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Preliminary communication

Hexa-phosphorus analogues of metallocenes: synthesis of the first paramagnetic sandwich complex containing two η^5-1,2,4-triphosphacyclopentadienyl rings. Crystal and molecular structures of $[Cr(\eta^5\text{-}C_2Bu^t_2P_3)_2]$

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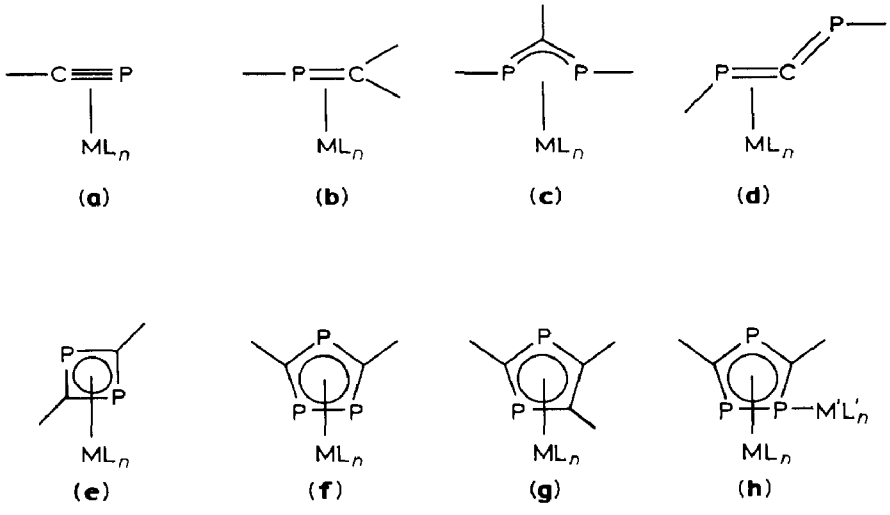
Abstract

The first paramagnetic sandwich complex containing η^5-1,2,4-triphosphacyclopentadienyl rings, has been synthesised, and its molecular structure determined.

In recent years several phosphorus analogues of unsaturated organo-transition metal complexes have been described [1]. Typical novel organophosphorus metal complexes are shown below (**a**–**j**), and continued rapid development of this field is to be expected [2–16].



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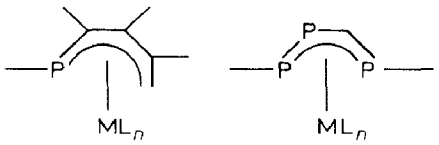
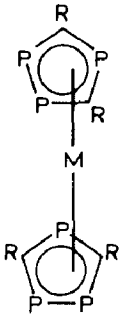
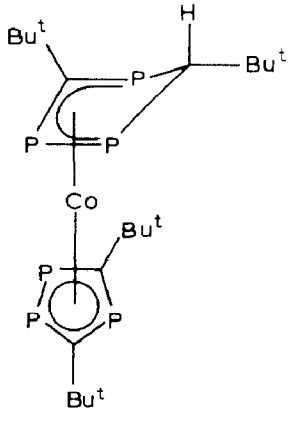


(i) (j)

Previously [14] we described the synthesis and structural characterisation of the diamagnetic 18-electron hexa-phosphorus analogues of ferrocene $[Fe(\eta^5\text{-}C_2R_2P_3)_2]$ (I: R = Bu^t, adamantyl), by treatment of $FeCl_2$ with $[Li(dme)_3][C_2R_2P_3)]$. An attempt to obtain the paramagnetic 19-electron cobaltocene analogue by a similar route gave instead the diamagnetic 18-electron (η^5-1,2,4-triphosphacyclopentadienyl)(η^4-1,2,4-triphosphacyclopentadiene)cobalt complex (II) [17]. Likewise, no evidence has yet been obtained for a 20 electron nickel complex.

We now report the successful synthesis of the paramagnetic 16 electron $[Cr(\eta^5\text{-}C_2R_2P_3)_2]$ complex (III: R = Bu^t), by treatment of the highly reactive complex $[CrCl_2(THF)_2]$ [18] with $[Li(dme)_3][C_2Bu^t_2P_3]$ in monoglyme at room temperature. The identity of the black solid complex, (olive green in solution), (μ 2.46 BM by the Evans' method) [19], was confirmed by a single crystal X-ray diffraction study * and the molecular structure is shown in Fig. 1.





(I : M = Fe ,(R = Bu^t ,adamantyl); (II)

III : M = Cr ,(R = Bu^t))

* Crystal data. $C_{20}H_{36}CrP_6$, M-514.4, orthorhombic, space group, $C222$, a 11.651(6), b 16.348(3), c 13.732(3) Å, U 2596.0 Å^3, $Z = 4$, $D_c = 1.31$ g cm^{-3}. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 7.9 cm^{-1}.

The coordinates for non-hydrogen atoms were taken from the isomorphous Fe complex and refined anisotropically by full matrix least squares to give $R = 0.049$ for 1087 reflections with $I > \sigma(I)$ measured on an Enraf–Nonius CAD4 diffractometer. The molecules lie on crystallographic two-fold rotation axes.

Tables of atomic coordinates and molecular parameters have been deposited with the Cambridge Crystallographic data centre.

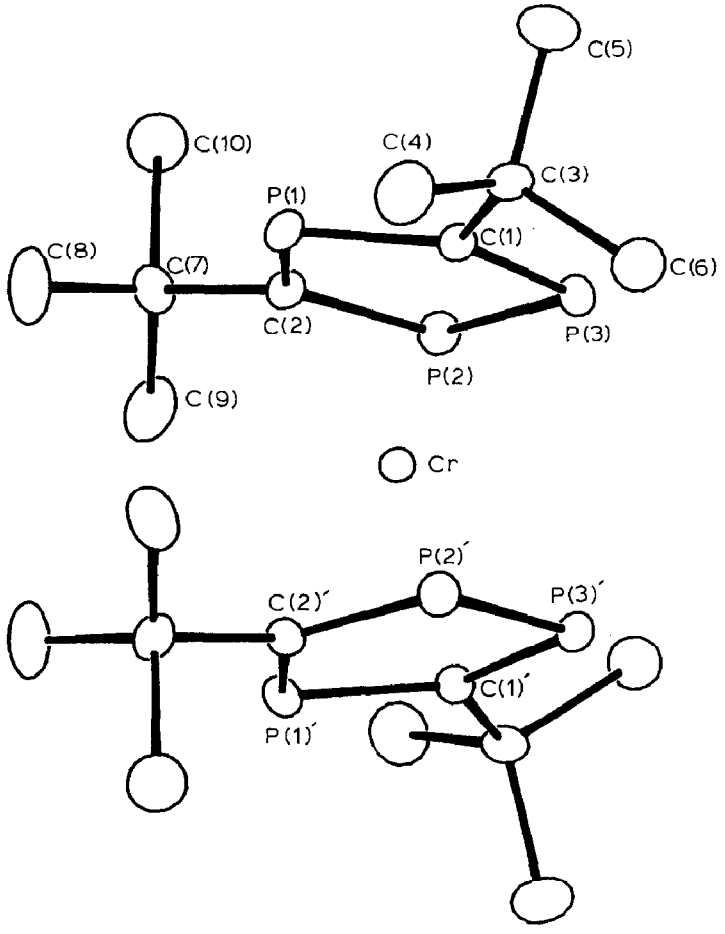


Fig. 1.

The two $[(\eta^5\text{-}C_2Bu^tP_3)_2]$ sandwich complexes (M = Cr, Fe) (I and III), are isomorphous, and in both the rings are eclipsed, with the Bu^t groups arranged to minimise inter-ring interactions. As expected the metal–ring distances are significantly longer for the chromium compound, e.g. Cr–P(1) 2.480(3); Cr–P(2) 2.454(3); Cr–P(3) 2.414(3) Cr–C(1) 2.274(9); Cr–C(2) 2.334(10 Å (compare Fe–P(1) 2.330(3); Fe–P(2) 2.358(3); Fe–P(3) 2.359(3); Fe–C(1) 2.197(11); Fe–C(2) 2.222(12) Å in I).

The mass spectrum of III shows a parent ion at *m/e* 514. Unlike that of I, the $^{31}P\{^1H\}$ NMR spectrum is featureless, but the ^1H NMR spectrum shows a broad Bu^t resonance. The ESR spectrum recorded at 77 K and 4.2 K exhibits a broad band. Further physical and chemical studies on III will be described in later publications.

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