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Preliminary communication

Synthesis, crystal and molecular structure of the "slipped" sandwich complex $[Ni(\eta^5\text{-}P_3C_2R_2)(\eta^3\text{-}P_2C_3R_3)]$ $(R = Bu^t)$

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Abstract

The synthesis of the novel "slipped" sandwich compound $[Ni(\eta^5\text{-}P_3C_2R_2)(\eta^3\text{-}P_2C_3R_3)]$ $(R = Bu^t)$ is described. The mode of attachment of the $P_3C_2R_2$ and $P_2C_3R_3$ rings has been determined by NMR spectroscopy and a single crystal X-ray diffraction study.

The field of organotransition metal chemistry involving unsaturated organic ligands in which CH fragments are replaced by P is rapidly developing [1]. Previously [2] we have described syntheses and full structural characterisation of the 18e sandwich complexes $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ (I) and $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$ (II) and more recently [3] the 16e paramagnetic compound $[Cr(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ (III).

Attempts to synthesise the 19e system $[Co(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ led instead [4] to the 18e diamagnetic $[Co(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^4\text{-}P_3C_2Bu^t{}_2H)]$ (IV).

We now report that treatment of a mixture of $Li(P_3C_2Bu^t{}_2)$ and $Li(P_2C_3Bu^t{}_3)$ with $[NiBr_2(monoglyme)_2]$ in monoglyme affords a low yield (ca. 5%) of the purple nickel complex $[Ni(P_3C_2Bu^t{}_2)(P_2C_3Bu^t{}_3)]$ (V) *, which exhibits the $^{31}P\{^1H\}$ NMR spectrum shown in Figure 1. No evidence was obtained for the formation of the paramagnetic 20e sandwich complexes $[Ni(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$, $[Ni(\eta^3\text{-}P_2C_3Bu^t{}_3)_2]$ or $[Ni(\eta^5\text{-}P_2C_3Bu^t{}_3)(\eta^5\text{-}P_3C_2Bu^t{}_2)]$. The sharpness of the $^{31}P\{^1H\}$ NMR spectra of V, which was fully analysed as an A_2BC_2 spin system (Figure 1), was indicative of a diamagnetic 18e complex, suggesting that one ring is η^5-ligated and the other is η^3-bonded to the metal as in Va or Vb. The low inter-ring coupling constant $^2J_{AC}$ (10.9 Hz) compared with the large value of ca. 50 Hz observed in I where the rings

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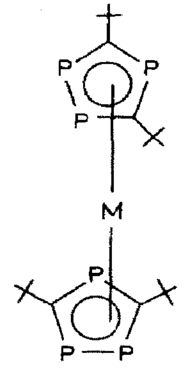
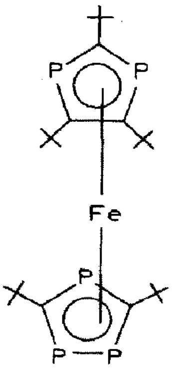
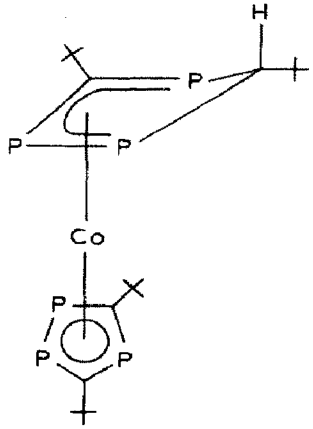
* Preparation of V. $NiBr_2(dme)_2$ (398 mg, 1 mmol) was added to 7 ml of a solution containing $Li[(C_2Bu_2{}^tP_3)]/Li[(C_3Bu_3{}^tP_2)]$ (1 mmol) in monoglyme and the mixture stirred at room temperature for 16 h. After removal of the solvent the residue was extracted with hexane and fractionated by column chromatography (kieselgel/hexane). V was obtained as purple solid (5% yield).



(I : M = Fe;
III : M = Cr)



(II)



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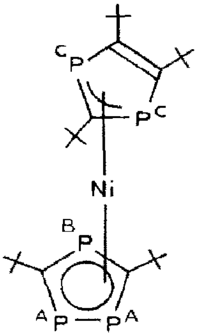

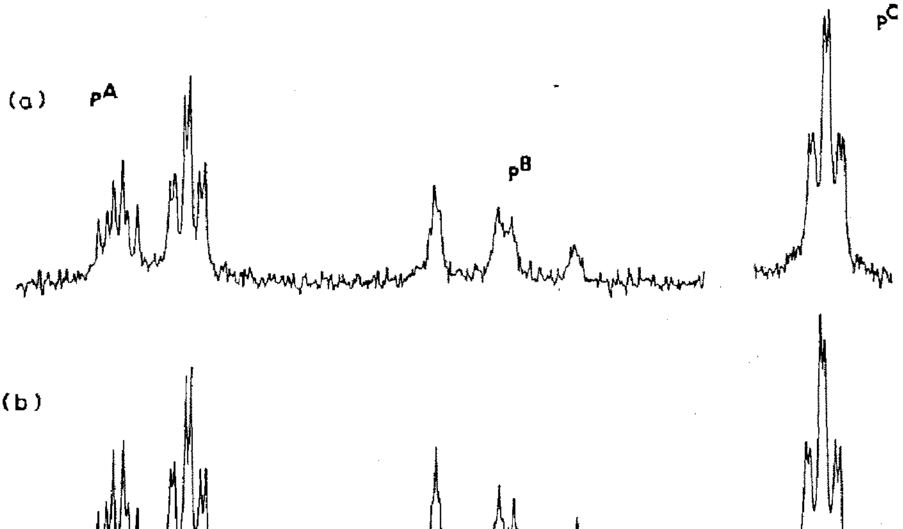

Fig. 1. Observed (a) and simulated (b) $^{31}P\{^1H\}$ NMR spectrum of V.

are eclipsed also suggested η^5-, η^3-ligation of the two rings. ^{31}P chemical shift data * supported structure Va, which does not have the localised P=P double bond in the ring.

The mass spectrum of V exhibits a parent ion at $m/e = 558$ and ions corresponding to the stepwise loss of the three Bu^{t}CP fragments. Of particular significance is the observation of the strongest peak at $m/e = 420$ corresponding to the $[Ni(P_3C_2Bu^t_2)(P_2CBu^t)]^+$ ion which arises from the loss of $Bu^t_2C_2$ from V. This strongly suggested that the $(P_2C_3Bu^t_3)$ ring is η^3-ligated to the metal as in Va.

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* ^{31}P NMR: $\delta(P^A)$ 115.0, $\delta(P^B)$ 153.2, $\delta(P^C)$ 111.4 ppm (rel. H_3PO_4); J_{AB} 51.2 Hz, J_{AC} 10.9 Hz, J_{BC} 2.9 Hz, ^{1}H NMR δ 1.18, 1.30, 1.54 ppm.

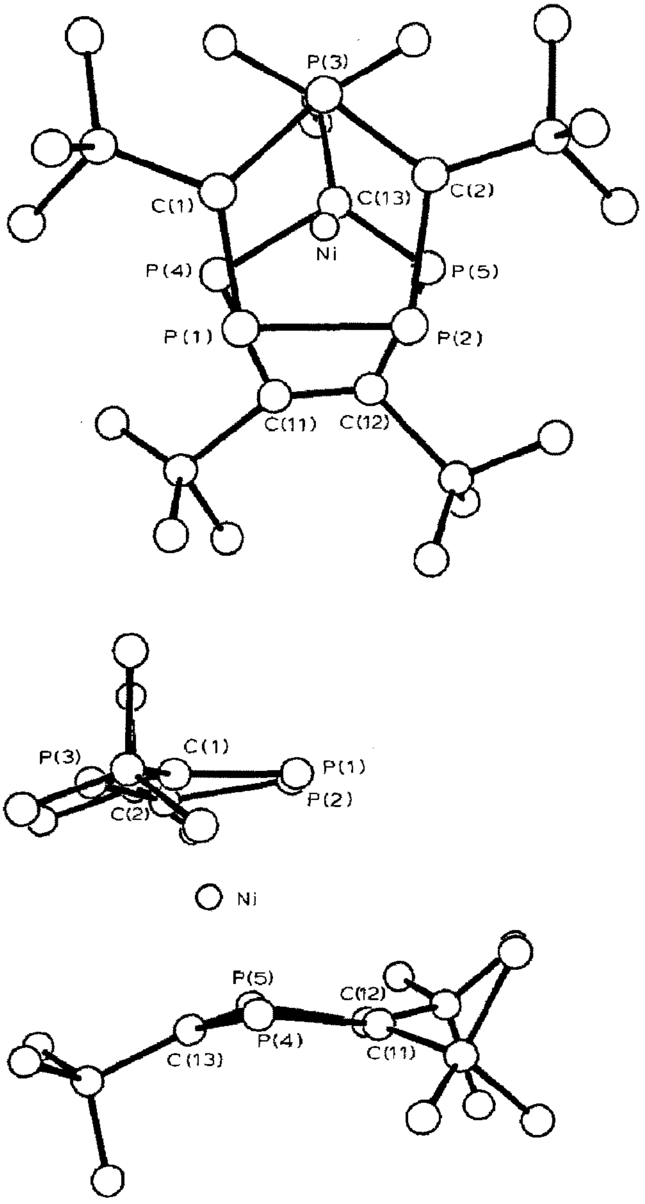

Fig. 2. Two views of the molecular structure of V.

Confirmation of the molecular structure came from a single crystal X-ray diffraction study (See Fig. 2) * where the planar ($P_3C_2Bu^t_2$) ring is η^5-bonded to the metal whereas the ($P_2C_3Bu^t_3$) ring is η^3-ligated and bent along the P(4)–P(5) vector so that the C=C fragment does not interact with the nickel atom.

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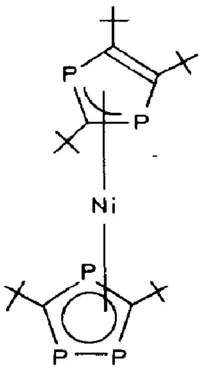
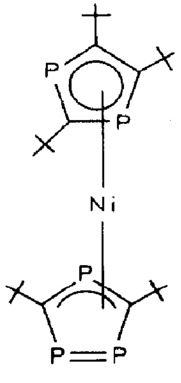
* Crystal data: $C_{25}H_{45}NiP_5$, $M = 559.2$, monoclinic, space group $P2_1/n$, a 11.902(4), b 18.777(3), c 27.341(9) Å, β 99.61(3)°, $Z = 8$. D_c 1.23 g cm^{-3}. The structure was solved by direct methods based on 7868 reflections collected on an Enraf–Nonius CAD4 diffractometer using mono-chromated Mo-K_α radiation, λ 0.71069 Å, μ 9.2 cm^{-1}, of which 2464 having $|F^2| > 3\sigma(F^2)$ were used in the refinement. The final residuals were $R = 0.136$, $R' = 0.193$.



(Va)



(Vb)

To our knowledge this is the first example of a complex containing one normal and one "slipped" ring in a simple metal sandwich complex containing no other attendant ligands [5,6]. The analogous 20e nickelocene compound has both C_5H_5 rings ligated in an η^5-fashion [7–9]. The preference in V by the nickel for the P–C–P rather than the C–C–P moiety within the five membered ring is in accord with our observations on η^2-monophosphaallene $R_2C{=}C{=}PR$ ($R = C_6H_2Bu^t_3$), complexes of palladium(0) and platinum(0) where it is the P=C bond rather than the C=C bond that interacts with the metal atom [1,10].

The non-formation of 19e and 20e metal complexes with the unsaturated five membered ring systems containing phosphorus presumably reflects the higher energy of the antibonding molecular orbitals in the $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ and $[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ complexes compared with those in their $[M(\eta^5\text{-}C_5H_5)_2]$ analogues.

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