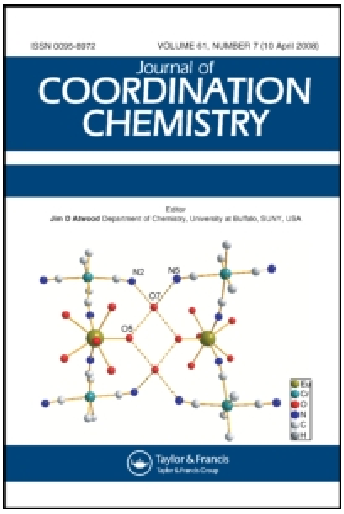

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SHORT COMMUNICATION

A New Chelating Diphosphorus Ligand and Some of its Complexes

J. H. MEINERS and J. G. VERKADE

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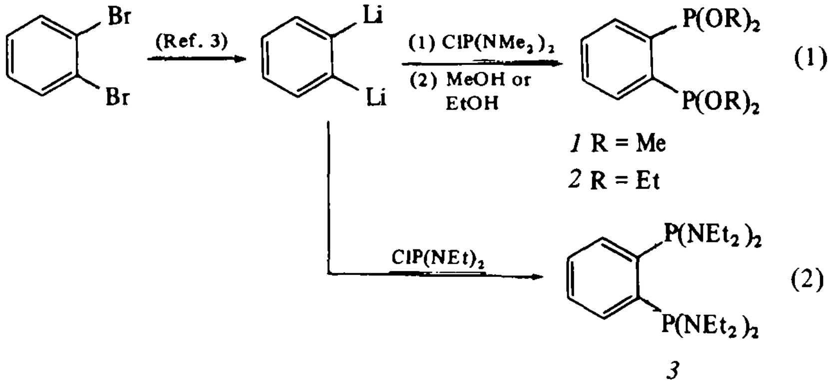
Chelating ligands of the type $o\text{-}(R_2P)_2C_6H_4$ have been prepared where R = OMe (*1*) OEt (*2*) and NEt_2 (*3*). The synthesis of the six coordinate $[\mathrm{Co(chel)}_3]^{+3}$ the five coordinate $[\mathrm{Co(chel)}_3]^{+1}$ and the four coordinate $[\mathrm{Cu(chel)}_2]^{+1}$ and $[\mathrm{Ag(chel)}_2]^{+1}$ complex ions where chel = *1* or *2* suggests that these electronegative phosphorus chelates provide high ligand fields.

Because of the excellent and somewhat unusual coordination properties of acyclic and cyclic phosphite esters,[1] it became of interest to incorporate $P(OR)_2$ groups into an appropriate backbone structure designed to display the chelate effect.[2] Employing reactions (1) and (2), ligands *1*–*3* were prepared in fair yield (25, 25 and 40%, respectively). All these compounds are distillable liquids under vacuum and they display parent peaks in the mass spectrum as well as ^1H and ^{31}P nmr spectra which are consistent with the structures shown. The ortho relationship of the phosphorus groups is supported by their chelating behaviour now described for several complexes.[4]

As is the case with $P(OR)_3$ ligands,[1] reaction of $Co(BF_4)_2 \cdot 6H_2O$ with *1* or *2* results in disproportionation of the cobalt to a colourless low-spin octahedral Co(III) complex and a yellow low-spin trigonal bipyramidal Co(I) complex. There do not appear to be any reports of this disproportionation reaction with $RP(OR)_2$ or $R_2P(OR)$ compounds. Moreover, the $[\mathrm{Co}(\mathit{2})_3]^{+3}$ and $[\mathrm{Co}(\mathit{1})_3]^{+3}$ ions to our knowledge represent the first instances in which Co(III) is completely chelated with only phosphorus atoms in the coordination sphere. Optical resolution attempts on these asymmetric systems are underway. That the Co(I) complex is five coordinate is supported by the ^1H nmr spectrum of $[\mathrm{Co}(\mathit{1})_3]^{+1}$ in which the OCH_3 resonances consist of a broad multiplet indicative of ^{31}P–^{31}P virtual coupling (intensity = 5) and a sharp doublet (^3JPH = 11.8 Hz) indicative of an uncoordinated phosphorus (intensity = 1). Although the equivalence of five of the OCH_3 resonances strongly suggests that this ion is stereochemically non-rigid (as are $\mathrm{Co}[P(OR)_3]_5{}^{+1}$ analogues[5]), intramolecular exchange of the coordinated phosphorus atoms with the uncoordinated phosphorus atom in $[\mathrm{Co}(\mathit{2})_3]^{+1}$ is apparently slow on the nmr time scale.

An unusual feature of the ^1H nmr spectrum of $[\mathrm{Co}(\mathit{2})_3]^{+3}$ in d_6-DMSO is the presence of two CH_3



triplets ($\delta = 1.37$ and 0.84; $^3JHH = 7.0$ Hz) of equal intensity at room temperature which completely collapse at 160° into one triplet ($\delta = 1.18$; $^3JHH = 7$ Hz) or upon standing for 15 months. Evaporation of the d_6-DMSO from the complex and redissolving it in the same solvent, gives rise to the original spectrum. The "two triplet" spectrum persisted in CD_3CN even at reflux temperature, however. Space filling models reveal that the two triplets could arise from the steric preference of a methyl group of the aromatic ring of an adjacent chelate. Thus with each "flat" side of the three benzene rings proximal to a methyl group, the remaining six methyl groups would be located at a greater distance from the shielding region of the rings. The CH_3 nmr spectrum of $[Co(\mathit{1})_3]^{+3}$ in CD_3CN consisted of a doublet ($\delta = 3.91$; $^3JPH + {}^5JPH = 16.8$ Hz). Low temperature nmr experiments are in progress to determine if non-equivalent CH_3 groups can be "frozen out."

Several crystalline zerovalent complexes have been realized with *2* as shown in reaction (3)–(5).

$$\mathit{2} \xrightarrow{M(CO)_4\,(\text{diolefin})} M(CO)_4(\mathit{2}) \quad (M = Cr, Mo, W) \qquad (3)$$

$$\mathit{2} \xrightarrow{Ni(CO)_4} Ni(CO)_2(\mathit{2}) \qquad (4)$$

$$\mathit{2} \xrightarrow{Ni(NCCH{=}CH_2)_2} Ni(\mathit{2})_2 \qquad (5)$$

Attempts to make $W(CO)_3(\mathit{2})_2$ by displacement of the olefin from $W(CO)_3$(cycloheptatriene) have failed thus far and only the disproportionation product $W(CO)_4(\mathit{2})$ was isolated. Further evidence for the "phosphite-like" nature of *2* stems from the CO stretching frequencies of these complexes which in each case are found to lie closer to the analogous $P(OMe)_3$[6] complex than to the PMe_3 compound.[7] Although *3* readily forms $Mo(CO)_4(\mathit{3})$ from $Mo(CO)_4$(norbornadiene), cationic complexes with this ligand have not yet been isolated in pure form.

The $[Ag(chel)_2]^{+1}$ cations where chel = *1* and *2* form stable solids when $AgNO_3$ or $AgClO_4$ is used as the source of Ag^{+1}. It is interesting in this regard that while $P(OMe)_3$ forms $[AgL_4]^+$ with $AgClO_4$, the neutral complex having the stoichiometry $[AgL_2NO_3]$ is formed from the nitrate and the latter compound is a nitrate-bridged dimer in the solid state.[8] Apparently the chelate effect militates against nitrate coordination in $[Ag(chel)_2]^{+1}$. Divalent copper is reduced to Cu(I) in the formation of $[Cu(\mathit{2})_2]BF_4$ from $Cu(BF_4)_2$.

The zerovalent complexes exhibited parent ion peaks in their mass spectra and the cationic complexes gave elemental analyses and equivalent conductances in acetonitrile which are commensurate with their formulations.

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