

Yttrium, Scandium, Lutetium, and Praseodymium Complexes of Tris(diphenylphosphinoyl)methanide¹

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The mesomerically stabilised anion tris(diphenylphosphinoyl)methanide reacts with yttrium (also scandium, lutetium, and praseodymium) chloride to form tris[tris(diphenylphosphinoyl)methanido]yttrium in which the ligand is bidentate and kinetically inert on an n.m.r. time-scale at room temperature and from whose ³¹P n.m.r. spectrum a ⁸⁹Y-³¹P nuclear spin coupling constant can be determined.

We report here the first complexes of the type M{[Ph₂P(O)]₃C}₃ where M is Sc, Y, Lu, or Pr, which have been prepared by metathesis from the recently synthesised, mesomerically stabilised, negative ligand tris(diphenylphosphinoyl)methanide,² {[Ph₂P(O)]₃C}⁻, (tdpm)⁻, and the respective metal chlorides or nitrates in methanol solution. The diamagnetic compounds M(tdpm)₃, where M is Sc, Y, or

Lu, are high melting, white solids which are readily soluble in polar organic solvents such as dichloromethane or chloroform. Unlike the previously reported³ sulphur analogue of tdpm, which behaves as a tripodal ligand to soft metal ions such as Ag^I⁴ and Hg^{II},⁵ the ³¹P n.m.r. spectra of the present M(tdpm)₃ complexes indicate that (tdpm)⁻ is bidentate as illustrated in Figure 1.

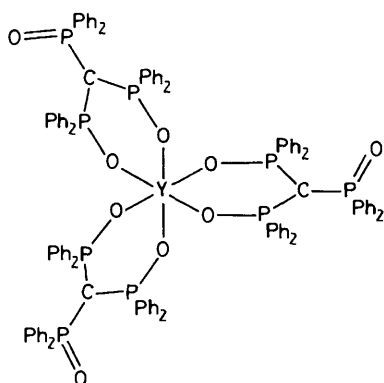


Figure 1. The structure of $Y(tdpm)_3$.

The ^{31}P n.m.r. spectra[†] of these complexes (except for the green paramagnetic praseodymium complex for which no ^{31}P n.m.r. signal was expected) consist of an upfield triplet (one P) due to the unco-ordinated phosphoryl group and a downfield doublet (two P) due to the co-ordinated phosphoryl groups. The observation of these P–P spin-couplings at room temperature indicates that the $(tdpm)^-$ ligand is kinetically inert in $M(tdpm)_3$ unlike the corresponding $M(MeCOCH-COMe)_3$ complexes.⁶ The ligand is also non-fluxional, *i.e.*, the unco-ordinated phosphoryl group does not displace the co-ordinated phosphoryl groups on this time scale. Addition of excess $Li(tdpm)$ to a solution of $Y(tdpm)_3$ results in a new singlet in the ^{31}P n.m.r. spectrum at δ 35.2 p.p.m. characteristic of the free $(tdpm)^-$ with no line-broadening or averaging of the chemical shifts in the original spectrum of $Y(tdpm)_3$.

[†] ^{31}P N.m.r. data for $M(tdpm)_3$. $M = Y$: δ 42.8 [2P, dd, $^2J(P-P)$ 30.0, $^2J(^{89}Y-P)$ 6.5 Hz] and 24.9 p.p.m. [1P, t, $^2J(P-P)$ 30 Hz]. $M = Sc$: δ 43.7 [2P, d, $^2J(P-P)$ 30.0 Hz] and 24.3 p.p.m. (1P, t). $M = Lu$: δ 43.9 [2P, d, $^2J(P-P)$ 29.9 Hz] and 24.9 p.p.m. (1P, t).

In the ^{31}P n.m.r. spectrum of $Y(tdpm)_3$ a nuclear spin coupling between ^{89}Y (100% abundance, $I = \frac{1}{2}$) and the phosphorus atoms of the two co-ordinated phosphoryl groups, $^2J(^{89}Y-P) = 6.5$ Hz, results in a pair of doublets in the downfield portion of the spectrum. This is the first observed yttrium–phosphorus coupling to our knowledge. No Y–P coupling is evident in the upfield triplet portion of the spectrum, $^4J(^{89}Y-P) < 1$ Hz, which further substantiates that the phosphoryl group giving rise to the triplet is not co-ordinated to Y.

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