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Novel η^2-ring edge coordination in the triphosphaferrocene complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)Rh(\eta^5\text{-}C_5Me_5)CO]$

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Abstract

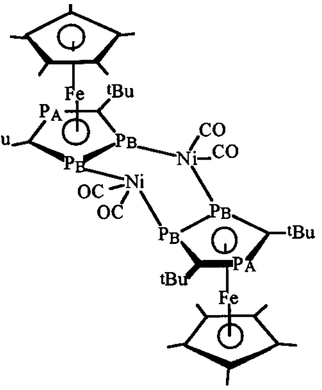
Single-crystal X-ray diffraction studies on the triphosphaferrocene $[Fe(\eta^5\text{-}C_5H_5)(\eta^5P_3C_2^tBu_2)]$ and its $[Rh(\eta^5\text{-}C_5Me_5)CO]$ complex reveal an unusual η^2-ring edge coordination mode in the latter resulting in a significant elongation of the triphosphacyclopentadienyl ring P–P bond. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ring edge coordination; Triphosphacyclopentadienyl ring; Triphosphaferrocene

1. Introduction

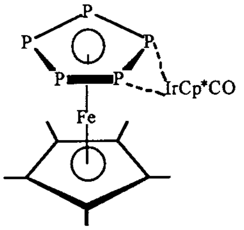
The η^1-ligating behaviour of the triphosphaferrocene $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$ (**1**) towards several transition metal–ligand ML_n centres ($M = Cr$, Mo, W, $L = CO$, $n = 5$; $M = Fe$, $L = CO$, $n = 4$) has been explored [1–4] and in all cases the bonding has been of the η^1-type involving lone pair electrons of one of the two directly bonded P atoms of the $(\eta^5\text{-}P_3C_2^tBu_2)$ ring as shown in Fig. 1.

Both lone pairs of electrons on adjacent P ring atoms of $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2^tBu_2)]$ (**2**) can be utilised [2] as in the tetrametallic dinickel(0) tetracarbonyl complex $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2^tBu_2)_2Ni_2(CO)_4]$ (**3**) shown below.



(3)

We have recently extended [5] the range of η^1-$[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)(ML_n)]$ complexes to square planar d^8-platinum (II) systems ($ML_n = [PtCl_2PR_3]_2$ ($R = Et$, Me and Ph) where unexpectedly only the *cis*-isomers are formed (Fig. 2), and it was therefore of interest to study analogous reactions with other d^8 metal complexes, particularly since Scherer et al. [6] previously established a novel η^2-ring-edge ligation of the pentaphosphaferrocene to iridium(I) in compound $[Ir(\eta^5\text{-}C_5Me_5)(CO)\eta^2\text{-}\{Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_5)\}]$ (**4**) and also described an analogous Rh(I) complex $[Rh(\eta^5\text{-}C_5Me_5)(CO)\eta^2\text{-}\{Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}As_5)\}]$ (**5**) involving the penta-arsaferrocene.



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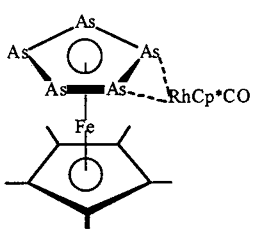

(5)

Unusually the bonding in **4** and **5** was found to involve an η^2-ligation mode through either the P–P or As–As multiple bond and not the usual η^1-ligation via P or As lone pair electrons. In view of this observation the synthesis of an η^2-ligated $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$-$[Rh(\eta^5\text{-}C_5Me_5)(CO)]$ complex was attempted to see whether edge-bonding might result and whether it would involve either a P–P, P–C or C–C multiple

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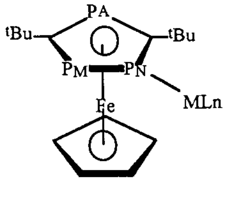


Fig. 1.

bond in the related triphosphaferrocene derivatives of (**1**).

2. Results and discussion

2.1. Synthesis of $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{CO})\eta^2\text{-}\{\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})\}]$ (6)

Treatment of $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$ with an excess of $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})]$ (**1**) in toluene under UV irradiation led to slow CO evolution and the progress of the reaction was monitored by infrared spectroscopy, showing the steady growth of the new complex $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{CO})\eta^2\text{-}\{\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})\}]$ (**6**). The product was characterised by mass spectroscopy, elemental analysis, infrared spectroscopy, multinuclear NMR spectroscopy and a single-crystal X-ray diffraction study.

The presence of a single band, ($\nu_{\mathrm{CO}} = 1938\ \mathrm{cm}^{-1}$), in the infrared spectrum of **6**, indicated that only one CO had been displaced from $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$ and the ^{1}H-NMR spectrum showed three singlets readily assigned to the $\mathrm{C_5H_5}$, $\mathrm{C_5Me_5}$ and ^{t}Bu groups, in the anticipated ratios 5:15:18, suggesting a structure in which the rhodium(I) fragment is coordinated to one phosphaferrocene in a *symmetrical* fashion.

The FAB mass spectrum of complex **6** exhibits a molecular ion, (*m/z* 618), consistent with the proposed formula $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{CO}\{\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})\}]$ together with peaks at (*m/z* 590, $\mathrm{M-CO})^+$and (*m/z* 352, $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})]^+$).

The ^{31}P{^{1}H}-NMR spectrum of (**6**) (Fig. 3) was particularly informative being typical of an [AM$_2$X] spin system ($\mathrm{A = P_A}$, $\mathrm{M = P_M}$, $\mathrm{X} = {}^{103}\mathrm{Rh}$, $\mathrm{I} = 1/2$, all 100% abundance) indicating that that there are only two distinct phosphorus sites.

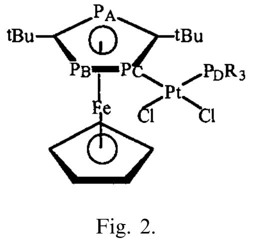


Fig. 2.

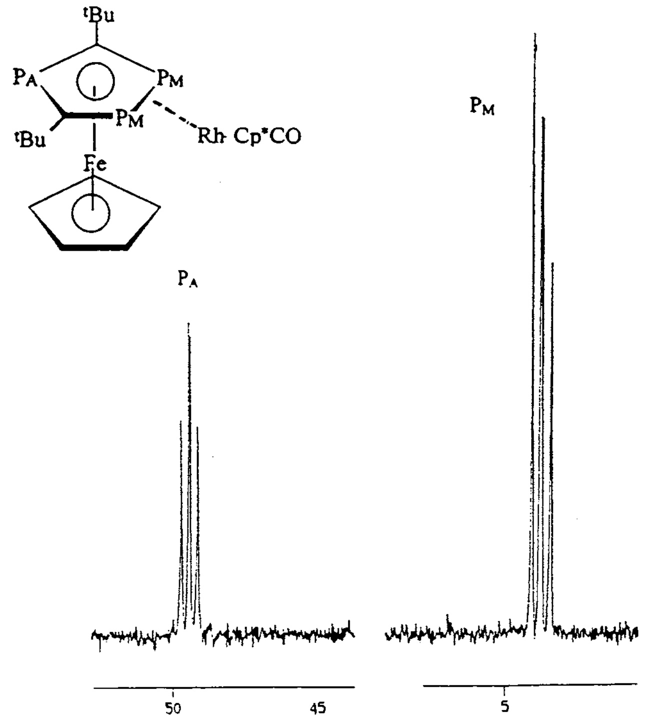
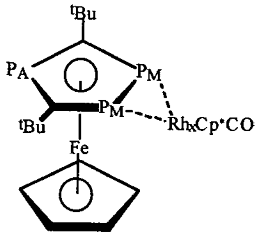


Fig. 3. ^{31}P{^{1}H}-NMR spectrum of $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{CO}\{\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})\}]$ (**6**) (25°C, $\mathrm{C_6D_5CD_3}$, 121.5 MHz).



(6)

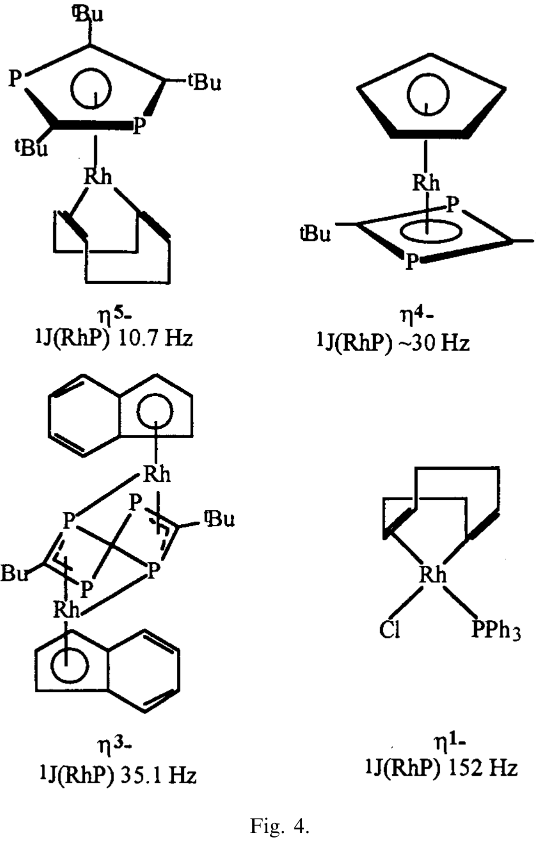
The main feature of interest in the ^{31}P{^{1}H}-NMR spectrum of $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{CO}\{\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{P_3C_2^tBu_2})\}]$ (**6**) is the lack of any large $^1J_{\mathrm{PP}}$ coupling constant characteristic of the spectra of conventional η^1-triphosphaferrocene complexes discussed above is observed for **6**, indicating that both the adjacent ring phosphorus atoms must be *chemically and magnetically equivalent*. The doublet of triplets resonance at $\delta = 49.5$, is assigned to phosphorus atom $\mathrm{P_A}$ $^2J_{\mathrm{RhP_A}}$ 4.3 Hz, $^2J_{\mathrm{P_MP_A}}$ 38.2 Hz) and the resonance of the $\mathrm{P_M}$ phosphorus atoms ($\delta = 4.9$) occurs as a doublet of doublets $^2J_{\mathrm{P_MP_A}}$ 38.2 Hz; $^1J_{\mathrm{RhP_A}}$ 41.1 Hz). The low value of both rhodium–phosphorus coupling constants is important since this can be related to the mode of bonding. A variety of rhodium(I) complexes of unsaturated phosphorus ring systems are known [7–10] in which η^1-, η^3-, η^4- and η^5-bonding modes are utilised. These are shown in Fig. 4 together with their corresponding $^1J_{\mathrm{RhP}}$ coupling constants.

As the mode of coordination decreases from η^5 to η^1 there is a corresponding increase in the magnitude of the $^1J_{RhP}$ coupling constant. The observation of $^1J_{RhP_M}$ (41.1 Hz) in **6** is clearly significantly smaller than would be expected for a typical η^1-ligation giving credence to the η^2-mode of coordination.

Since many rhodium(I) complexes often show dynamic behaviour in solution, although the $^{31}P\{^1H\}$-NMR spectrum of **6** is sharp, the possibility that a rapid 1,2-shift of the $[Rh(\eta^5\text{-}C_5Me_5)CO]$ fragment occurs between the adjacent phosphorus atoms (P_B) at room temperature, was also considered. This type of dynamic process has been reported in $[M(CO)_5[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2^tBu_2)]$ (M = Cr, Mo)[2]. A series of $^{31}P\{^1H\}$-NMR spectra for **6** were recorded at different temperatures but even at −90°C there was no observable change in the spectrum. Thus complex **6** is best formulated as $[Rh(\eta^5\text{-}C_5Me_5)(CO)\eta^2\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)\}]$ where the rhodium is edge-bonded to the phosphorus–phosphorus multiple bond. This structure was subsequently confirmed by a single-crystal X-ray diffraction study (vide infra).

2.2. Single-crystal X-ray diffraction study on complex *6*

Fig. 5 shows the molecular geometry of **6** as determined by a single-crystal X-ray diffraction study. The molecular structure of **6** shows all the expected features. The pentamethylcyclopentadienyl ring is η^5-ligated to the rhodium and the $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$ has the iron atom sandwiched between the η^5-cyclopentadienyl ring and the η^5-triphosphacyclopentadienyl ring. The rhodium centre is attached in an edge-fashion to *both* adjacent phosphorus atoms of the $(\eta^5\text{-}P_3C_2^tBu_2)$ ring system as previously inferred by solution multinuclear NMR spectroscopy. Particularly noteworthy is the resulting very elongated phosphorus–phosphorus bond (2.306(2) Å) which is comparable with the P–P bond distance in the η^2-edge ligated pentaphosphaferrocene complex (**4**) (2.359(2) Å), which is also significantly longer than in $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_5)]$ (2.085–2.111 Å). This mode of bonding can be considered as an ethene-like system where coordination through the P–P multiple bond, results in a decrease in bond order because of the synergic effect of back bonding from rhodium to ring π^* orbitals. In order to determine the extent of the P–P elongation in **6** compared with the starting complex $[Fe(\eta^5\text{-}C_2H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$ (**1**) a single-crystal X-ray diffraction study on the latter was carried out and the resulting molecular structure is shown in Fig. 6. As expected, the iron atom is sandwiched between two planar $(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}P_3C_2^tBu_2)$ five-membered rings. The carbon–carbon distances within the cyclopentadienyl ring have a range of 1.344–1.430 Å and phosphorus–carbon bonds lie in the range 1.752–1.770 Å. The phosphorus–phosphorus bond is 2.114(1) Å which is comparable with that in the anion [11] in $[Li(P_3C_2^tBu_2)TMEDA]$ (2.087(2) Å) and in $[WCO_5\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)\}]$ (2.098(2) Å) [1]. Shortly after completion of this study Zenneck et al. [12] have independently reported structural studies on **1** and their data are in good agreement with ours.



η5-
1J(RhP) 10.7 Hz

η4-
1J(RhP) ~30 Hz

η3-
1J(RhP) 35.1 Hz

η1-
1J(RhP) 152 Hz

Fig. 4.

A comparison of the P–P bond lengths in the starting complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$ (**1**) (P–P 2.114(1) Å) and in complex (**6**) $[Rh(\eta^5\text{-}C_5Me_5)(CO)\eta^2\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)\}]$ (P–P 2.306(2) Å) shows a pronounced elongation of ca. 0.2 Å resulting from the η^2-P–P edge ligation.

We recently reported a completely different novel kind of η^2-P–P ring edge-bonding complex in $[Ni(\eta^5\text{-}P_3C_2^tBu_2)\{\eta^2\text{-}P_3C_2^tBu_2CH(SiMe_3)_2Me)\}]$ (**7**) [13].

(7)

Complex **7**, like **6**, has an η^5-bound $(P_3C_2^tBu_2)$ ring, but in this case the $(P_3C_2^tBu_2CH(SiMe_3)_2Me)$ ring is η^2-coordinated to the nickel(II) centre by two *saturated*

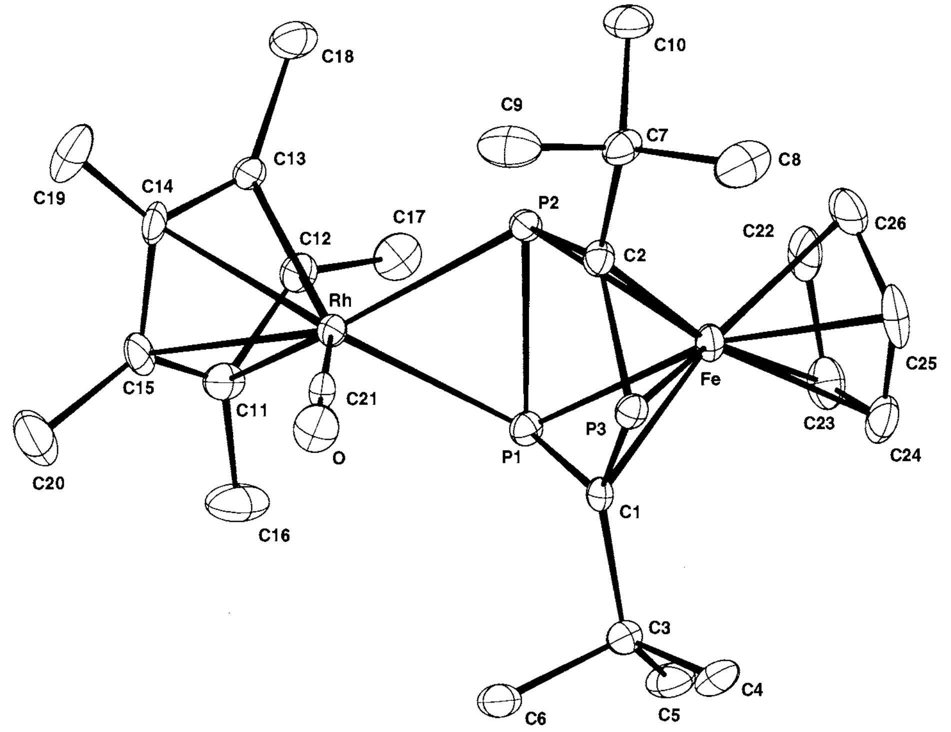
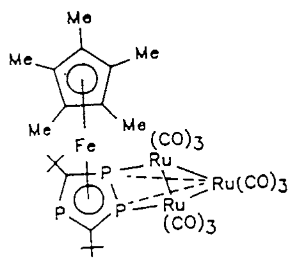


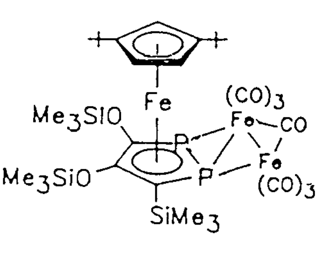
Fig. 5. Molecular geometry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)Rh(\eta^5\text{-}C_5Me_5)(CO)]$ (6) with selected bond lengths in Å. P(1)–P(2) 2.306(2), P(1)–C(1) 1.776(4), P(2)–C(2) 1.783(4), P(3)–C(2) 1.762(4), P(3)–C(1) 1.766(4). Rh–P(1) 2.384(1), Rh–P(2) 2.379(1).

(sp^3-hybridised) phosphorus atoms and not via the expected η^3-interaction with the allylic CPC part of the ring which is found in the isoelectronic organometallic complex $[Ni(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)]$. Thus there is no possible π-type bonding or significant bond lengthening of the P–P bond in the $P_3C_2{}^tBu_2CH(SiMe_3)_2Me$ ring because the bonding only involves the adjacent phosphorus lone pair electrons. This difference in ring edge-bonding is clearly borne out by a comparison of the P–P bond lengths in **6** (2.359(2) Å), and **7** (2.134(2) Å).

The above results enable further consideration of other recently reported complexes involving triphosphaferrocene and diphosphaferrocene compounds, typified by $[Ru_3(CO)_9\{Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2{}^tBu_2)\}]$ (**8**) [14] and $[Fe_2(CO)_7\{Fe(\eta^5\text{-}C_5H_3{}^tBu_2)(\eta^5\text{-}P_2C_3(OSiMe_3)_2(SiMe_3)\}]$ (**9**) [15].



(8)



(9)

In **8** two ruthenium atoms are bonded in an η^1-fashion to the lone pair of electrons on phosphorus and the third ruthenium atom is bonding to both ring phosphorus atoms. Comparison of the P–P bond lengths (P–P 2.131(2) Å) for **8**, compared to the parent triphosphaferrocene $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (**1**), (P–P 2.114(1)Å), shows no significant lengthening of the bond since bonding involves the two phosphorus lone pairs. and not via the ring edge. Likewise $[Fe_2(CO)_7\text{-}\{Fe(\eta^5\text{-}C_5H_3{}^tBu_2)(\eta^5\text{-}P_2C_3(OSiMe_3)_2(SiMe_3)\}]$ (**9**) containing a 1,2-diphosphaferrocene unit has one Fe coordinated in an η^1-mode via the phosphorus lone pair. The other Fe is attached to both phosphorus atoms but the (P–P) bond length in **9**, (P–P 2.281(4) Å), is slightly longer than that found in the η^1-complex $[Ni(CO)_3\{Fe(\eta^5\text{-}C_5H_3{}^tBu_2)(\eta^5\text{-}P_2C_3(OSiMe_3)_2SiMe_3)\}]$ (P–P 2.2126(2) Å).

Weber et al. [16] have also synthesised a structurally related complex $[Co_2(CO)_6\{Fe(\eta^5\text{-}C_5H_3{}^tBu_2)(P_2C_3(OSiMe_3)_2(SiMe_3)\}]$ exhibiting only η^1-bonding. The ring-edge ligated complexes **4**, **5** and **6** can all be considered as 'slipped' triple-decker sandwich compounds, if CO elimination is also considered, in which the Rh metal centre is only partly ligated to the appropriate heteroatom ferrocene, as opposed to being fully η^5-coordinated in a true triple-decker complex. We and others have synthesised triple-decker cationic sandwich complexes containing both the pentaphosphacyclopentadienyl ring [17] as in $[\{(\eta^5\text{-}C_5Me_4CH_2CH_3)Fe\}\mu\text{-}\eta^5\text{-}\eta^5\text{-}(P_5)\{Fe(\eta^5\text{-}C_5H_5)\}]PF_6$ **10** and the 1,2,4-triphosphacyclopentadienyl [18] ring as in $[\{(\eta^5\text{-}C_5Me_5)Ru\}\mu\text{-}\eta^5\text{-}\eta^5\text{-}(P_3C_2{}^tBu_2)\{Ru(\eta^5\text{-}C_5Me_5)\}]$

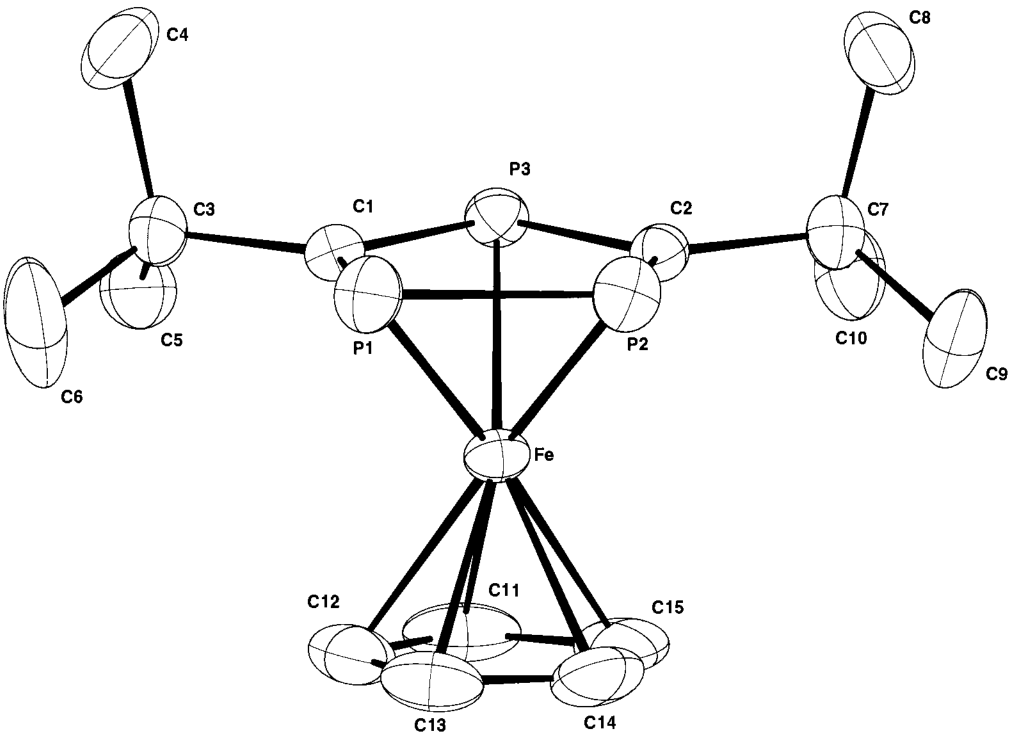
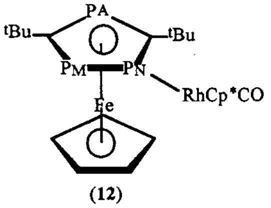


Fig. 6. Molecular geometry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (**1**), with selected bond lengths in Å. P(1)–C(1) 1.761(3), P(1)–P(2) 2.114(1), P(2)–C(2) 1.767(3), P(3)–C(2) 1.755(3), P(3)–C(1) 1.756(3).

PF_6 (**11**). In both **10** and **11**, the phosphorus–phosphorus and carbon–phosphorus bond lengths are only slightly longer than in the triphosphametallocenes themselves. Interestingly the mass spectrum of **6** shows a peak at (*m*/*z* 590) which corresponds to the 31 electron triple-decker cationic complex $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}P_3C_2{}^tBu_2)Rh(\eta^5\text{-}C_5Me_5)]^+$, formed by CO loss, and similarly the mass spectrum of **4** also shows a peak relating to the corresponding triple-decker complex.

2.3. Unexpected existence of the isomeric $[\{Rh(\eta^5\text{-}C_5Me_5)CO\}\eta^1\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)\}]$ *complex* (**12**)

Close inspection of the very weak lines which are only just visible above the base line in the $^{31}P\{^1H\}$-NMR spectrum of **6** (Fig. 7) unexpectedly showed evidence for a second isomeric compound assigned as the η^1-complex $[\{Rh(\eta^5\text{-}C_5Me_5)CO\}\eta^1\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)\}]$ (**12**) (1%).



(12)

This $^{31}P\{^1H\}$-NMR spectrum of **12** shown in Fig. 7 exhibits three distinct phosphorus environments typical of an [AMNX] (AMN = ^{31}P; X = ^{103}Rh, $I = 1/2$, 100% abundance) spin system, indicating that this species is an η^1-coordinated complex. The resonance of phosphorus P_C ($\delta = 89$) occurs as a doublet of doublets of doublets from coupling to P_B ($^2J_{P_AP_C}$) 446 Hz), P_A ($^2J_{P_AP_C}$ 47.3 Hz) and rhodium ($^1J_{RhP_C}$) 115 Hz). The magnitude of the phosphorus–rhodium coupling constant in **12** is much greater than that of **6** ($^1J_{RhP_M}$ 41.1 Hz) and is consistent with that expected for an η^1-coordinated rhodium. Furthermore the large size of the ($^1J_{P_BP_C}$) 446.1 Hz) coupling constant is also characteris-

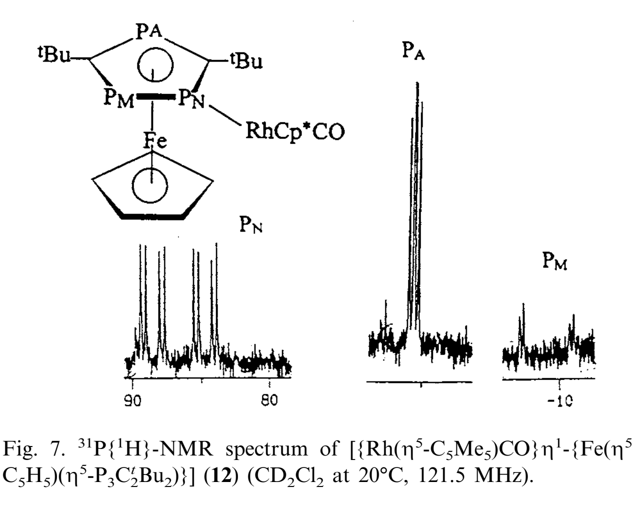


Fig. 7. $^{31}P\{^1H\}$-NMR spectrum of $[\{Rh(\eta^5\text{-}C_5Me_5)CO\}\eta^1\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)\}]$ (**12**) (CD_2Cl_2 at 20°C, 121.5 MHz).

tic of coupling between two adjacent nonequivalent ring phosphorus atoms suggesting that **12** is the isomeric η^1-complex $[\{Rh(\eta^5\text{-}C_5Me_5)CO\}\eta^1\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C^t_2Bu_2)\}]$. As expected ring phosphorus P_B shows a doublet of doublets, ($^1J_{P_BP_C}$) 446 Hz; $^2J_{P_AP_B}$ 50 Hz) and P_A exhibits a doublet of doublets with corresponding couplings to P_B and P_C. Unlike complex **6** no ^2J phosphorus–rhodium coupling constants were observed for either P_B or P_A, presumably because of the greater distance between the interacting nuclei.

Interestingly the reaction affording complexes **3** and **4** reported by Scherer et al. [6] also produce isomeric η^1-compounds, albeit in considerably larger yields (ca. 30%) than for compound **12**. The co-existence of both η^1- and η^2-ligated complexes is remarkable and not easily understood, but presumably reflects an unusual frontier orbital energy level pattern for the $[\{Rh(\eta^5\text{-}C_5Me_5)CO\}]$ fragment compared with other metal d^8-systems in its interaction with the phosphaferrocene ring systems.

3. Experimental

Standard methods for the handling of air- and moisture-sensitive materials were utilised throughout this work. Unless otherwise indicated, all manipulations were carried out at room temperature, under an atmosphere of dry nitrogen gas (or argon), using standard Schlenk, syringe and high vacuum-line techniques, with glassware that had been flame-dried in vacuo prior to use. Solvents were dried, degassed and redistilled before use.

Solution NMR spectra were recorded on a Bruker DPX 300, Bruker ACP-250 or AMX 500 Fourier transform instruments. Spectra were measured at room temperature unless otherwise stated. Mass spectra were recorded on Kratos MS80RF and Fisons instruments VG Auto Spec double focusing spectrometers. IR spectra were recorded in solution in a 2 mm cell with CaF_2 windows on a Perkin–Elmer 1710 Fourier transform instrument. Microanalyses were performed by Medac (UK).

The following materials were synthesised according to literature methods: $P(SiMe_3)_3$ [19]; $(Me_3Si)P{=}C(OSiMe_3)(^tBu)$ [20]; and $Fe(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}C_5H_5)]PF_6$ [21]. $[Li(P_3C^t_2Bu_2)]$ was prepared using a method developed in this laboratory [3], based on an initial communication by Becker et al. [22]. A hexane solution of butyllithium (1.6 M, 10 ml, 16 mmol) was added to a dme solution of $[P(SiMe_3)_3]$ (2.0 g, 8 mmol in 10 ml) at − 70°C. The resulting yellow solution was allowed to warm slowly to room temperature. Stirring was continued for a further 20 h to give a cream mixture and $[(Me_3Si)P{=}C(OSiMe_3)(^tBu)]$ was added drop-wise and the mixture stirred for 5 days, during which time an orange/red colour was seen which darkened to black. The volatile components were removed in vacuo and the oily residue washed with hexane (2 × 25 ml). The resulting oil was then redissolved in dme (10 ml). The solution was stirred for 30 min and the solvent removed. The resulting oil which was further purified by washing with hexane (2 × 25 ml), and was characterised by $^{31}P\{^1H\}$-NMR spectroscopy. This was then used as a stock solution in dme without further purification.

3.1. Synthesis of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C^t_2Bu_2)]$ (*1*)

To a green slurry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5Me)]PF_6$ (3 g, 7.0 mmol) in dme (100 ml), $[Li(\eta^5\text{-}P_3C^t_2Bu_2)]$ (10 ml, 7 mmol) in dme was added drop-wise. The mixture was stirred for 48 h and the solvent was removed in vacuo. The brown solid was washed with portions of petroleum ether until the washings were clear (60/80 ca. 200 ml), the volume reduced and the resulting red/brown oil was chromatographed (kieselgel/petroleum ether 60/80). The red product $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C^t_2Bu_2)]$ (**1**) (0.15 g, 50%) $^{31}P\{^1H\}$-NMR spectrum ($CDCl_3$, 25°C, 121.3 MHz): δ $P_A = 40.2$(t), δ $P_B = 39.6$(d) $^2J_{P_AP_B} = 45.4$ Hz. ^1H-NMR spectrum ($CDCl_3$, 25°C, 300 MHz): δ Cp = 4.71, δ $^tBu = 1.29$.

3.1.1. Crystallographic data for 1

$C_{15}H_{23}FeP_3$: $M = 352.1$; monoclinic; space group $P2_1/n$; $a = 13.749(5)$, $b = 9.659(3)$, $c = 12.839(5)$ Å; $\beta = 93.20.(3)°$; $U = 1702.4(10)$ Å^3; $Z = 4$; $D_{\text{calc.}} = 1.37$ Mg m^{-3}; crystal dimensions 0.4 × 0.35 × 0.2 mm; $F(000) = 736$; $T = 293(2)$ K; Mo–K_α radiation $\lambda = 0.71073$ Å. Data were collected on an Enraf–Nonius CAD4 diffractometer and of the total 2989 independent reflections measured, 2322 having $I > 2\sigma(I)$ were used in the calculations. The structure was solved by direct methods and refined by full matrix least squares on all F^2. There are two independent molecules of esssentially the same geometry. The final indices ($I > 2\sigma(I)$) were $R_1 = 0.036$, $wR_2 = 0.085$.

3.2. Synthesis of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C^t_2Bu_2)Rh(\eta^5\text{-}C_5Me_5)(CO)]$ (*6*)

$[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$ (0.05 g, 0.17 mmol) and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C^t_2Bu_2)]$ (0.18 g, 0.51 mmol) in toluene (20 ml) were irradiated with UV light for 24 h. The reaction which was monitored by IR spectroscopy and was complete after four repeated periods of irradiation, each for 24 h. Solvent was removed and the resulting brown/red solid was extracted with 60/80 petroleum ether and recrystallised from diethylether to afford $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C^t_2Bu_2)Rh(\eta^5\text{-}C_5Me_5)(CO)]$ (**6**) (0.06 g, 60%), (Found C 49.9%, H 6.4%;

$C_{16}H_{23}OP_3FeRh$; requires C 50.48%, H 6.14%). The structure was confirmed by $^{31}P\{^1H\}$-, ^1H-NMR spectroscopy, mass spectrometry, IR spectroscopy and a single crystal X-ray diffraction study. The $^{31}P\{^1H\}$-NMR spectrum also showed small amounts ($<1\%$) of an η^1-ligated product $[Rh(\eta^5\text{-}C_5Me_5)(CO)\eta^1\text{-}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)\}]$ (**12**) (see text). Complex **6** ^{31}P-NMR data ($C_6D_5CD_3$, 25°C, 121.5 MHz): δ $P_M = 4.9$(dd), δ $P_A = 49.5$(dd), $^2J_{P_AP_M} = 38.2$ Hz, $^3J_{RhP_A} = 4.3$ Hz, $^iJ_{RhP_M} = 41.1$ Hz, no change at −90°C. ^1H-NMR spectrum ($C_6D_5CD_3$, 25°C, 300 MHz): δ Cp* = 1.63(s), δ ^{t}Bu = 1.98(d), δCp = 4.64(s). IR (toluene 25°C) $\nu_{CO} = 1973$(vs) cm^{-1}. FAB MS: m/z 618, (M^+); 590, ($M^+ - CO$); 352, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2^tBu_2)]$

3.2.1. Crystallographic data for 6

$C_{26}H_{38}FeOP_3Rh$: $M = 618.2$; monoclinic, space group $P2_1/n$; $a = 10.698(3)$, $b = 31.464(11)$, $c = 16.693(4)$ Å; $\beta = 100.89(2)°$, $U = 5518(3)$ Å^3; $Z = 8$, $D_{calc.} = 1.49$ Mg m^{-3}; crystal dimensions 0.4 × 0.4 × 0.4 mm; $F(000) = 2544$; $T = 173(2)$ K; Mo–K_α radiation; $\lambda = 0.71073$ Å. Data were collected on an Enraf–Nonius CAD4 diffractometer and of the total 7657 independent reflections measured, 6273 having $I > 2\sigma(I)$ were used in the calculations. The structure was solved by direct methods and refined by full-matrix least squares on all F^2. There are two independent molecules of essentially the same geometry. The final indices ($I > 2\sigma(I)$) were R1 = 0.031 wR2 = 0.063.

^{31}P-NMR data for **12** ($C_5D_5CD_3$, 25°C, 121.5 MHz): δ $P_A = 17$(dd), δ $P_M = -8$(dd), δ $P_N = 87$(ddd) $^2J_{P_AP_M} = 36$ Hz, $^2J_{P_AP_N} = 47$ Hz, $^1J_{P_MP_N} = 450$ Hz, $J_{RhP_N} = 115$ Hz.

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