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Osmium 1996

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Contents

1. Introduction

This review covers the coordination chemistry of osmium published in 1996. I have tried to make the review as comprehensive as possible, although coverage is restricted to the more prominent journals. The main emphasis is on coordination chemistry, though some osmium clusters are also discussed. Organometallic compounds, including clusters where the primary interest is in the coordinated organic fragments, are not reviewed as they are covered elsewhere.

2. Osmium(VIII)

Lau and Siu have reported electrospray MS studies of several osmium nitride complexes including the Os(VIII) species $[Os(O)_3N]^-$. Relative intrinsic metal–ligand bond strengths were studied by examination of gas phase fragmentation

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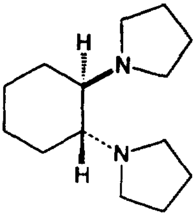
following collision induced dissociation (CID) [1]. The first cationic osmium(VIII) species, $[F(cis\text{-}OsO_2F_3)_2]^+$ and $[OsO_2F_3]^+$, have been synthesised and characterised by solution ^{19}F NMR spectroscopy. The solid state structure of the dinuclear complex has been determined by an X-ray diffraction study [2].

Kinetic studies on the asymmetric dihydroxylation of alkenes catalysed by OsO_4 and asymmetric nitrogen base ligands have been carried out [3] as well as theoretical studies on plausible reaction intermediates [4]. There has been some controversy over the mechanism [5–7] although a recent theoretical study gives strong support to the mechanism involving [3+2] cycloaddition of OsO_4 to the alkene through the concerted formation of two C–O bonds [8]. The asymmetric amine ligands (**1**), (**2**) and (**3**) have been synthesised and the formally 20-electron complex that (**1**) forms with OsO_4 has been characterised by a low temperature X-ray diffraction study [9]. A short review of asymmetric aminohydroxylation of alkenes using osmium with asymmetric amine catalysis has appeared [10].



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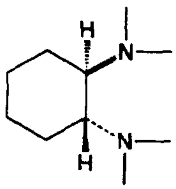

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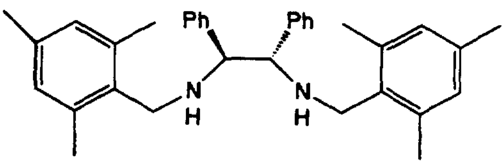

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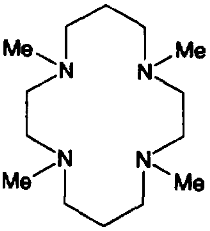
3. Osmium(VI)

Pulse radiolysis has been used to measure rate and equilibrium constants for the reaction of the $[Os^{VI}(4)(O)_2]^{2+}/[Os^{V}(4)(O)_2]^+$ couple with semiquinone/quinone couples and the solid state structure of $[Os^{VI}(4)(O)_2][PF_6]_2$ has been determined [11].

The compound $OsNCl_3$ has been prepared from the reaction of $[NH_4]_2[OsNCl_5]$ with chlorine at 300 °C and was characterised by IR spectroscopy and magnetic susceptibility measurements [12]. Alkanethiolate complexes of osmium(VI), $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$ (**5**, R = Et, ^{t}Bu, ^{i}Pr, CH_2^iPr, Bz), possessing bridging thiolate ligands have been prepared from the reaction of $[Os(N)(CH_2SiMe_3)_2Cl]_2$



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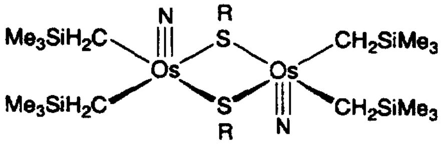
with alkali metal thiolates while terminal thiolate or alkoxide complexes $[PPh_4][Os(N)(EBz)_4]$ (E = O, S) are produced from the reaction of $[PPh_4][Os(N)Cl_4]$ with NaSBz or LiOBz [13].



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A theoretical study of $[OsH_5(\eta\text{-}C_5H_5)]$ has shown that it is probable that the hydride ligands undergo exchange through a trigonal twisting of three hydride ligands and that the formation of a non-classical dihydrogen species is unlikely [14].

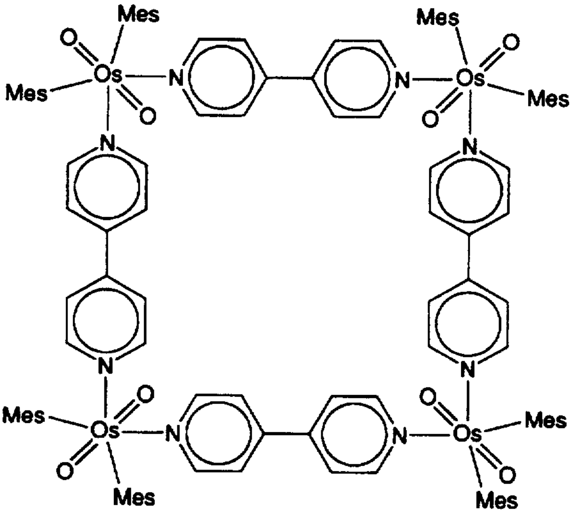
Reaction of OsO_2Mes_2 with pyrazine (pyz) gives the bridged species $[OsO_2Mes_2]_2(\mu\text{-pyz})$. If 4,4′-bipyridine is used instead, a tetraosmium species (**6**) is formed [15].

4. Osmium(V)

Metallic osmium will dissolve in a solution of difluorine in anhydrous HF to form anionic $[OsF_6]^-$. The unit cell of $Li[OsF_6]$ has been derived [16,17].

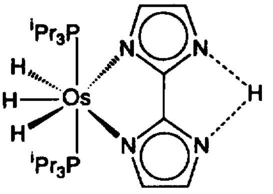
5. Osmium(IV)

Site selectivity has been observed in the abstraction of hydride or halide from $[Os(H)_2X_2P^iPr_3]$ (X = Cl, Br, I): protonation or methylation of the chloride or bromide complexes results in the abstraction of the halide whereas a hydrogen complex is formed on protonation of the iodide complex. Methyl triflate reacts with the iodide complex to form $[Os(H)_2(P^iPr_3)_2(OTf)_2]$ which has been shown to cocrystallise with its hydrated form by an X-ray diffraction study [18]. The hexahydrido complex $[OsH_6(P^iPr_3)_2]$ reacts with one equivalent of 2,2′-biimiazole



(6)

(H_2biim) or two equivalents of pyrazole to produce complexes (**7**) and (**8**). Complex (**7**) reacts with [M(μ-OMe)(COD)$_2$] to form [$OsH_3(P^iPr_3)_2$(μ-biim)M(COD)] (M = Rh or Ir) [19].



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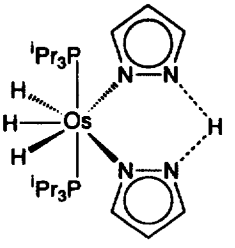
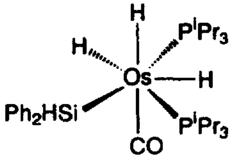


(8)

The first trihydrosilyl, trihydrogermyl and trihydrostannyl derivatives of osmium(IV) have been reported. The molecular structure of [$OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$] (**9**) has been determined by a combination of an X-ray diffraction study and *ab initio* calculations on the model compound [$OsH_3(SiH_3)(CO)(PH_3)_2$] [20].

A facile synthetic route to *trans*-dihalo(porphyrinato)osmium(IV) complexes [Os(TPP)X_2] and [Os(**10**)X_2] (X = Cl, Br, I) has been described. Synthesis is achieved by reacting the corresponding (carbonyl)osmium(II) complexes [Os(TPP)(CO)] or [Os(**10**)(CO)] with CCl_4, CBr_4 or CI_4. A relatively strong binding of carbon monoxide is thought to be an important factor in avoiding dimerisation of the osmium(III) intermediate shown to be involved in the reaction [21].



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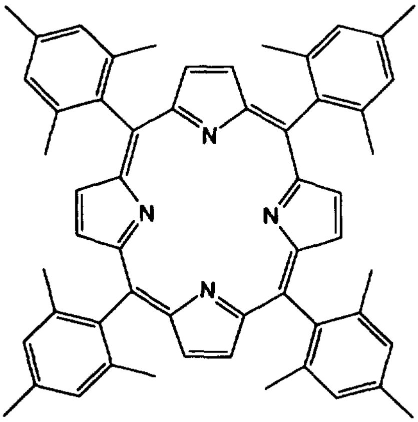

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Deprotonation of the imido ligand in $[(Cp)Os(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ produces the first osmium(IV) methyleneamido complex, $[(Cp)Os(N{=}CH_2)(CH_2SiMe_3)_2]$. The reaction is reversible, treatment of $[(Cp)Os(N{=}CH_2)(CH_2SiMe_3)_2]$ with HBF_4 producing $[(Cp)Os(NCH_3)(CH_2SiMe_3)_2][BF_4]$ [22].

The paramagnetic, octahedral complexes $[Os(SC_6F_5)_2(O_2CR_f)(PMe_2Ph)_2]$ (where R_f is a fluorinated alkyl/aryl fragment) have been prepared by treatment of $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ with the corresponding fluoro-carboxylic acid. Diamagnetic pentacoordinate osmium(IV) complexes $[Os(SR_f)_3X(PR_3)]$ ($X=Cl$, Br or SR_f; $PR_3=PMe_2Ph$, PPh_3, $P(C_6H_4Y\text{-}4)_3$ ($Y=F$, OMe, CF_3, Me, Cl)) have also been prepared and their electrochemistry studied [23].

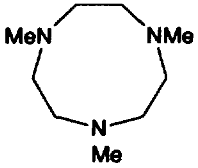
Osmium coordination compounds OsE_2Cl_{12} ($E=S$, Se, Te) and $OsS_2O_2Cl_3$ and OsS_4Cl_2 have been synthesised in halogen-containing non-aqueous solvents. The structures of the dodecachloro complexes were determined by X-ray diffraction. Determination of magnetic properties, vibrational (IR and Raman) spectra, ^{35}Cl NMR spectra and electronic diffusive reflectance spectra (DRS) was also carried out. The structures consist of complicated arrangements of $OsCl_6$ and EX_n polyhedra [24].

A series of mixed-ligand complexes of osmium(III/IV) 8-quinolinolates containing one ketoximate ligand have been studied. Mixed tris-chelates of the type $[OsAQ_2]$ [A = isonitrosoacetophenoate and isonitrosopropiophenoate; Q = deprotonated

8-quinolinol and 2-methyl-8-quinolinol] have been prepared and undergo reversible oxidation. The complexes have been characterised by physio-chemical, magnetic and spectroscopic methods and exhibit several spin-allowed and spin-forbidden charge transfer reactions in their electronic spectra [25].

6. Osmium(III)

Tetraazocyclononane complexes $[LOs(\eta^6\text{-}C_6H_6)][PF_6]_2$ (L = tacn) and $LOsCl_3$ [L = tacn and Me_3tacn (**11**)] have been prepared. Dinuclear species $[LOs(\mu\text{-}Cl)_3OsL][PF_6]_3$, formed on the reaction of $LOsCl_3$ with neat triflic acid, are successively reduced to Os(II)–Os(III) then Os(II)–Os(II) species. Addition of tetraphenylborate to $(Me_3tacn)OsCl_3$ results in the formation of $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)][BPh_4]$ (**12**) which has an unusual structure that has been characterised by an X-ray diffraction study [26].



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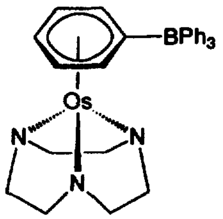


(12)

The MCD spectrum of $[Bu_4N]_3[Os(CN)_6]$ has been measured at 4.2 K and confirms the assignments of the LMCT transition and casts doubt on earlier d–d assignments made for $[Os(CN)_6]^{3-}$ [27].

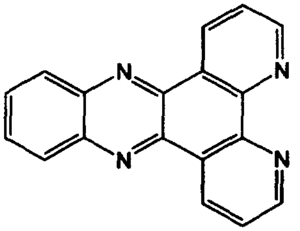
The adsorption and desorption processes of a new series of redox-active transition metal complexes of the type $[Os(bpy)_2Cl(Py\text{–}(CH_2)_n\text{–}SH)][PF_6]$, ($n = 4$, 6 or 9), capable of forming adsorbed monolayers on gold and platinum electrodes have been studied by cyclic voltammetry [28]. The 4-electron reduction of O_2 is catalysed by cobalt porphyrin derivatives containing $[(NH_3)_5Os]^{2+/3+}$ coordinated to the porphyrin ring [29].

The X-ray structure determination of $[Ph_4P][OsBr_4(CO)(H_2O)]$ has been reported [30].

7. Osmium(II)

7.1. Complexes with oligopyridine-based ligands

The photoinduced electron transfer chemistry between $[Os(phen)_2dppz]^{3+}$ [dppz = [3,2-*a*:2′,3′-*c*]phenazine, (**13**)] bound to DNA has been characterised [31]. The Stark spectra of bipyridine and a number of metal tris(2,2′-bipyridine) complexes (including $[Os(bpy)_3]^{2+}$) have been measured in the ligand-centred region in the near UV. Excitation into the ligand-centred absorption bands of the metal complexes leads to excited states with dipole moments that are substantially larger than would be expected were the transitions purely ligand centred. Mixing of ligand-centred excited states with MLCT states is a possible explanation for this [32]. Electrochemical studies on dense monolayers of $[Os(bpy)_2py(p3p)]^{2+}$, where p3p is 4,4′-trimethylenebipyridine (**14**), show three well-defined waves corresponding to osmium- and bipyridyl-based redox reactions [33]. The spectroscopic properties of a number of osmium complexes of tpy have been compared to those using a similar ligand (**15**). All of the complexes studied possess metal based oxidations and ligand based reductions localised on each polyazine ligand [34]. Cyclic voltammetry studies of osmium phthalocyanine complexes $[(CN)_2Os(pc)]^{2-}$ and $[(py)_2Os(pc)]$ have highlighted remarkably easy ring oxidations for the cyanide complex which shows half-wave oxidation potentials of 0.25 and 0.67 V (vs SCE) [35].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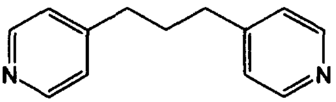
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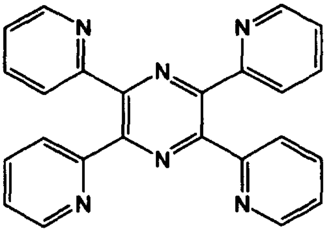
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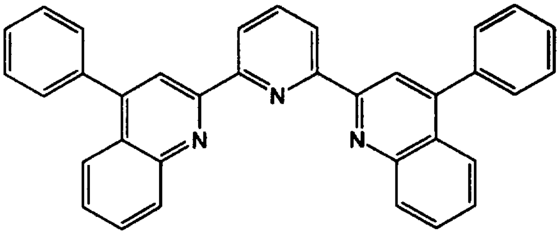
Complexes $[Os(\mathbf{16})_2][PF_6]_2$ and $[Os(\mathbf{16})(\mathbf{17})][PF_6]_2$ are reported to be the first mononuclear osmium complexes to show room temperature luminescence above 840 nm in the near-infrared region [36].

The redox-active polymers $[Os(bpy)_2(PVPS)_nClRu(edta)]$ ($n = 10, 15, 20$; PVPS = poly(vinylpyridine) co-styrene polymer) have been prepared and subjected to electrochemical investigation [37].

The monometallic complex $[(bpy)_2Os(\mathbf{18})]^{2+}$, has been obtained from the reaction of 5,6-diamino-1,10-phenanthroline with $[(bpy)_2Os(phenidione)]^{2+}$. Further reaction with an osmium precursor yields dimetallic $[(bpy)_2Os(\mathbf{18})Os(bpy)_2]^{4+}$. The com-



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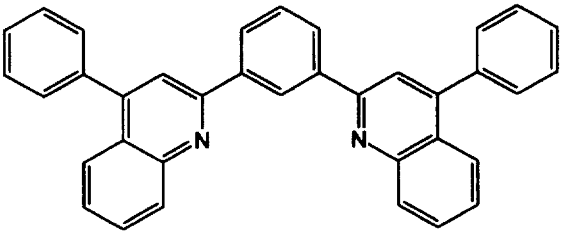
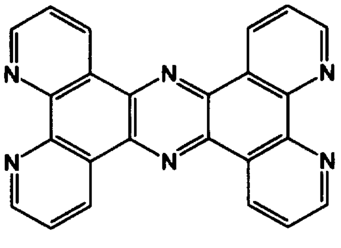


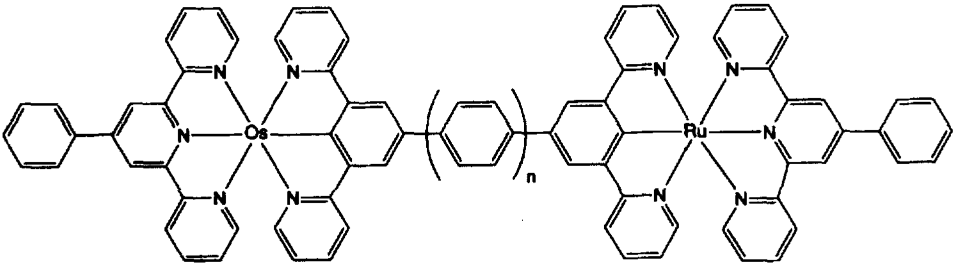
(17)

plexes show one reversible metal-centred oxidation and several reversible reductions which add one electron to (**18**) and bpy ligands. The complexes are luminescent in acetonitrile [38]. A building block approach has also been used to synthesise the mixed metal complexes $[(tpy)Os(\mathbf{15})RuCl_3][PF_6]$ and $[(tpy)Os(\mathbf{15})Ru(\mathbf{15})][PF_6]_4$. For both complexes the bridging ligand is the site of localisation of the LUMO. The HOMO is localised on the Ru atom for the chloride complex but this site shifts to Os when the chlorides are replaced by tpp [39]. The luminescence spectroscopy of a series of Ru(II)/Os(II) dinuclear complexes with bridging ligands containing a varying number of phenylene spacer units (**19**) has been investigated [40].



(18)

Adamantane has been employed as a spacer ligand in similar complexes $[(bpy)_2Os(\mathbf{20})M(bpy)_2]^{4+}$ and $[(bpy)_2Os(\mathbf{21})Os(bpy)_2]^{4+}$ [41]. In these complexes, each of the metal units displays its own absorption and electrochemical properties, regardless of the second metal based unit. The luminescence properties of these complexes have also been studied.



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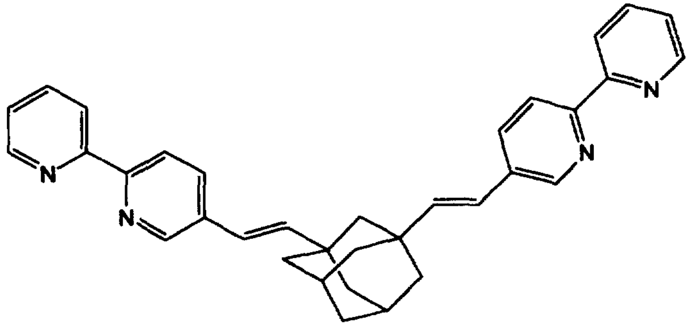

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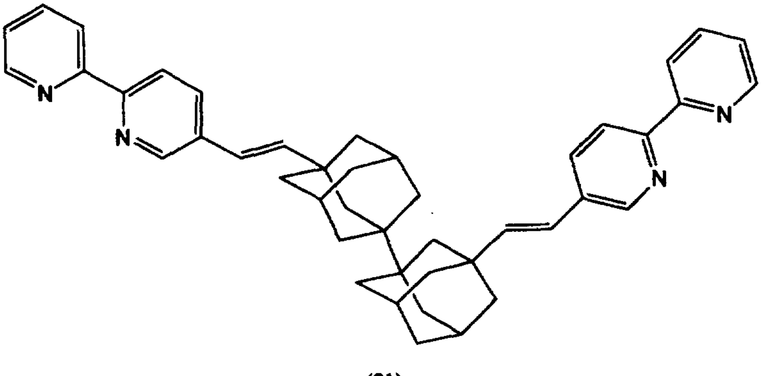
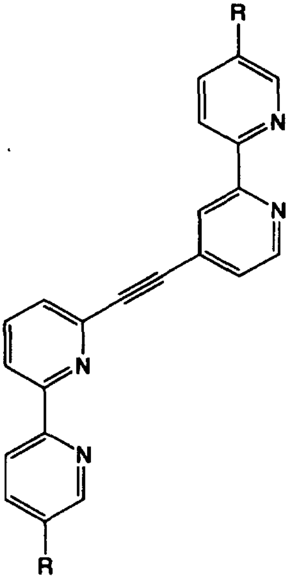


(21)

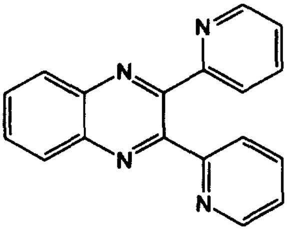
The photophysical and electrochemical properties of dinuclear complexes formed from ethynyl-bridged ditopic ligands (**22** and **23**) have been studied [42]. Electroabsorption studies of $[(NC)_5FeCNOs(NH_3)_5]^-$ show that light induced metal–metal charge transfer is accompanied by a dipole moment change of -12.5 ± 1.5 D along the charge transfer axis which corresponds to an electron transfer distance of only 2.5 ± 0.3 Å. This profoundly affects the estimates of solvent reorganisation and electronic coupling energies [43].



(22; R=H, Me)

(23)

The spectroscopic and electrochemical properties of a series of mixed metal complexes $[(bpy)_2M(BL)PtCl_2]^{2+}$ where BL is (**24**) or (**25**) have shown that these systems have lowest lying excited states that are M→BL charge-transfer in nature with optical excitation directing charge flow towards the coupled platinum site [44].



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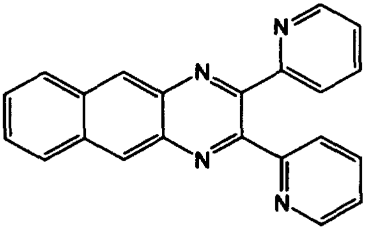

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7.2. Other coordination complexes

A number of osmium complexes containing hydrogen or hydride ligands have been prepared including $[Os(bpy)(PPh_3)_2(CO)(H_2)]^{2+}$ and $[Os(bpy)_2(CO)(H_2)]^{2+}$ [45]. Complexes $[Os(H\cdots H)Br(dppe)_2]^+$ have been synthesised from $[OsBr_2(dppe)_2]$ or $[OsHBr(dppe)_2]$ [46]. Microwave measurements for $[Os(CO)_4H_2]$ show it to have a classical *cis*-dihydride structure in the gas phase

[47]. A combination of *ab initio* and NMR studies on the complex $[OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]$ have shown it to have a *trans*-dihydro-hydrogen arrangement with a rapidly spinning H_2 ligand [48]. Density functional studies have been performed on the model complexes $[Os(NH_3)_4L^z(\eta^2\text{-}H_2)]^{(z+2)+}$ containing neutral ($z=0$) and anionic ($z=-1$) ligands giving estimates for the values of J_{HD}, gas phase equilibrium geometries and binding energies of the ligands [49,50]. A comparison with the results from *ab initio* methods has also been made [51]. Protonation of $[OsH(P\text{–}P)(\eta\text{-}C_5H_5)]$ (P–P = dppm, dppe, dppp) gives mixtures of *cis*- and *trans*-$[Os(H)_2(P\text{–}P)(\eta\text{-}C_5H_5)]$. The ratio of these isomers is dependent on the bite angle of the chelating phosphine [52].

Ground state electron transfer between tcne and 16-electron species including $[Os(P^iPr_3)_2(CO)(H)Cl]$ has been studied and shows that for Os (and Ru) electron transfer occurs only for the first metal coordination step in contrast to the other metals studied which show two consecutive metal-to-tcne electron transfers [53].

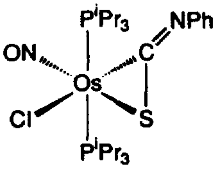
Complexes $[Cp^*Os(NO)(E_4)]$ (E = S, Se), formed from the reaction of Na_2S_4 or $[NEt_4]_2Se_6$ with $[Cp^*Os(NO)Br_2]$, are reported to be the first Cp* osmium half-sandwich complexes containing chalcogenido ligands. X-ray crystal structure analysis confirms the structure of the selenium compound. Dinuclear products, $[Cp^*Os(NO)(\mu\text{-}E)]_2$ (E = S, Se, Te) are obtained from the reactions of $Cp^*Os(NO)Br_2$ with Li_2E [54]. The tetrasulfido species $[PPh_4][Os(NS)(S_4)_2(H_2O)]$ has also been prepared and characterised crystallographically [55].

A high yield procedure has been reported for the preparation of the new water soluble, air-stable species $[Os(CO)_3Cl(OH)]_2$ and $[Os(CO)_3(OH)_2]_2$. The latter is thought to go on to form polymeric $[Os(CO)_3(OH)_2]_n$ [56].

8. Osmium(0)

The electronic structures of $Os(CO)_4L$ (L = CO, PMe_3) have been studied by variable energy photoelectron spectroscopy [57,58]. A relativistic Kohn–Sham Density-Functional Procedure has been used to model the structures of a number of mononuclear transition metal carbonyls including $Os(CO)_5$ [59].

Addition of carbon disulfide and other heteroallenes to *trans*-$[OsCl(NO)(P^iPr_3)_2]$ results in complexes *trans*-$[OsCl(NO)(SC{=}E)]$ (E = S, O, NPh). The product formed from the reaction with SCNPh (**26**) has been characterised by an X-ray diffraction study [60].



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9. Osmium carbonyl clusters

9.1. Clusters with only carbon-donor and hydride ligands

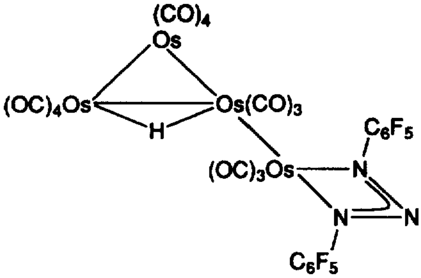
Metal–metal and metal–ligand bond lengths have been used to calculate bond strengths, relative stabilities and enthalpies of formation for a range of binary osmium carbonyl cluster compounds [61].

The ability of the carbide cluster $[PPN]_2[Os_{10}C(CO)_{24}]$ to act as an electron reservoir is demonstrated by the characterisation of five oxidation states $[Os_{10}C(CO)_{24}]^{0/1-/2-/3-/4-}$ which do not result in significant structural change. The structural rearrangement of bicapped tetrahedral $[Os_6(CO)_{18}]$ to octahedral dianion $[Os_6(CO)_{18}]^{2-}$ and the tetraanion $[Os_6(CO)_{18}]^{4-}$ has also been investigated [62].

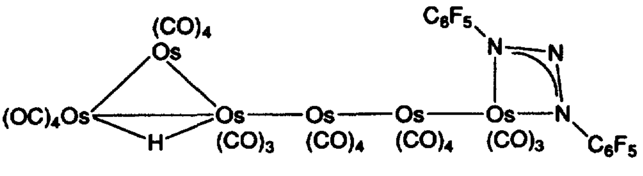
Cluster compounds $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[H_2Os_4(CO)_{12}]^{2-}$, $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ have been synthesised selectively and in high yields by carbonylation or hydrogenation of $OsCl_3$ or α-$[Os(CO)_3Cl_2]_2$ supported on silica in the presence of alkali carbonates [63].

9.2. Clusters with N- and P-donor ligands

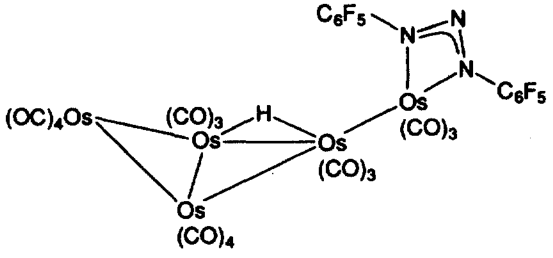
Reactions of the linear triosmium clusters $[Os_3H(CO)_{12-n}(NCMe)_n(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ ($n=1$ or 2) with clusters $[Os(CO)_{12-n}(NCMe)_n]$ ($n=1$ or 2) leads to the formation of "spiked" tetraosmium or hexaosmium clusters (**27**) and (**28**). A pentaosmium "spiked" butterfly cluster has also been made (**29**) [64].



(**27**)

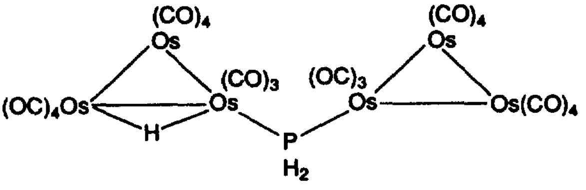


(**28**)

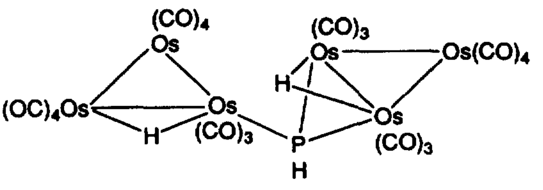


(29)

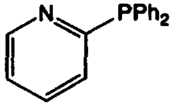
The solid state structures of the diphenylvinylphosphine substituted osmium carbonyl cluster $[Os_3(CO)_{11}\{PPh_2(CH{=}CH_2)\}]$ and its β-hydrogen eliminated partner $[Os_3H(CO)_9(\mu\text{-}PPh_2CH{=}CH)]$ have been determined [65]. The phosphido-bridged cluster $[Os_6H(CO)_{22}(\mu\text{-}PH_2)]$ (**30**) and the corresponding phosphinidene cluster $[Os_6H_2(CO)_{21}(\mu\text{-}PH)]$ (**31**) have been prepared from the reaction of $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{11}(PH_3)]$ in toluene [66]. A number of similar hexanuclear clusters incorporating phosphine, phosphite and isocyanide ligands have also been prepared [67]. Reaction of dppm or (**32**) in hexane with an equimolar amount of $[Os_3(H)_2(CO)_{10}]$ gave complexes $[Os_3(H)_2(CO)_{10}(dppm)]$ and $[Os_3(H)_2(CO)_{10}(\mathbf{32})]$, whereas when two equivalents of Os complex to dppm were used the compound $[(H)_2(CO)_{10}Os(\mu\text{-}dppm)Os_3(CO)_{10}(H)_2]$ was formed. Adding an equimolar amount of $[Os_3(H)_2(CO)_{10}]$ to $[(\eta^6\text{-}C_6H_6)RuCl_2(dppm)]$ gives the mixed metal cluster $[(\eta^6\text{-}C_6H_6)RuCl_2(dppm)Os_3(H)_2(CO)_{10}]$ [68]. The dppm cluster $[Os_3(CO)_{10}(\mu\text{-}dppm)]$ reacts with $^tBu_2PH$ to produce the electron deficient cluster $[Os_3(CO)_5(\mu\text{-}H)(\mu\text{-}P^tBu_2)_2(\mu\text{-}dppm)]$ for which the crystal structure has been determined [69].



(30)

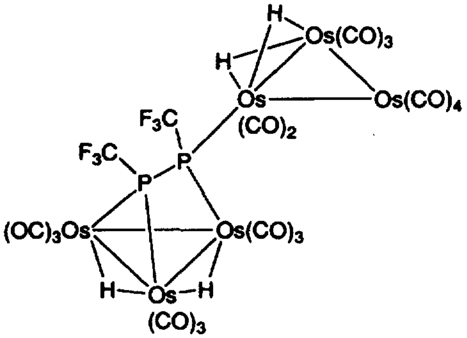


(31)



(32)

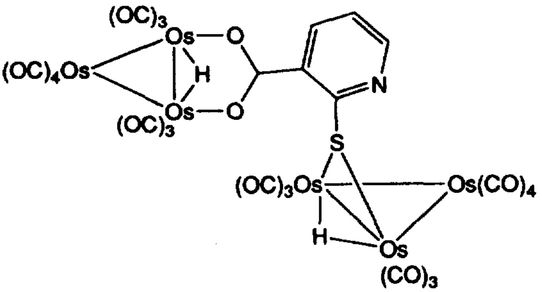
Pentaphenylcyclopentaphosphine $(PPh)_5$ has been coordinated to $[Os(CO)_{10}(NCMe)_2]$ to give mono and disubstituted species $[Os(CO)_{10}\{(PPh)_5\}_n]$ ($n=1$ or 2). Tri and hexanuclear species $[\{Os_3(CO)_{11}\}_n\{(PPh)_5\}]$ ($n=1$ or 2) were obtained from similar reactions of the phosphine with $[Os(CO)_{11}(NCMe)]$ and a mixed metal cluster $[Os_3(CO)_{11}\{(PPh)_5\}Ru_3(CO)_{11}]$ has also been produced [70]. Similar studies on the reactions of $[Os(CO)_{10}(NCMe)_2]$ and pentaethylcyclopentaphosphine have been carried out [71]. Reactions have also been performed on $[Os_3(CO)_{11}(NCMe)]$ using $(F_3CP)_5$ and $(F_3CP)_4$ to give clusters containing phosphinidene (PCF_3), phosphido $(HPCF_3)$ ligands as well as $[(CO)_9(\mu\text{-}H)_2Os_3(\mu_4\text{-}F_3CPPCF_3)Os_3(\mu\text{-}H)_2(CO)_9]$ (33) [72].



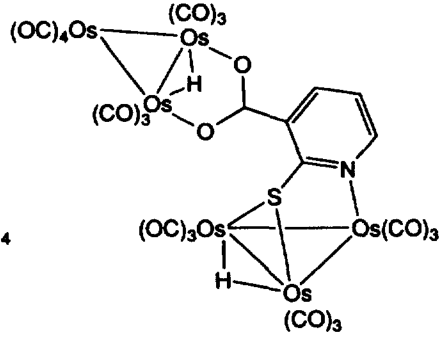
(33)

9.3. Clusters with other ligands

Clusters containing triosmium units linked by thiolato–carboxylato bridges have been prepared from the reaction of $[Os_3(CO)_{10}(NCMe)]$ with thiolate–carboxylate ligands, one example being complex (33). Photochemical activation of the triosmium 2-mercaptopyridine complex $[Os_3H(CO)_{10}(\mu\text{-}SC_5H_4N)]$ results in nitrogen coordination at the third metal atom yielding $[Os_3H(CO)_9(\mu_3\text{-}SC_5H_4N)]$. A similar reaction takes place for the hexanuclear species (34) to generate (35). The X-ray crystal structures of (34) and (35) have been established [73,74].

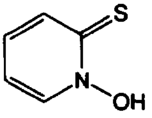


(34)

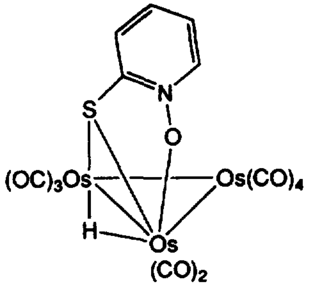


(35)

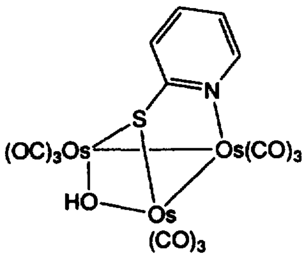
Ligand (**36**) reacts with $[Os_3(CO)_{11}(NCMe)]$ to produce (**37**) and similar complexes which involve additional coordination of the oxygen atom of (**36**). Heating (**37**) results in elimination of oxygen to produce complex (**38**) [75].



(36)

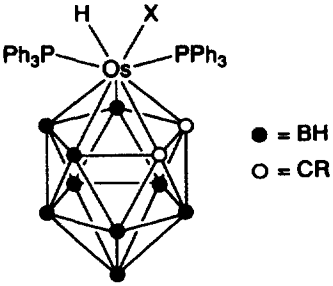


(37)



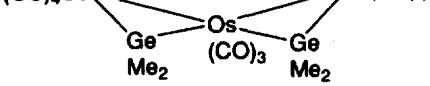
(38)

The first *closo*-hydrido complexes of osmium with carborane ligands have been reported. The structures of (**39**) have been established by X-ray diffraction studies [76].

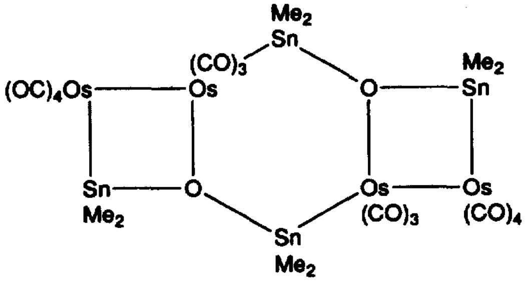


(39; X=Cl, R=H; X=H, R=Me)

A number of osmium–germanium clusters have been prepared from $[Os_2(CO)_8(\mu\text{-}GeMe_2)_3]$ including $[Os_2(CO)_6(\mu\text{-}GeMe_2)_3]$ and $[Os_3(CO)_{11}(\mu\text{-}GeMe_2)_2]$ (**40**). The structures of the products have been determined by X-ray diffraction studies [77]. Similar studies on the tin species $[Os_2(CO)_8(\mu\text{-}SnMe_2)_2]$ have produced a series of clusters including $[Os_4(CO)_{14}(\mu_3\text{-}O)_2(\mu\text{-}SnMe_2)_4]$ (**41**) [78].



(40)



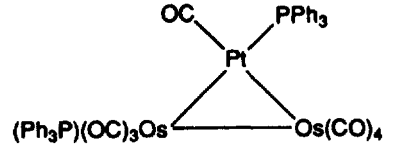
(41)

9.4. Clusters containing other transition metals

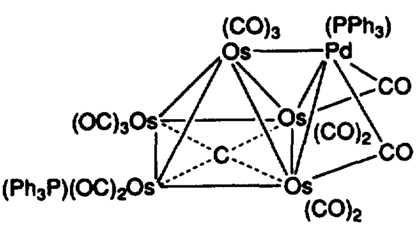
Protonation of $[Os_3(CO)_{12}]$ occurs readily in anhydrous HF to give a cation that can be isolated by reaction with WF_6 to yield crystals of $[Os_3H(CO)_{12}][W_2O_2F_6]$, thus allowing structure determination by X-ray diffraction [79].

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with ferrocenecarboxylic acid or ferrocenedicarboxylic acids yields complexes $[Os_3H(CO)_{10}(\mu\text{-}\eta\text{-}O_2CC_5H_4)Fe(\eta\text{-}C_5H_5)]$ and $[\{Os_3H(CO)_{10}\}_2(\eta\text{-}O_2CC_5H_4)_2Fe]$. Both complexes exhibit a reversible electron transfer process [80].

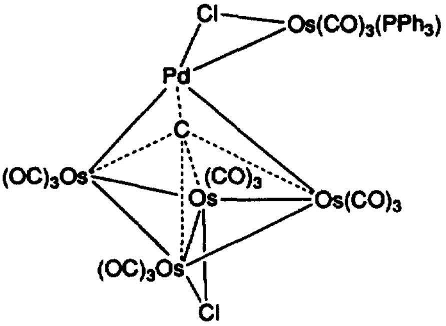
Reaction of $[Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)]$ with $[(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2]$ gives predominantly the heterotrinuclear cluster $[Os_2Pt(CO)_8(PPh_3)_2]$ (**42**). The solid state structure of (**42**) has been established by X-ray diffraction and the interchange of the three isomers it forms in solution has been studied [81]. The pentaosmium carbide cluster $[Os_5C(CO)_{15}]$ reacted with $[Pd(PPh_3)_4]$ to give a new hexanuclear osmium–palladium carbide cluster $[Os_5PdC(CO)_{12}(\mu\text{-}CO)_{12}(PPh_3)_2]$ (**43**), while heating the same osmium cluster and $[PdCl_2(PPh_3)_2]$ gave $[Os_5PdC(CO)_{15}(\mu\text{-}Cl)_2(PPh_3)]$ (**44**) [82].



(42)



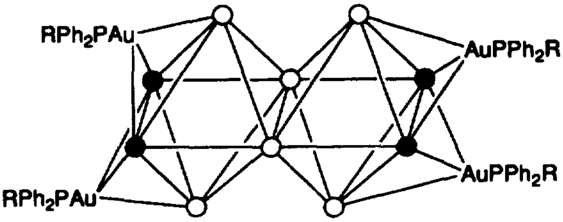
(43)



(44)

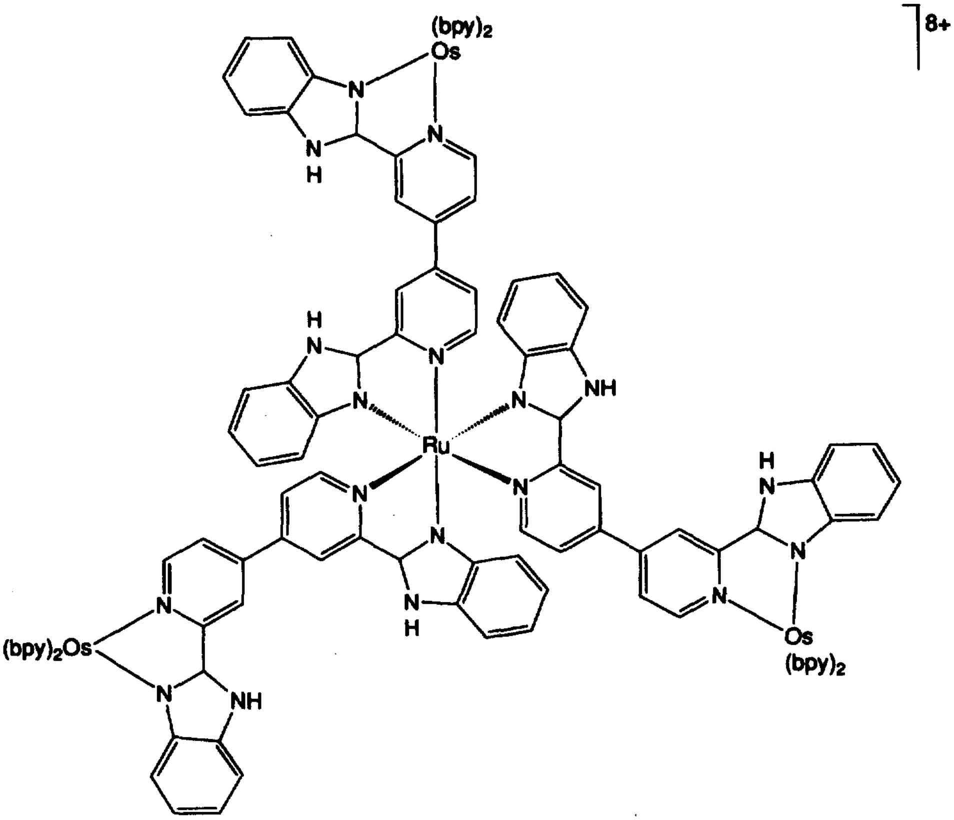
An osmium–palladium carbonyl bpy complex [$Os_6Pd(CO)_{18}$(bpy)] is formed from the reaction of [$Os_3(CO)_{10}(NCMe)_2$] with [Pd(bpy)$(CO_2Me)_2$]. Its cyclic voltammogram reveals an irreversible oxidation at around 0.75 V and no reduction wave. A similar reaction between [Pd(bpy)$(CO_2Me)_2$] and [$Os_3H_2(CO)_{10}$] produces [{(bpy)Pd(μ-CO)$_2$}$_2Os_3(CO)_8$] [83].

A tubular osmium–gold cluster, [$Os_{10}(CO)_{24}\{Au(PPh_2R)\}_4$] (**45**) has been prepared and characterised by single crystal X-ray diffraction [84].



(45)

The dendrimer-type complex (**46**) has been prepared whose redox chemistry can



(46)

be controlled through protonation/deprotonation of the basic sites on the nitrogen ligands. Oxidation of the complex can thus be made to follow one of two pathways. The first pathway involves simultaneous oxidation of all three Os(II) sites followed by oxidation of the central Ru(II) site. The second pathway involves initial oxidation of Ru(II) followed by oxidation of the peripheral Os(II) sites [85].

References

[1] T.C. Lau, Z.B. Wu, J.Y. Wang, K. Siu, R. Guevremont, Inorg. Chem. 35 (1996) 2169.
[2] W.J. Casteel, D.A. Dixon, H.P.A. Mercier, G.J. Schrobilgen, Inorg. Chem. 35 (1996) 4310.
[3] P.O. Norrby, K.P. Gable, J. Chem. Soc., Perkin Trans. 2 (1996) 171.
[4] G. Ujaque, F. Maseras, A. Lledos, Theor. Chim. Acta 94 (1996) 67.
[5] E.J. Corey, M.C. Noe, J. Am. Chem. Soc. 118 (1996) 11038.
[6] E.J. Corey, M.C. Noe, J. Am. Chem. Soc. 118 (1996) 319.
[7] P.O. Norrby, H. Becker, K.B. Sharpless, J. Am. Chem. Soc. 118 (1996) 35.
[8] S. Dapprich, G. Ujaque, F. Maseras, A. Lledos, D.G. Musaev, J. Am. Chem. Soc. 118 (1996) 11660.
[9] E.J. Corey, S. Sarshar, M.D. Azimioara, R.C. Newbold, M.C. Noe, J. Am. Chem. Soc. 118 (1996) 7851.
[10] O. Reiser, Angew. Chem. Int. Ed. Engl. 35 (1996) 1308.
[11] C. Kelly, D.J. Szalda, C. Creutz, H.A. Schwarz, N. Sutin, Inorg. Chim. Acta 243 (1996) 39.
[12] M. Rhiel, K. Dehnicke, A. Simon, R.K. Kremer, Z. Anorg. Allg. Chem. 622 (1996) 1205.
[13] P.A. Shapley, W.A. Reinerth, Organometallics 15 (1996) 5090.
[14] C.A. Bayse, M. Couty, M.B. Hall, J. Am. Chem. Soc. 118 (1996) 8916.
[15] W.H. Leung, J.Y.K. Cheng, T.S.M. Hun, C.M. Che, W.T. Wong, K.K. Cheung, Organometallics 15 (1996) 1497.
[16] G. Lucier, S.H. Elder, L. Chacon, N. Bartlett, Eur. J. Solid State and Inorg. Chem. 33 (1996) 809.
[17] J.H. Holloway, E.G. Hope, C.D. Puxley, Eur. J. Solid State and Inorg. Chem. 33 (1996) 821.
[18] R. Kuhlman, W.E. Streib, J.C. Huffman, K.G. Caulton, J. Am. Chem. Soc. 118 (1996) 6934.
[19] M.A. Esteruelas, F.J. Lahoz, A.M. Lopez, E. Onate, L.A. Oro, N. Ruiz, E. Sola, J.I. Tolosa, Inorg. Chem. 35 (1996) 7811.
[20] M.L. Buil, P. Espinet, M.A. Esteruelas, F.J. Lahoz, A. Lledós, J.M. Martínez-Ilarduya, F. Maseras, J. Modrego, E. Oñate, L.A. Oro, E. Sola, C. Valero, Inorg. Chem. 35 (1996) 1250.
[21] Z. Gross, A. Mahammed, Inorg. Chem. 35 (1996) 7260.
[22] P.A. Shapley, J.M. Shusta, J.L. Hunt, Organometallics 15 (1996) 1622.
[23] M.L. Abasq, C.J. Pickett, R.L. Richards, M. Arroyo, J.A. Chamizo, A. Calderon, P. Sosa, H. Torrens, Polyhedron 15 (1996) 3623.
[24] S.V. Volkov, V.I. Pekhnyo, Z.A. Fokina, V.B. Rybakov, Polyhedron 15 (1997) 4145.
[25] P.R. Basudhar, S. Sinha, P.K. Das, B.K. Ghosh, Transition Met. Chem. 21 (1996) 154.
[26] D.C. Ware, M.M. Olmstead, R. Wang, H. Taube, Inorg. Chem. 35 (1996) 2576.
[27] H.W. Kang, G. Moran, E. Krausz, Inorg. Chim. Acta 249 (1996) 231.
[28] R.L. Bretz, H.D. Abruna, J. Electroanal. Chem. 408 (1996) 199.
[29] C.N. Shi, F.C. Anson, Inorg. Chem. 35 (1996) 7928.
[30] M. Höhling, W. Preetz, Acta Crystallogr., Sect. C 52 (1996) 863.
[31] R.E. Holmin, E.D.A. Stemp, J.K. Barton, J. Am. Chem. Soc. 118 (1996) 5236.
[32] S.J. Hug, S.G. Boxer, Inorg. Chim. Acta 242 (1996) 323.
[33] R.J. Forster, Inorg. Chem. 35 (1996) 3394.
[34] L.M. Vogler, S.W. Jones, G.E. Jensen, R.G. Brewer, K.J. Brewer, Inorg. Chim. Acta 250 (1996) 155.
[35] M. Sekota, T. Nyokong, Polyhedron 15 (1996) 2901.
[36] A. Mamo, A. Juris, G. Calogero, S. Campagna, Chem. Commun. (1996) 1225.
[37] C.M. Lindall, J.A. Crayston, D.J. Cole-Hamilton, A. Glidle, R.D. Peacock, J. Mater. Chem. 6 (1996) 2937.

[38] J. Bolger, A. Gourdon, E. Ishow, J.P. Launay, Inorg. Chem. 35 (1996) 2937.
[39] L.M. Volger, K.J. Brewer, Inorg. Chem. 35 (1996) 818.
[40] F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowskikimmes, J.P. Collin, J.P. Sauvage, Inorg. Chem. 35 (1996) 136.
[41] M. Frank, M. Nieger, F. Vogtle, P. Belser, A. von Zelewsky, L. Decola, V. Balzani, F. Barigelletti, L. Flamigni, Inorg. Chim. Acta 242 (1996) 281.
[42] V. Grosshenny, A. Harriman, F.M. Romero, R. Ziessel, J. Phys. Chem. 100 (1996) 17472.
[43] L. Karki, H.P. Lu, J.T. Hupp, J. Phys. Chem. 100 (1996) 15637.
[44] M. Milkevitch, E. Brauns, K.J. Brewer, Inorg. Chem. 35 (1996) 1737.
[45] D.M. Heinekey, T.A. Luther, Inorg. Chem. 35 (1996) 4396.
[46] P.A. Maltby, M. Schlaf, M. Steinbeck, A.J. Lough, R.H. Morris, W.T. Klooster, T.F. Koetzle, R.C. Srivastava, J. Am. Chem. Soc. 118 (1996) 5396.
[47] S.G. Kukolich, S.M. Sickafoose, S.M. Breckenridge, J. Am. Chem. Soc. 118 (1996) 205.
[48] V.I. Bakhmutov, J. Bertran, M.A. Esteruelas, A. Lledos, F. Maseras, J. Modrego, L.A. Oro, E. Sola, Chem. Eur. J. 2 (1996) 815.
[49] G.B. Bacskay, I. Bytheway, N.S. Hush, J. Am. Chem. Soc. 118 (1996) 3753.
[50] I. Bytheway, G.B. Bacskay, N.S. Hush, J. Phys. Chem. 100 (1996) 14899.
[51] I. Bytheway, G.B. Bacskay, N.S. Hush, J. Phys. Chem. 100 (1996) 6023.
[52] G.C. Jia, W.S. Ng, J.Z. Yao, C.P. Lau, Y.Z. Chen, Organometallics 15 (1996) 5039.
[53] F. Baumann, M. Heilmann, W. Mathesis, A. Schulz, W. Kaim, J. Jordanov, Inorg. Chim. Acta 251 (1996) 239.
[54] M. Herberhold, G.X. Jin, L.M. Liable-Sands, A.L. Rheingold, J. Organomet. Chem. 519 (1996) 223.
[55] B. Vollmer, S. Wocaldo, W. Massa, K. Dehnicke, Z. Anorg. Allg. Chem. 622 (1996) 1306.
[56] E. Cariati, E. Lucenti, M. Pizzotti, D. Roberto, R. Ugo, Organometallics 15 (1996) 4122.
[57] Y.F. Hu, G.M. Bancroft, H.B. Davis, J.I. Male, R.K. Pomeroy, J.S. Tse, K.H. Tan, Organometallics 15 (1996) 4493.
[58] H.B. Davis, R.K. Pomeroy, Y.F. Hu, G.M. Bancroft, K.H. Tan, Chem. Phys. Lett. 252 (1996).
[59] C. van Wüflen, J. Chem. Phys. 105 (1996) 5485.
[60] R. Flügel, O. Gevert, H. Werner, Chem. Ber. 129 (1996) 405.
[61] A.K. Hughes, K.L. Peat, K. Wade, J. Chem. Soc., Dalton Trans. (1996) 4639.
[62] W.F. Lin, W.T. Wong, S.G. Sun, J. Phys. Chem. 100 (1996) 14904.
[63] D. Roberto, E. Cariati, R. Ugo, R. Psaro, Inorg. Chem. 35 (1996) 2311.
[64] H.G. Ang, L.L. Koh, S.G. Ang, S.Y. Ng, G.Y. Yang, J. Chem. Soc., Dalton Trans. (1996) 4083.
[65] B.F.G. Johnson, J. Lewis, E. Nordlander, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1996) 3825.
[66] B.F.G. Johnson, J. Lewis, E. Norlander, S.M. Owen, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1996) 1567.
[67] B.F.G. Johnson, J. Lewis, E. Nordlander, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1996) 755.
[68] R. Gobetto, C.G. Arena, D. Drommi, F. Faraone, Inorg. Chim. Acta 248 (1996) 257.
[69] F.W. Heinemann, H.C. Bottcher, J. Organomet. Chem. 526 (1996) 145.
[70] H.G. Ang, S.G. Ang, Q. Zhang, J. Chem. Soc., Dalton Trans. (1996) 3843.
[71] H.G. Ang, S.G. Aug, Q. Zhang, Phosphorus Sulfur 110 (1996) 145.
[72] H.G. Ang, K.W. Ang, S.G. Ang, A.L. Rheingold, J. Chem. Soc., Dalton Trans. (1996) 3131.
[73] E.W. Ainscough, A.M. Brodie, R.K. Coll, A.J.A. Mair, J.M. Waters, J. Organomet. Chem. 509 (1996) 259.
[74] E.W. Ainscough, A.M. Brodie, R.K. Coll, T.G. Kotch, A.J. Lees, A.J.A. Mair, J.M. Waters, J. Organomet. Chem. 517 (1996) 173.
[75] J.T. Hung, S. Kumaresan, L.C. Lin, Y.S. Wen, L.K. Liu, K.L. Lu, J.R. Hwu, Organometallics 15 (1996) 5605.
[76] I.T. Chizhevsky, P.V. Petrovskii, P.V. Sorokin, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovsky, Y.T. Struchkov, A. Demonceau, A.F. Noels, Organometallics 15 (1996) 2619.
[77] W.K. Leong, F.W.B. Einstein, R.K. Pomeroy, Organometallics 15 (1996) 1589.
[78] W.K. Leong, F.W.B. Einstein, R.K. Pomeroy, Organometallics 15 (1996) 1582.
[79] M.C. Crossman, J. Fawcett, E.G. Hope, D.R. Russell, J. Organomet. Chem. 514 (1996) 87.
[80] S.M. Lee, K.K. Cheung, W.T. Wong, J. Organomet. Chem. 506 (1996) 77.

[81] J. Cooke, R.E.D. McClung, J. Takats, R.D. Rogers, Organometallics 15 (1996) 4459.
[82] J.W.S. Hui, W.T. Wong, J. Chem. Soc., Dalton Trans. (1996) 2887.
[83] S. Chan, S.M. Lee, Z.Y. Lin, W.T. Wong, J. Organomet. Chem. 510 (1996) 219.
[84] Z. Akhter, S.L. Ingham, J. Lewis, P.R. Raithby, Angew. Chem. Int. Ed. Engl. 35 (1996) 992.
[85] M.A. Haga, M. Ali, R. Arakawa, Angew. Chem. Int. Ed. Engl. 35 (1996) 76.