Cl){Si(SiMe$_3$)$_3$}] that could be trapped by reaction with 2 mol of CO, thus yielding an isolable silylthoroxyketene compound: [Cp$_2^*$Th(Cl){O-C[Si(SiMe$_3$)$_3$] = C = O}]. The analogous [Cp$_2^*$Th(Cl)(Si^{t}BuPh$_2$)] could be isolated and its reaction with CO gave a similar silylthoroxyketene compound and in this case the transient η^2-acyl complex: [Cp$_2^*$Th(Cl){μ^2 − OC(Si^{t}Bu*Ph*2)}] could be detected [38].

3. Phosphorus, arsenic, antimony and bismuth-based ligands

Four classes of complexes have been catalogued according to the formal charge bome by the group-15 elements in the ligand: the organophosphines and arsines (R$_3$E), containing with no formal charge at the heteroatom; the organophosphides and arsenides (R$_2$E$^-$), bearing a negative charge at the heteroatom; the phosphinidene (RP^{2-}) and polyphosphide (P$_n$)$^{x-}$, with a negative charge greater than one;

and the heterocyclic phospholyl and arsolyl ligands ($R_4C_4E^-$) with a delocalized charge, together with other ligands of related structure.

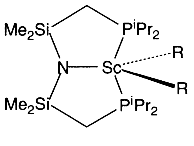
3.1. Phosphines and arsines

Complexes of neutral mono- or polyphosphines, but not of arsines or heavier analogs, have been isolated, although one experiment established that bonding of Eu to $AsPh_3$ or $SbPh_3$ was possible. Also, several complexes of multidentate phosphines and arsines where one atom in the side chain is negatively charged (carbanion, amide or alkoxide) have been made. Part of this topic has been recently reviewed by Fryzuk [11] so only summaries of the early results will be given whenever appropriate.

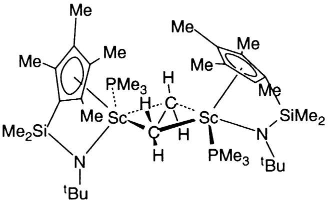
3.1.1. Scandium complexes

Trimethylphosphine is useful in scandium chemistry to stabilize low-coordinate cyclopentadienyl complexes by blocking a coordination site: treatment of [Cp*(L)ScCl] (L = Cp, $C_5Me_3H_2$) with MeLi yielded [Cp*(L)Sc(Me)(PMe_3)], in the presence of PMe_3, and intractable material only in its absence. Upon hydrogenolysis of the alkyl complexes, the more bulky [Cp*($C_5Me_3H_2$)Sc(H)(PMe_3)] was obtained whereas [Cp*(Cp)Sc(H)(PMe_3)] is unstable and the product of metalation at Cp: [Cp*(Cp)Sc(μ:η^5,η^1-C_5H_4)(μ-H)ScCp*] was isolated [39].

Although the mixed Cp/amide complex [{[(η^5-C_5Me_4)$SiMe_2$(η^1-N^{t}Bu)] Sc(μ-H)(PMe_3)}$_2$] [XR] [40] is already coordinatively unsaturated, it has been shown that phosphine-free 12-electron species such as [{(η^5-C_5Me_4)$SiMe_2$(η^1-N^{t}Bu)}Sc(R)] were the actual catalytically active species in the polymerization of α-olefins. An ethylene-bridged intermediate: [{[(η^5-C_5Me_4)$SiMe_2$(η^1-N^{t}Bu)] Sc(PMe_3)}$_2$(μ:η^2,η^2-C_2H_4)] [XR] has been isolated [41].



R = Et, CH(SiMe3)2



Treatment of $ScCl_3(thf)_3$ with the lithium salt of the diphosphinoamide: [Li{N($SiMe_2CH_2P^iPr_2$)$_2$}] (Li[^{i}Pr-P^{Si}N^{Si}P]) afforded [(^{i}Pr-P^{Si}N^{Si}P)ScC]$_2$(thf)] [XR], of which the solid-state structure is likely to be retained in solution (by NMR). [(^{i}Pr-P^{Si}N^{Si}P)ScR_2] (R = Me, Et [XR], CH_2SiMe_3 [XR]) can be obtained by reaction of the dichloride with the appropriate organolithium reagent. No agostic infractions were observed in the solid state despite the high degree of coordinative unsaturation. The Sc alkyl complexes are highly reactive towards small molecules (H_2, CO, CO_2) but complicated mixtures were obtained in which no definite scandium complex could be identified. A semiempirical MO study of the dimethyl complex suggests that the frontier orbitals, in the absence of phosphine dissociation, do not have the right symmetry for reaction, e.g. with CO [42].

Reaction of $Sc(OSO_2CF_3)_3$ with a diphosphinomethanide $[Li\{Me_2PC(SiMe_3)PMe_2\}]$ gave a homoleptic scandium complex: $[Sc\{Me_2PC(SiMe_3)PMe_2\}_3]$ [XR] in which the bonding pattern of the ligand is intermediate between η^2 and η^3 (Sc–C distance = 291 pm). A possible explanation is that the negatively charged C atom is attracted by the metal cation, but the small coordination number of Sc(III) and the size of the silyl group prevents it from coming too close to the metal; also, the nucleophilicity of the carbanion should be reduced by the adjacent silyl group. The similar $[Sc\{Me_2PC(PMe_2)PMe_2\}_3]$ has also been isolated [43,44].

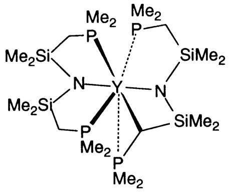
3.1.2. Yttrium, lanthanum and lanthanide complexes

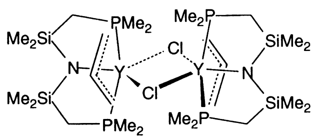
Early reports on phosphine adducts of inorganic and organometallic Ln(II) and Ln(III) complexes have been reviewed by Fryzuk [11]; see also Refs [45,46]. One striking feature is the easy replacement of the THF in $[(MeCp)_3Ce(thf)]$ by PMe_3 or $P(OCH_2)_3CEt$ to give $[(MeCp)_3Ce(PR_3)1$ [47,48], in opposition to what is expected from crude hard/soft considerations; complexometric measurements on 1:1 adducts of $[Cp_3Yb]$ with Lewis bases in benzene solution showed that PEt_3 was approximately as good a ligand as pyrrolidine and better than THF [49]. In contrast, whereas the sterically more demanding Ph_3P forms an adduct with $[Cp^*_2Sm]$, it cannot displace THF in $[Cp^*_2Sm(thf)_2]$; no Ph_3As adduct was observed with either $[Cp^*_2Sm]$ or $[Cp^*_2Sm(thf)_2]$ (E–C bond cleavage occurs with Ph_3Sb and Ph_3Bi, see later) [50]. The more labile Et_2O ligand in $[Yb\{CH(SiMe_3)_2\}_2(Et_2O)_2]$ is displaced by the chelating diphosphine dmpe to yield $[Yb\{CH(SiMe_3)_2\}_2(dmpe)]$, in which the dmpe ligand partially dissociates in toluene solution, however. This compound was isolated and characterized by multinuclear NMR (^{13}P, ^{13}C, ^{17}Yb) [51].

Although no arsine or stibine complexes with group 3 elements have been isolated, evidence for complex formation between Eu^{3+} and Ph_3E (E = As, Sb) in benzonitrile solution has been established by tracer experiments [52]. All other compounds described are di- or tridentate phosphine complexes with additional amido, alkoxy or carbanion functionality.

The results on the reaction of alkali metal salts of a tridentate amidodiphosphine $[M\{N(SiMe_2CH_2PR_2)_2\}]$ ($M[R\text{-}P^{Si}N^{Si}P]$) with $LnCl_3$ in THF that were reported in Fryzuk's review have now been published and completed [53–55]. The following complexes were prepared: $[(R\text{-}P^{Si}N^{Si}P)_2LnCl]$ (Ln = Y, R = Me, Ph, ^iPr; Ln = La, R = Me; Ln = Lu, R = Me, Ph); the monosubstituted $[(Me\text{-}P^{Si}N^{Si}P)YCl_2]$ could also be obtained with a 1:1 $K(Me\text{-}P^{Si}N^{Si}P):YCl_3$ ratio [55]. Reaction of the bis($Me\text{-}P^{Si}N^{Si}P$) chloro complexes with organolithiums gave $[(Me\text{-}P^{Si}N^{Si}P)_2LnR]$ (R = Ph, CH_2Ph, Ln = Y, Lu) that are unstable and decomposed by heating into a product of cyclometalation: $[(Me\text{-}P^{Si}N^{Si}P)Ln\{\eta^4\text{-}Me_2PCH_2(SiMe_2)N(SiMe_2)CHPMe_2\}]$ [XR] [54,11]; when $[(Me\text{-}P^{Si}N^{Si}P)_2LaCl]$ was reacted with PhLi, the intermediate La-Ph was not observed and the cyclometalated complex was isolated directly. These cyclometalated products reacted with dideuterium gas with incorporation of D atoms at the methylene and silylmethyl protons (not on the methyls on phosphorus), but did not react with hydrocarbons [54]. Although no

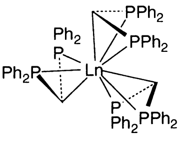
X-ray structure of the $[(\text{R-P}^{\text{Si}}\text{N}^{\text{Si}}\text{P})_2\text{Ln}(\text{X})]$ compounds has been reported, their pentagonal bipyramidal structure has been conclusively established by ^{31}P NMR. $[(\text{Me-P}^{\text{Si}}\text{N}^{\text{Si}}\text{P})_2\text{YCl}]$ reacted with allylmagnesium chloride or diallylmagnesium with elimination of one Me-$\text{P}^{\text{Si}}\text{N}^{\text{Si}}$P ligand (and not of the Cl atom) and formation of $[\{(\eta^3\text{-allyl})(\text{Me-P}^{\text{Si}}\text{N}^{\text{Si}}\text{P})\text{Y}(\mu\text{-Cl})\}_2]$, [XR] whereas elimination of $MgCl_2$ occurred in the reaction of $[(\text{Me-P}^{\text{Si}}\text{N}^{\text{Si}}\text{P})\text{YCl}_2]$ with diallylmagnesium where $[(\eta^3\text{-allyl})_2(\text{Me-P}^{\text{Si}}\text{N}^{\text{Si}}\text{P})\text{Y}]$ was obtained. This latter compound is an olefin polymerization catalyst [55].



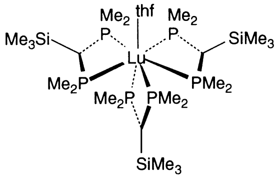


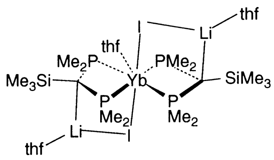
The homoleptic phosphinoalkoxide complexes: $[\text{Ln}(\text{OC}^t\text{Bu}_2\text{CH}_2\text{PMe}_2)_3]$ (Ln = Y, Nd) [56] have been reviewed in Ref. [11].

The diphosphinomethanide ligands $[\text{R}_2\text{PC}(\text{R}')\text{PR}_2]^-$ can be either η^2-coordinated to a metal by the two phosphorus atoms, or η^3 (π-allyl-like) with additional bonding of the central carbon atom. When the carbon atom is unsubstituted, incoordination is generally preferred: reaction of $LnCl_3$ with $[\text{Ph}_2\text{PCHPPh}_2]^-$ afforded the homoleptic $\{\text{Ln}(\eta^3\text{-Ph}_2\text{PCHPPh}_2)_3]$ ([XR]:Ln = La [57], Sm [58]), whereas with $[\text{Me}_2\text{PCHPMe}_2]$, a dimeric species: $[\{\text{Sm}(\eta^3\text{-Me}_2\text{PCHPMe}_2)_2(\mu{:}\eta^2,\eta^1\text{-Me}_2\text{PCHPMe}_2)\}_2]$ ([XR]: [59]) was obtained, presumably because the monomeric $[\text{Sm}(\eta^3\text{-Me}_2\text{PCHPMe}_2)_3]$ would be too coordinatively unsaturated.



Ln = La, Sm

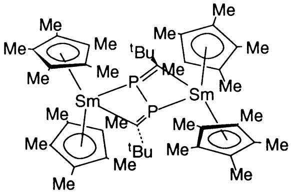




With the silyl-substituted diphosphinomethanide $[\text{Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2]^-$, only η^2-coordination has been observed so far. Reaction of this anion with $\text{Ln}(\text{OSO}_2\text{CF}_3)_3$ gave the unsolvated ate-complexes $[\text{Ln}\{\eta^2\text{-Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2\}_2\{\mu{:}\eta^2\text{-Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2\}_2\text{Li}]$, (Ln-Y, La [XR], Er), whereas with the smallest lanthanide (Lu) a neutral THF solvate $[(\text{thf})\text{Lu}\{\eta^2\text{-Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2\}_3]$ [XR] was isolated [43]. Reaction of this compound with MeLi gave $[(\text{thf})\text{Lu}(\text{Me})\{\eta^2\text{-Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2\}_2]$ but accidental contamination of the reaction mixture (presumably by silicone grease) led to the isolation of $[\{(\text{thf})_4\text{LiI}\{\text{Lu}(\text{OSiMe}_3)[\eta 2\text{-Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2]_3\}]$ [XR] [44]. The iodides on the divalent $\text{LnI}_2(\text{thf})_2$ were not substituted by the $[\text{Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2]$ anion and simple adducts such as $[(\text{thf})\text{Ln}(\mu\text{-I})_2[\mu{:}\eta^2,\eta^1\text{-Me}_2\text{PC}(\text{SiMe}_3)\text{PMe}_2]_2\{\text{Li}(\text{thf})\}_2]$

(Ln = Yb [XR], Sm) were isolated; [(thf)Yb(μ-I)$_2$[μ:η^2,η^1-Me$_2$PC(PMe$_2$)PMe$_2$]$_2${Li(thf)$_2$}] was similarly obtained. Increased steric crowding and reduced electron density at the central carbon atom in [Me$_2$PC(SiMe$_3$)PMe$_2$] may be responsible for η^2-coordination with this ligand rather than η^3-coordination as observed with [R$_2$PCHPR$_2$] [43].

Reductive dimerization of the phosphaalkyne ^{t}BuC≡P occurred with [Cp$^*_2$Sm(thf)$_2$] and a 2,3-diphosphabutadiene-1,4-diyl Sm(III) complex: [{Cp$^*_2$Sm(μ:η^2,η^2-E,E-^{t}BuC=P-P=C^{t}Bu)}$_2$] [XR] was isolated [60].



The metathetical reaction of [Cp$_2$Lu(Cl)(thf)] with LiCH$_2$PMe$_2$ afforded [Cp$_2$Lu(CH$_2$PMe$_2$)], in which the doublet structure of the ^{1}H NMR signal of the Cp ligands was attributed to Lu–P bonding [61]. Likewise, the arsine complexes [CpLu{(CH$_2$)$_3$AsR$_2$}$_2$] (R = ^{t}Bu, Me) were obtained when [CpLu(OSO$_2$CF$_3$)$_2$] was reacted with ClMg(CH$_2$)$_2$AsR$_2$ [62]. These complexes were further characterized by microanalysts and mass spectroscopy (for the As compounds).

3.1.3. Actinide complexes

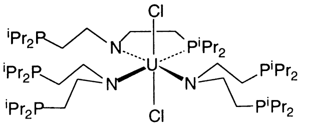
The reports on actinide phosphine complexes that were already reviewed in Ref. [11] are briefly summarized here. Many DMPE-chelated compounds of U(IV) and Th(IV) have been prepared. Inorganic compounds include complexes such as [(dmpe)$_2$AnX$_4$] (An = Th, U; X = Halogen, Me or OPh) or [(dmpe)An(R)(CH$_2$Ph)$_3$] (An = Th, U; R = Me, CH$_2$Ph); in these latter coordinatively unsaturated complexes, a close contact between the *ipso* carbon of the benzyl group and the metal is present [63,64]. U(IV) borohydrides such as [U(BH$_4$)$_4$(dmpe)$_2$] and [U(BH$_3$CH$_3$)$_4$(dmpe)$_x$] (x = 1, 2) as well as the analogous U(III) compounds: [U(BH$_4$)$_3$(dmpe)$_2$] and [U(BH$_3$CH$_3$)$_3$(dmpe)$_2$] have been isolated [65,66]. Organometallic complexes such as the Th(IV) compound [Cp$_2$Th(dmpe)(X)$_2$] (X = Cl, Me, CH$_2$Ph) [67,68] and the U(III) chloride [Cp$^*_2$UCl(PMe$_3$)x] [69,70] and hydride [Cp$^*_2$U(dmpe)(H)] [71] have also been made. A chelating phosphinopyridine has been used in [U(BH$_4$)$_3$(o-Ph$_2$PC$_5$H$_4$N)$_2$] [72].

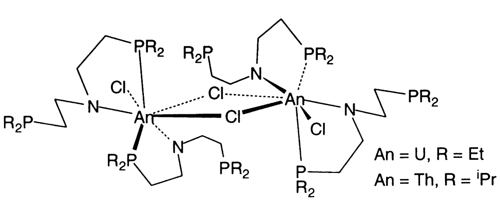
Monodentate complexes are much less common and have been so far limited to the Tris(Cp) or tris(MeCp) U(III) series: [(MeCp)$_3$U(PMe$_3$)] [73] and [(Cp$_3$U)$_2$(μ-dmpe)] [74], in which the dmpe ligand is now bridging, have thus been prepared. An interesting comparison has been made between the crystal structures of [(MeCp)$_3$M{P(OCH$_2$)$_3$CEt}] (M = U, Ce), on the one hand; and those of [(MeCp)$_3$M(quinuclidine)] (M = U, Ce), on the other. While the U–N and Ce–N bonds have similar lengths, which is expected from the ionic bond model since Ce(III) and U(III) are similar in size, the U–P bond is quite significantly shorter than the Ce–P bond, which is the best evidence so far for U–P π-backbonding in the case of uranium [48].

The lability of the phosphine ligand in [Cp^*_2U(dmpe)(H)] has been exploited recently: its reaction with 2,3,4,5-tetramethylfulvene gave the remarkable [Cp^*_3U] [75].

The adduct: [{η^5-C_5H_3($SiMe_2{}^t$Bu)$_2$-1,3}$_2$$ThCl_2$(dmpe)] was formed by reaction of DMPE with [{η^5-C_5H_3($SiMe_2{}^t$Bu)$_2$-1,3}$_2$$ThCl_2$] [76].

Chelating amidodiphosphines have also been used in actinide chemistry. Reaction of [Li{N($CH_2CH_2PR_2$)$_2$}] (Li[R-PNP], R = Et, ^{i}Pr) with $AnCl_4$ (An = Th, U) in THF yielded the following An(IV) compounds, depending on the stoichiometry: [{[η^2-(RPNP)]$_2$AnCl(μ-Cl)}$_2$] ([XR]: An = Th, R = ^{i}Pr; An = U, R = Et) or [(^{i}Pr-PNP)$ThCl_3$] [77]. The U(IV) compounds are oxygen-sensitive: reaction of [Li(R-PNP)] with UCl_4 in the presence of O_2 gave the rare U(V) complex [{η^2-(^{i}Pr-PNP)} {η^1-(^{i}Pr-PNP)}$_2$$UCl_2$] [XR]. All compounds are fluxional in solution. The NMR spectra of [(R-PNP)$_2$$ThCl_2$] are compatible with two isomeric μ-chloro dimers in equilibrium. One can note that THF does not compete with PR_3 for coordination with the actinide, even for the highly electrophilic U(V) complex [78].



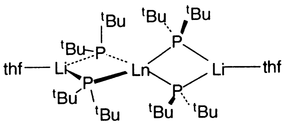


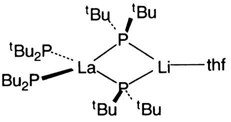
3.2. Phosphides and arsenides

3.2.1. Yttrium, lanthanum and the lanthanides

3.2.1.1. Inorganic complexes. Inorganic complexes of divalent and trivalent lanthanides with organophosphides and arsenides have been prepared. The substituents at phosphorus are usually bulky aliphatic, aromatic, or chelating. Most compounds have been described very recently.

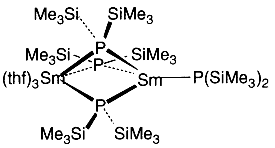
The outcome of the reaction of ^{t}Bu$_2$PLi with lanthanide halides or triflates depends on the size of the metal: with the biggest (La), an ate-complex: [(thf)$_2$Li (μ^tBu$_2$P)$_2$La(^{t}Bu$_2$P)$_2$] [XR] is obtained; ^{31}P NMR at low temperature suggests a structure in solution similar to that found in the solid state [79]. With the smaller Ho, Er, Tm, Yb, Lu and Y, neutral [(thf)$_x$Ln(^{t}Bu$_2$P)$_3$] ($x = 0$ or 2) were isolated. The Y complex gave ^{t}Bu$_2$PH after hydrolysis while the ^{31}P resonance of the Lu compound is broadened by quadrupolar relaxation by ^{175}Lu; these facts were taken as evidence for Ln–P bonding. The complexes were also characterized by elemental analysis [80]. When the same reaction was performed with the trivalent triflates of Sm, Eu and Yb, reduction occurred and the homoleptic Ln(II) ate-complexes [{(thf)Li(μ-^{t}Bu$_2$P)$_2$}$_2$Ln] were obtained; γ-agostic interactions are present in the three isomorphous solid state X-ray structures (Ln = Sm [81], Eu [82] and Yb [79]). ^{151}Eu Mössbauer spectroscopy confirms the divalent state of the metal in the Eu complex [82].


Ln = Eu, Yb, Sm

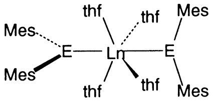


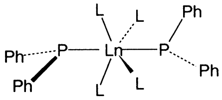
The reaction of $LnCl_3$ with $Li^{t}Bu_2As$ yielded $[(thf)_3Ln(^{t}Bu_2As)_3]$ (Ln = Y, La, Pr, Ho, Er, Tm, Lu) that were characterized by elemental analysis and NMR for the diamagnetic Y, La and Lu compounds. The corresponding TMEDA complexes were obtained by displacement of THF [83].

In the reaction of $[(SiMe_3)_2PK]$ with TmI_3 or NdI_3, precipitation of KI occurred and the neutral $[(thf)_2Ln\{(SiMe_3)_2P\}_3]$ were obtained ([XR]: Ln = Nd [84], Tm [85]) These complexes are distorted trigonal bipyramidal with the phosphides in the equatorial plane. Reaction of $[(SiMe_3)_2PK]$ with a divalent derivative such as SmI_2 yielded a dimeric Sm (II) complex: $[(thf)_3Sm\{\mu\text{-}SiMe_3)_2P\}_3Sm\{(SiMe_3)_2P\}]$ [XR]. NMR suggests that the structure in solution, yet unknown, is different from that obtained in the solid state [86].



THF- and *N*-methylimidazole (MeIm) solvated diphenylphosphides of divalent Yb and Sm: $[(MeIm)_4Ln(Ph_2P)_2]$ ([XR]: Ln = Sm [87], Yb [88]) and $[(thf)_4Ln(Ph_2P)_2]$ (Ln = Sm, Yb [XR] [87]) have been prepared by three different routes: (a) the metathesis of LnI_2 with $KPPh_2$; (b) a metathesis reaction of LnI_3 with $KPPh_2$ followed by a reduction step and formation of $Ph_2P\text{-}PPh_2$; (c) the acid–base reaction of $Ln\{N(SiMe_3)_2\}$ with Ph_2PH. ^{171}Yb satellites with a doublet structure are present in the ^{31}P NMR spectrum of $[(thf)_4Yb(Ph_2P)_2]$ in d-8 THF, which is evidence for a monomeric structure in solution.

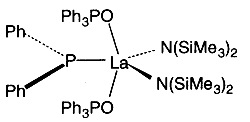

Ln = Yb, E = P
Ln = Sm, E = P, As

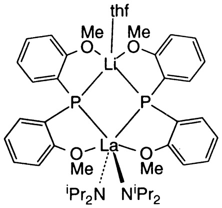

Ln = Yb, L = thf, MeIm
Ln = Sm, L = MeIm

In all the structurally characterized aforementioned complexes, the coordination at phosphorus is close to planarity, the sum of angles around phosphorus being intermediate between 328.4° (value for tetrahedral coordination) and 360° (value for planar coordination). For instance, in the $[(L)_4Ln(Ph_2P)_2]$ series, this value varies from 332.7° (L = thf, Ln = Yb) to 334.9° (L = MeIm, Ln = Yb). However, in the more crowded $[(thf)_4Ln(Mes_2P)_2]$ ([XR]: Ln = Sm [89], Yb [90]), conveniently made by the reaction of $KPMes_2$ with LnI_2, the coordination is rigorously planar, a crystallographic C_2 axis coinciding with the Yb–P bond. Planarity at arsenic is also achieved in the isomorphous $[(thf)_4Sm(Mes_2As)_2]$ [XR] [89] similarly made from $KAsMes_2$ and SmI_2.

Steric crowding by the mesityl group may thus be responsible of this planarity at the heteroatom, and also of the already noted absence of reaction of $Ln\{N(SiMe_3)_2]$ with Mes_2PH [87].

The acid–base reaction of $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La, Eu or Y) with just one equivalent of Ph_2PH gave the mixed amido/phosphido complexes $[Ln\{N(SiMe_3)_2\}_2(Ph_2P)]$ (Ln = La, Eu) or their triphenylphosphine oxide adducts $[(OPPh_3)Ln\{N(SiMe_3)_2\}_2(Ph_2P)]$ (Ln = La, Eu, Gd and Y). A ^{31}P NMR study of the La complex showed the expected broadening due to the quadrupolar moment of ^{135}La, while the ^{31}P NMR spectrum of the Y compound suggests a dimeric structure [91]. An additional equivalent of triphenylphosphine oxide caused the precipitation of $[(OPPh_3)_2La\{N(SiMe_3)_2\}_2(Ph_2P)]$ [XR], which partially dissociates at room temperature in solution. In the solid state, coordination around the phosphorus atom is planar, also for steric reasons [92].





Reactions of bis(*o*-methoxyphenyl) phosphine $[(MeOPh)_2PH]$ with $[Ln(N^iPr_2)_3]$ at room temperature led to the formation of the homoleptic $[\{(MeOPh)_2P\}_3Ln]$ (Ln = La, Y), presumably with the phosphido acting as a chelating ligand via the methoxy groups, whereas at 0 °C, it is possible to perform the substitution stepwise and to isolate the intermediate $[\{(MeOPh)_2P\}_2La(N^iPr_2)]$. The reaction of $[(MeOPh)_2PH]$ with $[Li(Ln(N^iPr_2)_4\}]$ gave an ate-complex: $[(thf)Li\{\mu{:}\eta^2,\eta^2\text{-}[(MeOPh)_2P]\}_2La(N^iPr_2)_2]$ [XR] with one *o*-methoxy group of the $[(MeOPh)_2P]$ ligand coordinated to Li and the other to La [93].

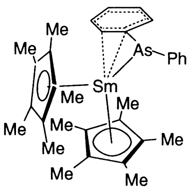
3.2.1.2. Organometallic complexes. All compounds in this group are diorganophosphide or arsenide bis-cyclopentadienyl lanthanide (III) complexes with one example of a mixed-valence Sm(II/III) binuclear compound.

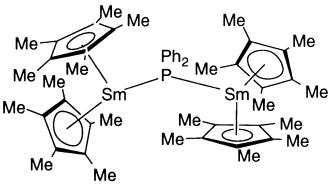
Early reports described the preparation of late lanthanide neutral derivatives: $[Cp_2Ln(^tBu_2P)]$ (Ln = Tb→Lu) from $[Cp_2LnCl]$ and $^tBu_2PLi$, and $[Cp_2Ln\{(^tBu)(Ph)P\}]$ (Ln = Tb, Ho, Er, Yb, Lu) from $[Cp_2LnCl]$ and $(^tBu)(Ph)PLi$; $[Cp_2Er(^tBu_2P)]$ has also been made from $[Cp_2ErCl]$ and $^tBu_2PSiMe_3$. The Gd and Sm compounds could not be obtained pure by this route. The isolated complexes were characterized by proton NMR and elemental analysis [94]; cryoscopic measurements suggest that the complexes are oligomeric in solution [95].

The neutral diphenylphosphide complex $[Cp_2Lu(Ph_2P)(thf)]$, characterized by NMR, has been observed in the reaction of $[Cp_2Lu(CH_2SiMe_3)]$ with Ph_2PH; it is not stable, however, and evolved into $[\{Cp_2Lu[\mu\text{-}O(CH_2)_4PPh_2]\}_2]$, a product of electrophilic opening of the THF ring by the $[Cp_2Lu^+]$ fragment. $[Cp_2Lu(Ph_2As)(thf)]$ obtained similarly is even less stable and was presumably hydrolyzed by traces of water into $[\{Cp_2Lu(thf)\}_2(\mu\text{-}O)]$ [96].

Protonation of the alkynyl ligand in $[(MeCp)_2Sm(C{\equiv}C^tBu)]$ by Ph_2PH afforded unsolvated $[(MeCp)_2Sm(Ph_2P)]$, monomeric in solution, characterized by ^1H and ^{13}C NMR and elemental analysis [97].

The unsolvated monomeric complexes: $[Cp^*_2Sm(Ph_2E)]$ (E = P, As [XR]) were obtained by oxidation of $[Cp^*_2Sm]$ by Ph_2EEPh_2. In the solid state, steric unsaturation was evidenced by a close contact of the *ipso* and α carbons of one phenyl group to Sm. Likewise, oxidation of $[Cp^*_2Sm(thf)_2]$ by Ph_2EEPh_2 afforded $[Cp^*_2Sm(Ph_2E)(thf)]$ (E = P, As [XR]) which further reacted upon heating to give THF ring-opened products: $[Cp^*_2Sm\{O(CH_2)_4EPh_2\}(thf)]$ (E = P, As) in the same way as noted above for $[Cp_2Lu(Ph_2P)(thf)]$. Reaction of $[Cp^*_2Sm(Ph_2E)]$ with $[Cp^*_2Sm]$ gave a Sm(II/III) mixed-valence adduct: $[(Cp^*_2Sm)_2(\mu\text{-}Ph_2E)]$ [XR], where magnetic measurements indicate that the two metals remain in their discrete oxidation states; however, NMR experiments suggest that a fast interchange (on the NMR time scale) occurs between these two oxidation states. Reactions of $[Cp^*_2Sm]$ or $[Cp^*_2Sm(thf)_2]$ with Ph_2EEPh_2 (E = Sb, Bi) did not occur with E–E bond cleavage, but with E–C bond cleavage and formation of $[Cp^*_2SmPh]$ or $[Cp^*_2SmPh(thf)_2]$ [50].



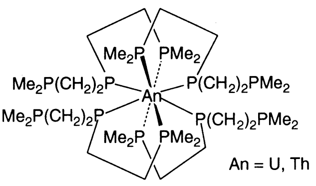


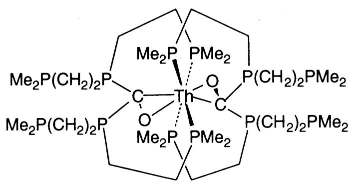
The absolute Sm–P bond disruption enthalpy of $[Cp^*_2Sm(Et_2P)]$ (synthesized by reaction of $[(Cp^*_2SmH)_2]$ with $HPEt_2$ and elimination of H_2) has been measured. Its value of 136.3 kJ mol^{-1} is, not unexpectedly, smaller than the corresponding value of 201.5 kJ mol^{-1} for the Sm–N bond in $[Cp^*_2Sm(Me_2N)]$ [98].

Anionic complexes: $[Cp_2Lu(\mu\text{-}Ph_2E)_2Li(tmeda)]$ ([XR]: E = P [99], As [100]) were obtained by protonolysis of $[Cp_2Lu(\mu\text{-}Me)_2Li(tmeda)]$ with $HEPh_2$. Stepwise replacement of the methyl groups is possible and $[Cp_2Lu(\mu\text{-}Me)(\mu\text{-}Ph_2E)Li(tmeda)]$ could be thus observed [99].

3.2.2. Actinides

3.2.2.1. Inorganic complexes. Applications of the chelating diphosphinophosphide $[(Me_2PCH_2CH_2)_2P]^-$ (PPP) in actinide chemistry have recently appeared. Reaction of AnX_4 with LiPPP or KPPP yielded the homoleptic $[An(PPP)_4]$ ([XR]: An = Th, U [101–103]) where the PPP ligand is bidentate. The eight-coordinate complexes are best described as dodecahedral, but distorted towards square antiprismatic. The most striking feature of these complexes is the complete or nearcomplete planarity at phosphorus for the coordinated phosphides; their U–P bond is approximately 20 pm shorter (see Table 1) than the U–P bond for the coordinated phosphines. These phenomena have been attributed to phosphide π-donation to U or Th. NMR of the Th complex revealed two dynamic processes: a low temperature exchange between coordinated and pendant phosphines, and a high temperature oscillation between seven- and eight-coordination around uranium.





Carbon monoxide reacted with [Th(PPP)$_4$] (but not with [U(PPP)$_4$]) by insertion into two Th–P (phosphide) bonds to give a bis(diphosphacarbonyl) thorium complex: [Th{(PPP)$_2$CO}$_2$] [XR] with η^2-acyl coordination to thorium; hydrolysis gave the diphosphinocarbinol (PPP)$_2$CHOH [114]. NMR experiments suggest the formation of [(PhO)$_2$Th(PPP)$_2$] by reaction of PHOH with Th(PPP)$_4$] [102].

3.2.2.2. Organometallic complexes. All complexes in this section are cyclopentadienyl or pentamethylcyclopentadienyl derivatives of U(IV) or Th(IV).

[Cp$_3$U(PPh$_2$)] was prepared either by the anionic route (reaction of [Cp$_3$UCl] and LiPPh$_2$) or by the acid–base reaction of [Cp$_2$U(NEt$_2$)$_2$] with HPPh$_2$. This latter route was found more practical, even though its maximum yield is 50% (redistribution must take place), because purification of the product was not necessary. The reaction of [Cp$_3$U(PPh$_2$)] with alcohols or diphenylamine gave [Cp$_3$U(OR)] or [Cp$_3$U(NPh$_2$)], respectively [243].

Several complexes such as [Cp^*_2An(PR$_2$)$_n$(L)$_p$] (L = Cl or Me) have been made by the anionic route:

$$[\mathrm{Cp}^*_2\mathrm{An}(\mathrm{X})_n(\mathrm{L})_p] + n\mathrm{MPR}_2 \rightarrow [\mathrm{Cp}^*_2\mathrm{An}(\mathrm{PR}_2)_n(\mathrm{L})_p] + n\mathrm{MX}.$$

Starting material	**Reagent**	**Product**	**Ref.**
[$\mathrm{Cp}^*_2\mathrm{ThCl}_2$]	LiPR$_2$ (R = Cy, Et)	[$\mathrm{Cp}^*_2\mathrm{Th(PR}_2)_2$]	[115]
[$\mathrm{Cp}^*_2\mathrm{ThCl}_2$]	LiPPh$_2$	[$\mathrm{Cp}^*_2\mathrm{Th(PPh}_2)_2$]	[115] [XR]
[$\mathrm{Cp}^*_2\mathrm{ThCl}_2$]	KP(SiMe$_3$)$_2$	[$\mathrm{Cp}^*_2\mathrm{Th(Cl)\{P(SiMe}_3)_2\}$]	[116]
[$\mathrm{Cp}^*_2\mathrm{UCl}_2$]	KP(SiMe$_3$)$_2$	[$\mathrm{Cp}^*_2\mathrm{U(Cl)\{P(SiMe}_3)_2\}$]	[116] [XR]
[$\mathrm{Cp}^*_2\mathrm{Th(Me)(Cl)}$]	KP(SiMe$_3$)$_2$	[$\mathrm{Cp}^*_2\mathrm{Th(Me)\{P(SiMe}_3)_2\}$]	[116] [XR]
[$\mathrm{Cp}^*_2\mathrm{U(Me)(Cl)}$]	KP(SiMe$_3$)$_2$	[$\mathrm{Cp}^*_2\mathrm{U(Me)\{P(SiMe}_3)_2\}$]	[116]

While disubstitution of the chlorine atoms in [$\mathrm{Cp}^*_2\mathrm{AnCl}_2$] by a dialkyl- or diarylphosphide is possible [115], only monosubstitution is achieved with potassium bis(trimethylsilylphosphide [116]. [$\mathrm{Cp}^*_2\mathrm{Th(Cl)\{P(SiMe}_3)_2\}$] could also be made from lithium bis(trimethylsilyl)phosphide, but, in the case of uranium, reduction occurred and [$\mathrm{Cp}^*_2\mathrm{UCl}$] was obtained. Restricted rotation around the P–An group is evidenced

Table 1
Table of metal–heteroelement bond lengths (pm).

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
	Sc–Si				
[Cp$_2$Sc{Si(SiMe$_3$)$_3$}(thf)]		286.3(2)	3	8	[16]
	Sm–Si				
[{Cp$^*_2$SmSi(H)(SiMe$_3$)[SiMe$_2$(μ-Me)]}$_2$]		305.2(8)	3	8	[28]
	Yb–Si				
[(thf)$_4$Yb(SiPh$_3$)$_2$]		315.8(2)	2	8	[18]
[Cp*Yb{Si(SiMe$_3$)$_3$}(thf)$_2$]		303.2(3)	2	8	[34]
	Lu–Si				
[{Li(dme)$_3$}{Cp$_2$Lu(SiMe$_3$)$_2$}]		288.8(2)	3	8	[33]
	Yb–Ge				
[{thf)$_4$Yb(GePh$_3$)$_2$]		315.6(5) (av.)	2	6	[18]
[(thf)$_4$Yb{η^2-GePh$_2$(GePh$_2$)$_2$Ph$_2$Ge}]		310.4(2)	2	6	[23]
	Eu–Sn				
[(thf)$_4$Eu(SnPh$_3$)$_2$]		342.4(1)	2	6	[13]
	Sm–Sn				
[(thf)$_4$Sm{Sn(SnMe$_3$)$_3$}$_2$]		339.4(4) (av.)	2	6	[22]
	Yb–Sn				
[(thf)$_4$Yb(SnPh$_3$)$_2$]		330.5(1)	2	6	[19]
[(thf)$_2$(Ph$_3$Sn)Yb(μ-Ph)$_3$Yb(thf)$_3$]		337.9(1)	2	6	[21]
[(thf)$_4$Yb{Sn(SnMe$_3$)$_3$}$_2$]		330.0(5)	2	6	[22]
[(thf)$_2$Yb{Sn(CH$_2$C^{t}Bu$_3$)$_3$}$_2$]		321.6(1)	2	4	[24]
	U–Sn				
[Cp$_3$U(SnPh$_3$)]		316.6(1)	4	10	[37]
	Sc–P				
[{[(η^5-C$_5$Me$_4$)SiMe$_2$(η^1-N^{t}Bu)]Sc(μ-H)(PMe$_3$)}$_2$]		299.6(1)	3	7	[40]
[{[(η^5-C$_5$Me$_4$)SiMe$_2$(η^1-N^{t}Bu)]Sc(PMe$_3$)}$_2$(μ:η^2-C$_2$H$_4$)]		282.5(3)	3	7	[41]
[(^{i}Pr-P^{Si}N^{Si}p)ScCl$_2$(thf)]		275.4(3) (av.)	3	6	[42]
[(^{i}Pr-P^{Si}N^{Si}P)ScEt$_2$]		277.9(2)	3	5	[42]
[(^{i}Pr-P^{Si}N^{Si}P)Sc(CH$_2$SiMe$_3$)$_2$]		279.1(2) (av.)	3	5	[42]
[Sc{Me$_2$PC(SiMe$_3$)PMe$_2$}$_3$]		261.7(1)	3	6	[44]
[{(η^5-P$_3$C$_2$^{t}Bu$_2$)Sc}$_2$(μ:η^6,η^6-P$_3$C$_3$^{t}Bu$_3$)]		274(4) (av.)	1	6	[104]
[{[(η^5-3-^{t}BuC$_5$H$_2$)$_2$SiMe$_2$]Sc(PMe$_3$)}$_2$(μ-Te)]		275.2(2) (av.)	3	8	[105]
	Y–P				
[(Me-P^{Si}N^{Si}P)Y{η^4-Me$_2$PCH$_2$(SiMe$_2$)N(SiMe$_2$)CHPMe$_2$}]		291(3) (av.)	3	7	[54]
[{(η^3-allyl)(Me-P^{Si}N^{Si}P)Y(μ-Cl)}$_2$]		291.2(7) (av.)	3	7	[55]

Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
	La–P				
[La{η^2-Me$_2$PC(SiMe$_3$)PMe$_2$}$_2${μ:η^2-Me$_2$PC(SiMe$_3$)-PMe$_2$}$_2$Li]		305(6) (av.)	3	8	[43]
[La(η^3-Ph$_2$PCHPPh$_2$)$_3$]		299(1)	3	9	[57]
[(thf)$_2$Li(μ-^{t}Bu$_2$P)$_2$La(^{t}Bu$_2$P)$_2$]		293(2) (av.)	3	4	[79]
[(OPPh$_3$)$_2$La{N(SiMe$_3$}$_2$(Ph$_2$P)]		316.5(6)	3	5	[92]
[(thf)Li{μ:η^2,η^2-[(MeOPh)$_2$P]}$_2$La(N^{i}Pr$_2$)$_2$]		314.1(4)	3	6	[93]
[{La[TeSi(SiMe$_3$)$_3$]$_3$(dmpe)$_2$}]		318(1) (av.)	3	7	[106]
	Nd–P				
[(thf)$_2${(SiMe$_3$)$_2$P}$_3$Nd]		282(4) (av.)	3	5	[84]
	Sm–P				
[Sm(η^3-Ph$_2$PCHPP$_2$)$_3$]		288.0(8) (av.)	3	9	[58]
[{Sm(η^3-Me$_2$PCHPMe$_2$)$_2$(μ:η^2,η^1-Me$_2$PCHPMe$_2$)}$_2$]		293(2) (av.)	3	9	[59]
[{Cp$^*_2$Sm(μ:η^2,η^2-E,E-^{t}BuC=P-P=C^{t}Bu)}$_2$]		294.9(2) (av.)	3	8	[60]
[{(thf)Li(μ-^{t}Bu$_2$P)$_2$}$_2$Sm		305.3(6) (av.)	2	4	[81]
[(thf)$_3$Sm{μ-(SiMe$_3$)$_2$P}$_3$Sm{(SiMe$_3$)$_2$P}]		302.7(3)	2	4/6	[86]
	μ	310(3) (av.)			
[(meim)$_4$Sm(Ph$_2$P)$_2$]		313.9(3)	2	6	[87]
[(thf)$_4$Sm(Mes$_2$P)$_2$]		303.4(2)	2	6	[89]
[(thf)$_2$Sm(η^5-Bdmp)$_2$]		307.75(1)	2	8	[107]
[(thf)$_4$Sm(η^1-Dbp)$_2$]		319.08(6)	2	6	[107]
[{(η^5-Dmp)$_2$(μ:η^5,η^1-Dmp)Sm}$_2$]		291.4(5) (av.)	3	10	[108]
	μ	299.2(2)			
[({(η^5-Tmp)Sm(μ:η^5, η^1-Tmp)(μ:η^1,η^5-Tmp)-(μ-Cl)K(η^6-toluene)}$_2$)$_\infty$]		293.9(5) (av.)	3	8	[108]
[(Et$_3$NH){(py)$_2$Sm(S$_2$TPPH)$_2$}]		297.7(2) (av.)	3	8	[109]
	Eu–P				
[{(thf)Li(μ-^{t}Bu$_2$P)$_2$}$_2$Eu]		305.1(6) (av.)	2	4	[82]
[{Eu[TeSi(SiMe$_3$)$_3$]$_2$(dmpe)$_2$}$_2$(μ-dmpe)]		321(1)(av.)	2	7	[110]
	Tm–P				
[(thf)$_2${(SiMe$_3$)$_2$P}$_3$Tm]		270.5(1) (av.)	3	5	[85]
	Yb–P				
[(thf)Yb(μ-I)$_2$(μ:η^2,η^1-Me$_2$PC(SiMe$_3$)PMe$_2$)$_2$-{Li(thf)}$_2$]		302(2) (av.)	2	7	[43]
[{thf)Li(μ-^{t}Bu$_2$P)$_2$}$_2$Yb]		295.9(2) (av.)	2	4	[79]
[(thf)$_4$Yb(Ph$_2$P)$_2$]		299.1(2)	2	6	[87]
[(meim)$_4$Yb(Ph$_2$P)$_2$]		302.8(1)	2	6	[88]
[(thf)$_4$Yb(Mes$_2$P)$_2$]		292.5(2)	2	6	[90]
[(thf)$_2$Yb(η^5-Dpp)$_2$]		297.3(5) (av.)	2	8	[111]
[(thf)$_2$Yb(μ:η^5,η^1-Tmp)$_2$Ru{*trans*-(H)$_2$}(Ph$_3$P)$_2$]		293.3(2)	2	8	[112]
[{(thf)$_2$(η^5-Tmp)Yb(μ-Cl)}$_2$]		291.1(1)	2	7	[113]
[{(thf)$_2$(η^5-Tmp)Yb(μ-SPh)}$_2$]		294.3(4) (av.)	2	7	[113]
	Lu–P				
[(thf)Lu{η^2-Me$_2$PC(SiMe$_3$)PMe$_2$}$_3$]		287(2) (av.)	3	7	[43]

Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
$[\{Li(thf)_4\}\{Lu(OSiMe_3)[\eta^2\text{-}Me_2PC(SiMe_3)PMe_2]_3\}]$		291(1)	3	7	[44]
$[Cp_2Lu(\mu\text{-}Ph_2P)_2Li(tmeda)]$		279.7(5) (av.)	3	8	[99]
	Th–P				
$[\{[\eta^2\text{-}(^iPr\text{-}PNP)]_2ThCl(\mu\text{-}Cl)\}_2]$		316(2)	4	7	[77]
$[Th\{\eta^2\text{-}P(CH_2CH_2PMe_2)_2\}_4]$	Phosphine	307.5(5) (av.)	4	8	[101]
(form a)	Phosphide	289.5(5) (av.)			
$[Th\{\eta^2\text{-}P(CH_2CH_2PMe_2)_2\}_4]$	Phosphine	309.5(2) (av.)	4	8	[102]
(form b)	Phosphide	288.3(2) (av.)			[103]
$[Th\{\eta^5\text{-}OC[P(CH_2CH_2PMe_2)_2]_2\}_2]$		309(3) (av.)	4	10	[114]
$[Cp^*_2Th(PPh_2)_2]$		287.5(8) (av.)	4	8	[115]
$[Cp^*_2Th(Me)\{P(SiMe_3)_2\}]$		288.8(4)	4	8	[116]
$[Cp^*_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2]$		288.5(5) (av.)	4	8	[117]
$[Cp^*_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)]$		292(1) (av.)	4	8	[118]
$[\{(^tBu_2Cp)_2Th\}_2(\mu{:}\eta^3,\ \eta^3\text{-}P_6)]$		288(1) (av.)	4	9	[119]
$[\{^tBu_2Cp)_2Th(\mu{:}\eta^3\text{-}P_3)Th(Cl)(^tBu_2Cp)_2]$		290(3) (av.)	4	9/10	[119]
	U–P				
$[\{[\eta^2\text{-}(Et\text{-}PNP)]_2UCl(\mu\text{-}Cl)\}_2]$		313(2) (av.)	4	7	[77]
$[\{\eta^2\text{-}(^iPr\text{-}PNP)\}\{\eta^1\text{-}(^iPr\text{-}PNP)\}_2UCl_2]$		299.5(2)	5	6	[78]
$[U\{\eta^2\text{-}P(CH_2CH_2PMe_2)_2\}_4]$	Phosphine	299.3(2)	4	8	[102]
	Phosphide	277.8(2) (av.)			
$[Cp^*_2U(Cl)\{P(SiMe_3)_2\}]$		278.9(4)	4	8	[116]
$[Cp^*_2U\{\eta^2\text{-}CH_2SiMe_2P(SiMe_3)\}]$		265.6(6)	4	8	[116]
$[\{Cp^*_2U(OMe)\}_2(\mu\text{-}PH)]$		274.3(1)	4	8	[120]
$[Cp^*_2U(PMes^*)(OPMe_3)]$		256.2(3)	3	8	[121]
$[(\eta^5\text{-}Tmp)UCl_3(dme)]$		292.6(4)	4	10	[122]
$[(\eta^5\text{-}Tmp)_3UCl]$		292.7(4)	4	8	[123]
$[(\eta^5\text{-}Tmp)_2U(BH_4)_2]$		290.5(3) (av.)	4	8	[124]
$[\{(\eta^5\text{-}Tmp)(\mu{:}\eta^5,\eta^1,Tmp)U(BH_4)\}_2]$		297.0(8) (av.)	3	8	[125]
$[\{Cl_2U(\mu{:}\eta^5,\eta^1\text{-}Tmp)\}_2Ni]$		238.4(7) (av.)	4	8	[126]
$[\{Cl_2U(\mu{:}\eta^5,\eta^1\text{-}Tmp)Ni(\mu\text{-}Tmp)\}_2]$		286(1)	4	8	[126]
	Sm–As				
$[Cp^*_2Sm(Ph_2As)]$		296.9(3) (av.)	3	7	[50]
$[Cp^*_2Sm(Ph_2As)(thf)]$		304.9(3)	3	8	[50]
$[(thf)_4Sm(Mes_2As)_2]$		306.1(3)	2	6	[89]
	Lu–As				
$[Cp_2Lu(\mu\text{-}Ph_2As)_2Li(tmeda)]$		288.3(4) (av.)	3	8	[100]
	Th–As				
$[\{(^tBu_2Cp)_2Th\}_2(\mu{:}\eta^3,\eta^3\text{-}As_6)]$		298(2) (av.)	4	9	[127]
	Sm–Sb				
$[(Cp^*_2Sm)_3(\mu{:}\eta^2,\eta^2,\eta^1\text{-}Sb_3)(thf)]$		318.4(7) (av.)	3	8	[128]
	Sm–Bi				
$[(Cp^*_2Sm)_2(\mu{:}\eta^2,\eta^2\text{-}Bi_2)]$		328.8(7) (av.)	3	8	[129]

Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
	La–S				
$[\{La[\eta^6\text{-}(18\text{-}C\text{-}6\text{-}S_2)](\eta^1\text{-}ClO_4)(\eta^2\text{-}ClO_4)(H_2O)\}\ (ClO_4)]$		303.8(3) (av.)	3	10	[130]
$[La\{(CH_2)_4NCS_2\}_3(thf)(H_2O)]$		298(1) (av.)	3	8	[131]
$[La(Me_2NCS_2)_3(dmso)_2]$		298(1) (av.)	3	8	[132]
$[NaLa(Et_2NCS_2)_4]$		297(3) (av.)	3	8	[133]
$[\{La(Et_2NCS_2)_4\}(H)(THF)]$		297(1) (av.)	3	8	[134]
$[\{La(Et_2PS_2)_4\}(AsPh_4)]$		299.8(5) (av.)	3	8	[135]
$[\{La[(OEt)_2PS_2]_4\}(AsPh_4)]$		298.6(9) (av.)	3	8	[136]
$[La\{(OEt)_2PS_2\}_3(Ph_3PO)_2]$		304(2) (av.)	3	8	[137]
$[La\{(OEt)_2PS_2\}_3\{(PhCH_2)_2SO\}_2]$		304(2) (av.)	3	8	[138]
$[La\{(O^iPr)_2PS_2\}_3\{Me(Me_2N)CO\}_2]$		301(1) (av.)	3	8	[139]
$[La\{(O^iPr)_2PS_2\}_3(dmso)_2]$		299.9(5) (av.)	3	8	[140]
	Ce–S				
$[\{Cp^*_2Ce(tht)_2\}(BPh_4)]$		306.8(3) (av.)	3	8	[141]
$[\{Ce(SPy)_4\}(PEt_4)]$		293.4(9) (av.)	3	8	[142]
$[\{(^tBuCp)_2Ce(\mu\text{-}S^iPr)\}_2]$		288.2(4) (av.)	3	8	[143]
$[\{Ce[(OMe)_2PS_2]_4\}(AsPh_4)]$		297(1) (av.)	3	8	[144]
$[\{Ce(Me_2PS_2)_4\}\{AsPh_4\}]$		298(1) (av.)	3	8	[145]
	Pr–S				
$[\{Pr(Et_2NCS_2)_4\}(H)(THF)]$		293.8(9) (av.)	3	8	[146]
$[\{Pr(Me_2PS_2)_4\}(PPh_4)]$		298(1)	3	8	[147]
$[\{Pr(Cy_2PS_2)_3]$		284(1) (av.)	3	6	[148]
$[\{Pr(H_2O)_3(\eta^1\text{-}OPSMe_2)_2(\mu\text{:}\eta^1,\eta^2\text{-}OPSMe_2)\}_2]$		301.7(1)	3	8	[149]
$[\{Pr(EtOH)(^nPrOH)(\eta^2\text{-}OPSMe_2)(\eta^1\text{-}OPSMe_2)(\mu\text{:}\eta^1,\eta^2\text{-}OPSMe_2)\}_2]$		307.1(3) 298.4(2)	3	8	[149]
	Nd–S				
$[\{Nd(SCN)_2(\mu\text{-}SCN)(thf)_4\}_2]$		310.0(9)	3	8	[150]
$[\{Nd(Me_2NCS_2)_4\}(NMe_2H_2)]$		291.3(9) (av.)	3	8	[151]
$[NaNd(Et_2NCS_2)_4]$		294(2) (av.)	3	8	[152]
$[\{Nd(Et_2NCS_2)_4\}(NEt_4)]$		291.5(7) (av.)	3	8	[153]
$[\{Nd(Et_2NCS_2)_4\}(H)(THF)]$		291(1) (av.)	3	8	[134]
$[\{Nd[(O^iPr)_2PS_2]_4\}(AsPh_4)]$		295.3(9)	3	8	[144]
$[Nd\{(O^iPr)_2PS_2\}_3\{Ph(NH_2)CO\}_2]$		293(1) (av.)	3	8	[154]
$[\{Nd[(O^iPr)_2PS_2]_2(^nBu_2SO)_3\}\{Nd[(O^iPr)_2PS_2]_4\}]$	Nd^- Nd^+	289.9(7) (av.) 291 (1) (av.)	3	7/8	[155]
$[\{Nd(H_2O)(\eta^1\text{-}OPSCy_2)(\eta^2\text{-}OPSCy_2)(\mu\text{:}\eta^1,\eta^2\ OPSCy_2)\}_2]$		293.8(3) 298.7(3)	3	7	[156]
	Sm–S				
$[(thf)_2(\eta^2\text{-}SPNPS)_2Sm]$		298.1(6) (av.)	2	6	[157]
$[\{Li(tmeda)\}_3Sm(\mu\text{-}S^tBu)_6]$		282.9(3) (av.)	3	6	[158]
$[\{[Sm(dme)]_7(\mu\text{-}SePh)_6([\mu_3\text{-}S)_4(\mu_4\text{-}S)(\mu_5\text{-}S)_2\}\{Hg_3(SePh)_7\}]$		279(5)	3	7/8	[225]
$[(hmpa)_3Sm(SPh)_3]$		282.4(4) (av.)	2	6	[159]

Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
$[\{(thf)_3Sm(SAr^{iPr} (\mu\text{-}SAr^{iPr})_2]$		290.8(6)	3	6	[160]
	μ	301.7(6) (av.)			
$[(py)_2(thf)Sm(SAr^{iPr})_3]$		273.5(5)	3	6	[160]
$[Sm(SMes^*)_3]$		264.3(9) (av.)	3	3	[161]
$[\{(hmpa)_3Sm(SPy)_2\}(I)]$		287.0(8) (av.)	3	7	[162]
$[\{(py)_2Sm(S_2TPPH)_2\}(Et_3NH)]$		285.8(9) (av.)	3	8	[109]
$[Cp_2^*Sm(S_2CNMe_2)]$		280.8(2)	3	8	[163]
$[\{(COT)Sm(thf)_2(\mu\text{-}SPh\}_2]$		292.4(8) (av.)	3	9	[164]
$[\{(COT)Sm(thf)(\mu\text{-}SAr^{iPr})\}_2]$		288.3(6) (av.)	3	8	[164]
$[\{Cp_2^*Sm(thf)\}_2(\mu\text{-}S)]$		266.4(1) (av.)	3	8	[165]
$\{[PPh_4\}\{(Cp_2^*Sm)_2Mo(\mu\text{-}S)_4\}]$		279.3(3) (av.)	3	8	[166]
$[\{PPh_4\}\{Cp_2^*Sm(\mu\text{-}S)_2WS_2\}]$		279.0(2) (av.)	3	8	[166]
$[\{Sm(Et_2NCS_2)_4\}\{Mo(Et_2NCS_2)_4)\}]$		288(1) (av.)	3	8	[167]
$[\{Sm[(OEt)_2PS_2]_2(OPPh_3)_3\}\{(OEt)_2PS_2\}]$		293(1)	3	7	[137]
$[Sm(Cy_2PS_2)_3]$		278.9(6) (av.)	3	6	[148]
$[\{Cp^*Sm\{\eta^2\text{-}S_2P(OMe)_2\}[\mu{:}\eta^2,\eta^1\text{-}S_2P(OMe)_2]\}_2]$		291.6(2) (av.)	3	9	[168]
	μ	304.7(2)			
$[\{[\eta^2\text{-}N(Ph)C(Ph)NC(S)(NEt_2)][\mu{:}\eta^2\text{-}SC(NEt_2)NH]SmBr(thf)\}_2]$		300(1)	3	8	[169]
	Eu–S				
$[\{Eu(SCN)_2(\mu\text{-}SCN)(thf)_4\}_2]$		311.2 (3)	3	8	[150]
$[\{(py)_3Eu(\mu_2\text{-}SPh)_2(\mu_3\text{-}SPh)Hg(SPh)_2\}]$	μ_2	301.4(9) (av.)	2	7	[170]
	μ_3	301.8(4) (av.)			
$[\{(py)_3Eu(\mu_2\text{-}SPh)_2(\mu_3\text{-}SPh)Cd(SPh)_2\}]$	μ_2	301.4(9) (av.)	2	7	[170]
	μ_3	304(1) (av.)			
$[\{(thf)_3Eu(\mu_2\text{-}SPh)_2(\mu_3\text{-}SPh)Zn(SPh)_2\}]$	μ_2	298.7(2) (av.)	2	7	[170]
	μ_3	305.2(7) (5)			
$[\{(py)_2Eu(\mu{:}\eta^1\text{-}SPy)_3(\mu{:}\eta^1,\eta^2\text{-}SPy)Sn\}_\infty]$		322(5) (av.)	2	9	[171]
$[\{(thf)_3Eu(SAr^{iPr})(\mu\text{-}SAr^{iPr})\}_2]$		289.8(4)	2	6	[160]
	μ	301.5(6) (av.)			
$[(py)_4Eu(SPy)_2]$		304.5(7) (av.)	2	8	[172]
$[(bipy)(thf)_2Eu(SPy)_2]$		300.6(2) (av.)	2	8	[172]
$[\{Eu(SPy)_4\}(PEt_4)]$		287(1) (av.)	3	8	[172]
$[NaEu(Et_2NCS_2)_4]$		287(3) (av.)	3	8	[173]
$[\{Eu(Et_2NCS_2)_4\}(H)(THF)]$		286.2(7) (av.)	3	8	[174]
$[\{Eu[(OiPr)_2PS_2]_2(dmso)_3\}\{Eu[(O^iPr)_2PS_2]_4\}]$	Eu^+	287.8(5) (av.)	3	7/8	[140]
	Eu^-	289.4(6) (av.)			
	Gd–S				
$[\{Li(thf)_4\}_2\{Gd(Br)_4(thf)(\mu\text{-}SMoCp_2\}_2]$		276.7(1)	3	6	[175]
$[\{[(Me_3Si)_2N]_2Gd(\mu\text{-}S^tBu)\}_2]$		279(1) (av.)	3	4	[176]
$[(Gd(thf)\}_8(\mu\text{-}SPh)_{12}(\mu_4\text{-}S)_6]$		283(1) (av.)	3	7	[177]
	μ_4	279(1) (av.)			
$[\{[\eta^2\text{-}N(Ph)C(Ph)NC(S)(NEt_2)][\mu{:}\eta^2\text{-}SC(NEt_2)NH]GdBr(thf)\}_2]$		300(2)	3	8	[169]
	Tb–S				
$[\{Tb[(O^iPr)_2PS_2]_2[Ph(NH_2)CO]_3\}\{(O^iPr)_2PS_2\}]$		282.8(7) (av.)	3	7	[178]
	Dy–S				

Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
$[\mathrm{Dy(Cy_2PS_2)_3}]$		273.9(3) (av.)	3	6	[179]
	Ho–S				
$[\{\mathrm{Ho[(^iPrO)_2PS_2]_4}\}\{\mathrm{AsPh_4}\}]$		287(2) (av.)	3	8	[144]
	Er–S				
$[\{\mathrm{Er(SCN)_2(\mu\text{-}SCN)(thf)_4}\}_2]$		328.3(4)	3	8	[150]
$[\mathrm{Er(Et_2NCS_2)_3(bipy)}]$		287.6(8) (av.)	3	8	[180]
$[\{\mathrm{Er[(MeO)_2PS_2]_4}\}\{\mathrm{AsPh_4}\}]$		281(3) (av.)	3	8	[144]
$[\{\mathrm{Er(Et_2PS_2)_4}\}\{\mathrm{AsPh_4}\}]$		286(2) (av.)	3	8	[135]
$[(\mathrm{Er[(EtO)_2PS_2]_4]}\}\{\mathrm{AsPh_4}\}]$		286(2) (av.)	3	8	[136]
$[\{\mathrm{Er[(O^iPr)_2PS_2]_2[Ph(NH_2)CO]_3}\{\mathrm{(O^iPr)_2PS_2}\}]$		280.0(6) (av.)	3	7	[178]
$[\{\mathrm{Er(H_2O)_2(\eta^1\text{-}OPSMe_2)_2(\mu{:}\eta^1,\eta^2\text{-}OPSMe_2)}\}_2]$		291.0(1)	3	7	[149]
	Tm–S				
$[\{\mathrm{Tm(Me_2PS_2)_4}\}\{\mathrm{AsPh_4}\}]$		290(4) (av.)	3	8	[145]
	Yb–S				
$[\{\mathrm{Li(tmeda)}\}_3\mathrm{Yb(\mu\text{-}S^tBu)_6}]$		273.7(2) (av.)	3	6	[158]
$[\mathrm{(py)_4Yb(SPh)_2}]$		282.7(3)	2	6	[181]
$[\mathrm{(hmpa)_3Yb(SPh)_3}]$		273.3(2) (av.)	3	6	[159]
$[\{\mathrm{(hmpa)_6Yb_2(\mu\text{-}SPh)_3}\}\mathrm{(SPh)}]$		291.6(7) (av.)	2	6	[159]
$[\mathrm{(py)_3Yb(SPh)_3}]$		264(1) (av.)	3	6	[182]
$[\mathrm{Yb}\{\mathrm{PhC(NSiMe_3)_2}\}_2\mathrm{(S_2CNMe_2)}]$		273.8(3) (av.)	3	6	[183]
$[\mathrm{(py)_3Yb(SAr^{iPr})_3}]$		264.3(7) (av.)	3	6	[160]
$[\mathrm{(dme)_2Yb(SMes^*)_2}]$		275.6(8) (av.)	2	6	[161]
$[\mathrm{(py)_3Yb(SPy)_2}]$		288(2) (av.)	2	7	[142]
$[\mathrm{(py)_2Yb(SPy)_3}]$		275.8(4) (av.)	3	8	[142]
$[\{\mathrm{(hmpa)_3Yb(SPy)_2}\}\mathrm{(I)}]$		280.0(9) (av.)	3	7	[162]
$[\{\mathrm{Cp_2Yb(\mu\text{-}S^nPr)]_2}]$		270.8(3) (av.)	3	8	[184]
$[\mathrm{Cp_2Yb(SAr^F)(thf)}]$		263.9(3)	3	8	[185]
$[\mathrm{Cp_2^*Yb(SPh)(NH_3)}]$		267.0(3)	3	8	[186]
$[\mathrm{Cp_2^*Yb(S_2CNMe_2)}]$		270(1)	3	8	[187]
	Lu–S				
$[\mathrm{Cp_2^*Lu(\mu\text{-}S^tBu)_2Li(thf)_2}]$		271.6(3) (av.)	3	8	[188]
$[\mathrm{Lu(Cy_2PS_2)_3}]$		269.0(3)	3	6	[179]
	Th–S				
$[\mathrm{(dmf)(OPyS)_4Th}]$		296(1)	4	9	[189]
$[\mathrm{Cp_2^*Th(S^nPr)_2}]$		271.8(3)	4	8	[190]
$[\mathrm{Cp_2^*Th(S)_5}]$	α	276.8(4)	4	10	[191]
	β	303.6(3)			
$[\mathrm{Th(S_2PMe_2)_4}]$		290.4(9) (av.)	4	8	[192]
$[\mathrm{Th(S_2PCy_2)_4}]$		291.0(4) (av.)	4	8	[192]
	U–S				
$[\{\mathrm{U(BH_3CH_3)_4(\mu\text{-}tht)}\}_2]$		318(2)(av.)	4	6	[193]
$[\mathrm{U(BH_3CH_3)_4(bmte))}]$		306(1)	4	6	[194]

Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
$[\{C_6H_4(O)(NCH_2CH_2S)\}_2(UO_2))]$		296(1)	4	7	[195]
$[\{(Cl)[CH(OEt)_2]C_6H_2(O)(NCH_2CH_2S)\}_2(UO_2)]$		300.3(3)	6	7	[196]
$[\{(Cl)C_6H_2(O)[NCH_2CH_2S]_2\}_2(UO_2)]$		301.8(4)	6	7	[197]
$[UO_2(bmppt)(NO_3)_3)_2]$		287.1(3)	6	8	[198]
$[UO_2(bmppt)_2(dmso)]$		287(1)	6	7	[198]
$[UO_2Cl_2(bhcs)]$		294(1)	6	7	[199]
$[(MeCp)_3U(tht)]$		298.6(5)	3	10	[200]
$[\{(hmpa)_4U({}^1PrS)_2\}\ (BPh_4)_2]$		265(7) (av.)	4	6	[201]
$[(py)_3U({}^iPrS)_2(I)_2]$		262(2) (av.)	4	7	[201]
$[(hmpa)_2U({}^iPrS)_4]$		272.2(5) (av.)	4	6	[202]
$[U_3(\mu_3\text{-}S)(\mu_3\text{-}S^tBu)(\mu_2\text{-}S^tBu)_3(S^tBu)_6]$		258(2)	4	6	[202]
	μ_2	279(1)			
	μ_3-SR	288(2)			
	μ_3-S	275(2)			
$[\{(Ph_3P)Cu(\mu\text{-}SPh)_3\}_2U]$		275(1)	4	6	[203]
$[(Et_2NH_2)_2\{U(SPh)_6\}]$		273(3) (av.)	4	6	[203]
$[\{(thf)_3Na(\mu\text{-}S^tBu)_3\}_2U]$		275.0(9)	4	6	[204]
$[\{(thf)_3Na(\mu\text{-}SPh)_3\}_2U]$		271.7(3)	4	6	[204]
$[\{(dme)Li\}_4\{(\mu{:}\eta^2\text{-}SCH_2CH_2S)_4U\}]$	Site A	282(1) (av.)	4	8	[205]
	Site B	288.5(8) (av.)			
$[U(SAr')(N(SiMe_3)_2\}_3]$		269.6(3)	4	4	[206]
$[(HBPz_3)_2U({}^iPrS)_2]$		268.0(6)	4	8	[207]
$[(dmso)(OPyS)_2(UO_2)]$		287(1)	6	7	[208]
$[\{(UO_2)_2(\mu{:}\eta^2,\eta^2\text{-}O_2)(SPym)_4\}(HNEt_3)_2]$		292.3(5)	6	8	[209]
$[\{(H)(UO_2)_2(\mu{:}\eta^2,\eta^2\text{-}O_2)(SMePym)_4\}(HNEt_3)_2]$		289.1(5)	6	8	[209]
$[\{(SPy)_2(UO)(\mu_2\text{-}O)\mu_3\text{-}O)(UO_2)\}_2(HNEt_3)]$		285.6(4)	6	7	[209]
$[Cp_3U(SMe)]$		269.5(4)	4	10	[210]
$[\{(COT)U(\mu\text{-}S^iPr)_2\}_2]$		285.5(9) (av.)	4	9	[211]
$[\{Na(18\text{-crown-}6)(thf)\}\{(COT)U(S^iPr)_3\}]$		269(3)	4	8	[211]
$[\{UO_2({}^nPr_2NCOS)_2(\eta^2\text{-}S_2)\}({}^nPr_2NH_2)_2]$		287.3(2)	6	8	[212]
	η^2-S_2	271.1(3)			
$[\{U(OAr^*)_3\}_2(\mu\text{-}S)]$		258.8(1)	4	4	[213]
$[\{(MeCp)_3U\}_2(\mu\text{-}S)]$		260(1) (av.)	4	10	[214]
$[Cp^*_3U_3(\mu_3\text{-}I)(\mu_3\text{-}S)(\mu_2\text{-}I)_3(I)_3]$		275(2) (av.)	4	8	[215]
$[\{UO_2(S_2CNMe_2)_3\}(NEt_4)]$		293.5(7) (av.)	6	8	[216]
$[\{UO_2(S_2CNEt_2)_3\}(NMe_4)]$		292.3(4) (av.)	6	8	[216]
$[\{UO_2[S_2CN(CH_2)_4]_3\}(NEt_4)]$		294.7(2) (av.)	6	8	[216]
$[\{UO_2[S_2CN(CH_2)_5]_3\}(NEt_4)]$		292.6(6) (av.)	6	8	[216]
$[\{UO_2(OSCNEt_2)_2(OEt)\}(H_2NEt_2)]$		286.6(4) (av.)	6	7	[217]
$[\{UO_2(OSCN^nPr_2)_2(OEt)\}(H_2N^nPr_2)]$		287.1(4) (av.)	6	7	[218]
$[UO_2(S_2PCy_2)_2(H_2O)]$		284.4(4) (av.)	6	7	[219]
$[UO_2(S_2PCy_2)_2(H_2O)]$ (orthorhombic)		285.2(5) (av.)	6	7	[219]
$[UO_2(S_2PCy_2)2(H_2O)]$ (monoclinic)		287.2(5) (av.)	6	7	[219]
$[UO_2(S_2PPh_2)_2(EtOH)]$		287.4(7) (av.)	6	7	[220]
$[UO_2(S_2PCy_2)_2(EtOH)]$		284.7(4) (av.)	6	7	[220]
$[UO_2(S_2PMe_2)_2(OPMe_3)]$		287.4(5) (av.)	6	7	[220]
$[\{UO_2(S_2PMe_2)_2(Cl)\}(NEt_4)]$		289.0(9) (av.)	6	7	[220]
$[\{UO_2(S_2PPh_2)_2(Cl)\}(NEt_4)]$		289(1) (av.)	6	7	[220]

Table 1 (*continued*)

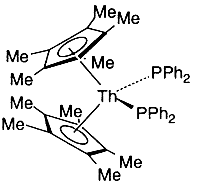
Compound	Bond type	Bond length	o.s.	c.n.	Ref.
$[\{\mathrm{U}(\eta^2\text{-}\mathrm{S_2PMe_2})_2(\eta^1\text{-}\mathrm{OPSMe_2})(\mu\text{-}\mathrm{O_2PMe_2})\}_2]$		285.8(4) (av.)	4	7	[221]
$[\{(\mathrm{MeCp})_3\mathrm{U}\}_2(\mu{:}\eta^1,\eta^2\text{-}\mathrm{CS_2})]$		279.2(3)	4	10/11	[222]
	Sc–Se				
$[\{\{\mathrm{Cp}^*_2\mathrm{Sc}\}_2(\mu\text{-}\mathrm{Se})]$		254.25(16)	3	7	[223]
	Y–Se				
$[\{(^t\mathrm{BuCp})_2\mathrm{Y}(\mu\text{-}\mathrm{SePh})\}_2]$		291.5(1)	3	8	[224]
	Sm–Se				
$[(\mathrm{thf})_2(\eta^2\text{-}\mathrm{SePNPSe})(\eta^3\text{-}\mathrm{SePNPSe})\mathrm{Sm}]$		314(1)	2	7	[157]
$[(\eta^3\text{-}\mathrm{SePNPSe})_2\mathrm{Sm}(\mathrm{SeMes})(\mathrm{thf})]$		294.3(1)	3	8	[157]
	η^3	304(2) (av.)			
$[\{\mathrm{Sm}(\mathrm{thf})\}_8(\mu\text{-}\mathrm{SePh})_{12}(\mu_4\text{-}\mathrm{Se})_6]$	μ	297(2)	3	7	[225]
	μ_4	291(2)			
$[\{[\mathrm{Sm}(\mathrm{dme})]_7(\mu\text{-}\mathrm{SePh})_6(\mu_3\text{-}\mathrm{S})_4(\mu_4\text{-}\mathrm{S})(\mu_5\text{-}\mathrm{S})_2\}\{\mathrm{Hg}_3(\mathrm{SePh})_7\}]$		303(3)	3	7/8	[225]
$[\{(\mathrm{thf})_2\mathrm{Sm}(\mathrm{SePh})(\mu_2\text{-}\mathrm{SePh})_2(\mu_3\text{-}\mathrm{SePh})\mathrm{Hg}(\mathrm{SePh})\}_2]$		285.9(2)	3	7	[226]
	μ_2	299.5(7) (av.)			
	μ_3	308.8(4) (av.)			
$[\{(\mathrm{py})_2\mathrm{Sm}(\mathrm{SePh})(\mu\text{-}\mathrm{SePh})_3\mathrm{Na}(\mathrm{py})_2\}_2]$		290.8(1)	3	7	[227]
	μ	301(1) (av.)			
$[\mathrm{Cp}^*_2\mathrm{Sm}(\mathrm{SeAr^F})(\mathrm{thf})]$		291.9(1)	3	8	[163]
$[\{(\mathrm{COT})\mathrm{Sm}(\mathrm{thf})_2(\mu\text{-}\mathrm{SePh})\}_2]$		309(3)	3	9	[228]
$[\{\mathrm{Cp}^*_2\mathrm{Sm}(\mathrm{THF})_2(\mu\text{-}\mathrm{Se})]$		278.1 (1) (av.)	3	8	[165]
$[\{\mathrm{Cp}^*_2\mathrm{Sm}\}_2(\mathrm{thf})(\mu{:}\eta^1,\eta^3\text{-}\mathrm{Se}_3)]$		291.7(1)	3	8/9	[165]
		319.8(1)			
	μ	300.7(1)			
$[(\mathrm{Cp^*Sm})_6(\mathrm{Se})_{11}]$		286–330	3	8/9	[229]
	Eu–Se				
$[\{(\mathrm{thf})_3\mathrm{Eu}(\mu_2\text{-}\mathrm{SePh})_2(\mu_3\text{-}\mathrm{SePh})\mathrm{Hg}(\mathrm{SePh})_2)\}_2]$	μ_2	309.8(4) (av.)	2	7	[226]
	μ_3	322.9 (av.)			
$[\{(\mathrm{py})_3\mathrm{Eu}(\mu_2\text{-}\mathrm{SePh})_2(\mu_3\text{-}\mathrm{SePh})\mathrm{Hg}(\mathrm{SePh})\}_2]$	μ_2	315.0 (av.)	2	7	[227]
	μ_3	318.4(1)			
$[(\mathrm{thf})_4\mathrm{Eu}(\mu\text{-}\mathrm{SePh})_3\mathrm{Zn}(\mathrm{SePh})]$		322(2) (av.)	2	7	[227]
$[(\mathrm{thf})_2\mathrm{Eu}\{\mu\text{-}\mathrm{SePh})_3\mathrm{Pb}\}_2]$		327(3) (av.)	2	8	[171]
$[(\mathrm{thf})_3\mathrm{Eu}(\mu\text{-}\mathrm{SePh})_2]_\infty$		314(1) (av.)	2	7	[230]
$[(\mathrm{py})_2\mathrm{Eu}(\{\mu\text{-}\mathrm{SePh})_2]_\infty$		310(3) (av.)	2	6	[230]
$[(\mathrm{dmf})_{13}\mathrm{Eu}_8(\mu_4\text{-}\mathrm{O})(\mu_3\text{-}\mathrm{OH})_{12}(\mathrm{Se}_3)(\mathrm{Se}_4)_2(\mathrm{Se}_5)_2]$		305(2) (av.)	3	6/7	[231]
	Tm–Se				
$[\{(\mathrm{py})_3\mathrm{Tm}(\mathrm{SePh})_2(\mu\text{-}\mathrm{SePh})\}_2]$		282.64(7)	3	7	[182]
	μ	293.01(8)			
	Yb–Se				
$[\{\mathrm{Yb}[(\mu\text{-}\mathrm{SePh})_3\mathrm{Yb}(\mathrm{dme})_2]_2\}\{(\mathrm{dme})\mathrm{Yb}(\mathrm{SePh})_4\}]$		278.1(4)	2/3	6/7	[232]
	μ	282.9(6)			
	μ	302.6(7)			
$[(\mathrm{thf})_6\mathrm{Yb}_4(\mathrm{SePh})_2(\mu\text{-}\mathrm{SePh})_6(\mu_3\text{-}\mathrm{O})_2]$		276.6(2)	3	6/7	[232]
	μ	286.9(6) (av.)			

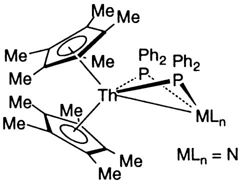
Table 1 (*continued*)

Compound	Bond type	Bond length	o.s.	c.n.	Ref.
	μ	305.6(6) (av.)			
[(thf)$_3$Yb(SePh)$_3$]		277.4(3)	3	6	[232]
[(py)$_4$Yb(SePh)$_2$]		296.0(1)	2	6	[181]
[(py)$_2$Yb(SePh)$_2$(μ-SePh)$_2$Li(py)$_2$]		277.1(3) (av.)	2	6	[233]
	μ	278(1) (av.)			
[(thf)Yb{PhC(NMe)$_2$}$_2$(SePh)]		280.5(1)	3	6	[183]
[(thf)Yb{PhC(NMe)$_2$}$_2$(SeMes)]		279.3(2)	3	6	[234]
[(tmeda)$_2$Yb{SeSi(SiMe$_3$)$_3$}$_2$]		287.0(1)	2	6	[110]
[{Cp$_2^*$Yb}$_2$(μ-Se)]		262.1(1)	3	8	[235]
	Lu–Se				
[Cp$_2$Lu(μ-SePh)$_2$Li(thf)$_2$]		279.9(7) (av.)	3	8	[236]
	U–Se				
[K$_4$U(η^2-Se$_2$)$_4$]		286.7(9)	4	8	[237]
	Sc–Te				
[{Cp$_2^*$Sc}$_2$(μ-Te)]		275.28(12)	3	7	[238]
[Cp$_2^*$Sc(TeCH$_2$Ph)]		283.37(14)	3	7	[223]
[{[(η^5-3-^{t}BuC$_5$H$_2$)$_2$SiMe$_2$]Sc(PMe$_3$)}$_2$(μ-Te)]		281(2) (av.)	3	8	[105]
	La–Te				
[{La[TeSi(SiMe$_3$)$_3$]$_3$(dmpe)$_2$}]		315.5(5) (av.)	3	7	[106] [239]
	Ce–Te				
[Ce$_5$(μ$_3$-Te)$_3${μ$_2$-TeSi(SiMe$_3$)$_3$}$_6${TeSi(SiMe$_3$)$_3$}$_3$]	μ$_2$	302.6(3)	3	5	[106]
	μ$_2$	320.9(9) (av.)			[239]
	μ$_3$	320.9(9) (av.)			
	Sm–Te				
[Cp$_2^*$Sm(TeMes)(thf)]		308.8(2)	3	8	[163]
[{Cp$_2^*$Sm(thf)$_2$}(μ-Te)]		299.3(2) (av.)	3	9	[165]
[(Cp$_2^*$Sm)$_2$(μ:η^2,η^2-Te$_2$)]		320.9(2)	3	8	[165]
	Eu–Te				
[(thf)$_3$Eu(μ$_3$-TePh)$_2$]$_\infty$	μ$_2$	332.4(2)	2	7	[240]
	μ$_3$	339(1) (av.)			
[(thf)$_2$Eu((μ-TePh)$_2$]$_\infty$	μ	335(1) (av.)	2	6	[240]
[{Eu[TeSi(SiMe$_3$)$_3$]$_2$(dmpe)$_2$}$_2$(μ-dmpe)]		319(1) (av.)	2	7	[110]
	Yb–Te				
[(py)$_5$Yb(TePh)$_2$]		328(3) (av.)	2	7	[181]
[(thf)$_2$Yb(μ-TePh)$_3$Yb(thf)$_2$(μ-TePh)]$_\infty$		317(1)(av.)	2	6	[240]
[Cp$_2^*$Yb(TePh)(NH$_3$)]		303.9(1)	3	8	[241]
[(Cp$_2^*$Yb)$_2$(μ:η^2,η^2-Te$_2$)]		315.6(1) (av.)	3	8	[242]

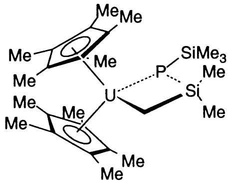
by the inequivalence of the silyl groups in the NMR spectra of the $[Cp^*_2An(X)\{P(SiMe_3)_2\}]$ complexes.

Thermal decomposition of $[Cp^*_2An(Me)\{P(SiMe_3)_2\}]$ resulted in elimination of methane and the formation of a phosphasilametalacyclobutane: $[Cp^*_2An\{\eta^2CH_2SiMe_2P(SiMe_3)\}]$ (An = Th, U [XR]). A thermodynamic analysis of this reaction has been made [116].





$ML_n = Ni(CO)_2, Pt(PMe_3)$



The environment around the P atoms of all structurally described compounds is pyramidal so there is no multiple bond character in the P–An bond [115,116].

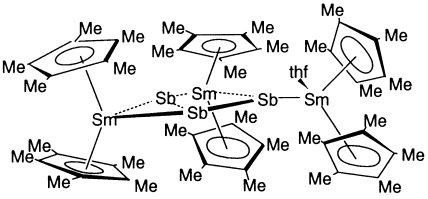
The phosphorus lone pairs on the phosphide ligands are available for complexation with other metals: reaction of $[Cp^*_2Th(PPh_2)_2]$ with $[Ni(COD)_2]$ and CO, or with $[Pt(COD)_2]$ and PMe_3, respectively, afforded $[Cp^*_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2]$ [XR] [117] and $[Cp^*_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)]$ [XR] [118]. The structure of these heterobimetallic complexes display short Th–M distances (Th–Ni = 320.6 pm, Th–Pt = 298.4 pm). In the platinum case, this very short value together with ^{31}P NMR data provide evidence for a direct Th–Pt bond in $[Cp^*_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)]$. Ab initio calculations suggest that this bond (which is the HOMO) is constituted by axial overlap of $6d(x^2-y^2)$ and $5d(x^2-y^2)$ orbitals, respectively, on thorium and platinum [118].

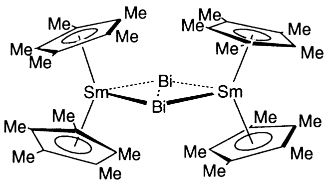
3.3. Phosphinidene and polyphosphides, antimonides and bismuthides

Compounds in this group consist of organometallic complexes with ligands bearing less than two substituents for each group 15 atom, or more than one formal charge. These are complexes with a phosphinidene (RP) ligand, or polyphosphides, antimonides and bismuthides $(E)_n$ ligands.

3.3.1. Lanthanide complexes

When Cp^*_2Sm was reacted with Sb^nBu_3, reductive cleavage of all Sb–C bonds occurred with the formation of a so-called Zintl ion (Sb_3^{3-}) stabilized by three Cp^*_2Sm units. Crystals of $[(Cp^*_2Sm)_3(\mu{:}\eta^2,\eta^2,\eta^1\text{-}Sb_3)(thf)]$ [XR] were thus obtained [128]. Although Cp^*_2Sm also reacted with $SbPh_3$, no products other than $[Cp^*_2SmPh]$ could be identified [50].

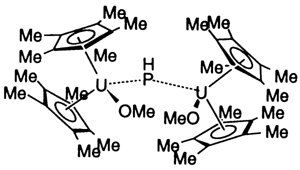


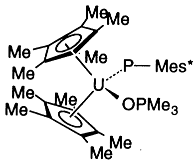


When the same reaction was performed with $BiPh_3$, reductive cleavage of Bi–C bonds also occurred and $[(Cp_2^*Sm)_2(\mu:\eta^2,\eta^2\text{-}Bi_2)]$ [XR] was formed; with the optimum stoichiometry of 4:1 Sm:Bi, only $[Cp_2^*SmPh]$ is formed as a side product, otherwise the reaction is much less clean and diphenyl is also formed. The Bi–Bi distance in the Bi_2^{2-} unit is not especially short and, thus, no definitive conclusion can be drawn with regard to the possible multiple bond character between the Bi atoms [129].

3.3.2. *Actinide complexes*

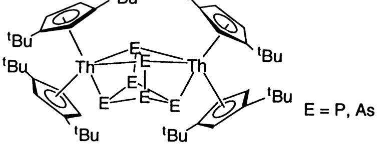
Reaction of the dihydrides $[Cp_2^*AnH_2]$ (An = Th, U) with $P(OMe)_3$ did not yield a phosphite adduct, but cleavage of the P–O bond occurred with simultaneous formation of $[Cp_2^*An(OMe)_2]$ and of the phosphinidene bridged $[\{Cp_2^*An(OMe)\}_2(\mu\text{-}PH)]$ (An = Th, U [XR]). Although the proton on phosphorus was not located on the X-ray structure of the U complex, it was detected in the NMR spectrum of the Th complex. Chemical evidence was provided by the reaction of $[\{Cp_2^*An(OMe)\}_2(\mu\text{-}PH)]$ with D_2O which yielded PD_2H [120].

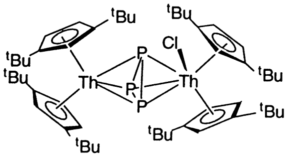




A monomeric phosphinidene complex: $[Cp_2^*U(PMes^*)(OPMe_3)]$ [XR] was obtained when $[Cp_2^*U(Me)(Cl)]$ reacted with KPHMes* in the presence of $OPMe_3$ after α-elimination of methane. No clean products were obtained in the absence of $OPMe_3$. It is quite clear from the very short U–P bond length (256.2 pm, see Table 1) that a P = U double bond is present in this compound. Reaction of $MesPH_2$ with two *ansa*-dimethyluranocenes gave phosphinidene dimers (by MW determination in solution) $[\{[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^5\text{-}C_5R_4)]U(\mu\text{-}PMes^*)\}_2]$ (R = H, Me) [121].

The reaction of $[(^tBu_2Cp)_2Th(\eta^4\text{-}C_4H_6)]$ with P_4 or As_4 afforded a hexapnictide complex: $[\{(^tBu_2Cp)_2Th\}_2(\mu:\eta^3,\eta^3\text{-}E_6)]$ ([XR]: E = P [119], As [127]). When the reaction with P_4 was performed in the presence of magnesium chloride, a triphosphide complex $[(^tBu_2Cp)_2Th(\mu:\eta^3\text{-}P_3)Th(Cl)(^tBu_2Cp)_2]$ [XR] was obtained instead. The cyclo-P_3 unit is freely rotating between the two $(^tBu_2Cp)_2Th$ units at room temperature and this rotation is blocked at 193 K.



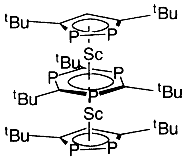


3.4. Phospholyl, arsolyl, and other phosphorus containing π-ligands

Selected compounds in this section include complexes of group 3 metals with heterocyclic phosphorus- or arsenic-containing π-ligands. They consist of π-phospholyl or π-arsolyl complexes (analogs of π-cyclopentadienyl complexes) in which the formal negative charge is delocalized in the ring; however, there is one example of a σ-phospholyl complex which will also be included in this section. In addition, two neutral phospha- or triphosphabenzene complexes are also listed here because, although bearing no formal charge on the ligand, they are π-complexed with the group 3 metal.

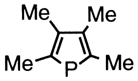
3.4.1. Scandium complex

Reaction of vaporized Sc atoms with ^{t}BuC$\equiv$P gave a formal 22-electron paramagnetic Sc(I) triple-decker complex with two π-1,2,4-triphosphacyclopentadienyl ligands and one π-1,3,5-triphosphabenzene ligand: $[\{(\eta^5\text{-}P_3C_2{}^tBu_2)Sc\}_2(\mu\text{:}\eta^6,\eta^6\text{-}P_3C_3{}^tBu_3)]$ [XR] [104].

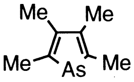


3.4.2. Yttrium and lanthanide complexes

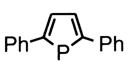
Two methods for the synthesis of divalent bis(phospholyl) complexes can be used: (a) the metathetical reaction of a phospholyl or arsolyl anion with a lanthanide diiodide; and (b) the insertion of a lanthanide metal (usually activated with $HgCl_2$) into the E–E bond of a biphospholyl or biarsolyl.



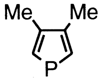
Tmp



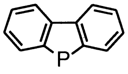
Tmas



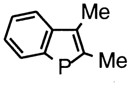
Dpp



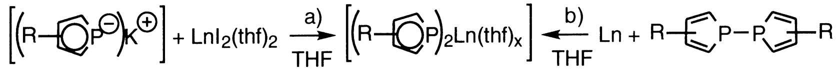
Dmp



Dbp



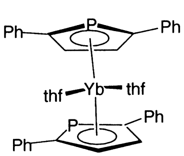
Bdmp

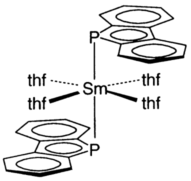


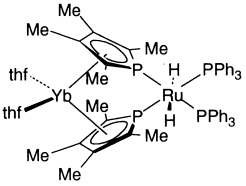
Method	Compound	Ref.
a,b	$[(Tmp)_2Ln(thf)_2]$ (Ln = Yb, Sm)	[244,111]
a,b	$[(Tmas)_2Ln(thf)_2]$ (Ln = Yb, Sm)	[111]
b	$[(Dpp)_2Ln(thf)_2]$ (Ln = Yb [XR], Sm)	[111]
a	$[(Bdmp)_2Sm(thf)_2]$ [XR]	[107]
b	$[(Dbp)_2Sm(thf)_4]$ [XR]	[107]

The THF ligand in [$(Tmp)_2Ln(thf)_2$] and [$(Tmas)_2Ln(thf)_2$] can easily be eliminated by extraction with toluene or vacuum pumping. The resulting [$(Tmp)_2Ln$] and [$(Tmas)_2Ln$] are insoluble in all non-coordinating solvents and their structure is unknown [244, 111]. However, unsolvated [$(Tmp)_2Yb$] could react in toluene with the stable nucleophilic carbene *N*,*N*-diisopropyl-2,3-dimethylimidazolylidene (Carb) to give the adduct [$(Tmp)_2Yb(Carb)$] [245].

In [$(Dpp)_2Yb(thf)_2$], the THF ligand is more tightly held. Its X-ray structure reveals η^5 bonding of the phospholyl ligand to Yb [111]. Although annelation of a benzo ring in the Bdmp ligand reduces the electronic density on the phospholyl ring, this ligand is still η^5-bonded to Sm in [$(Bdmp)_2Sm(thf)_2$], whereas the phospholyl ring no longer acts as a π-ligand when two benzo rings are annelated, and in [$(Dbp)_2Sm(thf)_4$], the phospholyl ligand is only η^1-bonded to Sm [107].



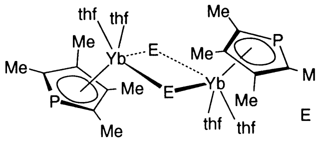




^{171}Yb satellites are clearly seen in the ^{31}P NMR spectra of [$(Dpp)_2Yb(thf)_2$] and of [{$Tmp)_2Yb(thf)_2$]. In addition, the triplet structure of the ^{171}Yb NMR spectrum of [$(Tmp)_2Yb(thf)_2$] confirms the presence of two Tmp ligands around Yb in solution [111].

Because the phosphorus atom in the phospholyl ligand still possesses a lone pair of electrons, σ–π bonding of this ligand is possible. Consequently, the reaction of [$(Tmp)_2Yb(L)$] with $(Ph_3P)_2RuH_4$ afforded the Ru–Yb heterobimetallic [$(L)Yb(\mu{:}\eta^5,\eta^1\text{-}Tmp)_2Ru\{$*trans*-$(H)_2\}(Ph_3P)_2$] ($L=(thf)_2$ [XR] [112], Carb [245]) where [$(Tmp)_2Yb(L)$] acts as a chelating ligand on Ru. The Ru–Yb distance of 425 pm precludes any bonding interaction between the two metals. These complexes are not very stable and decompose in solution over time or upon heating into mixtures of compounds among which a product of phospholyl transfer to ruthenium: [$(Tmp)Ru(H)(PPh_3)_2$] has been detected [245].

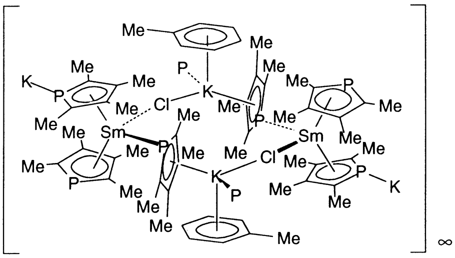
Insertion of Yb metal into the P–Cl bond of TmpCl gave the chloro-bridged Yb(II) dimer [$\{(\eta^5\text{-}Tmp)Yb(\mu\text{-}Cl)(thf)_2\}_2$] [XR] after an induction period during which the biphospholyl $(Tmp)_2$ could be detected in the reaction mixture. The dimer could also be obtained by comproportionation of [$(Tmp)_2Yb(thf)_2$] with $YbCl_2$. No induction period was necessary in the reaction of Yb with TmpSPh which gave [$\{(\eta^5\text{-}Tmp)Yb(\mu\text{-}SPh)(thf)_2\}_2$] [XR]; this μ-thiolato complex was also obtained by reaction of the chloro-bridged dimer with NaSPh [113].

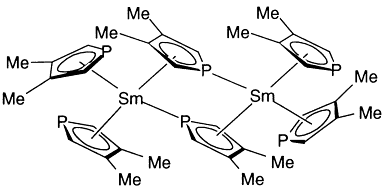


E = Cl, SPh

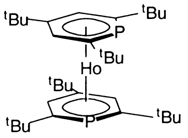
Reaction of TmpLi with YCl_3 and $LuCl_3$ in a 2:1 ratio afforded Ln(III) ate-complexes: $[(\eta^5\text{-Tmp})_2Y(\mu\text{-Cl})_2Li(dme)_2]$ and $[(\eta^5\text{-Tmp})_2Lu(\mu\text{-Cl})_2Li(Et_2O)_2]$, respectively. In the ^{31}P and ^{89}Y NMR spectra of the Y complex, the value of the $^1J_{PY}$ coupling constant, smaller than that found for σ-phosphine Y complexes [11] has been taken as evidence for π-complexation of Tmp to Y[246].

Tris(phospholyl) complexes can also be obtained: the reaction of DmpK with $SmCl_3$ in toluene in a 3:1 ratio gave a σ–π bridged dimer: $[\{(\eta^5\text{-Dmp})_2(\mu\text{:}\eta^5,\eta^1\text{-Dmp})Sm\}_2]$ [XR], but in the same conditions with the more bulky Tmp ligand, an adduct TmpK with $[Tmp_2SmCl]$: $[\{[(\eta^5\text{-Tmp})Sm(\mu\text{:}\eta^5,\eta^1\text{-Tmp})(\mu\text{:}\eta^1,\eta^5\text{-Tmp})(\mu\text{-Cl})K(\eta^6\text{-toluene})]_2\}_\infty]$ [XR] was obtained. Elimination of KCl from this adduct (which would have yielded $[Tmp_3Sm]$) could not be achieved, even under forcing conditions [108].





Finally, reaction of 2,4,6-tri-^{t}butylphosphabenzene with vapourized Ho atoms gave a sandwich complex of Ho(0): $[(\eta^6\text{-PC}_5H_2{}^tBu_3\text{-2,4,6})_2Ho]$ [XR] [247].



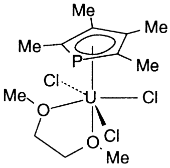
3.4.3. Actinide complexes

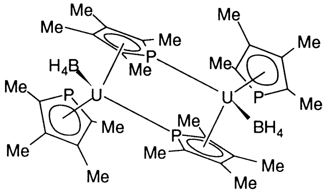
Reaction of KTmp with various U(IV) precursors can give, depending on the conditions used, neutral mono-, bis- or trisphospholyl complexes.

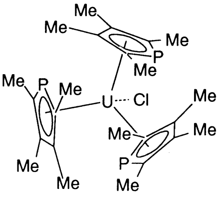
$$[L_nUX_p]+q(\text{TmpK})\rightarrow[L_nUX_{p-q}(\text{Tmp})_q]+q(\text{KX}).$$

Starting material	**Products**
$[UCl_4]$	$[(Tmp)_2UCl_2]$, $[(Tmp)UCl_3(dme)]$ [XR] [122] $[(Tmp)_3UCl]$ [XR] [123]
$[U(BH_4)_4]$	$[(Tmp)U(BH_4)_3]$ [248], $[(Tmp)_2U(BH_4)_2]$ [XR] [124]
$[Cp^*U(BH_4)_3]$	$[Cp^*(Tmp)U(BH_4)_2]$ [122]

Uranium(III) ate-complexes, e.g. $[\{(Tmp)U(BH_4)_3\}(K)]$ [248] and $[\{(Tmp)_2U(BH_4)_2\}(K)]$ were obtained when KTmp was reacted in THF with the U(III) precursor $[U(BH_4)_3(\eta\text{-mesitylene})]$ [124]. These complexes (as sodium salts) could also be made from sodium amalgam reduction of the corresponding U(IV) compounds in THF. Treatment of [(L)(Tmp)U(BH$_4$)$_2$] by sodium amalgam in toluene, however, gave neutral U(III) phospholyl-bridged dimers: [{(η^5-L)(μ:η^5,η^1-Tmp)U(BH$_4$)}$_2$] (L = Tmp [XR], Cp* [125]); [{(η^5-Tmp)(μ:η^5,η^1-Tmp)U(BH$_4$)}$_2$] was also obtained by treatment of [{(Tmp)$_2$U(BH$_4$)$_2$}(K)] with toluene and simultaneous precipitation of KBH$_4$ [124]. There is a dynamic equilibrium between the *meso* and *dl* isomers of the phospholyl-bridged dimers in toluene solution, as shown by ^{31}P NMR (the signals of the P atoms σ-bonded to uranium are extremely deshielded, approximately 3500–3900 ppm) [248,125]. Treatment of these dimers with Lewis bases gave neutral adducts, e.g. [(Tmp)$_2$U(BH$_4$)(OPPh$_3$)] [124].







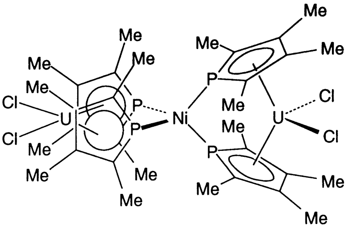
Substituents could easily be introduced at uranium in the mono-, bis- and tris-phospholyluranium compounds [122,123].

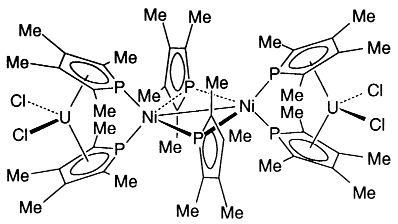
$$[\mathrm{L}_n\mathrm{UX}_p(\mathrm{Tmp})_q]+p[\mathrm{RM}]\rightarrow[\mathrm{L}_n\mathrm{UR}_p(\mathrm{Tmp})_q]+p(\mathrm{MX}).$$

Starting material	**RM**	**Products**
[(Tmp)UCl$_3$(dme)]	RLi	[(Tmp)U(CH$_2$Ph)$_3$(dme)]
[(Tmp)$_2$U(BH$_4$)$_2$]	RONa	[(Tmp)$_2$U(OR)$_2$] (R = Et, ^{i}Pr, ^{t}Bu)
[(Tmp)$_2$U(BH$_4$)$_2$]	RLi	[(Tmp)$_2$UMe$_2$], [(Tmp)$_2$U(CH$_2$SiMe$_3$)$_2$]
[(Tmp)(Cp*)U(BH$_4$)$_2$]	RLi	[(Tmp)(Cp*)UMe$_2$], [(Tmp)(Cp*)U(CH$_2$SiMe$_3$)$_2$]
[(Tmp)$_3$UCl]	MeLi	[(Tmp)$_3$UMe]
[(Tmp)$_3$UCl]	KBEt$_3$H	[(Tmp)$_3$UH]
[(Tmp)$_3$UCl]	^{i}PrONa	[(Tmp)$_2$U(O^{i}Pr)$_2$]

Reduction of [(Tmp)$_2$UR$_2$] (R = Me, CH$_2$SiMe$_3$) with H$_2$ in the presence of DMPE leads to the dmpe-stabilized U(III) hydride [(Tmp)$_2$U(H)(dmpe)] analogous to the known [Cp$^*_2$U(H)(dmpe)]. The ^{1}H NMR resonances of the U-bonded protons were respectively found at 856 ppm (Tmp compound) and 808 ppm (Cp* compound). The following pieces of evidence for the weaker electron-donating ability of the Tmp ligand relatively to that of the Cp* ligand have been put forward: (a) the redox potentials (versus ferrocene/ferocinium) of [(Cp*)$_n$(Tmp)$_{2-n}$U(BH$_4$)$_2$] that vary from -1.49 V ($n=0$) to -1.66 V ($n=1$) and -1.83 V ($n=2$); (b) the fact that only the Tmp complex is reduced when an equimolecular mixture of [(Tmp)$_2$U(BH$_4$)$_2$] and [Cp$^*_2$U(BH$_4$)$_2$] is reacted with 0.5 equivalent of Na/Hg [122].

The U–Ni heterobimetallics [{Cl$_2$U(μ:η^5,η^1-Tmp)}$_2$Ni] and [{Cl$_2$U(μ:η^5,η^1-Tmp)Ni(μ-Tmp)}$_2$], in which the [(Tmp)$_2$UCl$_2$] moiety acts as a chelating ligand on Ni, have been structurally described [126].





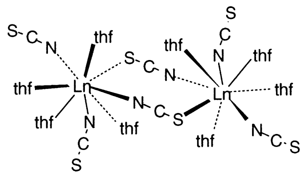
4. Sulphur, selenium and tellurium-based ligands.

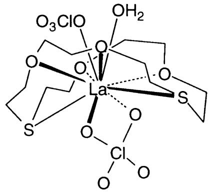
As for the group 15 elements, the chalcogen-based ligands are classified according to the formal charge on the heteroatom. Uncharged ligands are represented by the thioethers: (R–S–R) (and a related thiometallate: M–S–M) and thioketones: ($R_2C{=}S$). There are also a few examples of negatively charged α-amidophosphine sulphides or selenides: $[(E{=}PR_2)_2N]^-$ (E = S, Se) where the charge will be considered as mostly residing on the nitrogen atom. Singly charged ligands include the organic chalcogenolates: $(RE)^-$, a recent and expanding class of compounds, while multiply charged ligands comprise the mono- and polychalcogenides: $(E_n)^{2-}$. An additional class of ligands is constituted by sulphur or selenium-substituted anions of carboxylic, carbonic, phosphoric or phosphoric acids ligands where the formal negative charge is delocalized on two heteroatoms: $[E{\cdots}X{\cdots}Z]^-$ (E = S, Se; X = CR, PR_2; Z = heteroatom).

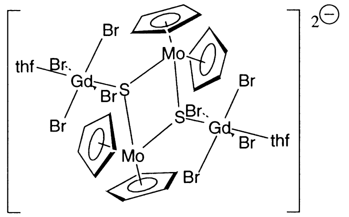
4.1. Thioethers, thioketones, phosphine sulphides and selenides

4.1.1. Lanthanum and lanthanide complexes

Adducts between lanthanide perchlorates and macrocyclic di-, tetra- or hexathioethers (sulphur-substituted derivatives of [18-crown-6]) have been obtained in polar aprotic solvents (CH_3CN or CH_2Cl_2). With the dithio ligand (18-C-6-S_2), the following compounds have been isolated: the unsolvated [(18-C-6-S_2)Nd(ClO_4)$_3$], the water-solvated [(18-C-6-S_2)Ln(ClO_4)$_3$(H_2O)] (Ln = La, Ce, Pr) and the water and acetonitrile-solvated [(18-C-6-S_2)Ln(ClO_4)$_3$(H_2O)(MeCN)$_x$] (Ln = Ce, Pr, Nd, Sm, Eu, Ho, Yb) ($x = 1.5$ or 2). With the tetrathio ligand (18-C-6-S_4) and the hexathio ligand (18-C-6-S_6), [(18-C-6-S_4)Eu(ClO_4)$_3$(H_2O)] and [(18-C-6-S_6)Ln (ClO_4)$_3$(H_2O)] (Ln = Sm, Eu, Yb) have been obtained, respectively. The X-ray structure of the lanthanum hydrate is that of [{La(η^6-18-C-6-S_2) (η^1-ClO_4)(η^2-ClO_4)(H_2O)}(ClO_4)] in which the 10-coordinate La atom is bonded with all heteroatoms of the macrocycle, two perchlorates (one η^1 and one η^2) and one water molecule in a decatetrahedral arrangement. The Eu, Yb and Sm compounds display S to metal CT bands in all compounds, which is indicative of metal–sulphur bonds also in the 18-C-6-S_4 and 18-C-6-S_6 complexes. All compounds are hygroscopic [130].



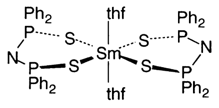


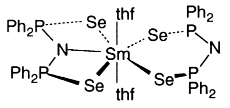


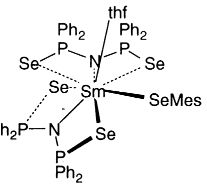
Thf-solvated lanthanide thiocyanates [{Ln(SCN)$_2$(μ-SCN)(thf)$_4$]$_2$] (Ln = Gd, [RX]: Ln = Nd, Eu and Er) are solid-state dimers with two bridging thiocyanate ligands. The large values of the S–Ln distances indicate a weak bond, and are remarkable because the variation is in reverse order than expected (increasing bond distance from Nd to Er). Steric factors might be responsible for this unusual phenomenon [150].

The reaction of $Cp_2Mo(S)(Li)$ with $GdBr_3$ did not lead to substitution of the Br atoms on gadolinium, but to the formation of an anionic complex: [{(thf)$_4$Li}$_2${(thf)$_2$Gd$_2$Br$_8$(μ-S$_2$Mo$_2$Cp$_4$)}] [RX] which is an adduct of two $GdBr_4^-$ anions with one $S_2Mo_2Cp_4$ unit acting as a μ-ligand [175].

The bis(thiophosphino)amide [S = P(Ph)$_2$-N-P(Ph)$_2$ = S] (SPNPS) is η^2-bonded to Sm(II) by the two S atoms (and not the amido group) in [(thf)$_2$Sm(η^2-SPNPS)$_2$], whereas one bis(selenophosphino)amide is η^2-bonded to Sm(II) and one η^3-bonded (also by the amido group) in [(thf)$_2$Sm(η^2-SePNPSe)(η^3-SePNPSe)]. Both compounds were made by reaction of K(EPNPE) (E = S, Se) with SmI_2. Oxidation of the Se compound with PhSeSePh or MesSeSeMes afforded the Sm(III) complexes: [(thf)Sm(η^3-SePNPSe)$_2$(SeR)] (R = Ph, Mes). All these complexes were characterized by X-ray [157].



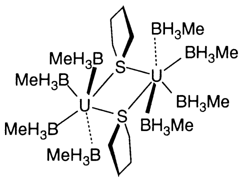


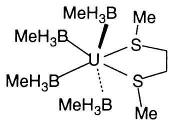


Only one organometallic lanthanide thioether complex has been reported. Protonation of [Cp^*_2CeCH(SiMe$_3$)$_2$] with HEt_3NBPh_4 in neat tetrahydrothiophene (THT) or THF solution gives the cationic complexes: [Cp^*_2Ce(tht)$_2$(BPh$_4$)] [XR] and [Cp^*_2Ce(thf)$_2$(BPh$_4$)], respectively. The THT ligand is more labile than THF: dissolution of [Cp^*_2Ce(tht)$_2$(BPh$_4$)] in THF results in quantitative formation of the THF adduct, and a reaction occurs between [Cp^*_2Ce(tht)$_2$(BPh$_4$)] and ^{t}BuC≡CH while in the same conditions, [Cp^*_2Ce(thf)$_2$(BPh$_4$)] does not react [141].

4.1.2. Actinide complexes

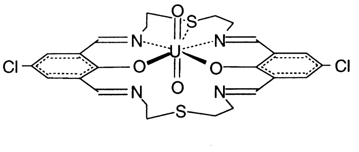
Thioether adducts of [U(BH$_3$CH$_3$)$_4$] have been prepared. With tetrahydrothiophene, a dimer was obtained: [{U(BH$_3$CH$_3$)$_4$(μ-tht)}$_2$] [XR]. NMR suggests that this structure is retained in solution below −90 °C [193]. With a bidentate ligand such as 1,2-bis(methylthio)ethane (BMTE) a monomeric distorted octahedral complex was obtained: [U(BH_3CH_3)$_4$(bmte)] [XR]. Ligand-exchange studies with other bidentate ligands indicate the following order of affinity for the U(BH_3CH_3)$_4$ moiety: dmpe > tmeda > bmte > dme; like for some other U(III) complexes, the phosphine adduct is more strongly bonded than the other heteroatom-based ligands [194].

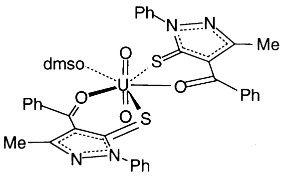


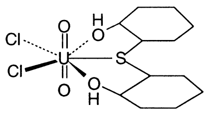


Several thioether complexes are pentagonal bipyramidal uranyl complexes with a pentadentate ligand constituted of two *o*-iminophenolate groups tethered by one -(CH_2)$_2$-S-(CH_2)$_2$- chain. The strong bonding of the axial uranyl with the *o*-iminophenolate fragments, which occupy four coordination sites in the equatorial plane, brings the connected sulphur atom in the fifth coordination site of this plane so that S–U bonding is somehow enforced. Two crystal structures have been published: the *N*,*N′*-bis (salicylidene) 1,5-diamino-3-thiapentane-dioxouranium [{C_6H_4(O)(NCH_2CH_2S)}$_2$(UO_2)] [195], and a tetrasubstitited derivative: [{4-ClC_6H_2[CH(OEt)$_2$](O)(NCH_2CH_2S)}$_2$(UO_2)] [196]. A macrocyclic version of this ligand exists where two *o*,*o′*-bis(imino)phenolate groups are linked by two -(CH_2)$_2$-S(CH_2)$_2$- chains, and an X-ray structure the an uranyl complex: [{4-ClC_6H_2(O)[NCH_2CH_2S]$_2$]$_2$(UO_2)] is also available [197,249]. Heterobimetallic uranyl-nickel and uranyl–copper compounds [{4-ClC_6H_2(CHO)(μ-O)(NCH_2CH_2S)}$_2$(UO_2)MCl_2] (M = Ni, Cu) have been also prepared. The second metal is believed to be tetracoordinated by the phenoxides now acting as μ-alkoxy ligands and the two *o*-aldehyde groups. No structural data are available for these compounds, however [250].

Complexation of the uranyl group with 4-benzoyl-2,4-dihydro-5-methyl-2phenyl-3H-pyrazol-3-thione (Hbmppt) can give, in a neutral medium, a simple adduct of uranyl nitrate: [UO_2(Hbmppt)(NO_3)$_2$] [XR], or, in basic medium, a salt of the delocalized pyrazol-3-thione anion: [UO_2(bmppt)$_2$(dmso)] [XR]. There is no significant variation of the U–S bond in both compounds [198].







The structure of an uranyl adduct of the tridentate bis(2-hydroxycyclohexyl) sulphide (bhcs): [UO_2Cl_2(bhcs)] has also been described [199]. A tetrakis(thiohydroxamato)Th(IV) complex has been briefly mentioned [251].

The organometallic adduct [(MeCp)$_3$U(tht)] [XR] was obtained by a ligand exchange reaction of $[(MeCp)_3U(thf)]$ with THT [200]. The affinity of $[(MeCp)_3U]$ for THF or THT is similar [252].

4.2. Thiolates, selenolates and tellurolates

The study of group 3 chalcogenolates is currently a very active area. Apart from the seminal study of Gilman [253] on the preparation of thiolates $U(SR)_4$, almost all studies on this subject appeared in the past 10 years and most of them in the past 5 years. Interest in this area has been in part stimulated by the value of solid M_xE_y binary materials that are accessible from controlled pyrolysis of inorganic or organometallic chalcogenolates [254].

4.2.1. Scandium complexes

Only substituted cyclopentadienyl scandium selenolates and tellurolates have been described so far. Insertion of elemental Se or Te into the metal–carbon σ-bond of $[Cp^*_2ScR]$ gave the corresponding selenolates and tellurolates $[Cp^*_2Sc(ER)]$ [238,223] (E = Te, R = CH_2SiMe_3, CH_2Ph [XR], $CH_2CH(D)(CH_2)_2{=}CMe_2$, $CH_2(C\text{-}C_5H_{11})$, Ph); E = Se, R = CH_2SiMe_3). Bu_3PTe could also be used as the Te source and the reaction was then more rapid, but possibly less convenient, since the Bu_3P byproduct can interfere in the purification process. Mechanistic studies with deuterated analogs have established that insertion of tellurium into the C–Sc bond proceeds with retention of configuration [223,255].

The ansa-scandocene tellurolate $[\{(\eta^5\text{-}3\text{-}{}^tBuC_5H_3)_2SiMe_2\}Sc(TeCH_2SiMe_3)]$ has likewise been obtained from $[\{(\eta^5\text{-}3\text{-}{}^tBuC_5H_3)_2SiMe_2\}Sc(CH_2SiMe_3)]$ and Te; A 1:1 adduct of this complex with PMe_3 could also be observed by NMR [105].

Thermolysis or photolysis of the above-described tellurolates produced μ-tellurido species that will be discussed in Section 4.3.1.

4.2.2. Yttrium, lanthanum and the lanthanides

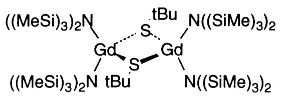
4.2.2.1. Inorganic complexes. The chemistry of this class of compounds is very rich. Both divalent (for Sm, Eu and Yb) and trivalent compounds have been characterized. The substituent R on the chalcogenolate ER^- can be alkyl or aryl (^{n}Bu, ^{t}Bu or Ph), bulky (Mes, Ar^{iPr} ($Ar^{iPr} = 2,4,6\text{-}{}^iPr_3C_6H_2$), Mes* and $Si(SiMe_3)_3$), or chelating.

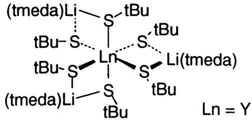
In an early report the synthesis of $(BuE)_2Yb$ (E = S, Se) and of $(BuSe)_3Ln$ (Ln = Pr, Sm) from the corresponding bis(trimethylsilyl)amides and BuEH was described, but the products were only characterized by microanalysis [256].

The first structurally characterized compound in this class was the t-butylthio bridged dimeric $[\{(Me_3Si)_2N\}_2Gd(\mu\text{-}S^tBu)\}_2]$ made by reaction of $[\{(Me_3Si)_2N\}_2Gd(\mu\text{-}Cl)\}_2]$ with ^{t}BuLi. The analogous Eu and Y thiolates could also be made similarly [176].

When an excess of ^{t}BuLi is reacted with $YbCl_3$ or with $LnI_2(thf)_2$ (Ln = Yb or Sm) in the presence of TMEDA, trivalent ate-complexes $[\{Li(tmeda)\}_3Ln(\mu\text{-}S^tBu)_6]$

(Ln = Yb, Sm) are obtained and the isomorphous structures were characterized by X-ray as homoleptic six-coordinated octahedral complexes [158].

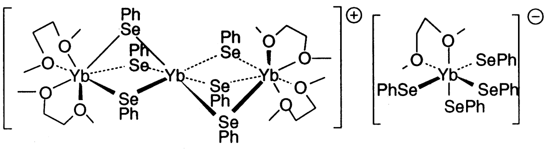


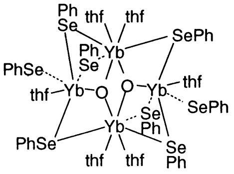


Ln = Yb, Sm

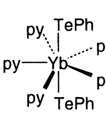
The earliest report on lanthanide thiolates describes the synthesis of trivalent arenethiolates $[Ln(SR)_3]$ by the acid–base reaction of $[Ln(O^iPr)_3]$ with RSH in refluxing benzene (Ln = Pr, Nd, Sm; R = 4-ClC_6H_4, 4-$^tBuC_6H_4$, 2-Me-4-$^tBuC_6H_3$). In some cases, mixed alkoxy/thiolato compounds of type $[Ln(O^iPr)_2(SR)]$ or $[Ln(O^iPr)(SR)_2]$ could also be isolated. IR spectra of the complexes were reported [257]. Since then, lanthanide arenethiolates have been the subject of intensive research.

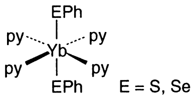
The outcome of the reactions of Yb metal with one equivalent of PhEEPh appears to be strongly dependent on the reaction conditions. Reaction of Yb with PhSeSePh in THF only solvent yielded the monomeric Yb(III) compound $[(thf)_3Yb(SePh)_3]$ [XR]; in a THF/toluene mixture, the bis (μ_3-oxo) Yb(III) polynuclear species $[(thf)_6Yb_4(SePh)_2(\mu\text{-}SePh)_6(\mu_3\text{-}O)_2]$ [XR] was isolated; and in DME solution, an ion pair: $[\{Yb[\mu\text{-}SePh)_3Yb(dme)_2]_2\}\{(dme)Yb(SePh)_4\}]$ [XR] was recovered. In this compound, the trimetallic cation possesses two Yb(II) and one Yb(III) atoms, whereas the anion is a ytterbate(III). The origin of oxygen in the μ-oxo compound or the reason for oxidation to Yb(III) are unknown [232].

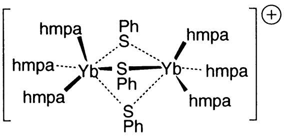




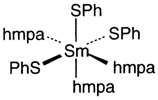
Reactions of Yb/Hg amalgam with one equivalent of PhEEPh in THF gave products that could be crystallized on addition of pyridine (E = S, Se) as divalent $[(py)_4Yb(SPh)_2]$ and $[(py)_4Yb(SePh)_2]$, while the reaction of $YbCl_3$ with NaTePh occurs with reduction to give the Yb(II) complex $\{(py)_5Yb(TePh)_2]$ and PhTeTePh. These complexes could also be obtained from Yb in liquid NH_3 with PhEEPh. The X-ray structures of the six-coordinated S and Se complexes are octahedral with four pyridines in the equatorial plane, as are the five pyridines in the pentagonal bipyramidal seven-coordinated Te complex. UV-vis spectoscopy suggest that the complexes are oligomeric in solution [181]. $[Sm(SePh)_2]$ prepared by reaction of Sm with PhSeSePh is unstable and decomposes into a Sm cluster that will be discussed in Section 4.3.2.1. [225]. In very similar conditions (lanthanide metals in the presence of catalytic amounts of diiodine + one equivalent PhSSPh), but with the stronger Lewis base HMPA as donor, the divalent cationic complexes $[\{Ln_2(hmpa)_6(\mu\text{-}SPh)_3\}\{SPh\}]$ (Ln = Sm, Eu and Yb) were obtained; the Yb compound has been structurally characterized [159].

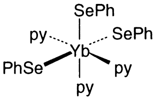


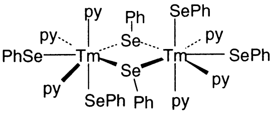




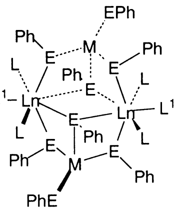
Ln/cat.I_2 or Ln/Hg amalgams can also react with more PhEEPh (1.5 equivalents) to give trivalent compounds such as [$(hmpa)_3Ln(SPh)_3$] (Ln = Sm, Eu and Yb) [159], [{$(py)_3Yb(SPh)_3$] and [$(py)_3Ln(SePh)_3$] [182] (Ln = Ho, Tm, Yb). X-ray crystallography reveals that while the Yb–S complexes [$(py)_3Yb(SPh)_3$], [$(hmpa)_3Yb(SPh)_3$] and [$(hmpa)_3Sm(SPh)_3$] are monomers, the Tm–Se compound is a phenylselenido bridged dimer: [{$(py)_3Tm(SePh)_2(\mu$-SePh)}$_2$]. The Yb complexes display intense LMCT absorption bands. Thermolysis of the Se complexes yielded [HoSe + $HoSe_2$], Yb_2Se_3 and Tm_2Se_3, respectively [182].



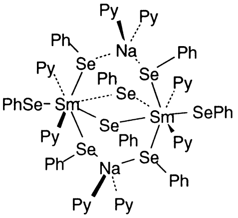


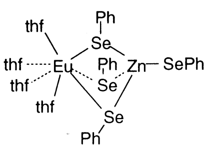


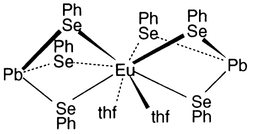
Reactions of Sm/Hg or Eu/Hg amalgams with two equivalents or more of PhEEPh (E = S, Se) had a different outcome than above: Hg atoms were now incorporated into an Eu(II)–Hg(II) cluster: [{$(L)_3Eu(\mu_2$-EPh$)_2(\mu_3$-EPh)Hg(EPh)}$_2$] (E = Se, L = THF [226] or py [227]; E = S, L = py [170]) and in a Sm(III)–Hg(II) cluster of similar structure: [{$(thf)_2$(SePh)Sm$(\mu_2$-SePh$)_2(\mu_3$-SePh)Hg(SePh)}$_2$] [226]. When the oxidation of PhSeSePh with Eu/Hg was performed in the presence of lead metal, this metal was also incorporated in an Eu/Pb bimetallic species: [$(thf)_2$Eu{$(\mu$-SePh$)_3$Pb}$_2$] [171]. Trans-metalation reactions of europium clusters are possible: redox displacement of Hg in [($(L)_3Eu(\mu_2$-SPh$)_2(\mu_3$-SPh)Hg(SPh)}$_2$] by the more electropositive Zn or Cd gave [{$(L)_3Eu(\mu_2$-SPh$)_2(\mu_3$-SPh)M(SPh)}$_2$] (M = Cd: L = py; M = Zn: L = thf) without modification of the structure [170], whereas reaction of Zn with [{$(py)_3Eu(\mu_2$SePh$)_2(\mu_3$-SePh)Hg(SePh)}$_2$] yielded an Eu(II)–Zn(II) cluster of different structure: [$(thf)_4Eu(\mu_2$-SePh$)_3$Zn(SePh)] [227]. Treatment of the Sm–Hg cluster with Zn did not give a Sm–Zn cluster but, not unexpectedly, reduction to Sm(II) occurred instead and the ion pair [{$(thf)_7$Sm} {$Zn_4(\mu$-SePh$)_6$(SePh$)_4$}], in which no Sm–Se bonds are any longer present, was obtained. A similar Yb compound: [{$(thf)_6$Yb}{$Hg_5(\mu$-SePh$)_8$(SePh$)_4$}] could be obtained when Yb was treated with a large excess of PhSeSePh and Hg. Reaction of Sm/Hg with PhSeSePh in the presence of NaSePh afforded a Sm(III) ate-complex: [{$(py)_2$Sm(SePh)$(\mu$-SePh$)_3$Na$(py)_2$}$_2$] with a structure resembling that of the Sm–Hg cluster [227]. All the isolated complexes described in this paragraph have been analysed by X-ray crystallography. Thermolysis of the Eu–Zn–S, Eu–Cd–S and Eu–Hg–S clusters produced [EuS + ZnS], [EuS + CdS] and EuS, respectively [170].



Ln = Eu : L = L^1 = py or thf
M = Hg, Zn or Cd
E = S or Se
Ln = Sm : L = thf, L^1 = PhSe
M = Hg
E = Se

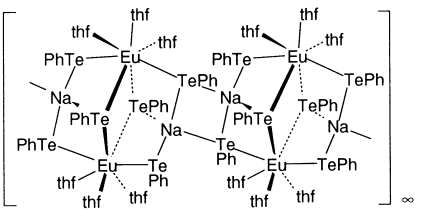


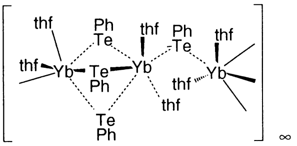




Reaction of LiSePh with $YbCl_3$ gave an octahedral Yb(III) ate-complex: $[(py)_2Yb(SePh)_2(\mu\text{-}SePh)_2Li(py)_2]$ [233], whereas in the reaction of NaSePh with $EuCl_3$, reduction occurred and the neutral divalent one-dimensional polymers $[(thf)_3Eu(\mu\text{-}SePh)_2]_\infty$ and $[(py)_2Eu(\mu\text{-}SePh)_2]_\infty$ were obtained [230].

Reduction also occurred in the reaction of NaTePh with $EuCl_3$, giving, depending on the conditions, the monomeric Eu(II) $[(py)_5Eu(TePh)_2]$, isomorphous with the aforementioned Yb(II) complex, or, with the weaker THF as donor, an anionic infinite 2-dimensional compound $[(thf)_3Eu(\mu_3\text{-}TePh)_2Na(\mu_2\text{-}TePh)]_\infty$. A neutral infinite polymer $[(thf)_2Eu(\mu\text{-}TePh)_2]_\infty$ was obtained when $[(py)_5Eu(TePh)_2]$ was treated with THF. Another convenient route to this complex is by a transmetalation reaction of $Hg(TePh)_2$ with Eu metal; $[(thf)_2Yb(\mu\text{-}TePh)_3Yb(thf)_2(\mu\text{-}TePh)]_\infty$ could be similarly obtained from $Hg(TePh)_2$ and Yb metal [240].





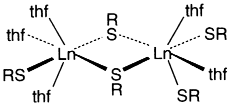
The Yb(II) benzamidinate $[(thf)_2Yb\{PhC(NSiMe_3)_2\}_2]$ was oxidized with PhSeSePh into a six-coordinated Yb(III) complex: $[(thf)Yb\{PhC(NSiMe_3)_2\}_2(SePh)]$ that was characterized by X-ray [183].

Several more bulky, and therefore more soluble and more kinetically stabilized, lanthanide mesitylthiolate, selenolates and tellurolates have also been made. Reaction of LnX_2 with 2KEMes gave $[(thf)_{2\text{-}3}Ln(EMes)_2]$ (Ln = Sm, Eu, Yb, E = Se, Te). Multinuclear NMR studies (^1H, ^{13}C, ^{77}Se, ^{125}Te and ^{171}Yb) of the diamagnetic Yb(II) complexes suggest that they are monomeric in solution. Pyrolysis of $[(thf)_{2\text{-}3}Yb(TeMes)_2]$ gave YbTe [258,259].

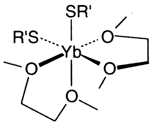
The presence of mesityl on tellurium enabled the synthesis of the spectroscopically characterized Yb(III) benzamidinate $[(thf)Yb(4\text{-}MeOPhC(NMe)_2\}_2(TeMes)]$ from $[(thf)_2Yb\{4\text{-}MeOPhC(NMe)_2\}_2]$ and MesTeTeMes as above. The analogous $[(thf)Yb\{PhC(NMe)_2\}_2(SeMes)]$ was characterized by X-ray [234].

With the even more bulky $Ar^{iPr}S$, soluble THF adducts of divalent lanthanide thiolates were obtained: the reaction of Ln/I_2 with $Ar^{iPr}SSAr^{iPr}$ (one equivalent) gave the crystalline, structurally characterized $[(thf)_3Ln(SAr^{iPr})(\mu-SAr^{iPr})_2]$ (Ln = Eu, Sm). The oily Yb adduct gave the monomeric $[(py)_4Yb(SAr^{iPr})_2]$ on addition of pyridine. With 1.5 equivalent of $Ar^{iPr}SSAr^{iPr}$ with Yb or Sm, the Ln(III) complexes: $[(py)_3Yb(SAr^{iPr})_3]$ [XR] and $[(py)_2(thf)Sm(SAr^{iPr})_3]$ [XR] were obtained in Eu(III) complex could be isolated in these conditions [159,160].

The use of "supermesityl" (2,4,6-$(^tBu)_3C_6H_2$ or Mes*) has also been reported. Thus, the acid–base reaction of Mes*SH with $[(dme)_2Yb\{N(SiMe_3)_2\}_2]$ afforded $[(dme)_nYb(SMes^*)_2$[259,161], and the reaction of Mes*SH with $[Sm\{HC(SiMe_3)_2\}_3]$ yielded the three-coordinate homoleptic $[Sm(SMes^*)_3]$, which was structurally characterized together with $[(dme)_2Yb(SMes^*)_2]$ [161].

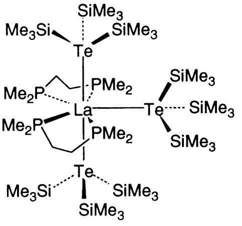


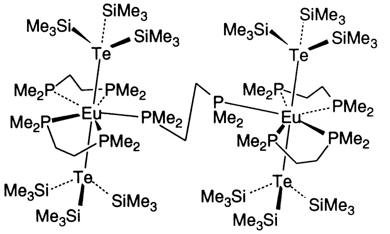
Ln = Eu, Sm
R = 1-(2,4,6-tri*iso*propyl)phenyl



R' = 1-(2,4,6-tri*tertio*butyl)phenyl

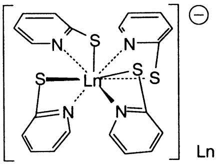
The acid–base-type reaction also yielded the divalent octahedral $[(tmeda)_2Ln(ESi(SiMe_3)_3\}_2]$ (Ln = Sm, Eu, Yb, E = Se, Te [XR]: Yb–Se) from the amides $[Ln\{N(SiMe_3)_2\}_2]$ and the bulky selenols or tellurols $HESi(SiMe_3)_3$. In the presence of excess DMPE, a dimeric seven-coordinate europium compound was obtained: $[\{Eu[ESi(SiMe_3)_3]_2(dmpe)_2\}_2(\mu\text{-dmpe})]$ (E = Te [XR], Se) which has a short Eu–Te bond (319 pm). Thermolysis of the Yb compounds at a relatively low temperature (300 °C) yielded YbSe and YbTe [110].



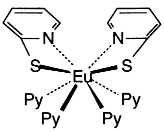


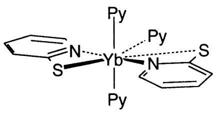
In the trivalent field, the same reaction has been used to prepare the homoleptic tellurolates $[Ln\{TeSi(SiMe_3)_3\}_3]$ that are unstable at room temperature. The La, Y, Ce complexes decompose into μ-tellurido clusters (detailed later in Section 4.3.1), and ultimately into Ln_2Te_3 after thermolysis, while the Eu, Sm, and Yb derivatives cleanly disproportionate into $[Ln\{TeSi(SiMe_3)_3\}_2]$ and $[\{TeSi(SiMe_3)_2\}_2]$. The dmpe adducts $[\{Ln[ESi(SiMe_3)_3]_3(dmpe)_2\}]$ are stable (Ln = Y, La [XR]) and NMR data suggest that the structure of the Y correspond in solution below −50 °C and that of the La compound in the solid-state are the same (trigonal bipyramidal). As for the Se compounds, the homoleptic $[Ln\{SeSi(SiMe_3)_3\}_3]$ (Ln = La, Y) are stable, whereas ^{77}Se NMR indicates a monomeric structure for $[La\{SeSi(SiMe_3)_3\}_3]$ and a dimeric structure for the base-free $[\{Y[SeSi(SiMe_3)_3]_2[\mu\text{-}SeSi(SiMe_3)_3]\}_2]$ in toluene solution. The THF adducts $[Ln\{SeSi(SiMe_3)_3\}_3(thf)_2]$ (Ln = La, Sm, Yb) could also be obtained [106].

The chelating pyridine-2-thiolate ligand (S-2-C_5H_4N[SPy]) has also been used. Transmetalation of $Hg(SPy)_2$ with Eu metal afforded the eight-coordinate divalent $[(py)_4Eu(SPy)_2]$ and $[(bipy)(thf)_2Eu(SPy)_2]$ [XR] [172], whereas the reaction of Yb/Hg with PySSPy afforded the seven-coordinate $[(py)_3Yb(Spy)_2]$ [XR]; further oxidation of this compound with PySSPy gave the eight-coordinated Yb(III) complex: $[(py)_2Yb(SPy)_3]$ [XR] [142]. The reaction of Ln/Hg with PySSPy in the presence of $(PEt_4)(SPy)$ yielded the Ln(III) anionic isomorphous complexes: $[(PEt_4)\{Ln(SPy)_4\}]$ (Ln = Ce [XR], Ho, Tm [142], Eu [XR] [172]); it is to be noted that the SPy ligand, in contrast to the nonchelating thiolates, is able to stabilize Eu(III). Reduction occurs during the thermolysis of $[(PEt_4)\{Eu(SPy)_4\}]$, and EuS (not Eu_2S_3) is obtained [172]. The intense colour of the Eu complexes is due to charge-transfer bands [LMCT for Eu(III), MLCT for Eu(II)], and that of $[(PEt_4)\{Ce(SPy)_4\}]$ is due to $f^1 \rightarrow d^1$ excitation, whereas both MLCT and f→d absorptions are detected in the visible spectrum of $[(py)_3Yb(SPy)_2]$.



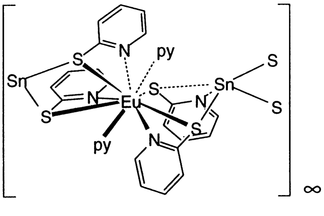
Ln = Ce, Eu





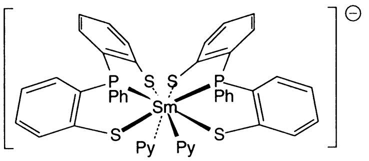
Similar reactions of Ln with PySSPy, but in the presence of 0.5 equivalent of I_2 and the stronger base HMPA, afforded the cationic Ln(III) complexes: $[\{(hmpa)_3Ln(SPy)_2\}(I)]$ (Ln = Pr, Nd, Sm [XR], Er and Yb [XR]) [162].

When Eu/Hg was reacted with PySSPy and tin metal in a 1:3:2 ratio, an infinite polymeric chain: $[(py)_2Eu(\mu{:}\eta^2,\eta^1\text{-}SPy)_3(\mu{:}\eta^1,\eta^2\text{-}SPy)Sn]_\infty$ was obtained [171].



Reaction of the chelating ligand 2-(dimethylaminomethyl)ferrocenthiolato as lithium salt (Me_2NCH_2FcSLi) with $YbCl_3$ afforded the heterobimetallic complexes $[(Me_2NCH_2FcS)_2Yb(Cl)]$ and $[Me_2NCH_2FcS)_3Yb]$ (presumably chelates) which both were characterized by NMR, mass spectroscopy and elemental analysis [260].

The di-2,2′thiotriphenylphosphine H_2S_2TPPH or its 3,3′-bis(trimethylsilyl) analogue $H_2S_2TPPSiMe_3$ reacted with SmI_3 in the presence of NEt_3 acting as a base to give the ion pair $[\{Et_3NH\}\{(py)_2Sm(\eta^3\text{-}S_2TPPR)_2\}]$ (R = H [XR], $SiMe_3$) with both S_2TPPR groups acting as tridentate ligands [109].



The amidobis (selenodiphenylphosphine derivatives: $[\eta^3 SePNPSe)_2 Sm(SeR)(thf)$ [175] have already been discussed in Section 4.1.1.

Finally, lanthanide thiolates have found an application in organic chemistry. Benzophenone-activated ytterbium reacts with disulphides (RSSR) to give $[Yb(SR)_3]$ that were used in situ as sulphenylating reagents: reaction of $[Yb(SR)_3]$ with α-enones gave selectively β-sulphenylketones, i.e. the products of conjugate 1,4-addition [261].

4.2.2.2. Organometallic complexes. All complexes in this class but one are trivalent, the exception being the already mentioned Yb(II) phospholyl complex $[\{(thf)_2(\mu\text{-}SPh)(\mu^5\text{-}C_4Me_4P)Yb\}_2]$ [112]. Most compounds reported are bis(η^5) complexes of the unsubstituted or monosubstituted cyclopentadienyl (Cp or R^1Cp) ligand, of the pentamethylcyclopentadienyl ligand Cp* and a few are η^8-cyclooctatetraenyl (COT) complexes.

Neutral bis-Cp or bis-R^1Cp lanthanide chalcogenolate complexes can be made by protonation of one ligand of $[(R^1Cp)_3Ln]$ with RSH, yielding $[(R^1Cp)_2Ln(SR)]$.

$$[(R^1Cp)_3Ln] + RSH \rightarrow [(R^1Cp)_2Ln(SR)] + [R^1CpH].$$

Starting material	**R**	**Compound**	**Ref.**
$[Cp_3Dy]$	^{n}Pr	$[\{Cp_2Dy(\mu\text{-}S^nPr)\}_2]$	[184]
$[Cp_3Dy]$	^{n}Bu	$[\{Cp_2Dy(\mu\text{-}S^nBu)\}_2]$	[184]
$[Cp_3Yb]$	^{n}Pr	$[\{Cp_2Yb(\mu\text{-}S^nPr)\}_2]$	[184] [XR]
$[Cp_3Yb]$	^{n}Bu	$[\{Cp_2Yb(\mu\text{-}S^nBu)\}_2]$	[184]
$[Cp_3Yb]$	$(2,4,6\text{-}CF_3)_3C_6H_2$ (Ar^F)	$[Cp_2Yb(SAr^F)(thf)]$	[185] [XR]
$[(^tBuCp)_3Ce]^iPr$	$[\{^tBuCp)_2Ce(\mu\text{-}S^iPr)\}_2]$	[143] [XR]	
$[(^tBuCp)_3Ce]$	Ph	$[\{^tBuCp)_2Ce(\mu\text{-}SPh)\}_2]$	[143]
$[(MeCp)_3Ce(thf)]$	^{t}Bu)	$[(MeCp)_2Ce(\mu\text{-}S^tBu)\}_2]$	[143]

All compounds are μ-thiolato bridged dimers except the Yb compound with the bulky SAr^F ligand, which is a mononomer. The dimers undergo chemical exchange in solution: a mixture of $[\{(^tBuCp)_2Ce(\mu\text{-}SPh)]_2]$ and $[\{(^tBuCp)_2Ce(\mu\text{-}S^iPr)\}_2]$ equilibrate into $[(^tBuCp)_4Ce_2(\mu\text{-}SPh)(\mu\text{-}S^iPr)]$, with Keq. = 1 [143]. ^{t}BuSH does not react with $[(^tBuCp)_3Ce]$ presumably for steric reasons. $[\{Cp_2Dy(\mu\text{-}SR)\}_2]$ disproportionates to $[Cp_3Dy(thf)]$ on prolonged refluxing in THF, whereas the less sterically unsaturated $[\{Cp_2Yb(\mu\text{-}SR)\}_2]$ does not [184].

Compounds of this type have also been made by the σ-bond metathesis reaction of $[\{(^tBuCp)_2Ln(\mu\text{-}Me)\}_2]$ with REER and elimination of MeER: $[\{(^tBuCp)_2 Ln(\mu\text{-}EPh)\}_2]$ (Ln = Y, Lu; E = S, Se) were thus obtained. $[\{(^tBuCp)_2 Y(\mu\text{-}SePh)\}_2]$ was structurally characterized [224].

Insertion of tellurium into the Y–Me bond of $[\{({}^t\mathrm{BuCp})_2\mathrm{Y}(\mu\text{-Me})\}_2]$ yielded the light-sensitive $[\{({}^t\mathrm{BuCp})_2\mathrm{Y}(\mu\text{-TeMe})\}_2]$ [262].

The X-ray characterized ate-complexes $[(\eta^5\text{-L})_2\mathrm{Lu}(\mu\text{-ER})_2\mathrm{Li(thf)}_2]$ (L = Cp*, Er = $\mathrm{S}^t\mathrm{Bu}$ [188]; L = Cp, ER = SePh [236]) could be obtained by protonolysis of $[(\eta^5\text{-L})_2\mathrm{Lu}(\mu\text{-Me})_2\mathrm{Li(thf)}_2]$ with REH. In the solid-state structure of the Se compound, the phenyl groups have the unusual syn configuration. Likewise, $[\{\mathrm{(tmeda)Li}\}\{\mathrm{Cp}^*_2\mathrm{Lu}(\mu\text{-S}^t\mathrm{Bu})_2(\mathrm{S}^t\mathrm{Bu})\}]$ could be obtained from $[\{\mathrm{(tmeda)_2Li}\}\{\mathrm{Cp^*Lu(Me)_3}\}]$ and ${}^t\mathrm{BuSH}$ [188].

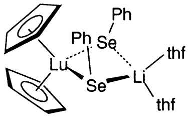
Many of the bis (Cp*) lanthanide chalcogenolates have been made by oxidation of the divalent $[\mathrm{Cp}^*_2\mathrm{Ln}]$ with REER

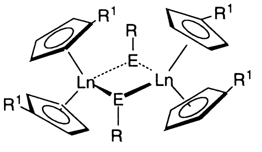
$$2[\mathrm{Cp}^*_2\mathrm{Ln}]+\mathrm{REER}\rightarrow 2[\mathrm{Cp}^*_2\mathrm{Ln(ER)}].$$

Starting material	ER	Compound	Ref.
$[\mathrm{Cp}^*_2\mathrm{NdCl}_2]^{2-}$	SeMes	$[\mathrm{Cp}^*_2\mathrm{Nd(SeMes)(thf)}]$	[263]
$[\mathrm{Cp}^*_2\mathrm{Sm(thf)}_2]$	EMes (E = S, Se, Te)	$[\mathrm{Cp}^*_2\mathrm{Sm(EMes)(thf)}]$	[163]
$[\mathrm{Cp}^*_2\mathrm{Sm(thf)}_2]$	$\mathrm{SeAr^F}$	$[\mathrm{Cp}^*_2\mathrm{Sm(SeAr^F)(thf)}]$	[163]
$[\mathrm{Cp}^*_2\mathrm{Yb(Et_2O)}]$	EPh (E = S, Se, Te)	$[\mathrm{Cp}^*_2\mathrm{Yb(EPh)(Et_2O)}]$	[241]
$[\mathrm{Cp}^*_2\mathrm{Yb(Et_2O)}]$	SR (R = *o*-tol, *m*-tol, Mes)	$[\mathrm{Cp}^*_2\mathrm{Yb(SR)(Et_2O)}]$	[241]
$[\mathrm{Cp}^*_2\mathrm{Yb(Et_2O)}]$	SMes*	$[\mathrm{Cp}^*_2\mathrm{Yb(SMes^*)}]$	[241]
$[\mathrm{Cp}^*_2\mathrm{Yb(NH_3)}]$	EPh (E = S, Se, Te)	$[\mathrm{Cp}^*_2\mathrm{Yb(EPh)(NH_3)}]$	[241]
$[\mathrm{Cp}^*_2\mathrm{Yb(NH_3)}]$	SR (R = *o*-tol, *m*-tol, Me, $\mathrm{CH_2Ph}$)	$[\mathrm{Cp}^*_2\mathrm{Yb(SR)(NH_3)}]$	[241]

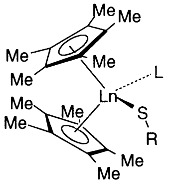
Both $[\mathrm{Cp}^*_2\mathrm{Sm}]$ and $[\mathrm{Cp}^*_2\mathrm{Yb}]$ have been used, but also the rare and ill-characterized Nd(II) ate-complex $[\mathrm{Cp}^*_2\mathrm{NdCl}_2]^{2-}$, of which the reaction with MesSeSeMes in fact has been proposed as evidence for its formation. Steric crowding of the two Cp* ligands resulted in all complexes in the above series being solvated omers, except in $[\mathrm{Cp}^*_2\mathrm{Yb(SMes^*)}]$ where the small Yb(III) is bonded to the bulkiest chalcogenolate ligand. As expected, coordinated ether is more labile than ammonia in the Yb series. $[\mathrm{Cp}^*_2\mathrm{Sm(TeMes)(thf)}]$, $[\mathrm{Cp}^*_2\mathrm{Sm(SeAr^F)(thf)}]$ [163], $[\mathrm{Cp}^*_2\mathrm{Yb(TePh)(NH_3)}]$ [241] and $[\mathrm{Cp}^*_2\mathrm{Yb(SPh)(NH_3)}]$ [186] have been chacterized by X-ray.

σ-bond metathesis of the hydride $[\{\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-H})\}_2]$ with ${}^n\mathrm{PrSH}$ in toluene resulted in elimination of $\mathrm{H_2}$ and the obtention of the solvent-free $[\{\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-S}^n\mathrm{Pr})\}_2]$ which dimeric structure in solution was determined by cryoscopy. Calorimetric studies revealed that the Sm–S bond in this complex ($D(\mathrm{Sm–S}) = 306.8\ \mathrm{kJ\ mol^{-1}}$) is only slightly weaker than the Sm–N bond in $[\mathrm{Cp}^*_2\mathrm{Sm(NMe_2)}]$ ($D(\mathrm{Sm–N}) = 342.8\ \mathrm{kJ\ mol^{-1}}$) or the Sm–O bond in $[\{\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-O}^t\mathrm{Bu})\}_2]$ ($D(\mathrm{Sm–O}) = 338.6\ \mathrm{kJ\ mol^{-1}}$) [98].





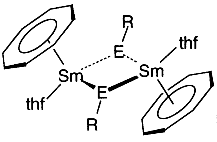
Ln = Y, Ce, Yb, E = S, Se
R = Ph, iPr, nBu, R1 = H, tBu



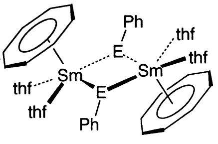
Ln = Sm, Yb, E = S, Se, Te
R = Ph, Mes, $\mathrm{Ar_F}$, L = $\mathrm{NH_3}$, thf

The ansa-samarocene (II) [(CpCMe$_2$CMe$_2$Cp)SM] was oxidized by MesSeSeMes into [(CpCMe$_2$CMe$_2$Cp)Sm(SeMes)] [264].

Cyclooctatetraenylsamarium (III) chalcogenolates were made by the one-pot reaction of two equivalents of I$_2$-activated Sm with two equivalents of C$_8$H$_8$ (COT) and one equivalent of REER. [{(COT)Sm(thf)$_2$(μ-EPh)}$_2$] (E = S [XR] [164], Se [XR] [228]) and [{(COT)Sm(thf)(μ-SR)}$_2$] (R = Ar^{iPr} [XR] [164], Mes [228]) could thus be made. A plausible mechanism can involve the reaction of REER with Sm giving [(RE)$_2$Sm] in the first step followed by oxidation with COT: The known [(thf)$_3$(Ar^{iPr}S)$_2$Sm] [160] does react with COT to give [{(COT)Sm(thf)(μ−SAr^{iPr})}$_2$]; however, the two steps might also occur in reverse order.



R = 1-(2,4,6tri*iso*propyl)phenyl



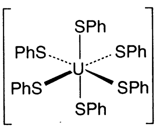
E = S, Se

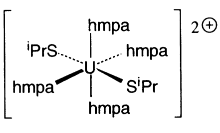
4.2.3. Actinides

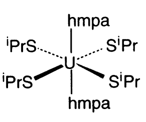
4.2.3.1. Inorganic complexes. Here again, apart from the early work of Gilman [253] who described in 1956 preparations of insoluble [U(SR)$_4$] (R = Et, ^{n}Bu) from U(NEt$_2$)$_4$] and four equivalents of RSH in ether, most work on this subject only appeared very recently, and almost all with uranium as the metal.

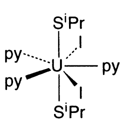
The original Gilman experiments can also be conducted in pentane, THF or benzene, and the new [U(^{i}PrS)$_4$] could thus be prepared. [U(SPh)$_4$] could not be directly obtained from [U(NEt$_2$)$_4$] and PhSH (the result is discussed later), but was conveniently made by an analogous reaction of PhSH with [U(BH$_4$)$_4$]. [U(SPh)$_4$] could also be made by a trans-thiolatation reaction of [U(^{n}BuS)$_4$] with PhSH or, more simply (but in low yield) by direct reaction of U metal with PhSSPh [201].

Uranium thiolates [U(SR)$_4$] are soluble in a strong donor solvent (HMPA or pyridine). Crystalline [(hmpa)$_2$U(^{i}PrS)$_4$] [XR] [202] could be isolated from solutions of [U(^{i}PrS)$_4$] in THF/HMPA, and controlled protonation of two thiolate ligands of this hmpa complex with two equivalents of the acid [(HNEt$_3$)(BPh$_4$)] afforded the cationic complex [{(hmpa)$_4$U(^{i}PrS)$_2$}{BPh$_4$}$_2$] [XR] [201]. When a solution of [U(^{i}PrS)$_4$] in pyridine was treated by diiodine, an oxydo-reduction occurred in the coordination sphere and [(py)$_3$U(^{i}PrS)$_2$(I)$_2$] [XR] [201] was obtained together with ^{i}PrSS^{i}Pr.





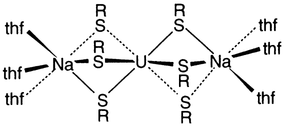




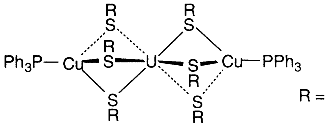
The reactions of $[U(NEt_2)_4]$ with ^{t}BuSH and PhSH did not give $[U(SR)_4]$. In pyridine, $[(py)_3U(^tBuS)_4]$ could be obtained from ^{t}BuSH and $[U(NEt_2)_4]$, but in the absence of this solvent, a μ_3-sulphido cluster is formed (which will be discussed later in Section 4.3.1). This cluster was also obtained by thermal decomposition of the pyridine adduct $[(py)_3U(^tBuS)_4]$ [201].

A soluble homoleptic dianion: $[\{(Et_2NH_2)_2\}\{U(SPh)_6\}]$ [XR] [203] was obtained from $[U(NEt_2)_4]$ and PhSH in the Gilman conditions.

Uranium thiolates could also be obtained by an anionic route. The reaction of $[UCl_4]$ or $[U(BH_4)_4]$ with six equivalents of NaSR afforded the homoleptic uranate $[\{(thf)_3Na(\mu\text{-}SR)_3\}_2U]$ (R = ^{n}Bu, ^{i}Pr, ^{t}Bu [XR], Ph [XR]) [204]. The Gilman product $[U(^nBuS)_4]$ could be obtained by controlled protonolysis of the corresponding anionic compound with $[(HNEt_3)(BPh_4)]$. Finally, the anionic reaction when performed in the presence of CuSPh and PPh3 gave an analogous heterobimetallic homoleptic complex: $[\{(Ph_3P)Cu(\mu\text{-}SPh)_3\}_2U]$ [XR] [203].



R = t-Bu, Ph



R = Ph

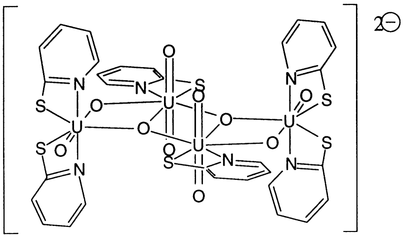
A homoleptic uranium tetraanionic chelate: $[\{(dme)Li\}_4\{(\mu{:}\eta^2\text{-}SCH_2CH_2S)_4U\}]$ [XR] could be made by reaction of ethanedithiolate with UCl_4. Variable-temperature NMR studies show that there are two fluxional processes: the conformational mobility of the S–U–S five-membered ring (frozen below -70 °C), and the degenerate rearrangement of two equivalent dodecahedral structures, above room temperature. An extended Hückel study reveals little participation of the 5f orbitals in bonding, and weak U–S π-interactions. Reaction of the chelate with CS_2 gave dilithium ethylenedithioxanthate $[\{Li(dme)_2\}_2(S_2CSCH_2CH_2SCS_2)]$ [205].

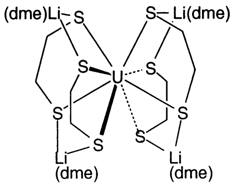
Reaction of the uranasilaazacyclobutane metalacycle $[U\{\eta^2\text{-}CH_2SiMe_2N(SiMe_3)\}\{N(SiMe_3)_2\}_2]$ with one equivalent of Ar′SH [Ar′= 1-(2,6-dimethyl)phenyl] gave $[U(SAr')\{N(SiMe_3)_2\}_3]$ [XR] in a σ-bond metathesis reaction. Addition of more Ar′SH gave intractable products [206].

The thiolate derivatives of actinide bis(hydrotrispyrazolylborates) $[(HBPz_3)_2An(S^tBu)_2]$ (An = U [265], Th [266]) could be made from $[(HBPz_3)_2AnCl_2]$ and NaS^{t}Bu. There is NMR evidence for the intermediate $[(HBPz_3)_2U(Cl)(S^tBu)]$, but it could not be isolated [265]. $[(HBPz_3)_2U(S^iPr)_2]$ could be made similarly and was characterized by X-ray. $[(HBPz_3)_2U(OEt)(S^tBu)]$ was isolated from $[(HBPz_3)_2U(Cl)(OEt)]$ and NaS^{t}Bu [207].

The 2-thiopyridine *N*-oxide (OPySH) as been used as a (O,S) chelatant. Reaction of OPySH with $Th(NO_3)_4$ in the presence of LiOH gave $[(dmsO)_2(OPyS)_4Th]$ or the nine-coordinated $[(dmf)(OPyS)_4Th]$ [XR] [189]. Likewise, reaction of uranyl nitrate with OPySLi afforded $[(Ph_3PO)(OPyS)_2UO_2]$ and $[(dmso)(OPyS)_2UO_2]$ [XR] [208].

When uranyl nitrate was reacted with 2-mercaptopyrimidine or (HSPym) or a 4-methyl 2-mercaptopyrimidine (HSMePym) in the presence of an amine, atmospheric oxygen was activated and incorporated into peroxo-bridged uranyl compounds such as $[(HNEt_3)_2](UO_2)_2(\mu{:}\eta^2,\eta^2\text{-}O_2)(SPym)_4\}]$ [XR] or the monoprotonated $[(HNEt_3)\{(H)(UO_2)_2(\mu{:}\eta^2,\eta^2\text{-}O_2)(SMePym)_4\}]$ [XR], whereas with 2-mercaptopyridine a tetranuclear μ-oxo species $[(HNEt_3)_2](SPy)_2(UO)(\mu_2\text{-}O)(\mu_3\text{-}O)(UO_2)(SPy)\}_2]$ was obtained [XR] [209].





4.2.3.2. Organometallic complexes. An early paper by Jamerson and Takats briefly described the reactivity of $[Cp_2U(NEt_2)_2]$ towards various thiols and dithiols. With chelating dithiols (HS-⌒-SH), $[Cp_2U$(S-⌒-S)] compounds (generally dimers) are obtained, whereas $[Cp_2U(SR)_2]$ compounds obtained with monothiols were unstable and disproportionated into $[Cp_3U(SR)]$ and other unidentified products. Isolated products were characterized by mass spectroscopy and ^1H NMR [267].

Most other compounds in this class are of the type $[(RCp)_3U(ER)]$ along with some other cyclopentadienyl and cyclooctatetraenyl complexes.

Oxidation of cyclopentadienyluranium (III) complexes with REER provided the following uranium (IV) complexes: $[(RCp)_3U(ER)]$

$$2[(RCp)_3U]+REER\rightarrow 2[(RCp_3)U(ER)].$$

Starting material	**ER**	**Compound**	**Ref.**
$[Cp_3U(thf)]$	SR (R = ^{i}Pr, ^{n}Bu, Ph), SeMe	$[Cp_3U(ER)]$	[210]
$[(Me_3SiCp)_3U]$	SR (R = Et, ^{i}Pr, ^{t}Bu), SeMe	$[(Me_3SiCp)_3U(ER)]$	[210]
$[(^tBuCp)_3U]$	SR (R = Et, ^{i}Pr, ^{t}Bu)	$[(^tBuCp)_3U(ER)]$	[210]

Most of the reactions studied were exploratory NMR tube experiments, but $[(RCp_3)U(S^iPr)]$ (R = Me_3Si, ^{t}Bu) were isolated. Several alternative routes to these complexes are possible: the σ-bond metathesis reaction of $[Cp_3U(uBu)]$ with ^{i}PrSH (R = ^{i}Pr, ^{n}Bu) and the reaction of $[Cp_3U(BH_4)]$ with ^{i}PrSH. Electronic effects are believed to be responsible for the sluggishness of the reaction of ^{t}BuSS^{t}Bu with $[(^tBuCp)_3U]$, since its reaction with the sterically equivalent $[(Me_3SiCp)_3U]$ is rapid [210].

Complexes $[Cp_3U(SR)]$ (R = Me [XR], ^{i}Pr, ^{t}Bu and Ph) have also been prepared by the classical anionic route (NaSR + $[Cp_3UCl]$). The value of U–S bond length in $[Cp_3U(SMe)]$ (269.5 pm) is in agreement with an ionic bonding model, the U–S–C bond angle is equal to 107.2°. These complexes and their substituted analogs $[(RCp)_3U(SR)]$ reacted with protic compounds XH (ROH, HBr) and halogens X_2 (X = I) to give $[(RCp)_3U(X)]$. The anionic U(III) complexes

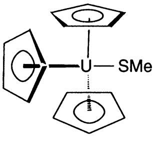
[{Na(thf)}{Cp_3U(SR)}] (R = Me, ^{i}Pr, ^{t}Bu and Ph) could be made by reduction of the corresponding neutral complexes with sodium amalgam or by addition of NaSR to [Cp_3U(thf)] [210].

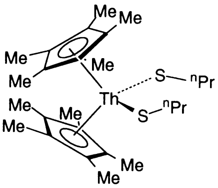
Earlier syntheses of [$(RCp)_3U$(SR)] involved reactions of [$(RCp)_3U$] with RSH, but the yield was always below 50%. The following explanation was put forward: The first step would be protonation of a Cp group to give another U(III) complex: [$(RCp)_2U$(SR)] which would then disproportionate into the isolated product [$(RCp)_3U$(SR)] and "$(RCp)_2U$" which would decompose. The dimeric U(III) complex [{$(^tBuCp)_2U$([μ-SPh)}$_2$] has, indeed, been isolated from the reaction of [$(^tBuCp)_3U$] and PhSH at low temperature. U(IV) complexes prepared by this route include [$(^tBuCp)_3U$(SPh)] and [$(MeCp)_3U(S^iPr)$] [143].

Uranium–sulphur bond disruption enthalpies [D(U–S)] have been measured for a series of organometallic uranium thiolates. The value for [$(Me_3SiCp)_3U$(SEt)], a compound that does not display steric crowding at the sulphur atom, is D(U–S) = 266 kJ mol^{-1}, slightly smaller than the estimated value of 310 kJ mol^{-1} for D(U–O) in a similar complex. The U–S bond is weaker for crowded complexes, e.g. D(U–S) = 158 kJ mol^{-1} for [$(Me_3SiCp)_3U(S^tBu)$] [268].

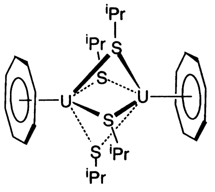
A U(IV) compound: [{η^5-$(SiMe_3)_2C_5H_3$}$_2$U(Cl)(SMes*)] displaying restricted rotation about the U–S bond has been briefly mentioned [269].

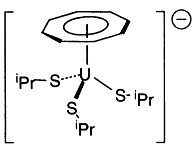
The Th complex: [$Cp^*_2Th(S^nPr)_2$] [XR] has been prepared from [$Cp^*_2ThMe_2$] and ^{n}PrSH. The Th–S bond length (271.8 pm), slightly smaller than expected (277 pm), might have a weak π character. Reaction with ^{t}BuOH gave the corresponding bis-alkoxide [$Cp^*_2Th(O^tBu)_2$] [190].





Finally, cyclooctatetraenyl compounds of U(IV) were reported. [{(COT)U(μ-SR)$_2$}$_2$] (R = ^{n}Bu, ^{i}Pr [XR]) could be obtained by reaction of [(COT)U$(BH_4)_2$] with RSH or RSNa. These compounds retain their dimeric structure in THF or toluene solutions whereas [{(COT)U(μ-S^{n}Bu)$_2$}$_2$] is partly dissociated in pyridine, presumably as a monomeric pyridine adduct. Reaction of [(COT)U$(BH_4)_2$] with ^{t}BuSNa gave an anionic complex: [{Na(18-crown-6)(thf)}{(COT)U$(S^iPr)_3$}] [XR] [211].





4.3. Mono- and polysulphides, selenides and tellurides

Acces to this category of compounds is generally obtained via two methods.

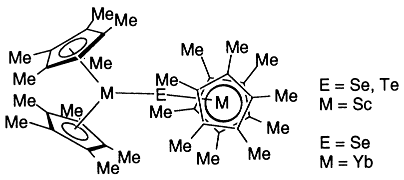
The first is the controlled decomposition of metal organochalcogenolates. The primary decomposition products are coordinatively unstable and, thus, prone to aggregation into polynuclear compounds.

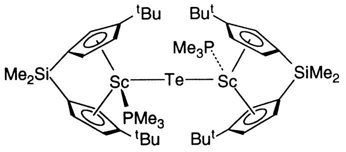
The second method involves reaction of chalcogens with metal complexes. The most frequent reaction is the oxidation of low-valent inorganic or organometallic complexes of Sm(II), Yb(II) or U(III) by chalcogens(0) in suitable form; Ln(III) or U(IV) compounds have been thus obtained. When the reaction cannot proceed by oxidation of the metal (like in Ln(III) complexes), chalcogenides can still be made by oxidative displacement of the ligands by elemental chalcogens. Insertion of a chalcogen in a M–H bond and elimination of H_2 has been used in the case of scandium.

There are two examples of molecular europium and uranium selenides with no organic ligands, that have been made from the elements or their halides.

4.3.1. Scandium

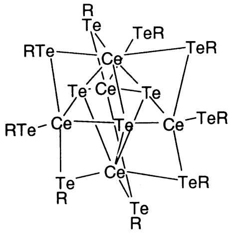
The reactions of $[Cp^*_2ScD]$ with elemental Se or Bu_3PTe yielded the μ-chalcogenolato $[(Cp^*_2Sc)_2(\mu\text{-}E)]$ (E = Se [XR], Te [XR]). Their X-ray structure shows an almost linear Sc–E–Sc configuration (approximately 173°) and a slightly longer bond (for Te) than in $[Cp^*_2Sc(TeCH_2Ph)]$, which may imply less π-bond character. The μ-tellurido species comproportionate photochemically with TeR_2 to give $[Cp^*_2Sc(TeR)]$, which in turn disproportionates thermally to give back TeR_2 and $[(Cp^*_2Sc)_2(\mu\text{-}Te)]$; these reactions were not observed with the Se complexes [238,223]. Decomposition of an ansa-scandocene telluride also yielded a μ-tellurido derivative. Steric crowding in its phosphine adduct: $[\{[(\eta^5\text{-}3\text{-}^t BuC_5H_3)_2SiMe_2]Sc(PMe_3)\}_2(\mu\text{-}Te)]$ has for consequence a linear Sc–Te–Sc configuration. [105].





4.3.2. Yttrium, lanthanum and the lanthanides

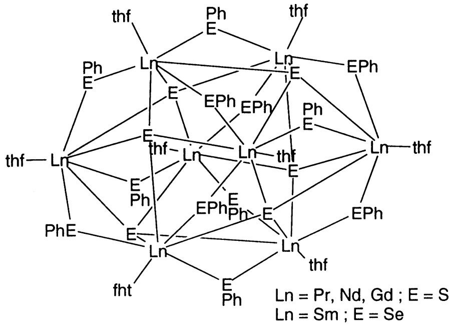
4.3.2.1. Inorganic complexes. Decomposition of the homoleptic tellurolates $[Ln(TeSi(SiMe_3)_3)_3]$ in hexane solution directly gave crystalline μ-tellurido clusters $[Ln_5(\mu_3\text{-}Te)_3\{\mu\text{-}TeSi(SiMe_3)_3\}_6\{TeSi(SiMe_3)_3\}_3]$ (Ln = La, Ce [XR]); the reaction failed with Ln = Y [106,239].

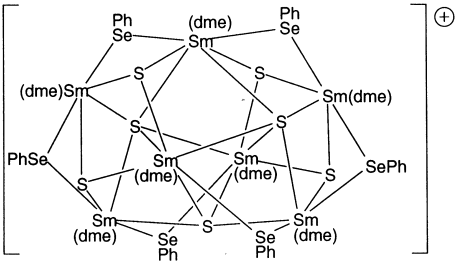


$R = Si(SiMe_3)_3$

The reaction of $Ln(SPh)_3$ with elemental sulphur proceeded with elimination of PhSSPh and formation of a Ln(III) cluster: $[\{Ln(thf)\}_8(\mu\text{-}SPh)_{12}(\mu_4\text{-}S)_6]$ (Ln = Pr, Nd, Gd [XR]). The structure can be described as a cubic array of Ln atoms with each face capped by sulphides and each edge bridged by a thiolate group [177].

Decomposition of $[Sm(SePh)_2]$ with or without added elemental Se yielded a Sm(III) cluster: $[\{Sm(thf)\}_8(\mu\text{-}SePh)_{12}(\mu_4\text{-}Se)_6]$ [XR] similar to the above-mentioned Ln/S clusters, whereas reaction of elemental sulphur with $[Sm(SePh)_3]$ (prepared in situ from Sm/Hg and PhSeSePh) afforded a cationic Sm(III) cluster: $[\{[Sm(dme)]_7(\mu\text{-}SePh)_6(\mu_3\text{-}S)_4(\mu_4\text{-}S)(\mu_5\text{-}S)_2\}\{Hg_3(SePh)_7\}]$ [XR] [225].





Reaction of $EuCl_3$, K_2Se and Se in DMF yielded an Eu(III) cluster: $[(dmf)_{13}Eu_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2]$ in which the μ_4-oxo group is at the centre of an Eu polyhedron. The oxygen and OH groups might come from residual water in commercial $EuCl_3$ [231].

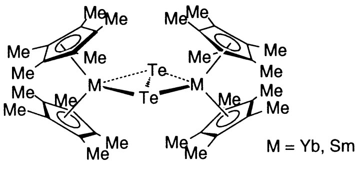
4.3.2.2. Organometallic complexes. Most compounds in this class are pentamethylcyclopentadienyl complexes of Sm or Yb (III) prepared by the oxidation of the divalent precursors with chalcogens.

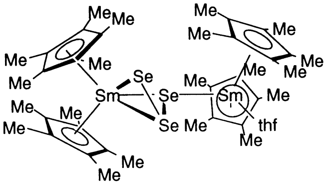
$$[Cp^*_2Ln]+[E]\rightarrow[(Cp^*Ln)_2E].$$

Starting material	**Chalcogen source**	**Compound**	**Ref..**
$[Cp^*_2Yb(Et_2O)]$	Ph_3PS, COS or As_2S_3	$[\{Cp^*_2Yb\}_2(\mu\text{-}S)]$	[235]
$[Cp^*_2Yb(Et_2O)]$	Ph_3PSe or Se	$[\{Cp^*_2Yb\}_2(\mu\text{-}Se)]$	[235] [XR]
$[Cp^*_2Yb(Et_2O)]$	BU_3PTe or Te	$[\{Cp^*_2Yb\}_2(\mu\text{-}Te)]$	[235]
$[Cp^*_2Yb(Et_2O)]$	Te (large excess)	$[Cp^*_2Yb\}_2(\mu\text{:}\eta^2,\eta^2\text{-}Te_2)]$	[242] [XR]
$[Cp^*_2Sm(thf)_2]$	Ph_3PS	$[\{Cp^*_2Sm(thf)\}_2(\mu\text{-}S)]$	[165] [XR]

[$\mathrm{Cp}_2^*\mathrm{Sm(thf)}_2$]	Se (0.5 equivalent)	[$\{\mathrm{Cp}_2^*\mathrm{Sm(thf)}\}_2(\mu\text{-Se})$]	[165] [XR]
[$\mathrm{Cp}_2^*\mathrm{Sm(thf)}_2$]	Te (0.5 equivalent)	[$\{\mathrm{Cp}_2^*\mathrm{Sm(thf)}\}_2(\mu\text{-Te})$]	[165] [XR]
[$\mathrm{Cp}_2^*\mathrm{Sm(thf)}_2$]	S (1.5 equivalent)	[$\{\mathrm{Cp}_4^{\ddagger}\mathrm{Sm}_2\mathrm{(thf)}\}(\mathrm{S})_3$]	[165]
[$\mathrm{Cp}_2^*\mathrm{Sm(thf)}_2$]	Te (1.5 equivalent or more)	[$\{\mathrm{Cp}_4^{\ddagger}\mathrm{Sm}_2\mathrm{(thf)}\}(\mathrm{Te})_3$]	[165]
[$\mathrm{Cp}_2^*\mathrm{Sm(thf)}_2$]	Se (excess)	[$\{\mathrm{Cp}_2^*\mathrm{Sm}\}_2(\mu{:}\eta^1,\eta^3\text{-Se}_3)$ (thf)]	[165] [XR]

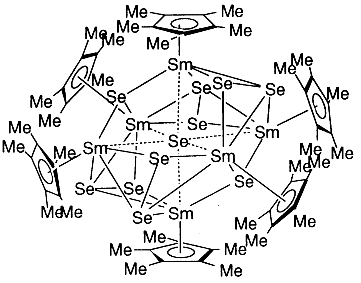
Depending on the stoichiometry, mono- or polychalcogenides can be obtained. Their interconversion is possible: the selective removal of two chalcogen atoms with PPh_3 produced [$\{\mathrm{Cp}_2^*\mathrm{Sm(thf)}\}_2(\mu\text{-E})$ from [$\{\mathrm{Cp}_4^{\ddagger}\mathrm{Sm}_2\mathrm{(thf)}\}(\mathrm{E})_3$] (E = S, Se) and that of one Te atom with pme$_3$ yielded [$\{\mathrm{Cp}_2^*\mathrm{Sm}\}_2(\mu{:}\eta^2,\eta^2\text{-Te}_2)$] [XR] from [$\{\mathrm{Cp}_4^{\ddagger}\mathrm{Sm}_2\mathrm{(thf)}\}(\mathrm{Te})_3$]; conversely, mixed chalcogenides like [$\{\mathrm{Cp}_4^{\ddagger}\mathrm{Sm}_2\mathrm{(thf)}\}(\mathrm{Se})_x(\mathrm{Te})_y$] could be obtained from [$\{\mathrm{Cp}_2^*\mathrm{Sm(thf)}\}_2(\mu\text{-Te})$] and Se [165].

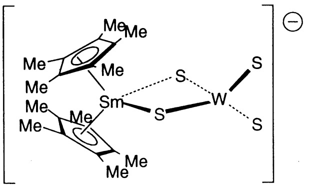




In the μ-monochalcogenido structures, the Ln–X–Ln angle are close to 180° (8–11° deviation), as in the Cp*Sc example. In the η^2-E_2 and the η^3-E_3 species, the E–E distances denote single bonds, which are expected in a formal E–E or E–E–E dianions.

When toluene solutions of [$\{\mathrm{Cp}_2^*\mathrm{Sm}\}_2(\mu{:}\eta^1,\eta^3\text{-Se}_3)\mathrm{(thf)}$] were allowed to stand at room temperature, crystals of [$\{\mathrm{Cp^*Sm}\}_6\mathrm{Se}_{11}$] [XR], a Sm–Se cluster, deposited [229].



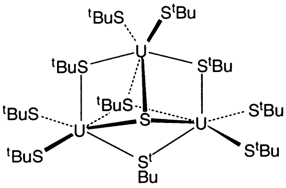


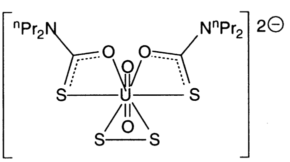
The reaction of $\mathrm{Cp}_2^*\mathrm{Sm}$ with inorganic M(VI) sulphides MS_4^{2-} (M = Mo, W) result in the formation of μ-sulphido bimetallic complexes. With molybdenum, reduction occurs and a [Sm(III), Mo(V)] is obtained: [$\{\mathrm{PPh}_4\}\{(\mathrm{Cp}_2^*\mathrm{Sm})_2\mathrm{Mo}(\mu\text{-S})_4\}$] [XR], whereas tungsten remains in the +6 oxidation state in [$\{\mathrm{PPh}_4\}\{\mathrm{Cp}_2^*\mathrm{Sm}(\mu\text{-S})_2\mathrm{WS}_2\}$] [XR] [166].

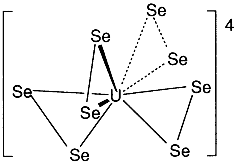
4.3.3. Actinides

4.3.3.1. Inorganic complexes. As stated in Section 4.2.3.1, $[U(S^tBu)_4]$ is unstable and its decomposition gives the μ_3-sulphido compound $[U_3(\mu_3\text{-}S)(\mu_3\text{-}S^tBu)(\mu_2\text{-}S^tBu)_3(S^tBu)_6]$ [XR]. A tentative mechanism for this reaction has been proposed: 1 mol of $[U(S^tBu)_4]$ would decompose with formation of 2-methylpropene (which has, indeed, been detected by GLC), ^tBuSH and $[(S^tBu)_2U{=}S]$ which would then condense with two more moles of $[U(S^tBu)_4]$ to give the μ_3-sulphido compound. This compound can also be obtained from the more stable $[(py)_3U(S^tBu)_4]$ upon heating [202].

Solutions of the mixed bis (thiocarbamate)-alkoxy uranyl compound $[(^nPr_2NH_2)\{UO_2(^nPr_2NCOS)_2(OMe)\}]$ are unstable and, with time, deposit crystals of the disulphido ion $[(^nPr_2NH_2)_2\{UO_2(^nPr_2NCOS)_2(\eta^2\text{-}S_2)\}]$ [XR]. It decomposes in polar solvents and deposits sulphur upon standing in air for several weeks [212].





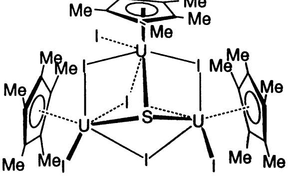


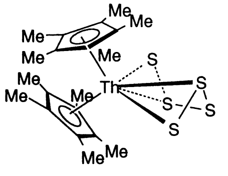
Oxidation of the kinetically stabilized homoleptic U(III) complex $[U(OAr^*)_3]$ ($Ar^* = 1\text{-}(2,6\text{-}di(^tbutyl)phenyl)$) with COS or Ph_3PS gave the μ-sulphido $[\{U(OAr^*)_3\}_2(\mu\text{-}S)]$ [XR] with a linear U–S–U bond, presumably for steric reasons [213].

Finally, one can note the high temperature (300 °C) solid-state synthesis of $[K_4U(\eta^2\text{-}Se_2)_4]$ [XR] from the appropriate amounts of U, Se and K_2Se. The structure consists of a homoleptic $[U(\eta^2\text{-}Se_2)_4]^{4-}$ tetraanion linked with potassium ions in an infinite array. $[K_4U(\eta^2\text{-}Se_2)_4]$ is soluble in polar solvents (DMF, ethylenediamine, or acetonitrile in the presence of crown ethers or cryptands). The $[U(\eta^2\text{-}Se_2)_4]^{4-}$ tetraanion may be stable in these solvents [237].

4.3.3.2. Organometallic complexes. Oxidation of the U(III) complex $[(MeCp)_3U(thf)]$ with R_3PE (or COS) gave $[(MeCp)_3U\}_2(\mu\text{-}E)]$ (E = S [XR], Se, Te). The S–U–S angle in $[\{(MeCp)_3U\}_2(\mu\text{-}E)]$ is 165°, a value similar to that reported for other E–M–E angles (M being a group 3 metal) [214].

Likewise, oxidation of $[Cp^*UI_2(thf)_3]$ with CS_2 or ethylene sulphide yielded $[\{Cp^*UI_2(thf)_3\}_2(S)]$, presumably a μ-sulphido dimer, that underwent slow decomposition in solution to give a tri-μ-sulphido polynuclear complex: $[Cp^*_3U_3(\mu_3\text{-}I)(\mu_3\text{-}S)(\mu_2\text{-}I)_3(I)_3]$ [XR] with the same polynuclear framework as $[U_3(\mu_3\text{-}S)(\mu_3\text{-}S^tBu)(\mu_2\text{-}S^tBu)_3(S^tBu)_6]$ [215].





A unique example of a thorium polysulphide has been recently reported: The reaction of $Cp^*_2ThCl_2$ with Li_2S_5 gives $[Cp^*_2Th(S_5)]$ [XR] in which the (S_5) ligand is a twist-boat conformation. Bonding of this ligand to Th is best characterized as η^4, since the β sulphur atoms interact with Th in a weaker dative bond. This bonding pattern was confirmed in an extended Hückel study on the model compound $[Cp_2Th(S_5)]$. Variable-temperature NMR data show that the twist-boat is fluxional at room temperature.[191]

4.4. Mono and dithio- (seleno-) carboxylates, phosphates and phosphinates

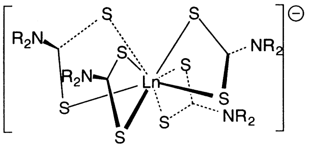
Sulphur or selenium derivatives of carboxylic and phosphoric acids in combination with lanthanides and actinides have been studied for quite a long time, the first paper mentioning thorium, uranyl and neodymium dithiocarbamates having been reported by Delépine in 1908 [270]. The carboxylic acid complexes include lanthanide and actinide thio- and dithioacetates, xanthates, mono- and dithio- and selenocarbamates, whereas the phosphorus acid complexes comprise mostly dithiophosphates and phosphinates. Interest in this class of compounds, in particular the inorganic uranyl complexes, stemmed from their potential use in spent nuclear fuel reprocessing [271]. The vast majority of complexes are air-stable inorganic compounds of U(VI) that were prepared by the straightforward reaction of uranyl salts with anions of the appropriate acids. Some An(IV) (An = Th, U, Np, Pu) and Ln(III) compounds and quite a few organometallic complexes have also been described.

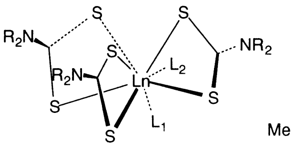
4.4.1. Yttrium, lanthanum and the lanthanides

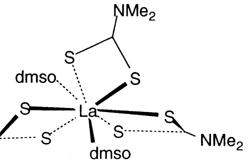
4.4.1.1. Inorganic complexes. The molecules reported hereafter are Ln(III) chelates with *N*,*N′*-dialkyldithiocarbamates (R_2NCS_2), O,O′-dialkyldithiophosphates $[(RO)_2PS_2]$, dialkylthiophosphinates $[R_2P(O)S]$ or dialkyldithiophosphinates (R_2PS_2) as ligands; there is one example of a chelating thioureato ligand: $[Et_2NC(S)NH]$. The dithioacid derivatives (S = X-SH) [X = $C(NR_2)$, PR_2] generally occur in three categories: the seven-coordinate cationic complexes $[M(S_2X)_2(L)_3]^+$, the neutral seven- or eight-coordinate $[M(S_2X)_3(L)_2]$ (L being an auxiliary donor ligand) and the anionic eight-coordinate $[M(S_2X)_4]^-$, the last category being the most common, whereas the monothio acid derivatives can have a more complex structure. The seven-coordinate compounds generally have the pentagonal bipyramidal structure while that of the eight-coordinate compounds are either distorted dodecahedral or distorted square antiprism.

N,*N′*-diethyldithiocarbamates were the first ligands to be used. Reaction of anhydrous $LnBr_3$ (Ln = La→Nd, Sm→Lu) with $[Na(Et_2NCS_2)]$ in anhydrous ethanol neutral $[Ln(Et_2NCS_2)_3]$, when crystallized in acetonitrile. X-ray powder diffraction studies have shown that two isomorphous series were present: (La–Nd) and (Sm–Lu) [272,273]. Other examples of neutral complexes include $[Ln(RCS_2)_3(H_2O)_3]$ where R = 3-ferrocenyl-5-(2-furyl)-pyrazolin-1-yl [274], $[Ln(Et_2NCS_2)_3(bipy)]$ (Ln = Y, La→Nd, Sm→Lu [XR] for Ln = Er) [180], $[La\{(CH_2)_4NCS_2\}_3(thf)(H_2O)]$ [XR]

[131], and [Ln(Me_2NCS_2)$_3$(dmso)$_2$] (Ln = La [XR], Pr, Nd, Sm→Tb) [132]. The ancillary ligands can be either cisoïd [180,131] or transoïd [132].



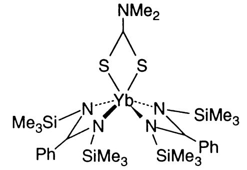




Further reaction of [Ln(Et_2NCS_2)$_3$] with [Na(Et_2NCS_2)] and Et_4NBr gave lanthanates: [(NEt_4){Ln(Et_2NCS_2)$_4$}] (Ln = La→Nd, Sm→Lu) that are all isomorphous by X-ray powder diffraction [272,273].

Several other lanthanates have been made: [(NEt_4){Ln($^n Bu_2NCS_2$)$_4$}] (Ln = La, Pr, Nd, Sm, Eu) [275], [(H_2R)(Ln(RCS_2)$_4$}] (R = pyrrolidyl [276], morpholyl [277], (Me)(H)N, (Et)(H)N [278], Ln = La, Pr, Nd, Sm, Eu, Gd) and [(NMe_2H_2){Ln(Me_2NCS_2)$_4$}] (Ln = La, Pr, Nd, Sm→Ho) [151]. X-ray crystal structures of the following lanthanates have been published: [NaLn(Et_2NCS_2)$_4$] (Ln = La [133], Nd [152], Eu [173]), [(NEt_4){Nd(Et_2NCS_2)$_4$}] [153], [(H)(THF){Ln(Et_2NCS_2)$_4$}] (Ln = La, Nd [134], Pr [146], Eu [174]), [(NMe_2H_2){Nd(Me_2NCS_2)$_4$}] [151]. All compounds have a distorted dodecahedral structure. Both metals have this same dodecahedral structure in the [Mo(V), Sm(III)] zwitterion: [{Mo(Et_2NCS_2)$_4$}{Sm(Et_2NCS_2)$_4$}] [167].

A mixed dithiocarbamate/benzamidinate compound has been made in a completely different way, which looks more like a method used for organometallic compounds: reaction of the already mentioned Yb(II) benzamidinate complex [(thf)$_2$Yb(PhC($NSiMe_3$)$_2$}$_2$] with tetramethylthiuramdisulphide Me_2NC-(S)SSC(S)NMe_2 resulted in cleavage of the S–S bond and oxidation into the Yb(III) compound: [Yb{PhC($NSiMe_3$)$_2$}$_2$(Me_2NCS_2)] [XR] [183].



There are more examples of diethyldithiophosphate and phosphinate complexes.

Yttrium, lanthanum and all lanthanides (except promethium) give anionic eight-coordinate tetrakis-chelates [Ln(S_2PR_2)$_4$]$^-$ (type a)

$$4[\mathrm{Na}\{(\mathrm{R})_2\mathrm{PS}_2\}]+\mathrm{LnX}_3(+[\mathrm{C}^+\mathrm{X}^-])\rightarrow[\mathrm{Ln}\{(\mathrm{R})_2\mathrm{PS}_2\}_4]^-[\mathrm{Na}]^+\ (\text{or }[\mathrm{C}]^+)\ (\text{type a}).$$

Ln	**Compound (type a)**	**Ref.**
La→Nd, Sm→Tm	[{Ln[$(OMe)_2PS_2$]$_4$}($AsPh_4$)]	[144]
Y, La→Nd, Sm→Ho	[{Ln[$(OEt)_2PS_2$]$_4$}(Na)]	[279]
Y, La→Nd, Sm→Lu	[{Ln[$(OEt)_2PS_2$]$_4$}($AsPh_4$)]	[279]
La→Nd, Sm, Eu, Tb, Ho	[{Ln[$(OEt)_2PS_2$]$_4$}(NEt_4)]	[280]

La→Nd, Sm→Lu	$[\{Ln[(O^iPr)_2PS_2]_4](AsPh_4)]$	[144]
La→Nd, Sm→Tm	$[\{Ln(Me_2PS_2)_4\}(EPh_4)](E=P, As)$	[147,281,145,282]
La, Er	$[\{Ln(Et_2PS_2)_4\}(AsPh_4)]$	[135]

In this series, the arrangement of the sulphur atoms around the metal in the crystal structures is best described as dodecahedral. This structure is almost perfect for the dithiophosphate derivatives $[\{Ln[(OR)_2PS_2]_4\}(AsPh_4)]$ ($R=Et$, $Ln=La$, Er [136] $R=Me$, $Ln=Ce$, Er; $R={}^iPr$, $Ln=Nd$, Ho [144]) and slightly distorted towards square antiprismatic for the dithiophosphinates $[\{Ln(R_2PS_2)_4\}(AsPh_4)]$ ($R=Et$, $Ln=La$, Er [135], $R=Me$, $Ln=Ce$, Tm [145]) and $[\{Pr(R_2PS_2)_4\}(PPh_4)]$ [147]. However, NMR data suggest that there is a structural change in solution as one progresses along the lanthanide series. This change, occurring at Ho for the dithiophosphates [144,283,284] and at Dy for the dithiophosphinates [282] is proposed to be from dodecahedral to square antiprismatic.

The coupling of phosphorus to yttrium in the NMR spectra of $[Ln\{(OEt)_2PS_2)_4]$ has been interpreted as a partial covalent character in the Ln–S bond [285].

Three more types of complexes could be obtained when the reaction of a sodium dithiophosphate or phosphinate with a lanthanide halide was performed in the presence of a donor ligand L (a Lewis base): (b): a neutral eight-coordinated tris-chelate; (c) a seven-coordinated cationic bis-chelate; (d) a zwitterion including a cationic complex of type b together with an anionic tetrakis-chelate of type a in the same crystallographic lattice. Complexes of types b and c can also be made by displacement of one or two chelating dithiophosphates from $[Ln\{(R)_2PS_2\}_4]^-$ (type a) by a neutral ligand.

$$3[Na\{(R)_2PS_2\}]+LnX_3+2(L)\rightarrow[Ln\{(R)_2PS_2\}_3(L)_2] \text{ (route 1).}$$

$$[Ln\{(R)_2PS_2\}_4]^-+2(L)\rightarrow[Ln\{(R)_2PS_2\}_3(L)_2]+(R)_2PS_2^- \text{ (route 2).}$$

Ln	**Compound (type b)**	**Route**	**Ref.**
La [XR]	$[La\{(OEt)_2PS_2\}_3(Ph_3PO)_2]$	2	[137]
La [XR], Nd	$[Ln\{(OEt)_2PS_2\}_3\{(PhCH_2)_2SO\}_2]$	1	[138]
La→Nd [XR], Sm, Eu, Gd	$[Ln\{(O^iPr)_2PS_2\}_3\{Ph(NH_2)CO\}_2]$	1	[154]
La [XR]	$[La\{(O^iPr)_2PS_2\}_3\{Me(Me_2N)CO\}_2]$	1	[139]
La [XR], Nd	$[Ln\{(OEt)_2PS_2\}_3(dmso)_2]$	1	[140]

$$3[Na\{(R)_2PS_2\}]+LnX_3+3(L)\rightarrow[Ln\{(R)_2PS_2\}_2(L)_3]^+[(R)_2PS_2]^- \text{ (route 1).}$$

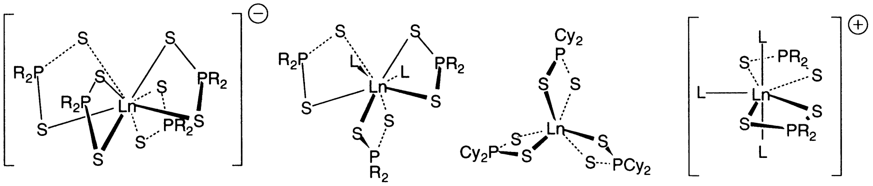
$$[Ln\{(R)_2PS_2\}_4]^-+3(L)\rightarrow[Ln\{(R)_2PS_2\}_2(L)_3]^+(R)_2PS_2]^-+(R)_2PS_2^- \text{ (route 2).}$$

Ln	**Compound (type c)**	**Route**	**Ref.**
Sm [XR]	$[\{Sm[(OEt)_2PS_2]_2(Ph_3PO)_3\}\{(OEt)_2PS_2\}]$	2	[137]
Gd, Tb [XR], Dy, Er [XR], Yb.	$[(Ln[(O^iPr)_2PS_2]_2[Ph(NH_2)CO]_3\}\{(O^iPr)_2PS_2\}]$	1	[178]

$$6[Na\{(R)_2PS_2\}]+2LnX_3+3(L)\rightarrow[Ln\{(R)_2PS_2\}_2(L)_3]^+[Ln\{(R)_2PS_2\}_4]^-.$$

Ln	Compound (type d)	Ref.
Eu [XR]	$[\{Eu[(O^iPr)_2PS_2]_2(dmso)_3\}\{Eu[(O^iPr)_2PS_2]\}_4]$	[140]
Nd [XR]	$[\{Nd[(O^iPr)_2PS_2]_2(^nBu_2SO)_3\}\{Nd[(O^iPr)_2PS_2]_4\}]$	[155]

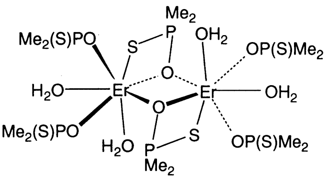
The early lanthanides prefer eight-coordination in type b, whereas the late lanthanide prefer seven-coordination in type c. With benzamide as auxiliary ligand, both type b and type c can be obtained in the borderline case of gadolinium. In type b, the transoïd arrangement of the donor ligands is generally preferred except for $[La\{(O^iPr)_2PS_2\}_3\{Me(Me_2N)CO\}_2]$ where the dimethylacetamide ligands are cisoïd [139].

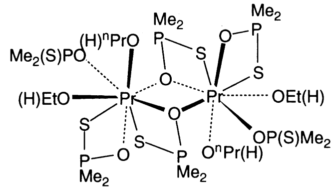


When the phosphorus substituent is bulky (cyclohexyl), there is no need to add a donor ligand to saturate the coordination sphere and six-coordinated neutral tris-chelates: $[Ln(Cy_2PS_2)_3]$ could be obtained (Ln = Y, La→Nd, Sm→Lu) [281]. The coordination pattern in the solid state is that of distorted trigonal prisms (Pr, Sm [148], Dy, Lu [179]). $[Ln(Me_2PS_2)_3]$ are also known and they are monomeric in chloroform solution, but their solid-state structure is unknown [286].

Solid-state dimers were observed with monothiophosphinates. Reaction of sodium dimethylthiophosphinate with lanthanide halides or perchlorates gave eight-coordinated oxygen-bridged La, Pr and Nd dimers, and a seven-coordinated Er dimer. The water adducts:$[\{Ln(H_2O)_n(\eta^1\text{-}OPSMe_2)_2(\mu{:}\eta^1,\eta^2\text{-}OPSMe_2)\}_2]$([XR]: Ln = Pr, $n=3$; Ln = Er, $n=2$) or the alcohol adducts: $[\{Ln(ROH)_2(\eta^2\text{-}OPSMe_2)(\eta^1\text{-}OPSMe_2)(\mu{:}\eta^1,\eta^2,\text{-}OPSMe_2)\}_2]$ (Ln = La and Pr [XR], Nd) were isolated. It can be noted that with water as a donor ligand, two thiophosphinates are bonded by the oxygen, whereas with the weaker ROH as ligand one of these thiophosphinates becomes bridging [149].

With the bulkier dicyclohexylthiophosphinate, Nd is only seven-coordinated in $[\{Nd(H_2O)(\eta^2\text{-}OPSCy_2)(\eta^1\text{-}OPSCy_2)(\mu{:}\eta^1,\eta^2\text{-}OPSCy_2)\}_2]$ whereas with the smaller erbium, only six-coordination is possible and the monomeric anionic $[(NH_4)(H_2O)_2\{ER(OPSCy_2)_4\}]$ was obtained, in which the presumably weaker S–Ln bonds are no longer present [156].





The dimeric thioureato bridged complexes $[\{[\eta^2\text{-}N(Ph)C(Ph)\text{-}$

$NC(S)(NEt_2)][\mu{:}\eta^2\text{-}SC(NEt_2)NH]LnBr(thf)\}_2]$ ([XR]: Ln = Sm, Gd) also contain a bidentate *N*,*N*-benzamidinato(thiocarbonyl) ligand [169].

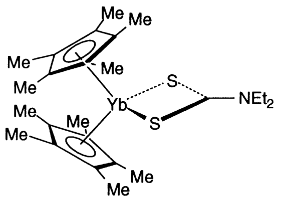
4.4.1.2. Organometallic complexes. Most compounds in this class are chelated Sm and Yb complexes: $[(RCp)_2Ln(S_2PR_2)]$ or $[(RCp)_2Ln\{S_2C(NR_2)_2\}]$ that have been prepared by oxidation of low-valent dicyclopentadienyl Ln(II) species. The oxidants used are generally S–S bonded thiuram disulphides $[R_2NC(S)S]_2$ or bis(thiophosphoryl) disulphides $[(RO)_2P(S)S]_2$.

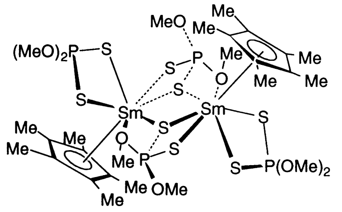
$$[(RCp)_2Ln] + [X(S)S]_2 \rightarrow [(RCp)_2LnS(S)X].$$

Starting material	Reagent	Compound	Ref.
$[Cp^*_2NdCl_2]^{2-}$	$[Me_2NC(S)S]_2$	$[Cp^*_2Nd(S_2CNMe_2)]$	[263]
$[Cp^*_2Sm(thf)_2]$	$[Me_2NC(S)S]_2$	$[Cp^*_2Sm(S_2CNMe_2)][XR]$	[163]
$[Cp^*_2Yb(Et_2O]$	$[Et_2NC(S)S]_2$	$[Cp^*_2Yb(S_2CNEt_2)]$	[241]
$[(CpCMe_2CMe_2Cp)Sm]$	$[Me_2NC(S)S]_2$	$[(CpCMe_2CMe_2Cp)Sm(S_2CNMe_2)]$	[264]
$[(CpCMe_2CMe_2Cp)Sm]$	$[(OMe)_2P(S)S]_2$	$[(CpCMe_2CMe_2Cp)Sm\{S_2P(OMe)_2\}]$	[264]
$[(CpCMe_2CMe_2Cp)Yb]$	$[Me_2NC(S)S]_2$	$[(CpCMe_2CMe_2Cp)Yb(S_2CNMe_2)]$	[264]
$[(CpCMe_2CMe_2Cp)Yb]$	$[(OMe)_2P(S)S]_2$	$[(CpCMe_2CMe_2Cp)Yb\{S_2P(OMe)_2\}]$	[264]

$[Cp^*_2Yb(S_2PR_2)]$ (R = Me, Et) could also be made from $[Cp^*_2Yb]$ and P–P bonded diphosphine disulphides such as $R_2P(S)P(S)R_2$, but an excess of this reagent had to be used since redistribution takes place, and $R_2PP(S)R_2$ and R_2PPR_2 were obtained as side products [241]

The reaction of $[Cp^*_2Sm(thf)_2]$ with $[(OMe)_2P(S)S]_2$ had a different outcome since a Cp* ligand was eliminated and a dimeric structure: $[\{Cp^*Sm[\eta^2\text{-}S_2P(OMe)_2][\mu{:}\eta^2,\eta^1,\eta^1\text{-}S_2P(OMe)_2]\}_2]$ [XR] was obtained, in which two bridging $(OMe)_2PS_2$ ligands are coordinated to Sm with one bridging S atom, one non-bridging S atom and additional coordination of a methoxy group [168]; this is in contrast to the reaction of $[(OMe)_2P(S)S]_2$ with the ansa-samarocene $[(CpCMe_2CMe_2Cp)Sm]$ where the chelate effect prevents the elimination of one Cp ligand and the "normal" $[(CpCMe_2CMe_2Cp)Sm(S_2P(OMe)_2\}]$ is obtained [264].





The Nd and Yb complexes $[Cp^*_2Ln\{S_2C(NEt_2)_2\}]$ have also been made by reaction of $[Cp^*_2LnCl_2]^-$ with sodium diethyldithiocarbamate ([XR]: Yb). The Yb complex could not be reduced into $[Cp^*_2Yb]$ by sodium amalgam in toluene [187].

Table 2

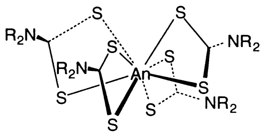
Actinide	Oxidation state	Type of complex
Th	(IV)	$[Th(S_2CNR_2)_4]$(E = S, R = Me, Et; E = Se, R = Et) $[Th(S_2CNEt_2)_2(salen)]$ $[Th(SOCNR_2)_4]$ (R = Me, Et)
Pa	(V)	$[Pa(S_2CNR_2)_4(X)]$ (X = Cl, Br)
U	(IV)	$[U(E_2CNEt_2)_4]$, (E = S, Se) $[U(S_2CNEt_2)_2(salen)]$ $[U(SOCNEt_2)_4]$
U	(VI)	$[UO_2(E_2CNEt_2)_2(L)]$ (E = S, Se; L = Ph_3PO, Ph_3AsO, Me_3NO, hmpa) $[\{UO_2(S_2CNEt_2)_3\}(C)]$, (C = K, NEt_4) $[UO_2(S_2CR)_2(L)]$ (R = Me, Ph; L = Ph_3PO, Ph_3AsO) $[UO_2(S_2COR)_2]$ (R = alkyl, aryl)
Np	(III)	$[\{Np(E_2CNEt_2)_4\}(NEt_4)]$
Np	(IV)	$[Np(S_2CNR_2)_4]$
Pu	(III)	$[Pu(S_2CNR_2)_3]$ $[\{Pu(E_2CNEt_2)_4\}(NEt_4)]$
Pu	(IV)	$[Pu(S_2CNR_2)_4]$

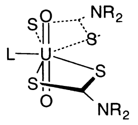
4.4.2. Actinides

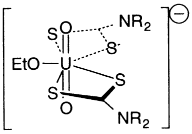
4.4.2.1. Inorganic complexes. Work on this subject prior to 1978 has been extensively reviewed [12] and will only be briefly summarized. Mostly actinide (III), (IV), (V), and uranyl (UO_2^{2+}, U(VI)) dithio- or diselenocarbamates have been reported up to 1997 with some examples of dithiocarboxylates and xanthates. Other complexes, including thiocarbamates and dithiophosphates and phosphinates have been reported later. Table 2 summarizes the type of compounds described in this review.

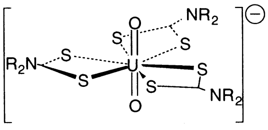
The An(III), (IV) and (V) compounds were usually made straightforwardly by reaction of, respectively, AnX_3, AnX_4 or AnX_6^{2-}, or AnX_5 and the appropriate amount of chelating anion. Anionic uranyl compounds $[\{UO_2(S_2CNR_2)_3\}(C)]$ were made from a uranyl salt and three equivalents of $(S_2CNR_2)^-$ anion and optional exchange of the cation C^+, while neutral complexes $[UO_2(E_2CNEt_2)_2(L)]$ were prepared from the anionic complexes and a suitable donor ligand L. The dithiocarbamate anions are sometimes made in situ by reaction of a diamine with CS_2 in the presence of a protic base.

The U(IV), Np(III) and Pu(III) are air-sensitive while the other compounds are air-stable. In fact, $[U(S_2CNEt_2)_4]$ cleanly transformed into the uranyl complex $[UO_2(S_2CNEt_2)_3(thf)_{1.5}]$ upon exposition to dioxygen [287].









In the reported crystal structures of these complexes, four type of geometries can be found: dodecahedral for the neutral An(IV) or anionic An(III) complexes: $[An(E_2CNR_2)_4]$, pentagonal bipyramidal for the neutral uranyl complexes: $[UO_2(E_2CNEt_2)_2(L)]$ and distorted hexagonal bipyramidal for the anionic $[UO_2(E_2CNEt_2)_3]$. More recent examples of $[UO_2(S_2CNR_2)_2(OPPh_3)]$ (R_2 = ^{n}Pr$_2$, ^{i}Pr$_2$, ^{n}Bu$_2$, ^{i}Bu$_2$, Ph$_2$, $(PhCH_2)_2$, -$(CH_2)_4$-, -$(CH_2)_5$-, -$(CH_2)_2O(CH_2)_2$-, -CHC(Me)$(CH_2)_3$-, (Me)Ph) [288] and of anionic $[\{UO_2(S_2CNR_2)_3\}(NEt_4)]$ ([XR]: R_2 = $(CH_2)_4$-, -$(CH_2)_5$-) have been described and the X-ray structure of $[\{UO_2(S_2CNEt_2)_3\}(NEt_4)]$ redetermined [289,216] and improved over the previous one [290].

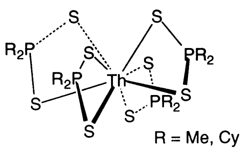
A few examples of air-stable uranyl monothiocarbamate alkoxides: $[\{UO_2(OSCNR_2)_2(OR')\}(H_2NR_2)1$ (R' = Et, R = Et [XR] [217], ^{n}Pr [XR] [218]; R' = Me, ^{n}Pr, R = Me, Et [291] have been described. They were prepared simply by bubbling COS into a solution of UO_2Cl_2 and HNR_2 in an alcohol R′OH. Their X-ray structure shows the classical pentagonal bipyramidal coordination pattern. They are not indefinitely stable in solution and decompose into a disulphido complex as already discussed in Section 4.3.1 [212]. The X-ray photoelectron spectrum of $[\{UO_2(OSCNEt_2)_2(OEt)\}(H_2NEt_2)]$ is indicative of a small S to U charge transfer [291].

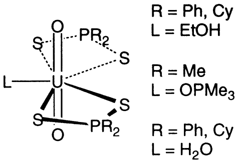
Dithiophosphate and phosphinate complexes of thorium and uranyl have been reported. The thorium compounds are neutral Th(IV) complexes of composition $[Th(S_2PR_2)_4]$ (R = Me, Et, ^{i}Pr, Cy or Ph) that were made by reaction of $ThCl_4$ with the appropriate dithiophosphinate salt. In the solid state, the structures (R = Me, Cy) are almost perfectly dodecahedral whereas NMR indicates dynamic behaviour for the cyclohexyl derivative in solution. The nature of the process is unknown, however [192].

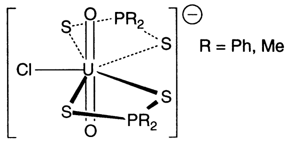
Uranyl complexes: $[UO_2(S_2PR_2)_2(L)]$ could be prepared from the suitable dithiophosphinate salt and $UO_2Cl_2.3H_2O$ or UCl_4; L can be an alcohol or water. In the UCl_4 case, air oxidation and four equivalents of dithiophosphinate are required for the transformation of U(IV) into U(VI) and the concomitant oxidation of dithiophosphinate into $(S_2PR_2)_2$, that could be isolated. Anionic compounds: $[\{(UO_2(S_2PR_2)_2(Cl)\}(NEt_4)]$ were likewise obtained either from UO_2Cl_2 or UCl_4 with addition of NEt_4Cl or from $[(UCl_6)(NEt_4)_2]$. Air and excess of dithiophosphinate are necessary with UCl_4 and $[(UCl_6)(NEt_4)_2]$ as starting materials. $[UO_2(S_2PMe_2)_2(OPMe_3)]$ has been once obtained as a side product, however the origin of $OPMe_3$ has not been determined.

Compound	**R**	**Starting material**	**Ref.**
$[UO_2(S_2PR_2)_2(HOH)]$	^{i}Pr	$UO_2Cl_2.3H_2O$	[219]
$[UO_2(S_2PR_2)_2(HOEt)]$	Me, Et, ^{i}Pr, OEt, Ph, Cy	$UO_2Cl_2.3H_2O$	[220]
$[UO_2\{S_2P(OR)_2\}_2(HOR)]$	Me, ^{i}Pr	$UO_2Cl_2.3H_2O$	[220]
$[UO_2(S_2PR_2)_2(HOEt)]$	Et, Ph	UCl_4	[220]
$[\{UO_2(S_2PR_2)_2(Cl)\}(NEt_4)]$	Me, Et, ^{i}Pr, OEt, Ph, Cy, OMe, O^{i}Pr	$UO_2Cl_2.3H_2O$	[220]
$[\{UO_2(S_2PR_2)_2(Cl)\}(NEt_4)]$	Et, Ph	UCl_4	[220]
$[\{UO_2(S_2PR_2)_2(Cl)\}(NEt_4)]$	Et, Ph, Cy	$[UCl_6]^-$	[220]

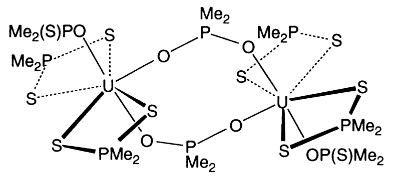
The crystal structures of several of these complexes have been determined; they are all pentagonal bipyramidal.







Red reaction mixtures $[UO_2(S_2PMe_2)_2(OH_2)]$ gradually turned green and deposited crystals of the reduced U(IV) phosphinato-bridged dimer: $[\{U(\eta^2\text{-}S_2PMe_2)_2(\eta^1\text{-}OPSMe_2)(\mu\text{-}O_2PSMe_2)\}_2]$ in which dithiophosphinate chelates and O-bonded monothiophosphinate ligands are present. The reductive step is believed to be a photochemical elimination of sulphur from $[UO_2(S_2PMe_2)_2(OH_2)]$ giving $[\{U(OPSMe_2)_2(S_2PMe_2)_2(H_2O)\}_2]$ followed by elimination of H_2S. The coordination around uranium is pentagonal bipyramidal, as usual [221].



4.4.2.2. Organometallic complexes. All compounds listed here are di- or tricyclopentadienyl derivatives of U(IV), and only one has been structurally characterized.

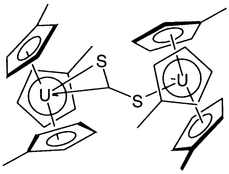
$[Cp_2U(SYCNEt_2)_2]$ (Y = O or S) have been prepared by insertion of COS or CS_2 into the U–N bond of $[Cp_2U(NEt_2)_2]$ [267,292]. They are monomeric in benzene solution, and NMR data show that they are fluxional. A comparative study of $[Cp_2U(S_2CNEt_2)_2]$, $[Cp_2U(NEt_2)_2]$ and $[Cp_2U(BH_4)_2]$ by photoelectron spectroscopy has been performed. In all cases, the HOMO corresponds to the 5f electrons on uranium, but the NHOMO (which should then control the nucleophilic reactivity of the complexes) is mostly centred on nitrogen for $[Cp_2U(NEt_2)_2]$ and on the Cp ligands on the other two complexes. This is in agreement with the higher lability of the amido group in $[Cp_2U(NEt_2)_2]$ and of the Cp ligand in $[Cp_2U(S_2CNEt_2)_2]$ and $[Cp_2U(BH_4)_2]$ in acidic conditions [293].

As an illustration, $[Cp_2U(NEt_2)_2]$ reacted with RC(O)SH to give the thiocarboxylates $[Cp_2U(SOCR)_2]$ (R = Me, Ph). These complexes are also monomeric and fluxional in solution [294].

Insertion of CS_2 into the U–S bond of $[Cp_3U(S^iPr)]$ followed by redistribution resulted in the formation of $[Cp_2U(S_2CS^iPr)_2]$ that was not isolated, but characterized by NMR [210].

Oxidation of $[(Me_3SiCp)_3U]$ or $[(MeCp)_3U(thf)]$ with CS_2 yielded the metallathiocarboxylate dimers: $[\{(RCp)_3U\}_2(\mu\text{:}\eta^1,\eta^2\text{-}CS_2)]$ (R = Me [XR], $SiMe_3$) where one

C–S unit of the CS_2 ligand η^2-bonded to one U atom and the extra S atom η^1 bonded to the other U atom [222].



5. Conclusion

The volume of research on the compounds that are the subject of this survey is steadily increasing. There are some areas that are less well studied than the others: to name a few, complexes with arsenic-based ligands are still relatively underrepresented, and also no examples of actinide selenolates or tellurolates have been reported to date. There are no obvious chemical reasons why these classes of compounds could not be better explored.

Regarding the nature of the chemical bond between the group 3, lanthanide or actinide metals and the heavier heteroelements, there are a few cases in which this bond may have some significant covalent character: the best example is found in tris(cyclopentadienyl)U(III) compounds that prefer coordination by phosphines than by conventional hard donor ligands such as amines or ethers, so the metal centre would, thus, acquire soft character; an important piece of evidence is brought about by the short value of the U–P bond length in tris(cyclopentadienyl)U(III) phosphine complexes. The analogous tris(cyclopentadienyl)Ce(III) complexes also prefer phosphine over amines or ethers, but the preference is not as significant and no short Ce–P bond length was observed in this case [48]. In most other cases, there is neither structural nor chemical evidence for significant covalency of the M–E bond, in agreement with earlier conclusions [295]. The degree of covalency indicated by the presence of phosphorus–yttrium or phosphorus–ytterbium(II) NMR coupling constants in several diamagnetic complexes should be assessed by a detailed analysis, since there is ample evidence that for organolithium compounds, despite the presence of $^1J(^6Li,^{13}C)$ coupling constants, the Li–C bond is almost exclusively ionic [296].

Few calorimetric studies have assessed the strengths of bonds between lanthanides or actinides and heavier heteroelements, yet they have shown that, when bond disruption enthalpies were compared in some analogous organometallic complexes, M–S bonds were not so much weaker than M–O bonds (M = U, Sm), whereas the Sm–P bond was significantly weaker than the Sm–N bond [98,268]. A case in point is also provided by the chemical behaviour of $[Cp_2Lu(Ph_2P)(thf)]$ [96] and of $[Cp^*_2Sm(Ph_2E)(thf)]$ (E = P, As) [50] where the three following factors: high Lewis acidity of the metal fragment; high nucleophilicity of the Ph_2E^- ligand; and weakness of the Ln–E bond contribute to the instability of the complexes and their transformation into products of THF ring opening. However, the possible weakness of the metal–heteroelement bond has not acted as a deterrent to the exploration of new and interesting compounds: what appears clearly from this survey is that provided that the right ligands and conditions are chosen, a great variety of complexes can be made, and that their chemistry is potentially very rich: as an example, advantage can be taken of their reactivity and/or instability to the synthesis of very interesting clusters.

Acknowledgements

Financial support from CNRS and Ecole Polytechnique is gratefully acknowledged. We also thank Professor J. Brennan for the communication of results prior to publication.

References

[1] M.P. Hogerheide, J. Boersma, G. van Koten, Coord. Chem. Rev. 155 (1996) 87.
[2] F.A. Hart, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 3: Main group and early transition elements, Pergamon press, NY, 1987, p. 1059.
[3] K.W. Bagnall, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 3: Main group and early transition elements, Pergamon press, NY, 1987, p. 1129.
[4] F.T. Edelmann, in: E.W. Abel, F.G.A. Stone (Eds.), Comprehensive Organometallic Chemistry II, vol. 4: Scandium, Yttrium, Lanthanides, Actinides and Titanium group, Pergamon Press, NY, 1995, p. 11.
[5] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev 95 (1995) 865.
[6] C.J. Schavieren, Adv. Organometallic Chem. 36 (1995) 283.
[7] G.B. Deacon, Q. Shen, J. Organometallic Chem. 511 (1996) 1.
[8] F.G.N. Cloke, Chem. Soc. Rev. (1993) 17.
[9] F.G.N. Cloke, in: E.W. Abel, F.G.A. Stone (Eds.), Comprehensive Organometallic Chemistry II, vol. 4: Scandium, Yttrium, Lanthanides, Actinides and Titanium group, Pergamon Press, NY, 1995, p. 1.
[10] S.A. Cotton, Coord. Chem. Rev. 160 (1997) 93.
[11] M.D. Fryzuk, T.S. Haddad, D.J. Berg, Coord. Chem. Rev. 99 (1990) 137.
[12] U. Casellato, M. Vidali, P.A. Vigato, Coord. Chem. Rev. 28 (1979) 231.
[13] L. Zakarov, Y.T. Struchkov, J. Organometallic Chem. 536 (1997) 65.
[14] B.K. Campion, R.H. Heyn, T.D. Tilley, J. Am. Chem. Soc. 112 (1990) 2011.
[15] B.K. Campion, R.H. Heyn, T.D. Tilley, Inorg. Chem. 29 (1990) 4355.
[16] B.K. Campion, R.H. Heyn, T.D. Tilley, Organometallics 12 (1993) 2584.
[17] L.N. Bochkarev, M.N. Kholodilova, S.F. Zhiltsov, T.V. Guseva, M.N. Bochkarev, G.A. Razuvaev, Zh. Obshch. Khim. 56 (1986) 723.
[18] L.N. Bochkarev, V.M. Makarov, Y.N. Hrzhanovskaya, L.N. Zakharov, G.K. Fukin, A.I. Yanovsky, Y.T. Struchkov, J. Organometallic Chem. 467 (1994) C3.
[19] M.N. Bochkarev, V.V. Khramenkov, Y.F. Rad'kov, L.N. Zakharov, Y.T. Struchkov, J. Organometallic Chem. 408 (1991) 329.
[20] L.N. Bochkarev, O.V. Grachev, S.F. Zhiltsov, L.N. Zakharov, Y.T. Struchkov, J. Organometallic Chem. 436 (1992) 299.
[21] M.N. Bochkarev, V.V. Khramenkov, Y.F. Rad'kov, L.N. Zakharov, Y.T. Struchkov, J. Organometallic Chem. 421 (1991) 29.

[22] L.N. Bochkarev, O.V Grachev, N.E. Molosnova, S.F. Ziltsov, L.N. Zakharov, G.K. Fukin, A.I. Yanovsky, Y.T. Struchkov, J. Organometallic Chem. 443 (1993) C26.
[23] L.N. Bochkarev, V.M. Makarov, L.N. Zakharov, G.K. Fukin, A.I. Yanovsky, Y.T. Struchkov, J. Organometallic Chem. 490 (1995) C29.
[24] F.G.N. Cloke, C.I. Dalby, P.B. Hitchcock, H. Karamallakis, G.A. Lawless, J. Chem. Soc. Chem. Commun. (1991) 779.
[25] D.J. Berg, C.K. Lee, L. Walker, G.W. Bushnell, J. Organometallic Chem. 493 (1995) 47.
[26] W.S. Rees, Jr, O. Just, H. Schumann, R. Weimann, Angew. Chem. Int. Ed. Engl. 35 (1996) 419.
[27] H. Schumann, M. Cygon, J. Organometallic Chem. 144 (1978) C43.
[28] N.S. Radu, T.D. Tilley, A.L. Rheingold, J. Am. Chem. Soc. 114 (1992) 8293.
[29] N.S. Radu, T.D. Tilley, A.L. Rheingold, J. Organometallic Chem. 516 (1996) 41.
[30] N.S. Radu, T.D. Tilley, Phosphorus Sulfur Silicon 87 (1994) 209.
[31] H. Schumann, S. Nickel, J. Loebel, J. Pickardt, Organometallics 7 (1988) 2004.
[32] H. Schumann, S. Nickel, E. Hahn, M.J. Heeg, Organometallics 4 (1985) 800.
[33] H. Schumann, J.A. Meese-Marktscheffel, F.E. Hahn, J. Organometallic Chem. 390 (1990) 301.
[34] M.M. Corradi, A.D. Frankland, P.B. Hitchcock, M.F. Lappert, G.A. Lawless, J. Chem. Soc. Chem. Commun. (1996) 2323.
[35] M. Porchia, N. Brianese, U. Casellato, F. Ossola, G. Rossetto, P. Zanella, R. Graziani, J. Chem. Soc. Dalton Trans. (1989) 677.
[36] M. Porchia, F. Ossola, G. Rossetto, P. Zanella, and N. Brianese, J. Chem. Soc. Chem. Commun. (1987) 550.
[37] M. Porchia, U. Casellato, F. Ossola, G. Rossetto, P. Zanella, R. Graziani, J. Chem. Soc. Chem. Commun. (1986) 1034.
[38] N.S. Radu, M.P. Engeler, C.P. Gerlach, T.D. Tilley, J. Am. Chem. Soc. 117 (1995) 3621.
[39] W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett, (1990) 74.
[40] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.
[41] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.
[42] M.D. Fryzuk, G. Giesbrecht, S.J. Rettig, Organometallics 15 (1996) 3329.
[43] H.H. Karsch, G. Ferazin, O. Steigelmann, H. Kooijman, W. Hiller, Angnew. Chem. Int. Ed. Engl. 32 (1993) 1739.
[44] H.H. Karsch, G. Ferazin, H. Kooijman, O. Steigelmann, A. Schier, P. Bissinger, W. Hiller, J. Organometallic Chem. 482 (1994) 151.
[45] T.D. Tilley, R.A. Andersen, A. Zalkin, J. Am. Chem. Soc. 104 (1982) 3725.
[46] T.D. Tilley, R.A. Andersen, A. Zalkin, Inorg. Chem. 22 (1983) 856.
[47] S. Stults, A. Zalkin, Acta Cryst. C43 (1987) 430.
[48] J.G. Brennan, S.D. Stults, R.A. Andersen, A. Zalkin, Organometallics 7 (1988) 1329.
[49] C.J. Schlesener, A.B. Ellis, Organometallics 2 (1983) 529.
[50] W.J. Evans, J.T. Leman, J.W. Ziller, S.I. Khan, Inorg. Chem. 35 (1996) 4283.
[51] J.R. van den Hende, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, S. Tian, J. Chem. Soc. Dalton Trans. (1995) 3933.
[52] G.F. Payne, O.L. Keller, J. Halperin, W.C. Wolsey, J. Chem. Soc. Chem. Commun. (1989) 50.
[53] M.D. Fryzuk, T.S. Haddad, J. Chem. Soc. Chem. Commun. (1990) 1088.
[54] M.D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 10 (1991) 2026.
[55] M.D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 11 (1992) 2967.
[56] P.B. Hitchcock. M.F. Lappert, I.A. MacKinnon, J. Chem. Soc. Chem. Commun. (1988) 1557.
[57] H.H. Karsch, A. Appelt, G. Müller, Angew. Chem. Int. Ed. Engl. 25 (1986) 823.
[58] S. Hao, J.I. Song, H. Aghabozorg, S. Gambarotta, J. Chem. Soc. Chem. Commun. (1994) 157.
[59] H.H. Karsch, G. Ferazin, P. Bissinger, J. Chem. Soc. Chem. Commun. (1994) 505.
[60] A. Recknagel, D. Stalke, H.W. Roesky, F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 28 (1989) 445.
[61] H. Schumann, F.W. Reier, E. Palamidis, J. Organometallic Chem. 297 (1985) C30.
[62] H. Schumann, J.A. Meese-Marktscheffel, A. Dietrich, J. Pickardt, J. Organometallic Chem. 433 (1992) 241.
[63] P.G. Edwards, R.A. Andersen, A. Zalkin, J. Am. Chem. Soc. 103 (1981) 7792.

[64] P.G. Edwards, R.A. Andersen, A. Zalkin, Organometallics 3 (1984) 293.
[65] H.J. Wasserman, D.C. Moody, R.R. Ryan, J. Chem. Soc. Chem. Commun. (1984) 532.
[66] J. Brennan, R. Shinomoto, A. Zalkin, N. Edelstein, Inorg. Chem. 23 (1984) 4143.
[67] A. Zalkin, J.G. Brennan, R.A. Andersen, Acta Cryst. C43 (1987) 421.
[68] A. Zalkin, J.G. Brennan, R.A. Andersen, Acta Cryst. C43 (1987) 418.
[69] J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day, V.W. Day, J. Am. Chem. Soc. 101 (1979) 5075.
[70] P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer, V.W. Day, Organometallics 1 (1982) 170.
[71] M.R. Duttera, P.J. Fagan, T.J. Marks, V.W. Day, J. Am. Chem. Soc. 104 (1982) 865.
[72] H.J. Wasserman,, D.C. Moody, R.T. Paine, R.R. Ryan, K.V. Salazar, J. Chem. Soc. Chem. Commun. (1984) 533.
[73] J.G. Brennan, A. Zalkin, Acta Cryst. C41 (1985) 1038.
[74] A. Zalkin, J.G. Brennan, R.A. Andersen, Acta Cryst. C43 (1987) 1706.
[75] W.J. Evans, K.J. Forrestal, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 36 (1997) 774.
[76] M.A. Edelmann, P.B. Hitchcock, J. Hu, M.F. Lappert, New J. Chem. 19 (1995) 481.
[77] S.J. Coles, A.A. Danopoulos, P.G. Edwards, M.B. Hursthouse, P.W. Read, J. Chem. Soc. Dalton Trans. (1995) 3401
[78] S.J. Coles, P.G. Edwards, M.B. Hursthouse, P.W. Read, J. Chem. Soc. Chem. Commun. (1994) 1967.
[79] G.W. Rabe, J. Riede, A. Schier, Inorg. Chem. 35 (1996) 40.
[80] H. Schumann, G.M. Frisch, Z. Naturforsch 34B (1979) 748.
[81] G.W. Rabe, J. Riede, A. Schier, Inorg. Chem. 35 (1996) 2680.
[82] G.W. Rabe, G.P.A. Yap, A.L. Rheingold, Inorg. Chem. 36 (1997) 3212.
[83] H. Schumann, G.M. Frisch, Z. Naturforsch 37B (1982) 168.
[84] G.W. Rabe, J.W. Ziller, Inorg. Chem. 34 (1995) 5378.
[85] G.W. Rabe, J. Riede, A. Schier, J. Chem. Soc. Chem. Commun. (1995) 577.
[86] G.W. Rabe, J. Riede, A. Schier, Organometallics 15 (1996) 439.
[87] G.W. Rabe, G.P.A. Yap, A.L. Rheingold, Inorg. Chem. 34 (1995) 4521.
[88] G.W. Rabe, J. Riede, A. Schier, Main Group Chem. 1 (1996) 273.
[89] F. Nief, L. Ricard, J. Organometallic Chem. 529 (1997) 357.
[90] S. Atlan, F. Nief, L. Ricard, Bull. Soc. Chim. Fr. 132 (1995) 649.
[91] H.C. Aspinall, D.C. Bradley, K.D. Sales, J. Chem. Soc. Dalton Trans. (1988) 2211.
[92] H.C. Aspinall, S.R. Moore, A.K. Smith, J. Chem. Soc. Dalton Trans. (1992) 153.
[93] H.C. Aspinall, S.R. Moore, A.K. Smith, J. Chem. Soc. Dalton Trans. (1993) 993.
[94] H. Schumann, H. Jarosch, Z. Anorg. Allg. Chem. 426 (1976) 127.
[95] H. Schumann, G.M. Frisch, Z. Naturforsch. 36B (1981) 1244.
[96] H. Schumann, E. Palamidis, J. Loebel, J. Organometallic Chem. 384 (1990) C49.
[97] W. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, Organometallics 2 (1983) 709.
[98] S.P. Nolan, D. Stern, T.J. Marks, J. Am. Chem. Soc. 111 (1989) 7844.
[99] H. Schumann, E. Palamidis, G. Schmid, R. Boese, Angew. Chem. Int. Ed. Engl. 25 (1986) 718.
[100] H. Schumann, E. Palamidis, J. Loebel, J. Pickardt, Organometallics 7 (1988) 1008.
[101] P.G. Edwards, M.B. Hursthouse, J.S. Parry, J. Chem. Soc. Chem. Commun. (1992) 1469.
[102] P.G. Edwards, J.S. Parry, P.W. Read, Organometallics 14 (1995) 3649.
[103] S.J. Coles, P.G. Edwards, M.B. Hursthouse, P.W. Read, Acta Cryst. C51 (1995) 1060.
[104] P.L. Arnold, F.G.N. Cloke, P.B. Hitchcock, J.F. Nixon, J. Am. Chem. Soc. 118 (1996) 7630.
[105] W.E. Piers, G. Ferguson, J.F. Gallagher, Inorg. Chem. 33 (1994) 3784.
[106] D.R. Cary, G.E. Ball, J. Arnold, J. Am. Chem. Soc. 117 (1995) 3492.
[107] F. Nief, L. Ricard, J. Organometallic Chem. 464 (1994) 149.
[108] H.J. Gosink, F. Nief, L. Ricard, F. Mathey, Inorg. Chem. 34 (1995) 1306.
[109] N. Froehlich, P.B. Hitchcock, J. Hu, M.F. Lappert, J.R. Dilworth, J. Chem. Soc. Dalton Trans. (1996) 1941.
[110] D.R. Cary, J. Arnold, Inorg. Chem. 33 (1994) 1791.
[111] F. Nief, L. Ricard, F. Mathey, Polyhedron 12 (1993) 19.

[112] P. Desmurs, M. Visseaux, D. Baudry, A. Dormond, F. Nief, L. Ricard, Organometallics 15 (1996) 4178.

[113] F. Nief, L. Ricard, J. Chem. Soc. Chem. Commun. (1994) 2723.

[114] P.G. Edwards, M.B. Hurshouse, K.M. Abdul Malik, J.S. Parry, J. Chem. Soc. Chem. Commun. (1994) 1249.

[115] D.A. Wrobleski, R.R. Ryan, H.J. Wasserman, K.V. Salazar, R.T. Paine, D.C. Moody, Organometallics 5 (1986) 90.

[116] S.W. Hall, J.C. Huffman, M.M. Miller, L.R. Avens, C.J. Burns, D.S.J. Arney, A.F. England, A.P. Sattelberger, Organometallics 12 (1993) 752.

[117] J.M. Ritchey, A.J. Zozulin, D.A. Wrobleski, R.R. Ryan, H.J. Wasserman, D.C. Moody, R.T. Paine, J. Am. Chem. Soc. 107 (1985) 501.

[118] P.J. Hay, R.R. Ryan, K.V. Salazar, D.A. Wrobleski, A.P. Sattelberger, J. Am. Chem. Soc. 108 (1986) 313.

[119] O.J. Scherer, B. Werner, G. Heckmann, G. Wolmershäuser, Angew. Chem. Int. Ed. Engl. 30 (1991) 553.

[120] M.R. Duttera, V.W. Day, T.J. Marks, J. Am. Chem. Soc. 106 (1984) 2907.

[121] D.S.J. Arney, R.C. Schnabel, B.C. Scott, C.J. Burns, J. Am. Chem. Soc. 118 (1996) 6780.

[122] P. Gradoz, D. Baudry, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, J. Organometallic Chem. 466 (1994) 107.

[123] P. Gradoz, C. Boisson, D. Baudry, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Chem. Commun. (1992) 1720.

[124] D. Baudry, M. Ephritikhine, F. Nief, L. Ricard, F. Mathey, Angew. Chem. Int. Ed. Engl. 29 (1990) 1485.

[125] P. Gradoz, M. Ephritikhine, M. Lance, J. Vigner, M. Nierlich, J. Organometallic Chem. 481 (1994) 69.

[126] T. Arliguie, M. Ephritikhine, M. Lance, M. Nierlich, J. Organometallic Chem. 524 (1996) 293.

[127] O.J. Scherer, J. Schultze, G. Wolmershäuser, J. Organometallic Chem. 484 (1994) C5.

[128] W.J. Evans, S.L. Gonzales, J.W. Ziller, J. Chem. Soc. Chem. Commun. (1992) 1138.

[129] W.J. Evans, S.L. Gonzales, J.W. Ziller, J. Am. Chem. Soc. 113 (1991) 9880.

[130] M. Ciampolini, C. Mealli, N. Nardi, J. Chem. Soc. Dalton Trans. (1980) 376.

[131] J. Huang, S. Lin, M. Wang, Q. Zhang, J. Lu, Wuji Huaxue 3(1) (1989) 1; Chem. Abstr. 107 (1987) 185548b.

[132] C. Su, N. Tang, M. Tan, W. Lu, X. Gan, K. Yu, J. Coord. Chem. 36 (1995) 41.

[133] M. Ciampolini, N. Nardi, P. Colamarino, P. Orioli, J. Chem. Soc. Dalton Trans. (1977) 379.

[134] J. Huang, S. Lin, M. Wang, Q. Zhang, J. Lu, Wuji Huaxue 3(2) (1989) 1; Chem. Abstr. 107 (1987) 248901m.

[135] A.A. Pinkerton, D. Schwarzenbach, S. Spiliadis, Inorg. Chim. Acta 128 (1987) 283.

[136] A.A. Pinkerton, D. Schwarzenbach, J. Chem. Soc. Dalton Trans. (1981) 1470.

[137] A.A. Pinkerton, D. Schwarzenbach, J. Chem. Soc. Dalton Trans. (1976) 2466.

[138] T. Imai, M. Shimoi, A. Ouchi, Bull. Chem. Soc. Jpn 59 (1986) 669.

[139] K. Nagai, Y. Sato, S. Kondo, A. Ouchi, Bull. Chem. Soc. Jpn 56 (1983) 2605.

[140] T. Imai, M. Nakamura, K. Nagai, Y. Ohki, Y. Suzuki, M. Shimoi, A. Ouchi, Bull. Chem. Soc. Jpn 59 (1986) 2115.

[141] H.J. Heeres, A. Meetsma, J.H. Teuben, J. Organometallic Chem. 414 (1991) 351.

[142] M. Berardini, J. Lee, D. Freedman, J. Lee, T.J. Emge, J.G. Brennan, Inorg. Chem. 36 (1997) 5772.

[143] S.D. Stults, R.A. Andersen, A. Zalkin, Organometallics 9 (1990) 1623.

[144] S. Spiliadis, A.A. Pinkerton, D. Schwarzenbach, Inorg. Chim. Acta 75 (1983) 115.

[145] S. Spiliadis, A.A. Pinkerton, D. Schwarzenbach, J. Chem. Soc. Dalton Trans. (1982) 1809.

[146] M. Wang, Q. Zhang, J. Huang, J. Lu, Xiamen Daxue Xuebao, Ziran Kexueban 26 (1987) 65; Chem. Abstr. 107 (1987) 88470q.

[147] A.A. Pinkerton, D. Schwarzenbach, J. Chem. Soc. Dalton Trans. (1976) 2464.

[148] Y. Meseri, A.A. Pinkerton, G. Chapuis, J. Chem. Soc. Dalton Trans. (1977) 725.

[149] K.M. Mühlsiepen, R. Mattes, Z. Anorg. Allg. Chem. 506 (1983) 115.

[150] G. Depaoli, P. Ganis, P.L. Zanonato, G. Valle, Polyhedron 12 (1993) 671.

[151] C. Su, M. Tan, N. Tang, X. Gan, Z. Zhang, Q. Xue, K. Yu, Polyhedron 16 (1997) 1643.
[152] Y. Tian, F. Zhao, J. Liu, Y. Liang, Jiegou Huaxue, 4 (1985) 115; Chem. Abstr. 105 (1986) 202088g.
[153] Z. Zhang, W. Zhang, S. Nyu, L. Ye, Y. Fan, Wuji Huaxue 5 (1989) 8; Chem. Abstr. 111 (1989) 184650b.
[154] R. Nakamura, K. Nagai, M. Shimoi, A. Ouchi, Bull. Chem. Soc. Jpn 57 (1984) 2919.
[155] Y. Ohki, M. Nakamura, Y. Suzuki, K. Nagai, M. Shimoi, A. Ouchi, Bull. Chem. Soc. Jpn 58 (1985) 1593.
[156] K.M. Mülsiepen, R. Mattes, Z. Anorg. Allg. Chem. 506 (1983) 125.
[157] M. Geissinger, J. Magull, Z. Anorg. Allg. Chem. 623 (1997) 755.
[158] K. Tatsumi, T. Amemiya, H. Kawaguchi, K. Tani, J. Chem. Soc. Chem. Commun. (1993) 773.
[159] K. Mashima, Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, Inorg. Chem. 35 (1996) 93.
[160] K. Mashima, Y. Nakayama, H. Fukumoto. N. Kanehisa, Y. Kai, A. Nakamura, J. Chem. Soc. Chem. Commun. (1994) 2523.
[161] B. Çetinkaya, P.B. Hitchcock, M.F. Lappert, R.G. Smith, J. Chem. Soc. Chem. Commun. (1992) 932.
[162] K. Mashima, T. Shibahara, Y. Nakayama, A. Nakamura, J. Organometallic Chem. 501 (1995) 263.
[163] A. Recknagel, M. Noltemeyer, D. Stalke, U. Pieper, H.G. Schmidt, F.T. Edelmann, J. Organometallic Chem. 411 (1991) 347.
[164] K. Mashima, Y. Nakayama, N. Kanehisa, Y. Kai, A. Nakamura, J. Chem. Soc. Chem. Commun. (1993) 1847.
[165] W.J. Evans, G.W. Rabe, J.W. Ziller, R.J. Doedens, Inorg. Chem. 33 (1994) 2719.
[166] W.J. Evans, M.A. Ansari, J.W. Ziller, S.I. Khan, Organometallics 14 (1995) 3.
[167] C. Sun, Y. Zhu, X. Liu, S. Yi, L. Li, X. Zheng, Chem. Res. Chin. Univ. 10 (1994) 236; Chem. Abstr. 122 (1995) 176915d.
[168] M. Rieckhoff, M. Noltemeyer, F.T. Edelmann, I. Haiduc, I. Silaghi-Dumitrescu, J. Organometallic Chem. 469 (1994) C19.
[169] M. Geissinger, J. Magull, Z. Anorg. Allg. Chem. 622 (1996) 734.
[170] M. Brewer, J. Lee, J.G. Brennan, Inorg. Chem. 34 (1995) 5919.
[171] J. Lee, T.J. Emge, J.G. Brennan, Inorg. Chem. 36 (1997) 5064.
[172] M. Berardini, J.G. Brennan, Inorg. Chem 34 (1995) 6179.
[173] T. Kobayashi, H. Naruke, Y. Yamase, Chem. Lett. (1997) 907.
[174] M. Wang, G. Guo, J. Huang, Q. Zhang, J. Lu, Jiegou Huaxue 8(2) (1989) 86; Chem. Abstr. 112 (1990) 129534n.
[175] J. Magull, A. Mandell, Z. Anorg. Allg. Chem. 620 (1994) 819.
[176] H.C. Aspinall, D.C. Bradley, M.B. Hursthouse, K.D. Sales, N.P.C. Walker, J. Chem. Soc. Chem. Commun. (1985) 1585.
[177] J.H. Melman, T.J. Emge, J.G. Brennan, J. Chem. Soc. Chem. Commun. (1997) 2269.
[178] K. Nagai, R. Nakamura, M. Shimoi, A. Ouchi, Bull. Chem. Soc. Jpn 57 (1984) 2725.
[179] A.A. Pinkerton, D. Schwarzenbach, J. Chem. Soc. Dalton Trans. (1980) 1300.
[180] C. Su, N. Tang, M. Tan, K. Yu, Polyhedron 15 (1996) 233.
[181] M. Brewer, D. Khasnis, M. Buretea, M. Berardini, T.J. Emge, J.G. Brennan, Inorg. Chem. 33 (1994) 2743.
[182] J. Lee, M. Brewer, M. Berardini, J.G. Brennan, Inorg. Chem. 34 (1995) 3215.
[183] M. Wedler, M. Noltemeyer, U. Pieper, H.G. Schmidt, D. Stalke, F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 29 (1990) 894.
[184] Z.Z. Wu, Z.E. Huang, R.F. Cai, X.G. Zhou, Z. Xu, X.Z. You, X.Y. Huang, J. Organometallic Chem. 506 (1996) 25.
[185] P. Poremba, M. Noltemeyer, H.G. Schmidt, F.T. Edelmann, J. Organometallic Chem. 501 (1995) 315.
[186] A. Zalkin, T.J. Henly, R.A. Andersen, Acta Cryst. C43 (1987) 233.
[187] T.D. Tilley, R.A. Andersen, A. Zalkin, D.H. Templeton, Inorg. Chem. 21 (1982) 2644.
[188] H. Schumann, I. Albrecht, E. Hahn, Angew. Chem. Int. Ed. Engl. 24 (1985) 985.
[189] U. Casellato, S. Sitran, S. Tamburini, P.A. Vigato, R. Graziani, Inorg. Chim. Acta 95 (1984) 37.
[190] Z. Lin, C.P. Brock, T.J. Marks, Inorg. Chim. Acta 141 (1988) 145.

[191] D.A. Wrobleski, D.T. Cromer, J.V. Ortiz, T.B. Rauchfuss, R.R. Ryan, A.P. Sattelberger, J. Am. Chem. Soc. 108 (1986) 174.

[192] A.A. Pinkerton, A.E. Storey, J.M. Zellweger, J. Chem. Soc. Dalton Trans. (1981) 1475.

[193] R. Shinomoto, A. Zalkin, N.M. Edelstein, Inorg. Chim. Acta 139 (1987) 91.

[194] R. Shinomoto, A. Zalkin, N.M. Edelstein, D. Zhang, Inorg. Chem. 26 (1987) 2868.

[195] D.E. Fenton, P.A. Vigato, U. Casellato, R. Graziani, M. Vidali, Inorg. Chim. Acta 51 (1981) 195.

[196] S. Sitran, D. Fregona, U. Casellato, P.A. Vigato, R. Graziani, G. Faraglia, Inorg. Chim. Acta 132 (1987) 279.

[197] U. Casellato, S. Sitran, S. Tamburini, P.A. Vigato, R. Graziani, Inorg. Chim. Acta 114 (1986) 111.

[198] G.D. Jarvinen, R.R. Ryan, B.F. Smith, J.M. Ritchey, Inorg. Chim. Acta 129 (1987) 139.

[199] L. Baracco, G. Bombieri, S. Degretto, E. Forsellini, G. Marangoni, G. Paolucci, R. Graziani, J. Chem. Soc. Dalton Trans. (1975) 2161.

[200] A. Zalkin, J.G. Brennan, Acta Cryst. C41 (1985) 1295.

[201] P.C. Leverd, M. Lance, J. Vigner, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1995) 237.

[202] P.C. Leverd, T. Arliguie, M. Ephritikhine, M. Nierlich, M. Lance, J. Vigner, New J. Chem. 17 (1993) 769.

[203] P.C. Leverd, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1994) 3563.

[204] P.C. Leverd, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1993) 2251.

[205] K. Tatsumi, I. Matsubara, Y. Inoue, A. Nakamura, R.E. Cramer, G.J. Tagoshi, J.A. Golen, J.W. Gilje, Inorg. Chem. 29 (1990) 4928.

[206] D.L. Clark, M.M. Miller, J.G. Watkin, Inorg. Chem. 32 (1993) 772.

[207] Â. Domingos, A. Pires de Matos, I. Santos, Polyhedron 11 (1992) 1601.

[208] U. Casellato, P.A. Vigato, S. Tamburini, R. Graziani, M. Vidali, Inorg. Chim. Acta 72 (1983) 141.

[209] D. Rose, Y.D. Chang, J. Zubieta, Inorg. Chem. 33 (1994) 5167.

[210] P.C. Leverd, M. Ephritikhine, M. Lance, J. Vigner, M. Nierlich, J. Organometallic Chem. 507 (1996) 229.

[211] P.C. Leverd, T. Arliguie, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1994) 501.

[212] D.L. Perry, A. Zalkin, H. Ruben, D.H. Templeton, Inorg. Chem. 21 (1982) 237.

[213] L.R. Avens, D.M. Barnhart, C.J. Burns, S.D. McKee, W.H. Smith, Inorg. Chem. 33 (1994) 4245.

[214] J.G. Brennan, R.A. Andersen, A. Zalkin, Inorg. Chem. 25 (1986) 1761.

[215] D.L. Clark, J.C. Gordon, J.C. Huffman, J.G. Watkin, B.D. Zwick, New J. Chem. 19 (1995) 495.

[216] N.W. Allcock, A. Pennington, J. Chem. Soc. Dalton Trans. (1989) 471.

[217] D.L. Perry, D.H. Templeton, A. Zalkin, Inorg. Chem. 17 (1978) 3699.

[218] D.L. Perry, D.H. Templeton, A. Zalkin, Inorg. Chem. 18 (1979) 879.

[219] A.A. Pinkerton, F.P. Ahlers, H.F. Greiwing, B. Krebs, Inorg. Chim. Acta 257 (1997) 77.

[220] A.E. Storey, F. Zonnevijle, A.A. Pinkerton, D. Schwarzenbach, Inorg. Chim. Acta 75 (1983) 103.

[221] H. Greiwing, B. Krebs, A.A. Pinkerton, Inorg. Chim. Acta 234 (1995) 127.

[222] J.G. Brennan, R.A. Andersen, A. Zalkin, Inorg. Chem. 25 (1986) 1756.

[223] W.E. Piers, D.J. Parks, L.R. MacGillivray, M.J. Zaworotko, Organometallics 13 (1994) 4547.

[224] I.P. Beletskaya, A.Z. Voskoboynikov, A.K. Shestakova, A.I. Yanovsky, G.K. Fukin, L.N. Zacharov, Y.T. Struchkov, H. Schumann, J. Organometallic Chem. 468 (1994) 121.

[225] D. Freedman, T.J. Emge, J.G. Brennan, J. Am. Chem. Soc. 119 (1997) 11112.

[226] M. Berardini, T.J. Emge, J.G. Brennan, J. Am. Chem. Soc. 116 (1994) 6941.

[227] M. Berardini, T.J. Emge, J.G. Brennan, Inorg. Chem. 34 (1995) 5327.

[228] K. Mashima, Y. Nakayama, A. Nakamura, N. Kanehisa, Y. Kai, H. Takaya, J. Organometallic Chem. 473 (1994) 85.

[229] W.J. Evans, G.W. Rabe, M.A. Ansari, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 33 (1994) 2110.

[230] M. Berardini, T.J. Emge, J.G. Brennan, J. Am. Chem. Soc. 115 (1993) 8501.

[231] C.G. Pernin, J.A. Ibers, Inorg. Chem. 36 (1997) 3802.

[232] M. Geissinger, J. Magull, Z. Anorg. Allg. Chem. 621 (1995) 2043.

[233] M. Berardini, T.J. Emge, J.G. Brennan, J. Chem. Soc. Chem. Commun. (1993) 1537.
[234] M. Wedler, A. Recknagel, J.W. Gilje, M. Noltemeyer, F.T. Edelmann, J. Organometallic Chem. 426 (1992) 295.
[235] D.J. Berg, C.J. Burns, R.A. Andersen, A. Zalkin, Organometallics 8 (1989) 1865.
[236] H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Muchmore, J. Pickardt, J. Organometallic Chem. 349 (1988) 103.
[237] A.C. Sutorik, M.G. Katzanidis, J. Am. Chem. Soc. 113 (1991) 7754.
[238] W.E. Piers, L.R. MacGillivray, M. Zaworotko, Organometallics 12 (1993) 4723.
[239] D.R. Cary, J. Arnold, J. Am. Chem. Soc. 115 (1993) 2520.
[240] D.V. Khasnis, M. Brewer, J. Lee, T.J. Emge, J.G. Brennan, J. Am. Chem. Soc. 116 (1994) 7129.
[241] D.J. Berg, R.A. Andersen, A. Zalkin, Organometallics. 7 (1988) 1858.
[242] A. Zalkin, D.J. Berg, Acta Cryst. C44 (1988) 1488.
[243] G. Paolucci, G. Rossetto, P. Zanella, R.D. Fischer, J. Organometallic Chem. 284 (1985) 213.
[244] F. Nief, F. Mathey, Synlett (1991) 745.
[245] P. Desmurs, A. Dormond, F. Nief, D. Baudry, Bull. Soc. Chim. Fr. 134 (1997) 683.
[246] F. Nief, F. Mathey, J. Chem. Soc. Chem. Commun. (1989) 800.
[247] P.L. Arnold, F.G.N. Cloke, P.B. Hitchcock, J. Chem. Soc. Chem. Commun. (1997) 481.
[248] P. Gradoz, D. Baudry, M. Ephritikhine, F. Nief, F. Mathey, J. Chem. Soc. Dalton Trans. (1992) 3047.
[249] U. Casellato, S. Sitran, S. Tamburini, P.A. Vigato, R. Graziani, J. Less-common Metals 122 (1986) 257.
[250] U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato, R. Graziani, Inorg. Chim. Acta 119 (1986) 215.
[251] K. Abu-Dari, K.N. Raymond, Inorg. Chem. 21 (1982) 1676.
[252] J.G. Brennan, S.D. Stults, R.A. Andersen, A. Zalkin, Inorg. Chim. Acta 139 (1987) 201.
[253] R.G. Jones, G. Karmas, G.A. Martin, Jr, H. Gilman, J. Am. Chem. Soc. 78 (1956) 4285.
[254] A. Stein, S.W. Keller, T.E. Mallouk, Science 259 (1993) 1558.
[255] W.E. Piers, J. Chem. Soc. Chem. Commun. (1994) 309.
[256] Y.F. Rad'kov, E.A. Fedorova, S.I. Khorchev, G.S. Kalinina, M.N. Bochkarev, G.A. Razuvaev, Zh. Obshch. 55 (1985) 2153.
[257] K.S. Gharia, M. Singh, S. Mathur, R. Roy, B.S. Sankla, Synth. React. Inorg. Met-Org. Chem. 12 (1982) 337.
[258] A.R. Strzelecki, P.A. Timinski, B.A. Helsel, P.A. Bianconi, J. Am. Chem. Soc. 114 (1992) 3159.
[259] A.R. Strzelecki, C.L. Lihar, B.A. Helsel, T. Utz, M.C. Lin, P.L. Bianconi, Inorg. Chem. 33 (1994) 5188.
[260] H. Gornitzka, F.T. Edelmann, K. Jacob, J. Organometallic Chem. 436 (1992) 325.
[261] Y. Taniguchi, M. Maruo, K. Takaki, Y. Fujiwara, Tetrahedron Lett. 35 (1994) 7789.
[262] I.P. Beletskaya, A.Z. Voskoboynikov, A.K. Shestakova, H. Schumann, J. Organometallic Chem. 463 (1993) C1.
[263] M. Weidler, A. Recknagel, F.T. Edelmann, J. Organometallic Chem. 395 (1990) C26.
[264] F.T. Edelmann, M. Rieckhoff, I. Haiduc, I. Silaghi-Dimitrescu, J. Organometallic Chem. 447 (1993) 203.
[265] I. Santos, N. Marques, A. Pires de Matos, Inorg. Chim. Acta 139 (1987) 89.
[266] Â. Domingos, J. Marçalo, A. Pires de Matos, Polyhedron 11 (1992) 909.
[267] J.O. Jamerson, J.A. Takats, J. Organometallic Chem. 78 (1974) C23.
[268] X. Jemine, J. Goffart, P.C. Leverd, M. Ephritikhine, J. Organometallic Chem. 469 (1994) 55.
[269] P.C. Blake, M.F. Lappert, R.G. Taylor, J.L. Atwood, H. Zhang, Inorg. Chim. Acta 139 (1987) 13.
[270] M. Delépine, Bull. Soc. Chim. Fr. 3 (1908) 643.
[271] D. Pattee, C. Musikas, A. Faure, C. Chachaty, J. Less-common Metals 122 (1986) 295.
[272] D. Brown, D.G. Holah, J. Chem. Soc. Chem. Commun. (1968) 1545.
[273] D. Brown, D.G. Holah, C.E.F. Rickard, J. Chem. Soc. A (1970) 786.
[274] W. Lu, X. Wang, S. Han, M. Chen, Polyhedron 11 (1992) 1815.
[275] T.H. Siddall III, W.E. Stewart, J. Inorg. Nucl. Chem. 32 (1970) 1147.
[276] H. Zhu, N. Tang, X. Gan, W. Zhang, M. Tan, A. Wang, Polyhedron 12 (1993) 945.

[277] N. Tang, X. Gan, H. Zhu, M. Tan, Polyhedron 9 (1990) 859.
[278] C. Su, N. Tang, M. Tan, W. Liu, X. Gan, Polyhedron 15 (1996) 73.
[279] A.A. Pinkerton, Inorg. Nucl. Chem. Lett. 10 (1974) 495.
[280] M. Ciampolini, N. Nardi, J. Chem. Soc. Dalton Trans. (1977) 2121.
[281] A.A. Pinkerton, Y. Meseri, C. Rieder, J. Chem. Soc. Dalton Trans. (1978) 85.
[282] S. Spiliadis, A.A. Pinkerton, J. Chem. Soc. Dalton Trans. (1982) 1815.
[283] A.A. Pinkerton, W.L. Earl, J. Chem. Soc. Dalton Trans. (1978) 267.
[284] S. Spiliadis, A.A. Pinderton, Inorg. Chim. Acta 75 (1983) 125.
[285] A.A. Pinkerton, W.L. Earl, J. Chem. Soc. Dalton Trans. (1979) 1347.
[286] P.N. Mohan Das, W. Kuchen, H. Keck, G. Hägele, J. Inorg. Nucl. Chem. 39 (1977) 833.
[287] F. Calderazzo, G. Dell'Amico, R. Netti, M. Pasquali, Inorg. Chem. 17 (1978) 471.
[288] C.C. Hadjikostas, G.A. Katsoulos, M.P. Sigalas, Inorg. Chim. Acta 134 (1987) 175.
[289] M. Pennington, N.W. Allcock, D. Brown, Inorg. Chim. Acta 139 (1987) 49.
[290] K. Bowman, Z. Dori, J. Chem. Soc. Chem. Commun. (1968) 636.
[291] D.L. Perry, Inorg. Chim. Acta 48 (1981) 117.
[292] A.I. Arduini, J.D. Jamerson, J. Takats, Inorg. Chem. 20 (1981) 2474.
[293] A.L. Arduini, J. Malito, J. Takats, E. Ciliberto, I. Fragala, P. Zanella, J. Organometallic Chem. 326 (1987) 49.
[294] A.L. Arduini, J. Takats, Inorg. Chem. 20 (1981) 2480.
[295] K.N. Raymond, C.W. Eigenbrot, Jr, Acc. Chem. Res. 13 (1989) 276.
[296] C. Lambert, P. von Ragué Schleyer, Angew. Chem. Int. Ed. Engl. 33 (1996) 1129.