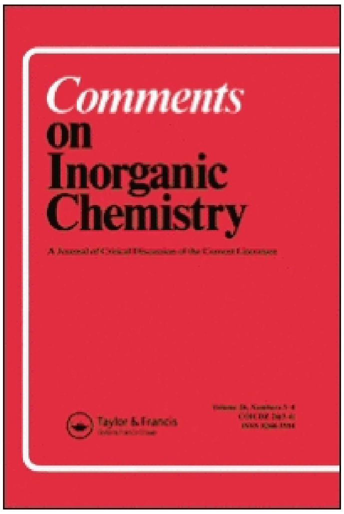

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High Oxidation States of the Later 3d Transition Elements in Phosphorus and Arsenic Donor Ligand Complexes

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The syntheses and properties of phosphorus and arsenic donor ligand complexes containing high formal oxidation states of the later 3d elements (Fe, Co, Ni, and Cu) are reviewed. The physical and structural data upon these materials are presented, and interpreted to show that the unusually high oxidation states are genuine. The features of the ligands which are particularly effective are elucidated, and the possibilities of obtaining several presently unknown types of complex discussed.

Key Words: *phosphine, arsine, iron, cobalt, nickel, copper*

INTRODUCTION

This article is concerned with the stabilization of high oxidation states of the later 3d transition elements (Fe, Co, Ni, and Cu) by phosphine and arsine ligands. For many years such oxidation states were found only in fluoro and oxo anions, and in a few, often incompletely characterized coordination complexes. However, recent work, particularly with nitrogen donor ligands such as aza-

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macrocycles and multidentate oximes, has revealed an extensive chemistry in this area, especially of nickel(III) and copper(III).[1-4] Early examples with phosphorus or arsenic donors include $[Ni(PEt_3)_2Br_3]$ prepared by Jensen in 1936[5] and Ni(III), Ni(IV), and Fe(IV) diarsine complexes reported by Nyholm and co-workers in the 1950's.[6-8] The apparent stabilization of such unusually high oxidation states by neutral ligands which are not strongly electronegative, and indeed are reducing agents *in the free state*, was unexpected. Moreover, the fact that the most successful by far of the ligands known at that time, the diarsine $o\text{-}C_6H_4(AsMe_2)_2$, contained an unsaturated backbone raised doubts in the minds of some workers about the site of the redox chemistry.[9,10] It is well known, for example, that diimines such as 2,2′-bipyridyl bind as neutral ligands to normal oxidation state transition metals, but that species such as $[Ru(2,2'\text{-bipyridyl})_3]^+$ apparently Ru(I) are best described as Ru(II) with the "extra" electron in the π^* orbitals of the ligands. Conversely the formally Fe(IV) $[Fe(2,2'\text{-bipyridyl})_3]^{4+}$ is best formulated as Fe(III) with the bipyridyl rings having lost an electron from the π orbitals.[11] The extensive studies of 1,2-dithiolene chemistry in the 1960's, where the ligand orbitals are intimately involved in the redox chemistry, seemed at one time to have significant parallels with the diarsine compounds, although it should be noted that 1,1-dithiolenes and dithiocarbamates do stabilize high oxidation states very effectively.[12] Jorgensen[13] introduced the term "non-innocent" for ligands which participate in the redox process.

In principle, whether, for example, $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$ contains d^6 Ni(IV), or is better described as perhaps d^8 Ni(II) with cation radical $L\text{-}L\cdot^+$ ligands, can be determined by detailed physical measurements, but for these unstable compounds, both the preparation of pure samples and the collection of high quality physical and spectroscopic data present a considerable challenge. As a result of recent studies made possible both by improved instrumentation and the introduction of new techniques, such data is now available and is the subject of this article.

IRON

Few tertiary phosphine complexes of either Fe(II) or Fe(III) have been described,[14,15] and it seems highly unlikely that Fe(IV) analogues will be obtainable. The yellow "iron(IV)" hydrides $[FeH_4(PR_3)_3]$ which always appeared anomalous are now known to be iron(II) η-H_2 complexes.[16]

Alkyl substituted diphosphines and diarsines produce stable low-spin Fe(III) *trans*-$[Fe(L\text{-}L)_2X_2]^{+}$[14]; the structures have been assigned mostly from spectroscopic data, being recently confirmed by an X-ray crystal structure determination of $[Fe(o\text{-}C_6F_4(PMe_2)_2)_2Cl_2]BF_4$.[17] Oxidation of these Fe(III) complexes with concentrated HNO_3, containing some concentrated HX at −5°C, followed by addition of HBF_4 generates green-black or purple-black *trans* $[Fe(L\text{-}L)_2X_2](BF_4)_2$ (L-L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(AsMe_2)$; X = Cl, Br). The complexes $[Fe(o\text{-}C_6F_4(PMe_2)_2)_2X_2]^{2+}$ were identified in solution, but not isolated, while $[Fe(Me_2PCH_2CH_2PMe_2)_2Cl_2](BF_4)_2$ was made by Cl_2 oxidation of the Fe(III) analogue in CF_3CO_2H solution.[16,18-22] The choice of counter-anion proved crucial to the production of pure materials, and BF_4^- was the only uniformly successful ion.[18,22] Of others tried, PF_6^- and ReO_4^- gave impure products, $CF_3SO_3^-$ did not precipitate the complexes from solution, and the ClO_4^- complexes are dangerously explosive.[6] Attempts to produce Fe(IV) complexes of other ligands $o\text{-}C_6H_4(PPh_2)_2$, $o\text{-}C_6H_4(PMe_2)(SbMe_2)$, or $o\text{-}C_6H_4(PMe_2)(SMe)$ failed.[22]

Cyclic voltammetry upon the $[Fe(L\text{-}L)_2X_2]^+$ in MeCN revealed the oxidation to Fe(IV) was electrochemically reversible and occurred at highly positive potentials, with the redox potential becoming more positive with L-L in the order $Me_2PCH_2CH_2PMe_2$ < $o\text{-}C_6H_4(PMe_2)_2$ ~ $o\text{-}C_6H_4(AsMe_2)_2$ < $o\text{-}C_6F_4(PMe_2)_2$.[20,22] The isolated Fe(IV) complexes can be kept for ca. 48 h at −20°C before significant decomposition occurs, but decompose in a few hours at room temperature, and very rapidly in most solvents. Indeed only conc. HNO_3 and anhydrous CF_3CO_2H are suitable solvents for spectroscopic work. The magnetic moments $\mu = 2.7\text{–}3.2$ B.M.[18,22] are consistent with a low spin d^4 ion (t_{2g}^4) corresponding to 2 unpaired electrons and a partially quenched orbital contribution. The electronic spectra (Fig. 1) are readily distinguished from those of the Fe(III) starting materials, and the major features have been satisfactorily assigned as L → Fe charge transfer transitions. Final spectroscopic confirmation of the Fe(IV) formulation is provided by the ^{57}Fe Mössbauer spectra of the series $[Fe(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2](BF_4)_n$ (n = 0,1,2) which show[23,24] progressive

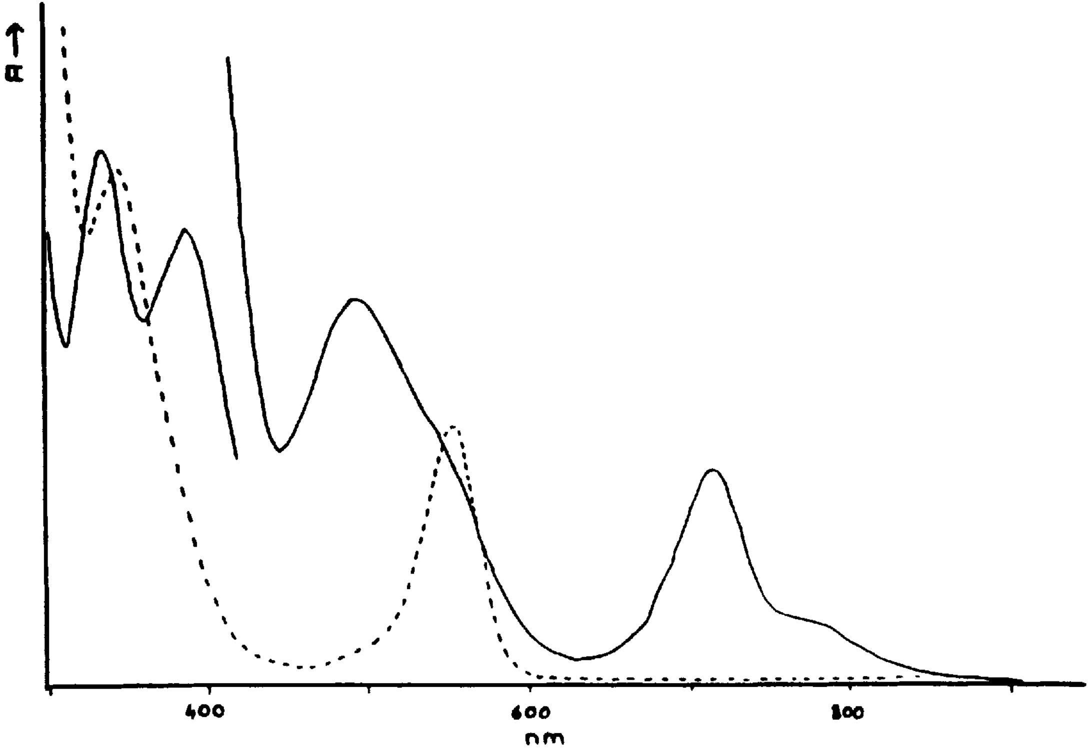


FIGURE 1 UV-visible spectra of $[Fe(o\text{-}C_6F_4(PMe_2)_2)_2Cl_2]^{2+}$ (——) and $[Fe(o\text{-}C_6F_4(PMe_2)_2)_2Cl_2]^{+}$ (---) in CF_3CO_2H. From Ref. 22 by permission of the American Chemical Society.

changes in the isomer shift with changes in the iron oxidation state, and indicate the Fe(IV) complex has a strong axially compressed ligand field. Thus the spectroscopic data provides good support for the Fe(IV) formulation, but supporting structural data has been unavailable, since the solution instability of these materials precludes attempts to grow single crystals for an X-ray study.

However, we[21,22] have recently shown that first coordination sphere bond lengths can be obtained via the metal K-edge EXAFS (extended X-ray absorption fine structure), the data being obtained from powdered samples. Providing the nature and symmetry of the donor set is established by spectroscopic means as in the present case, EXAFS data can provide the bond lengths about the metal center, and hence an essentially complete structural characterization. The results from such a study on the series $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2](BF_4)_n$ ($n = 0,1,2$) are shown in Table I, the reliability of the data being confirmed for the Fe(II) and Fe(III) complexes by comparison with X-ray single crystal data upon related complexes. The lengthening of the d(Fe–P) and the shortening of d(Fe–Cl) along the series $n = 0 \rightarrow 2$ seems eminently reasonable; as the metal oxidation state increases, the result is relatively stronger interaction with the anionic halide and weaker binding to the phosphorus.

The complexes described above are the only presently known Fe(IV) complexes with any neutral ligands, and the essential features of the ligands are discussed further below. It seems likely that examples with other anions (OR^-, even R^-) in place of Cl or Br may be obtainable, and given the stability of $[Fe^{IV}O(porphyrin)]$ species $[FeO(diphosphine)_2]^{2+}$ may form if suitable synthetic routes can be found.

COBALT

Cobalt(III) complexes of diphosphines, diarsines, and multidentates are well established, stable compounds, and there are a smaller number of often less stable materials containing tertiary phosphines. Although cobalt(III) is a familiar oxidation state and the reality of the d^6 constitution of these complexes has never been questioned, some treatment of them is appropriate here for two

TABLE I

Structural data

Complex	d^n	d(M-X)Å	d(M-P(As))Å	Technique	Ref.
trans $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]$	d^6	2.35	2.23	EXAFS[a]	22
trans $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^+$	d^5	2.245	2.245	EXAFS	22
trans $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^{2+}$	d^4	2.16	2.33	EXAFS	22
trans $[Co(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^+$	d^6	2.235(av)	2.251(av)	X-ray	19
trans $[Co(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^-$	d^6	2.256(3)	2.334(av)	X-ray	41
trans $[Co(o\text{-}C_6H_4(SbMe_2)_2)_2Cl_2]^+$	d^6	2.263(4)	2.491(av) (Co-Sb)	X-ray	43
$[Co(o\text{-}C_6H_4(AsMe_2)_2)_3]^{3+}$	d^6	–	2.365-2.395(2)	X-ray	42
cis $[Co(Ph_2PCH{=}CHPPh_2)_2O_2]^+$	d^6	–	2.232-2.251(4)	X-ray	68
cis $[Co(Me_2PCH_2CH_2PMe_2)_2O_2]^+$	d^6	–	2.194-2.234(4)	X-ray	69
cis $[Co(Me_2P(CH_2)_3PMe_2)_2O_2]^+$	d^6	–	2.208-2.246(2)	X-ray	69
$[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$	d^7	2.346(3) 2.417(3) 2.363(3)	2.225(5) 2.236(5)	X-ray	80
trans $[Ni(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^+$	d^7	2.424(2)	2.255(3)	X-ray	83
		2.42	2.25	EXAFS	84
trans $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^+$	d^7	2.425(3)	2.342(2)	X-ray	41
		2.42	2.34	EXAFS	84
trans $[Ni(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^{2+}$	d^6	2.275	2.225	EXAFS	84
trans $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$	d^6	2.275	2.39	EXAFS	84
$[Cu(o\text{-}C_6H_4(PMe_2)_2)_2Cl]^{2+}$	d^8	2.46(1)	2.263(av)	X-ray	19

[a] With current data analysis packages, EXAFS distances are accurate to ± 0.02 Å.

reasons. First, the Co(III) formulation rests upon the same types of structural and spectroscopic results interpreted in the same way as those used for the less familiar oxidation state materials discussed elsewhere in this article; and second, the greater stability of the Co(III) complexes means that a wider variety of types can be easily obtained, which serve as models for the types of materials which may be obtainable with less stable metal ions under suitably controlled conditions.

A small number of six-coordinate tertiary phosphine complexes are known, including *mer*-$[CoMe_3(PMe_3)_3]$,[25] *mer*-$[Co(PMe_3)_3(NCS)_3]$,[26] and $[Co(PF_2Ph)_3Cl_3]$,[27] but more interesting are the five-coordinate $[Co(PR_3)_2X_3]$, first obtained by Jensen[28,29] for PR_3 = PEt_3 by NOX oxidation of $[Co(PEt_3)_2X_2]$. The complexes are intensely colored, extremely soluble in most organic solvents, and decompose in a few days. An X-ray study of $[Co(PEt_3)_2Cl_3]$ showed a *trans* trigonal bipyramidal structure.[30] A recent reinvestigation[31] found that $[Co(PR_3)_2X_3]$ (X = Cl, Br; R_3 = Me_3, Et_3, Me_2Ph, Et_2Ph, $EtPh_2$; X = Br, R_3 = Ph_3) are best made by NOX oxidation of the corresponding tetrahedral Co(II) complex at −80°C in dichloromethane. Iodocomplexes have not been reported, but may be stable enough to isolate. The products are paramagnetic (μ = 2.9–3.3 B.M.) consistent with a $(d_{xz},d_{yz})^4$ $(d_{xy}, d_{x^2-y^2})^2$ $(d_z^2)^0$ $[(e'')^4(e')^2(a_1)^0]$ configuration in D_{3h} symmetry. The dichroic complexes vary in color from blue-purple to dark red or dark green, the color largely arising from an intense $P(\sigma) \rightarrow Co(e')$ charge transfer transition in the visible region (ca. (16–20) × 10^3 cm^{-1}). Cobalt and bromine K-edge EXAFS data again provided structural information with d(Co–P) ca. 2.30 Å, d(Co–Cl) ca. 2.20 Å, and d(Co–Br) ca. 2.36 Å. These complexes show no tendency to take up X^- to become six-coordinate, and in marked contrast to the heavier analogues $[M(PR_3)_2X_4]^-$ (M = Rh, Ir),[32] haloanions are unknown, although $[Co(PPh_3)_2(CN)_4]^-$ and $[Co(PPh_3)(CN)_5]^{2-}$ have been obtained.[33,34] Cyclic voltammetry showed that $[M(PR_3)_2X_4]^-$ (M = Rh, Ir)[32] undergo 1e oxidations, the Ir complexes reversibly, and the Ir(IV) analogues are easily isolated by chemical oxidations. In contrast, for the rhodium complexes, oxidation which occurs at more positive potentials than for iridium is completely irreversible even at fast scan rates, and it appears that the Rh(IV) complexes are kinetically unstable. Extrapolation suggests that Co(IV) complexes will not be obtainable.

Attempts to obtain five-coordinate Co(III) complexes with diphosphines have had limited success. The dark-blue or dark-green paramagnetic $[Co\{Ph_2P(CH_2)_nPPh_2\}X_3]$ (n = 4,5) are formed from NOX and the Co(II) analogues, and their spectroscopic properties are consistent with distorted five-coordination.[35] Analogues with 2-carbon backbone diphosphines are unknown, probably because these ligands fail to form the required Co(II) starting materials $[Co(L\text{-}L)X_2]$. Usually such ligands favor a $[Co(L\text{-}L)_2X]^+$ type, and even when materials of a 1:1 stoichiometry are isolated, on investigation they are found to have a $[Co(L\text{-}L)_2][CoX_4]$ constitution.[14,35] This illustrates a common problem in the synthesis of high oxidation state materials, where the major barrier is the absence of suitable lower oxidation state starting materials.

The most familiar complexes with bidentate ligands are the *trans*-$[Co(L\text{-}L)_2X_2]^+$ (Table II). Where L-L is an alkyl substituted bidentate, air-oxidation of a mixture of CoX_2 and L-L in alcohol is the usual synthetic route,[19,36,42,45,49] but for aryl substituted ligands air-oxidation to Co(III) does not occur (although Co(II) phosphine oxides are sometimes produced), and halogen oxidation is necessary.[46,47] Curiously complexes of $Ph_2PCH_2CH_2PPh_2$ have not been isolated, probably due to the steric hindrance of the nonplanar backbones and the *o*-H's of the phenyl groups.[46] It is noteworthy that a wide variety of X groups can be incorporated in place of the usual Cl or Br, including I, NO_2, NO_3, CNS, etc., and that relatively stable complexes occur even with weaker σ-donor neutral ligands such as distibines, $o\text{-}C_6H_4(PPh_2)(SMe)$ and $o\text{-}C_6H_4(PPh_2)(SeMe)$.[43] Indeed we subsequently found that even the poorly coordinating group 16 bidentates $MeSCH_2CH_2SMe$, $MeSeCH_2CH_2SeMe$, and $o\text{-}C_6H_4(TeMe)_2$[50,61] form Co(III) complexes when mixtures of CoX_2, L-L, and $NaBPh_4$ are air-oxidized in nitromethane solution. All of the *trans*-$[Co(L\text{-}L)_2X_2]^+$ are diamagnetic (t_{2g}^6) and have characteristic single antisymmetric CoX_2 vibrations in the IR spectra at ca. 400 cm^{-1} (Cl) and ca. 350 cm^{-1} (Br).[39,47] The UV-visible spectra are also very characteristic (Fig. 2), with the lowest energy transition corresponding (in D_{4h} symmetry) to ${}^1A_{1g} \rightarrow {}^1E_g$, and a second feature ${}^1A_{1g} \rightarrow {}^1A_{2g}$ is usually apparent to low energy of the intense charge transfer transitions.[38,40,43,44,54]

Cis-$[Co(L\text{-}L)_2X_2]^+$ are obtained from the *trans* isomers via che-

TABLE II

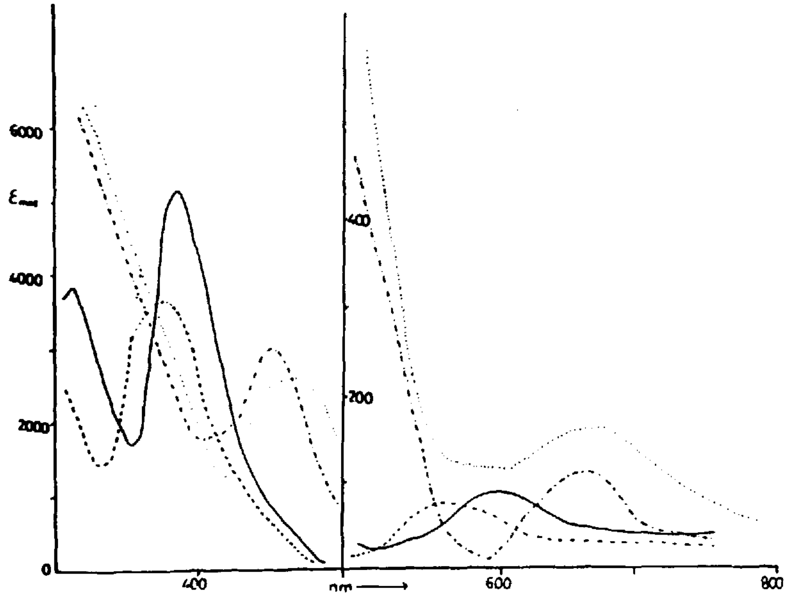
Cobalt(III) complexes of Bi and multidentates

trans $[Co(L\text{-}L)_2X_2]^+$	Ref.
L-L = o-$C_6H_4(PMe_2)_2$	19
o-$C_6H_4(AsMe_2)_2$	19, 36–41
o-$C_6F_4(PMe_2)_2$	20
o-$C_6H_4(PMe_2)(AsMe_2)$	42
o-$C_6H_4(PMe_2)(SbMe_2)$	43
o-$C_6H_4(SbMe_2)_2$	43
$Me_2PCH_2CH_2PMe_2$	42, 44
$Me_2P(CH_2)_3PMe_2$	44, 45
cis-$Ph_2PCH{=}CHPPh_2$	46
o-$C_6H_4(PPh_2)_2$	47
$Me_2Sb(CH_2)_3SbMe_2$	43
$Et_2PCH_2CH_2PEt_2$	48
cis-$Me_2AsCH{=}CHAsMe_2$	49, 50
$PhHPCH_2CH_2PHPh$	51
$Me_2AsCH_2CH_2AsMe_2$	54
$Me_2As(CH_2)_3AsMe_2$	54
${}^nBu_2PCH_2CH_2P^nBu_2$	44

cis $[Co(L\text{-}L)_2X_2]^+$	Ref.
L-L = o-$C_6H_4(AsMe_2)_2$	37,38,52,53
$Me_2As(CH_2)_3AsMe_2$	54
$Me_2PCH_2CH_2PMe_2$	44
$Me_2P(CH_2)_3PMe_2$	44
fac-(?)$[Co\{PhP(CH_2CH_2PPh_2)_2\}X_3]$	47
fac-$[Co\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}X_3]$	55
fac-$[Co\{MeC(CH_2AsMe_2)_3\}I_3]$	64
cis-$[Co\{P(CH_2CH_2PPh_2)_3\}X_2]^+$	47
cis-$[Co\{P(o\text{-}C_6H_4PPh_2)_3\}X_2]^+$	56
cis-$[Co\{E(CH_2CH_2CH_2AsMe_2)_3\}X_2]^+$	47,57
(E = P, As, Sb)	
$[Co\{(Ph_2PCH_2CH_2P(Ph)CH_2\text{-})_2\}X_2]^+$	47
$[Co\{(Me_2AsCH_2CH_2CH_2As(Ph)CH_2\text{-})_2\}X_2]^+$	58,59
$[Co\{(o\text{-}Me_2AsC_6H_4As(Me))_2C_6H_4\}X_2]^+$	60
$[Co\{(Me_2AsCH_2CH_2CH_2As(Me))_2C_6H_4\}X_2]^+$	60

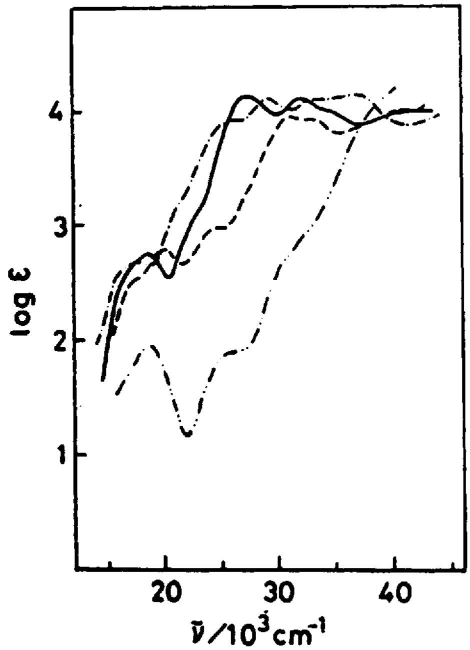
X = Cl, Br, sometimes I, NCS, NO_2, etc.

late complexes such as $[Co(L\text{-}L)_2CO_3]^+$ or $[Co(L\text{-}L)_2OAc]^{2+}$ followed by treatment with HX.[37,38,44,52–54] They are less stable than the *trans* into which they revert easily and often unpredictably. Mechanistically isomerization is catalyzed by Co(II) or may be photochemically induced. Most known examples are with alkyl substituted ligands, and X is usually an anion with little or no reducing power (Cl, Br, NO_3, $1/2C_2O_4$, OAc). Attempts to prepare *cis* isomers with reducing X groups usually bring about isomerization to the *trans*. The *cis* isomers can be readily distinguished from the *trans* by IR,[37,39] UV-visible,[38,44,53,54] and ^{1}H NMR[37,52] spectroscopy. The ^{59}Co NMR chemical shifts (relative to $K_3Co(CN)_6$ in water $\delta = 0$) although characteristic of the donor set present, ranging, for example, from $\delta + 1710$ ppm in $[Co(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^+$ to $\delta + 6560$ ppm in $[Co(o\text{-}C_6H_4(SbMe_2)_2)_2I_2]^\bullet$, are not usually sensitive to stereochemistry.[42,43] The fast relaxation of the quadrupolar ^{59}Co nucleus ($I = 7/2$ 100%) means that the linewidths are substantial ($W_{1/2} \leq$ ca. 20000 Hz) which obscures any small difference in the chemical shift between the isomers. X-



(a)

FIGURE 2 (I) UV-visible spectra of (a) *trans* $[Co(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^+$ (---), (b) *trans* $[Co(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^+$ (——), (c) *trans* $[Co(o\text{-}C_6H_4(PMe_2)(SbMe_2))_2Cl_2]^+$ (-·-·), (d) *trans* $[Co(o\text{-}C_6H_4(SbMe_2)_2)_2Cl_2]^+$ (···), from Ref. 43 by permission of the American Chemical Society. (II) UV-visible spectra of *cis*-$[Co(Me_2As(CH_2)_3AsMe_2)_2X_2]^+$ X = Cl (——, X = Br (······); *cis* $[Co(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^+$ (---), and *cis* $[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ from Ref. 54 by permission of the Chemical Society of Japan.



(b)

FIGURE 2 (*continued*)

ray studies are available for three *trans* isomers (Table I, Fig. 3), but there appears to be no example of a *cis* form with halide ligands, although complexes with chelating peroxo ligands are known.[68,69]

Multidentate ligand complexes are listed in Table II. The steric constraints of the tripodal tetradentates require that they form *cis* isomers if all four neutral donors chelate to the metal center (Fig. 4); however, linear tetradentates which exist in *rac* and *meso* forms can produce up to five isomers (Fig. 4).[58–60]

Cobalt(III) also forms $[CoE_6]^{3+}$ type complexes (E = P, As, etc.). The only examples with monodentate ligands are with phosphites $[Co\{P(OR)_3\}_6]^{3+}$,[62,63] and it is probable that the larger cone angles of tertiary phosphines preclude arranging six around the cobalt center. Complexes with bidentates $[Co(L\text{-}L)_3]^{3+}$ (L-L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(AsMe_2)$, $o\text{-}C_6H_4(PMe_2)(SbMe_2)$, *cis*-$Me_2AsCH{=}CHAsMe_2$, $Me_2PCH_2CH_2PMe_2$, $o\text{-}C_6H_4(PPh_2)_2$) and tridentates $[Co(L_3)_2]^{3+}$

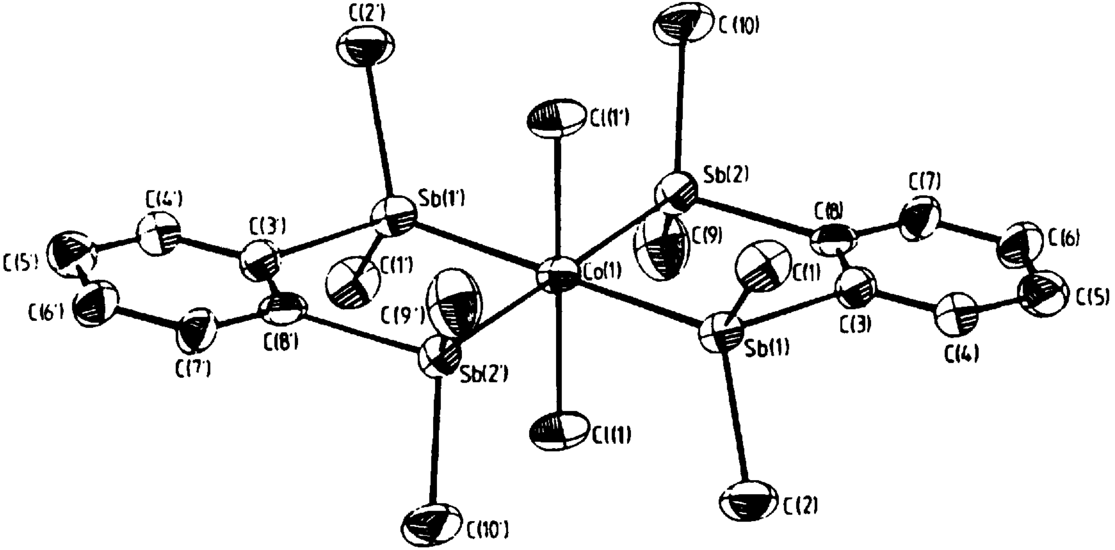


FIGURE 3 The typical structure of *trans* $[M(L\text{-}L)_2X_2]^{n+}$ cations. *Trans* $[Co(o\text{-}C_6H_4(SbMe_2)_2)_2Cl_2]^+$ from Ref. 43 by permission of the American Chemical Society.

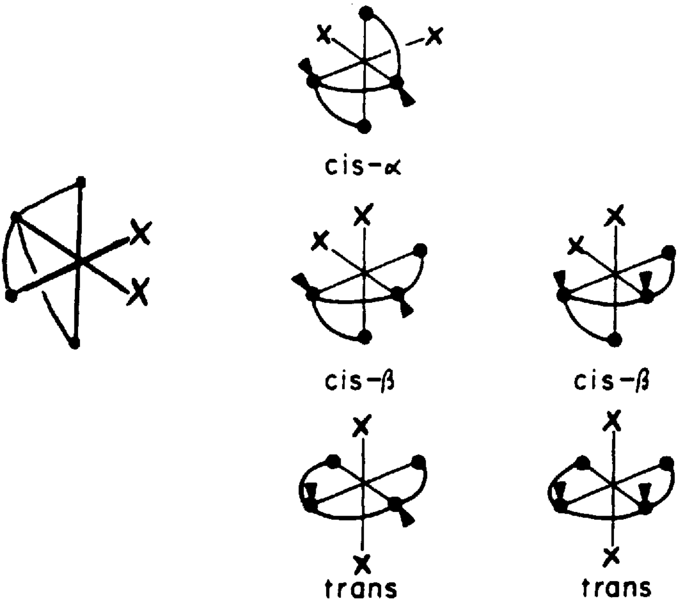


FIGURE 4 The geometric isomers of some octahedral complexes with multidentate ligands.

(L_3 = $MeAs(o\text{-}C_6H_4AsMe_2)_2$, $MeC(CH_2AsMe_2)_3$) are formed by air-oxidation of mixtures of cobalt(II) acetate and excess ligand, followed by addition of HY (Y = ClO_4 or BF_4), or in some cases from $[Co(L\text{-}L)_2X_2]^+$, Ag^+, and L-L.[42,43,49,55,64,65] The complexes are yellow or orange solids with characteristic ^{59}Co chemical shifts ranging from −2600 ppm in $[Co(o\text{-}C_6H_4(PMe_2)_2)_3]^{3+}$ to +2620 ppm in $[Co(o\text{-}C_6H_4(PMe_2)(SMe))_3]^{3+}$, and the structure of the tris(diarsine) complex has been determined (Table I).

No cobalt(IV) complexes are known, and cyclic voltammetry reveals no oxidations of *trans*-$[Co(L\text{-}L)_2X_2]^+$ in MeCN out to +2.2 V (versus SCE).[19,66] This contrast with the generation of Fe(IV) and Ni(IV) complexes demonstrates the great stability of the low-spin d^6 configuration of Co(III) in a pseudooctahedral geometry, especially with strong field ligands such as heavy group 15 donors. The ready generation of Co(IV) in pseudotetrahedral fields in $[CoO_4]^{4-}$ or $[Co(1\text{-norbornyl})_4]$[67] shows the effect of promoting some of the electrons in the Co(III) analogues into less stabilized orbitals.

NICKEL

The three main types of nickel(III) complex are $[Ni(PR_3)_2X_3]$, $[Ni(L\text{-}L)X_3]$, and *trans*-$[Ni(L\text{-}L)_2X_2]^+$, of which the last are the most stable. Jensen's early synthesis of $[Ni(PEt_3)_2Br_3]$ provided the first clear example of a nickel(III) complex.[5] This bromide was obtained by bromine oxidation of $[Ni(PEt_3)_2Br_2]$ in benzene, and subsequently P^nPr_3, P^nBu_3, and PMe_2Ph analogues were obtained.[29,70] The corresponding chlorides were made using NOCl as oxidant.[29] On the basis of a dipole moment measurement, a D_{3h} structure was assigned to $[Ni(PEt_3)_2Br_3]$.[71] Using NOCl or Br_2 in CH_2Cl_2 solution at −78°C as oxidant as appropriate, Higgins[72] prepared pure samples of $[Ni(PR_3)_2X_3]$ (R_3 = Me_3, Et_3, $^nBu_3$, Me_2Ph, Et_2Ph, $MePh_2$, X = Cl, Br) with magnetic moments in the range of 1.7–2.1 B.M. consistent with a d^7 ion. The tetrahedral $[Ni(PPh_3)_2X_2]$ were not oxidized, but the unstable red isomer *trans*-$[Ni(PPh_3)_2Cl_2]$ gave an impure green $[Ni(PPh_3)_2Cl_3]$ on treatment with NOCl, suggesting that the mechanism may involve oxidative addition of NOCl to the planar Ni(II) complexes, followed by loss of NO as the temperature is raised. ESR evidence was obtained for the formation of complexes with $AsEt_3$, $P(OMe)_3$ and PCy_3 in solution, but these were too unstable to isolate.[72] The $[Ni(PR_3)_2X_3]$ are unstable, decomposing to Ni(II) phosphine oxides in moist air in a few hours, and more slowly at low temperatures; the approximate order of stability is Br > Cl, and $PMe_3 \sim PEt_3 > PMe_2Ph \sim P^nBu_3 > PEt_2Ph > PMePh_2$. The structure of $[Ni(PMe_2Ph)_2Br_3]$ was determined by X-ray crystallography (in a mixed crystal of composition $Ni(PMe_2Ph)_2Br_2.\ 2Ni(PMe_2Ph)_2Br_3 \cdot 2C_6H_6$).[70,73] The molecule has a distorted trigonal bipyramidal geometry (Fig. 5), the disparate Ni–Br bond lengths in the trigonal plane being ascribed to the Jahn–Teller effect. Like the Co(III) analogues, the complexes are intensely colored, dichroic materials, and although the UV-visible spectra have previously been assigned in terms of d-d transitions,[72] it seems likely that the major features are L → Ni charge transfer type.[74] There is no evidence that $[Ni(PR_3)_2X_4]^-$ can be made, the ESR spectra of $[Ni(PR_3)_2X_3]$ are unchanged on

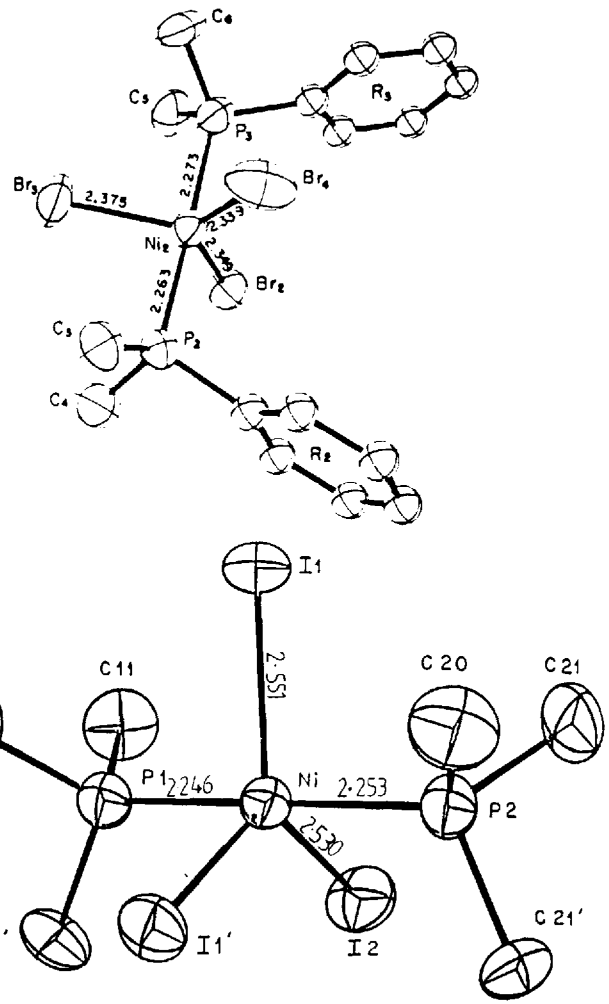


FIGURE 5 (I) The structure of [Ni(PMe$_2$Ph)$_2$Br$_3$] from Ref. 73 by permission of the American Chemical Society. (II) The structure of [Ni(PMe$_3$)$_2$I$_3$] from Ref. 76 by permission of Gordon and Breach, Inc.

addition of X$^-$ to their solutions, and Ni(II) anions such as [Ni(PPh$_3$)Br$_3$]$^-$ decompose on treatment with bromine.[72]

Iodine does not oxidize [Ni(PEt$_3$)$_2$I$_2$] in CH$_2$Cl$_2$,[75] but [Ni(PMe$_3$)$_2$I$_3$] is formed on treatment of [{Ni(μ-^{t}Bu$_2$As)(PMe$_3$)}$_2$] with I$_2$ in toluene.[76] The black product has been characterized by an X-ray study, and has the expected TBP structure (Fig. 5), although the distortion due to the Jahn–Teller effect operates in a different way from that in the bromide, as can be seen from comparison of the bond lengths in the trigonal plane.[76]

A number of dark-brown [Ni(L-L)Br_3] ($Ph_2PCH_2CH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Me_2PCH_2CH_2PMe_2$, $Et_2PCH_2CH_2PEt_2$) were first reported in "postscripts" to papers dealing with their nickel(II) chemistry, and are obtained by Br_2 oxidation of the corresponding [Ni(L-L)Br_2].[48,77–79] A detailed study[80] of these complexes included new examples with *o*-$C_6H_4(PPh_2)_2$ and *o*-$C_6H_4(PPh_2)(AsPh_2)$, but attempts to make complexes with diphosphines with smaller ($Ph_2PCH_2PPh_2$) or larger ($Ph_2P(CH_2)_4PPh_2$) rings were unsuccessful. Notably the aryl diarsine *o*-$C_6H_4(AsPh_2)_2$ gave a very unstable black bromocomplex, but attempts to obtain analogues with *cis*-$Ph_2AsCH{=}CHAsPh_2$ or $Ph_2AsCH_2CH_2AsPh_2$ failed.[80] The olive-green [Ni(L-L)Cl_3] (L-L as for the bromocomplexes $\neq$ *o*-$C_6H_4(AsPh_2)_2$) were made from [Ni(L-L)Cl_2] and NOCl in CH_2Cl_2, although subsequently chlorine was found to be a suitable oxidant under carefully controlled conditions. All these [Ni(L-L)X_3] complexes have μ = 1.7–2.1 B.M. as expected for low-spin d^7 ions, and characteristic ESR and UV-visible spectra,[80] although detailed assignments of the spectra have not been reported due to the low symmetry. In contrast to the [$Ni(PR_3)_2X_3$], the [Ni(L-L)X_3] clearly lose X_2 on heating and revert to the Ni(II) complexes. The X-ray structure of [$Ni(Ph_2PCH_2CH_2PPh_2)Br_3$]·PhMe showed a distorted square-pyramidal geometry with a long apical Ni–Br bond (Table I, Fig. 6). The ESR spectrum shows coupling to a single bromine which suggests that the unpaired electron resides in dz^2 (configuration $(d_{xz},d_{yz})^4\ (d_{xy})^2\ (dz^2)^1\ (dx^2\text{-}y^2)^0$), and the presence of this σ-antibonding electron accounts for the long apical Ni–Br bond.[80] It seems likely that the other [Ni(L-L)X_3] will have similar structures.

Usually the *o*-$C_6H_4(EMe_2)_2$ (E = P, As, etc.) type ligands form only 2:1 nickel complexes, but the unstable hygroscopic [Ni(*o*-$C_6H_4(AsMe_2)_2$)X_3] (X = Cl, Br) were made by halogenation of [Ni(*o*-$C_6H_4(AsMe_2)_2$)$(CO)_2$].[80,81] In solution they decompose rapidly with partial rearrangement into [Ni(*o*-$C_6H_4(AsMe_2)_2)_2X_2]^+$ on the basis of ESR evidence. In contrast to Co(III), no Ni(III) complexes with group 16 donor bidentates have been reported,

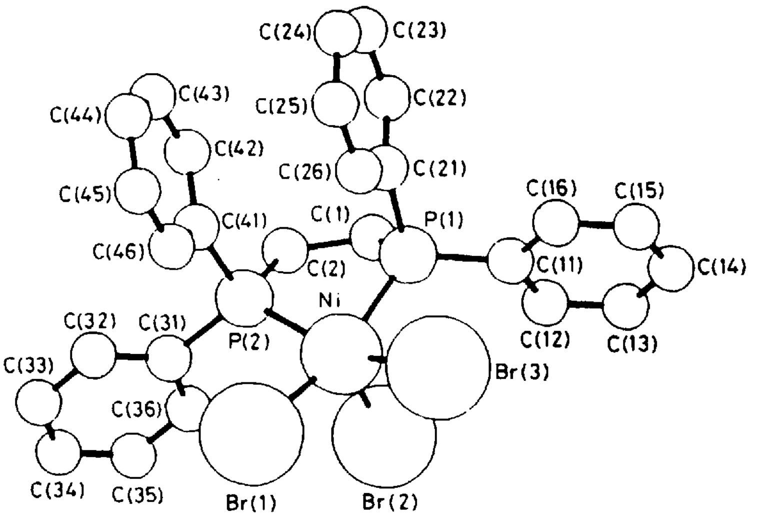


FIGURE 6 The structure of [Ni($Ph_2PCH_2CH_2PPh_2$)Br_3] from Ref. 80 by permission of the Royal Society of Chemistry.

but rare examples of Ni^{III}-E (E = S or Se) linkages are present in the black [Ni(o-C_6H_4(PPh_2)(EMe))Br_3].[82] Attempts to prepare the chloride analogues failed since Cl_2 decomposes the Ni(II) complexes and NOCl gave nitrosyls.

Iodonickel(III) complexes with bidentates have not yet been synthesized. The reaction of a variety of [Ni(L-L)I_2] with excess iodine in CH_2Cl_2 resulted in most being recovered unchanged, although two very unstable black products, analytically [Ni($Ph_2PCH_2CH_2PPh_2$)I_6] and [Ni(o-C_6H_4($AsPh_2$)$_2$)I_4], were obtained. These are ESR silent, lose iodine very easily even at room temperature, and are almost certainly Ni(II) polyiodides.[75] The [Ni(o-C_6H_4($AsMe_2$)$_2$)I_4] made from the dicarbonyl and iodine is similar.[75,81]

The *trans*-[Ni(L-L)$_2X_2$]$^+$ (X = Cl, Br; L-L = o-C_6H_4(PMe_2)$_2$, o-C_6H_4($AsMe_2$)$_2$, o-C_6H_4(PMe_2)($AsMe_2$), o-C_6F_4(PMe_2)$_2$, $Me_2PCH_2CH_2PMe_2$, *cis*-$Me_2AsCH{=}CHAsMe_2$) are readily made from the Ni(II) analogues and O_2/H^+, X_2, FeX_3, Ce(IV), etc.[7,19,20,77,80,85]; the chlorides are pale-green or pale-brown, the bromides orange or brown. In contrast to Co(III), complexes with weaker donor ligands are rare; for example, the only isolated stibine complex is the red $[Ni(o\text{-}C_6H_4(PMe_2)(SbMe_2))_2Br_2]^{\bullet}$ formed by bromination of the Ni(II) analogue, but the corresponding chloride is decomposed by chlorine.[80] The nickel(II) complexes of $Me_2Sb(CH_2)_3SbMe_2$ and $o\text{-}C_6H_4(SbMe_2)_2$ are decomposed by halogens at room temperature, although there is ESR spectral evidence that the addition of bromine to the Ni(II) complexes in CH_2Cl_2 and immediate freezing in liquid nitrogen generates transient Ni(III) species which decompose in seconds upon warming.[86] Group 16 donor complexes are also highly unstable, but conc. HNO_3 oxidation of $[Ni(o\text{-}C_6H_4(EMe_2)(SeMe))_2Br_2]$ (E = P, As), followed by the addition of HBF_4, gave deep-green $[Ni(o\text{-}C_6H_4(EMe_2)(SeMe))_2Br_2](BF_4)$[82]; neither the corresponding chlorides nor complexes with $o\text{-}C_6H_4(EMe_2)(SMe)$ could be prepared. Halogen oxidations of $[Ni(L\text{-}L)_2X_2]$, where L-L is an aryl substituted diphosphine, cleave one ligand from the metal, and the products are mixtures of $[Ni(L\text{-}L)X_3]$ and oxidized ligand.[80,82] This behavior again contrasts with that of Co(III). There are no reports of *cis* isomers of $[Ni(L\text{-}L)_2X_2]^+$ nor are iodocomplexes known.

The reaction of $[Ni(L\text{-}L)_2I_2]$ (L-L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$) with excess I_2 in MeCN solution gave dark-green $[Ni(L\text{-}L)_2I_6]$ which are Ni(II) triiodide(1-) complexes $[Ni(L\text{-}L)_2](I_3)_2$, while in CH_2Cl_2 solution $[Ni(o\text{-}C_6H_4(PMe_2)_2)_2I_{10}]$ was formed.[75] An X-ray study showed the latter to contain a planar Ni(II) diphosphine core, I_3^- ions and weakly associated I_2 molecules. Treatment of the $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{+/2+}$ in CF_3CO_2H with KI gave the same insoluble, black, ESR silent $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2I_3]$ which is almost certainly a Ni(II) polyiodide.[7,75] Although $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]$ was reported to form $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]I$ on refluxing in aqueous HI in air,[77] reexamination of this reaction found that the product was the diphosphine dioxide complex of Ni(II).[75]

All these Ni(III) complexes have magnetic moments corresponding to one unpaired electron, and a variable temperature study of $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]Cl$ found that it obeyed the Curie–Weiss law with $\vartheta = 10°K$.[87] X-ray studies of two examples have been reported,[41,83] and the Ni K-edge EXAFS data on the same complexes are in excellent agreement with respect to the bond lengths about the Ni center (Table I).[84] Particularly notable in comparison with the Co(III) X-ray data are the long axial Ni–Cl bonds which correlate with the presence of a single σ-antibonding electron in the dz^2 orbital in the d^7 nickel complexes which is absent in the d^6 cobalt compounds. The long Ni–X bonds are also evident in the IR spectra where $\nu(Ni-X_2)_{antisym}$ occur at unusually low frequency.[19,80,85,88]

The $[Ni(L\text{-}L)_2X_2]^+$ exhibit highly structured ESR spectra.[10,84,86,87,89,90] The fine details of the spectra prove to be very sensitive to the conditions under which they were recorded (solvent, temperature, glass, powder, host crystal, etc.); for example, $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^+$ gave a rhombic spectrum (3 g values) as a powder or in fairly concentrated solid solution (>10%) in the Co(III) analogue as host, but at lower concentrations in $[Co(o\text{-}C_6H_4(AsMe)_2)_2)_2Cl_2]^+$ or $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$ axial ESR spectra (2 g values) are seen. In principle, since these spectra are rich in hyperfine coupling to the donor atoms, the site(s) of the unpaired electron can be established, and a choice made between the extremes of localized d^7 Ni(III), cation radical ligands and Ni(II), or some intermediate model. In practice the very complexity of the spectra and the simplifications introduced to solve the spin Hamiltonians have made it very difficult to arrive at reliable estimates of the unpaired spin density on the various sites. Detailed studies of $[Ni(o\text{-}C_6H_4(PMe_2)_2)_2X_2]^+$ and $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2X_2]^+$ have been carried out, including one on the diphosphine chlorocomplex enriched in ^{61}Ni.[91] Although a preliminary study[10] proposed a highly unusual σ-arsine radical formulation for $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^+$, more detailed studies[87,89,90] favor a Ni(III) formulation with a $^2A_{2g}$ ground state $[(dz^2)]^1$ but with the unpaired electron extensively delocalized over the six donor atoms. The UV-visible spectra are also very characteristic, consisting of a very weak feature at ca. $(12-14) \times 10^3$ cm^{-1}, further d-d bands $\geq$ ca. 20,000 cm^{-1}, and charge transfer transitions > ca. 25,000 cm^{-1}.[19,80,92] The polarized single crystal optical spectrum of $[Ni(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]PF_6$ has been reported.[92] The interesting electrochemical properties of these complexes are discussed along with those of the Ni(IV) analogues below.

Multidentate ligand Ni(III) complexes are limited to *mer*-$[Ni(MeAs(o\text{-}C_6H_4AsMe_2)_2)Br_3]$,[93] *mer*-$[Ni(MeAs(CH_2CH_2CH_2AsMe_2)_2)Br_3]$,[80,94] and *mer*-$[Ni(PhP(CH_2CH_2PPh_2)_2)X_3]$ (X = Cl, Br),[80] obtained by halogen oxidation of the corresponding five-coordinate Ni(II) complexes. All are reasonably stable as solids, but decompose rapidly in solution. The reported[95] Ni(III) complexes of $As(CH_2CH_2CH_2AsMe_2)_3$ were subsequently shown to be trigonal bipyramidal Ni(II) complexes,[96] and our own attempts to obtain complexes with tetradentate phenylphosphines or alkylarsines were unsuccessful.[80] Multidentate methylphosphines such as $P(CH_2CH_2PMe_2)_3$ or $P(o\text{-}C_6H_4PMe_2)_3$ may be more successful due to the stronger σ-donor power and small steric requirements.

The chemistry of nickel(IV) is much less extensive than that of nickel(III) and complexes are restricted to a few examples of the $[Ni(L\text{-}L)_2X_2]^{2+}$ type. Nyholm[8] found that Ce(IV), Cl_2, or best conc. HNO_3 converted $[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^+$ to dark-blue *trans*-$[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$, and the dark-green bromoanalogue was produced using conc. HNO_3. Subsequently impure $[Ni(\textit{cis}\text{-}Me_2AsCH{=}CHAsMe_2)_2Cl_2](PF_6)_2$[85] and more stable *trans*-$[Ni(o\text{-}C_6H_4(PMe_2)_2)_2X_2]^{2+}$ [19] were prepared. A detailed reinvestigation of these and new examples with *o*-$C_6F_4(PMe_2)_2$,[20] *o*-$C_6H_4(PMe_2)(AsMe_2)$, and $Me_2PCH_2CH_2PMe_2$ has been reported.[84] As with the Fe(IV) complexes, the synthetic conditions are critical to the production of pure complexes. The hygroscopic purple *trans*-$[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2](BF_4)_2$ was made by chlorine oxidation of $[Ni(Me_2PCH_2CH_2PMe_2)_2](BF_4)_2$ in CCl_4, but the others are best made by conc. HNO_3/conc. HX oxidation of $[Ni(L\text{-}L)_2](ClO_4)_2$ at 0°C, followed by precipitation with conc. $HClO_4$ (CARE: explosion hazard). Precipitation with HPF_6 or HBF_4 resulted in complexes containing substantial amounts of Ni(III) impurities. Attempts to produce complexes with phenyl diphosphines such as *o*-$C_6H_4(PPh_2)_2$ or with *o*-$C_6H_4(PMe_2)(SbMe_2)$ failed. These small numbers of complexes are the only Ni(IV) complexes known with any neutral ligands; curiously even diamine complexes have not been prepared, although Ni(IV) moieties are present in the mixed-valence linear chains such as $[\{Ni^{II}(H_2NCH_2CH_2NH_2)_2\cdot Ni^{IV}(H_2NCH_2CH_2NH_2)_2Cl_2\}_nCl_{4n}]$.[97,98]

The Ni(IV) complexes are diamagnetic ($\mu \leq 0.6$ B.M.), and the purest samples are either ESR silent or exhibit very weak ESR spectra due to Ni(III) impurities.[8,84] Convincing evidence for the t_{2g}^6 configuration and hence for the Ni(IV) formulation comes from the UV-visible spectra which are very similar to those of the isoelectronic Co(III) (Figs. 2 and 7). The far IR spectra exhibit single $\nu(\mathrm{Ni{-}X_2})_{\mathrm{antisym}}$ vibrations at much higher frequencies than the Ni(III) complexes, consistent with the removal of the σ antibonding electron in the Ni(III) complexes upon oxidation.[88] The *trans*[Ni(L-L)$_2$X$_2$](ClO$_4$)$_2$ are measurably decomposed in about 1 day at room temperature, and decomposition is rapid in solution even in CF_3CO_2H, and instantaneous in most organic solvents.[84] This instability prevented single crystals from being produced for an X-ray study, but Ni K-edge EXAFS data were obtained on two examples and are shown in Table I,[84,99] and a typical EXAFS spectrum is displayed in Fig. 8. The structural data are similar to those of the Co(III) complexes, and when compared with the data on Ni(III) analogues, they show that d(Ni–P) and d(Ni–As) change by only small amounts upon oxidation, but that d(Ni–Cl) shortens

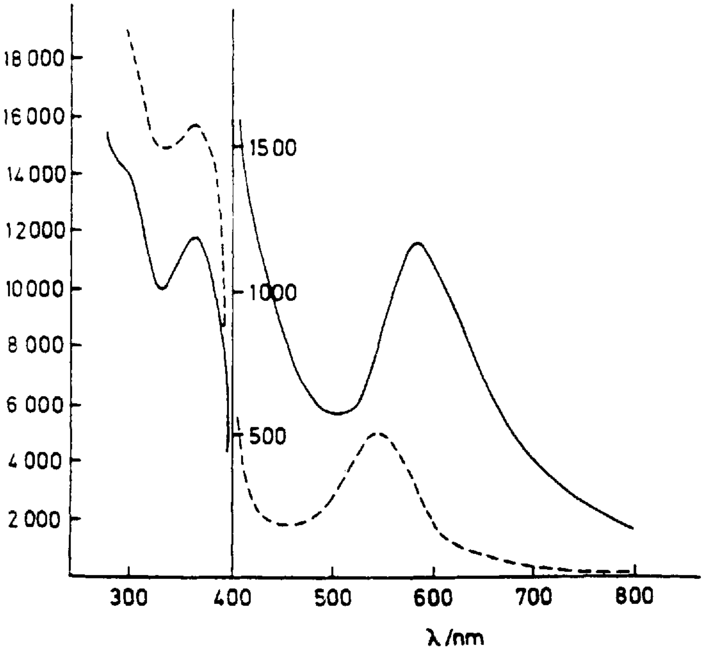


FIGURE 7 The UV-visible spectra of *trans* [Ni(o-$C_6H_4(PMe_2)_2)_2X_2]^{2+}$ X = Br (——), X = Cl (---) from Ref. 84 by permission of the Royal Society of Chemistry.

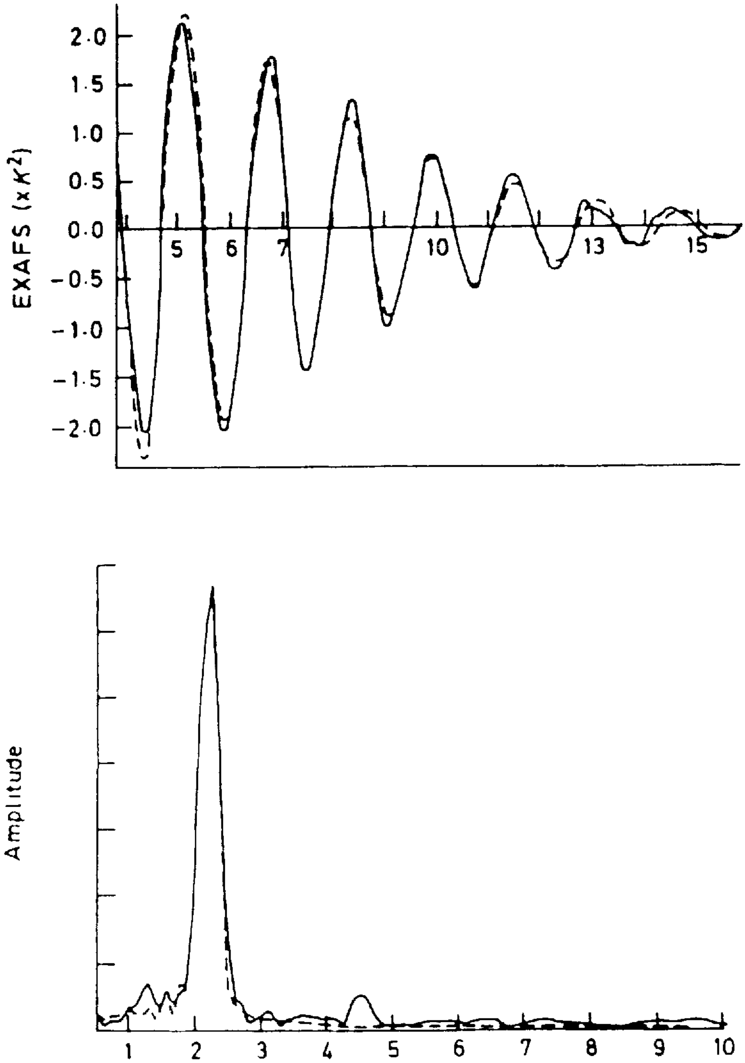


FIGURE 8 The background subtracted EXAFS of *trans* [Ni(*o*-$C_6H_4(PMe_2)_2)_2Cl_2](ClO_4)_2$ and its Fourier transform, from Ref. 84 by permission of the Royal Society of Chemistry.

by ca. 0.15 Å, consistent with removal of the electron in the dz^2 orbital, and providing good evidence that oxidation is metal centered. Attempts to prepare *cis*-$[Ni(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$ from the *trans* isomer via a silver salt (cf. Co(III)) failed.[84] It is possible that a tripod tetradentate such as $P(o\text{-}C_6H_4PMe_2)_3$, which combines *o*-phenylene backbones, small terminal groups with high σ donor power, and which is sterically constrained to generate *cis* pseudooctahedral geometry, might be more successful.

Cyclic voltammetry has provided some interesting insights into the $Ni^{II}/Ni^{III}/Ni^{IV}$ systems.[19,20,86] The Ni^{II}/Ni^{III} couples are electrochemically irreversible in MeCN with $^nBu_4NBF_4$ as background electrolyte, but approach quasi-reversible with $^nBu_4NCl$. This is due to the change in coordination number between Ni(III) (6) and Ni(II) (4 or 5), with the chloride shifting the equilibria in the Ni(II) systems in favor of the higher coordination numbers. Interestingly, the chlorocomplex of $o\text{-}C_6F_4(PMe_2)_2$ exhibits effectively reversible behavior in chloride media, which correlates with the fact that this ligand forms a rare pseudooctahedral (P_4Cl_2) complex with Ni(II).[20] Although the irreversibility of the couples complicates comparison of the changes with L-L, two features emerge: (a) the low positive values of the redox couples, ca. 0.2–0.4 V versus SCE which shows how successfully the $o\text{-}C_6H_4(EMe_2)_2$ type ligands stabilize Ni(III) and (b) the differences between $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, and $Me_2PCH_2CH_2PMe_2$ are small. In fact only the complexes of $o\text{-}C_6F_4(PMe_2)_2$ show significantly higher redox potentials which probably indicate reduced σ donor power of this ligand due to the $-I$ effect of the tetrafluorophenyl backbone.[20] The Ni(III)/Ni(IV) couples are reversible and occur at much more positive potential. In this case $^nBu_4NBF_4$ has to be used as base electrolyte, since the couples are close to that of $Cl^-/1/2Cl_2$. These couples vary little whether L-L is $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, or $o\text{-}C_6H_4(PMe_2)(AsMe_2)$, but are again more positive for $o\text{-}C_6F_4(PMe_2)_2$ complexes.[19,20,84] The *trans*-$[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2]^+$ shows only ill-defined completely irreversible oxidation processes, and this correlates with the instability of the chemically prepared Ni(IV) complex in solution. Possible reasons for the effectiveness of the *o*-phenylene backboned ligands are discussed in a subsequent section.

Until 15 years ago the only oxidation state of copper known in simple phosphine complexes was Cu(I), and there were a very small number of Cu^{II}-PR_3 linkages claimed in mixed donor ligand systems.[14] A few references to unpublished work in which unstable Cu(II)-*o*-$C_6H_4(AsMe_2)_2$ complexes had been observed appeared in papers in the 1960's, but these claims were never substantiated.

Warren and Bennett[100] reported the first Cu(III) diphosphine complex in 1974. In retrospect, since the synthetic route is the same as that used for many complexes discussed in this article, viz. HNO_3 oxidation of a lower oxidation state precursor, it is surprising that such complexes were not discovered earlier. The yellow $[Cu(L\text{-}L)_2](ClO_4)_3$ (L-L = *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$) are planar, diamagnetic d^8 complexes, which add Cl^- to give unstable five-coordinate $[Cu(L\text{-}L)_2Cl](ClO_4)_2$.[19] Attempts to isolate $[Cu(L\text{-}L)_2Cl_2]ClO_4$ have failed, although they may be the cause of the orange-red color seen when Cl^- is added to the monochlorocomplex at low temperatures. An X-ray study of $[Cu(o\text{-}C_6H_4(PMe_2)_2)_2Cl](ClO_4)_2$ (Table I) revealed a square pyramidal cation with a weak interaction with a perchlorate ion in the sixth site (Cu. . .$OClO_3$ = 2.89 Å).[19] Electrochemical reduction of these complexes is an irreversible 2e process, with no evidence for Cu(II) intermediates. Spectroscopic data is fragmentary and the UV-visible spectra are in need of a detailed study.

Chlorine oxidation of Cu(I) diphosphines or diarsines mostly of type $[Cu(L\text{-}L)_2]BF_4$ yield bright-yellow $[Cu(L\text{-}L)Cl_2]BF_4$ (L-L = *o*-$C_6H_4(PPh_2)_2$, $Ph_2PCH_2CH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Cy_2PCH_2CH_2PCy_2$, *o*-$C_6H_4(AsPh_2)_2$, $Ph_2AsCH_2CH_2AsPh_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$), which are unstable in solution, the phosphines in particular converting to phosphine oxides in the presence of moisture.[101] Suitable crystals for an X-ray study have not yet been obtained, but the UV-visible spectra are very similar indeed to those of square-planar Ni(II) complexes, and a similar planar d^8 geometry is almost certainly present. In contrast to the Cu(I) complexes which exhibit broad resonances with only small coordination shifts in their ^{31}P NMR spectra due to fast exchange, the ^{31}P NMR spectra of the Cu(III) complexes are sharp with large high frequency shifts.[101] Complexes

$[Cu(L\text{-}L)Cl_2]Cl$ have also been made, but show no tendency to become five-coordinate by coordination of the third chlorine. All attempts to prepare bromide analogues have failed, and it appears that the copper systems are rare examples of the bromide and chloride systems behaving in fundamentally different ways; as described elsewhere in this article, the differences for most of the other metals considered between complexes of the two halogens is one of degree at most. Copper(III) phosphine and arsine chemistry has been little studied and it is probably too early to speculate on the extent of the field.

Only one Cu(IV) complex is known, the very unstable $[CuF_6]^{2-}$,[102] and the formation of coordination complexes with neutral ligands seems highly unlikely.

SUMMARY AND CONCLUSIONS

The spectroscopic and structural data reviewed in some detail in previous sections provides convincing evidence that the phosphines and arsines are behaving as innocent ligands and that the high oxidation states are genuine. The failures to obtain certain complexes adds support to these conclusions; for example, if $[M(L\text{-}L)_2Cl_2]^{2+}$ are cation radical ligand complexes of lower oxidation state metal centers, it is rather hard to understand why they should form for M = Fe or Ni but not Co. However, if the oxidation is metal centered, then the absence of $[Co^{IV}(L\text{-}L)_2Cl_2]^{2+}$ is readily explained in terms of the unusually great stability of the d^6 Co(III) precursor. The absence of Pd(III) and Rh(IV) complexes[19] further supports the innocent nature of these ligands. Complexes of high oxidation state transition metals form highly covalent bonds with neutral ligands which of course results in delocalization of electrons, but this should not invalidate the ready assignment of the metal oxidation state from physical data any more than it does in other covalent complexes. The only measurements on the present complexes which could lead to a quantification of the delocalization are the ESR spectral studies on the $[Ni(L\text{-}L)_2X_2]^+$ complexes. Unfortunately the extent of delocalization estimated by different workers varies quite widely, in part a reflection of the great difficulties in accurate calculations.

Turning to the types of ligands which are most effective at promoting these high oxidation states, it is apparent from the complexes reported that diphosphines and diarsines with methyl substituents are most successful. The weaker coordinating abilities of phenyl substituted diphosphines and diarsines, of ligands containing the large soft antimony, or group 16 donor groups are evident in normal oxidation state chemistry,[14] and these effects become more pronounced in the more demanding systems considered in this article. Methyl substituted diphosphines and diarsines combine high σ-donor power with modest steric requirements, both important properties when binding to small hard acceptors such as high oxidation states of the later 3d metals. Analysis of the UV-visible spectra of the compounds shows that these ligands are high in the spectrochemical series, which contributes significantly to ligand field stabilization effects with low-spin d^4-d^7 in D_{4h} or O_h fields and to d^8 in planar or C_{4v} fields. The presence of halide coligands also improves stability—$[M(L\text{-}L)_2X_2]^{n+}$ the X ligands reduce the effective charge on the metal center and hence promote M-L binding. The lower relative stability of $[M(L\text{-}L)_3]^{3+}$ (M = Fe or Co) compared[40,42] with $[M(L\text{-}L)_2X_2]^+$ is at least partially attributable to this effect, although the tris(ligand) complexes may also experience destabilizing steric crowding.[42]

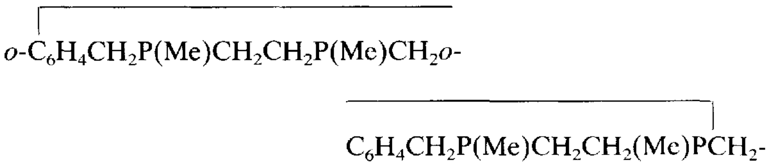
The lack of $[M(L\text{-}L)X_4]$ complexes may reflect the weaker ligand field stabilization when L-L is replaced by $2X^-$. Studies of $[Pt(L\text{-}L)X_4]$ and $[Pd(L\text{-}L)X_4]$[104,105] show that stability decreases markedly, Pt > Pd, the *cis* X groups making reductive elimination a facile decomposition route, and it is possible that $[M(L\text{-}L)X_4]$ where M is a late 3d metal are thermodynamically unstable even at room temperature.

There is also a marked effect of ligand backbone, particularly evident in the most demanding cases (i.e., the least stable complexes) where o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)_2$, and o-$C_6H_4(PMe_2)(AsMe_2)$ are especially effective. Although o-$C_6H_4(AsMe_2)_2$ is no longer unique, indeed in extreme cases such as Mn(II) or Fe(IV),[19,22] the diphosphine produces more robust complexes; the particular abilities of this "type" of ligand deserve some comment. o-phenylene backbones produce 5-membered chelate rings, as do ligands with *cis*-CH=CH- or $-CH_2CH_2-$ linkages, but the stability of the complexes with o-phenylene groups is greater.

The data is admittedly incomplete in that *cis*-$Me_2PCH{=}CHPMe_2$ is not known,[106] and $Me_2AsCH_2CH_2AsMe_2$ is obtainable only in very poor yield and its chemistry has been little studied.[54] It was concluded[85] that *cis*-$Me_2AsCH{=}CHAsMe_2$ was less able to stabilize Ni(III) or Ni(IV) complexes than *o*-$C_6H_4(AsMe_2)_2$. Many complexes of $Me_2PCH_2CH_2PMe_2$ are known[14,103] and it is an excellent ligand towards low and normal oxidation state metal ions and towards the hard early transition metals. For many systems the differences between $Me_2PCH_2CH_2PMe_2$ and *o*-$C_6H_4(PMe_2)_2$ as ligands are small (this includes, e.g., Fe(III) or Ni(III)), but for the highest states (Fe(IV), Ni(IV), Cu(III))[22,84,101] the *o*-$C_6H_4(PMe_2)_2$ complexes are more readily obtained and appear to be significantly more stable. As first suggested by Warren and Bennett[19] and since supported by other studies,[22,80,82,84] the major factor in the greater stabilizing ability of *o*-$C_6H_4(EMe_2)_2$ lies in the rigidity of the *o*-phenylene backbone, which effectively resists dissociation of the ligand from the metal center. In high oxidation state complexes of phosphines and arsines, a potentially unstable combination is present—a highly oxidizing metal center and ligands which are reducing agents *in the free state* (but not when coordinated). Dissociation of the ligands must be avoided, and the rigid *o*-phenylene backbone is more successful than more flexible analogues. Other results demonstrating this effect are the successful synthesis of a Ni(III) complex of *o*-$C_6H_4(AsPh_2)_2$ but not with $Ph_2AsCH_2CH_2AsPh_2$,[80] and the formation of similar complexes with weaker donor groups in *o*-$C_6H_4(PMe_2)(SbMe_2)$, *o*-$C_6H_4(PPh_2)(EMe)$ and *o*-$C_6H_4(PMe_2)(EMe)$ (E = S, Se),[80,82] where the combined effect of the strongly binding PR_2 group and the rigid *o*-C_6H_4 backbone "encourage" binding of the weaker donor.

Electronic effects are most clearly evident in the comparison of the redox potentials in *o*-$C_6H_4(PMe_2)_2$ and *o*-$C_6F_4(PMe_2)_2$ systems,[20] where the reduced donor power of the fluorinated ligand shifts the potentials to more positive values.

It is difficult to generalize about the effects of multidentate ligands, due to the subtle balance of steric and electronic effects built in to such ligands. Most work to date has been with phenyl substituted phosphines or with $MeAs(CH_2CH_2CH_2AsMe_2)_2$ which has the less desirable ring size (6) on chelation, and studies with $P(CH_2CH_2PMe_2)_3$ or preferably $P(o\text{-}C_6H_4PMe_2)_3$ should be more interesting. The latter, combining the favorable features of PMe_2 donors and the o-C_6H_4 linkages, may be particularly effective, and since it is constrained to coordinate *cis* to an O_h metal center, may be a way of forcing *cis* stereochemistry upon high valent ions such as Ni(IV). The most attractive ligands for further development of this area are undoubtedly tetraphosphine or tetraarsine macrocycles, which, with the correct "hole" size and MeP(As) substituents, should be very good at stabilizing $[M(\text{macrocycle})X_2]^{n+}$. The studies will be complicated by the stereoisomers present, but this should be compensated by gains in stability. At present the synthetic difficulties in obtaining the ligands has restricted work to a few groups, and virtually nothing is known about their high oxidation state chemistry. However, one example shows the potential. Stelzer *et al.* prepared a Pd(IV) complex of



$$o\text{-}C_6H_4CH_2P(Me)CH_2CH_2P(Me)CH_2o\text{-}C_6H_4CH_2P(Me)CH_2CH_2(Me)PCH_2\text{-}$$

which is made by H_2O_2/HCl oxidation of the Pd(II) and is stable in solution.[107] In contrast $[Pd(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2](ClO_4)_2$ is made by Cl_2 or HNO_3 oxidation and is relatively unstable in organic solvents.[105]

Finally it is worth drawing attention to the importance of studying pure samples of high oxidation state materials. Impure samples, in our experience, have much shorter "shelf-lives" and often quite different spectroscopic properties due to the presence of impurities or rapid decomposition. The likely impurities are the lower oxidation state analogues, which are usually more labile, and it is possible that these catalyze decomposition and ligand dissociation. (The *cis/trans* isomerization of Co(III) complexes catalyzed by Co(II) is a rather similar phenomenon.)

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