Use of the 2,5-bis-(*tert*-butyl)phospholide Anion as an η^5-Ligand: Stabilisation of η^5-phospholyl Complexes of Ruthenium and Rhodium

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The 2,5-bis-(*tert*-butyl)phospholide anion promotes η^5-complexation to late transition metals in cases where unhindered phospholyls may favour η^1-ligation through the phosphorus lone pair.

A phospholyl ligand may bind to metals either through its lone pair of electrons, in η^1-coordination mode, or through its delocalised 6π aromatic system. In the second case, it gives a series of η^5-complexes which are analogous to the well-known metal cyclopentadienyls, and which are potentially interesting in synthesis and catalysis. Therefore, it is important to develop syntheses which lead selectively and predictably to this η^5-mode.

Calculations of phospholide anions have shown that the homo and the negative charge are localised mainly upon the heteroatom,[1] so the initial interaction of a metal salt with a phospholide anion occurs at phosphorus. The M–P bond which is formed during this process is strong for the later transition metals, and this favours η^1 over η^5 coordination. Furthermore, where π complexes of the 'softer' metals are known, they show a strong tendency towards oligomerisation through their phosphorus lone pairs.[2]

In this paper, we outline an approach to new types of mononuclear η^5-phospholyl complexes. To prevent σ-coordination, we used the previously unknown 2,5-bis-(*tert*-butyl)-phospholide anion, whose phosphorus lone pair is sterically blocked. Kuhn,[3] Nixon[4] and their coworkers have shown that *tert*-butyl groups tend to favour η^5-complexation of heterocyclopentadienides: here we demonstrate that they permit the synthesis of η^5-monophospholyl complexes of ruthenium and rhodium.

The colourless, crystalline phosphole **1** was prepared through the butyllithium-catalysed[5] addition of phenylphosphane to 1,4-di(*tert*-butyl)buta-1,3-diyne, and isolated by chromatography on silica with a hexane eluent. Routine coupling and chromatography gave the air-stable pale yellow 1,1'biphosphole **2**, which serves as a clean source of the 2,5-bis(*tert*-butyl)phospholide anion **3**. Chlorotrimethylsilane reacts with **3** to give the P–silyl compound **4**, which shows unusual stability with respect to thermal dimerisation ($t_{1/2}$ *ca* 3 h at 80 °C) and demonstrates the influence of the α-*tert*-butyl substituents. These block the 1,5-silyl shifts through which such compounds generally decompose.[6]

The coordinating behaviour of **3** was investigated through reactions with ruthenium and rhodium complexes. A straight-

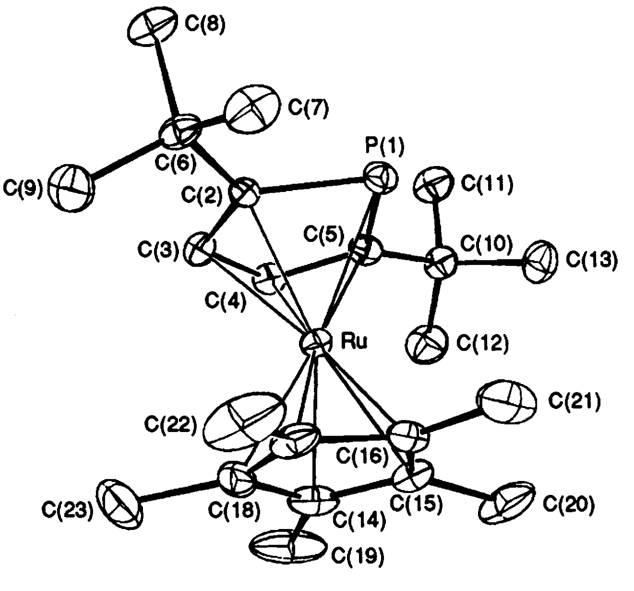
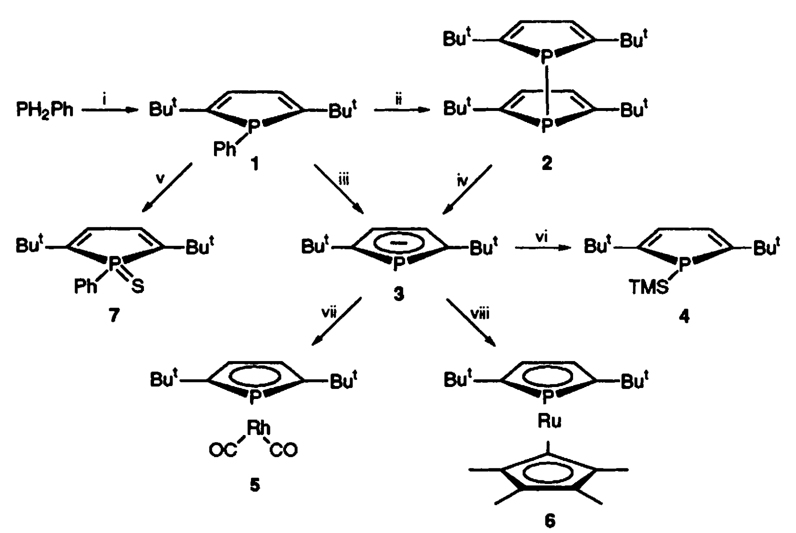
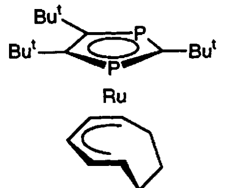


Fig. 1 Molecular stucture of $[Ru(\eta^5\text{-}C_5Me_5)\ (Bu^t{}_2C_4H_2P)]$ **6**, as determined by a single crystal X-ray diffraction study.‡ Selected bond lengths (Å) and angles (°): Ru–P(1) 2.397(1), Ru–C(2) 2.217(4), Ru–C(3) 2.185(4), Ru–C(4) 2.178(3), Ru–C(5) 2.221(4), Ru–Cp*(centroid) 1.838(2), P(1)–C(2) 1.793(4), P(1)–C(5) 1.785(4), C(2)–C(3) 1.408(6), C(3)–C(4) 1.422(5), C(4)–C(5) 1.422(6), C(2)–P(1)–C(5) 90.1(2), P(1)–C(2)–C(3) 112.0(3), P(1)–C(5)–C(4) 111.6(3), C(2)–C(3)–C(4) 113.0(3), C(3)–C(4)–C(5) 113.2(3).



Scheme 1 *Reagents and conditions*: i, $Bu^tC_4Bu^t$, 1 h, 50 °C, THF, 40%; ii, Li, 15 min, 20 °C, THF, then $AlCl_3$ (0.25 equiv.) then I_2 (0.5 equiv.), 15 min, 20 °C, THF, 65%. iii, Li, 15 min, 20 °C, THF, then TMSCl (chlorotrimethylsilane) (1 equiv.), 1 min, 0 °C, THF, 90%; iv, Li, 2 h, 20 °C, THF, 95%; v, S_8, N-methylimidazole (cat.) 45 min, 0 °C, THF, 80%; vi, TMSCl, 5 min, 20 °C, THF, 80%; vii, $[Rh(CO)_2Cl]_2$, 45 min, 0 °C, THF, 20%; viii, mixture of $[Ru(\eta^5\text{-}C_5Me_5)Cl_2]_2$, and Li, 5 h, 20 °C, THF, 95%



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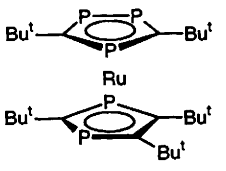

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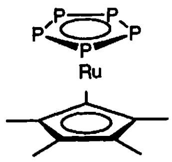

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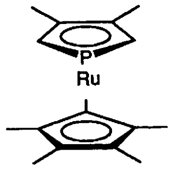

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forward interaction with $[Rh(CO)_2Cl]_2$ gave the red crystalline complex $[Rh(Bu^t{}_2C_4H_2P)(CO)_2]$ **5**, albeit in poor yield. The air-stable $[Ru(\eta^5\text{-}C_5Me_5)\ (Bu^t{}_2C_4H_2P)]$ **6** was prepared by two methods. The first, a redox reaction between **3** and $[Ru(\eta^5\text{-}C_5Me_5)\ Cl_2]_2$, produced **2** as a side-product: a more efficient route involved stirring lithium metal with a THF solution of $[Ru(\eta^5\text{-}C_5Me_5)\ Cl_2]_2$ and the biphosphole **2**.†

$[Ru(\eta^5\text{-}C_5Me_5)(Bu^t{}_2C_4H_2P)]$ **6**, is one of the simpler members of a series of ruthenium complexes which includes $[Ru(C_8H_{11})(Bu^t{}_3C_3P_2)]$ **8**,[7] $[Ru(Bu^t{}_2C_2P_3)(Bu^t{}_3C_3P_2)]$ **9**[8] and $[Ru(\eta^5\text{-}C_5Me_5)\ (P_5)]$ **10**.[9] It should be underlined that a wide range of 'soft' transition metals has been shown to coordinate to these latter anions[4] but relatively few complexes having monophospholyl rings have appeared. Furthermore, our attempts to prepare the unknown $[Ru(\eta^5\text{-}C_5Me_5)\text{-}(Me_2H_2C_4P)]$ **11**, by routes which are analogous to the synthesis of **6**, have failed. Thus, we feel that the 2,5-bis-(*tert*-butyl)phospholyl ligand has rather unusual properties, which should allow an expansion of the chemistry of π-coordinated monophospholyls.

Received, 26th January 1994; Com. 4/00503A

Footnotes

† *Selected spectroscopic data*: ^{31}P ^{13}C and ^1H NMR in $CDCl_3$ unless otherwise stated: δ in ppm, +ve to high frequency of external H_3PO_4 or Me_4Si, J in Hz: **1**: $\delta^{31}P$: 0.7; $\delta^{13}C$: 162.2 [J_{PC} 7.6 (ring C)], 132.9 [(br) (ring CH)]; δ^1H: 6.5 [J_{PH} 12.3 (ring CH)]. **2**: $\delta^{31}P$: −28.0. **3**: $\delta^{31}P$: 60.4. $\delta^{13}C$: 160.1. [J_{PC} 46.9 (ring C)], 113.0 [J_{PC} 0 (ring CH)] (THF); **4**: $\delta^{31}P$: −41.3 (THF). **5**: $\delta^{31}P$: 1.0,(J_{RhP} 6.4); $\delta^{13}C$: 192.0 [J_{RhC} 87.6, J_{PC} 4.3 (CO)], 143.0 [J_{RhC} 5.6, J_{PC} 66.5 (ring C)], 94.4 [J_{RhC}) 3.9, J_{PC} 3.9 (ring CH)]; δ^1H: 5.92 [J_{PH} 3.8, J_{RhH} 0.6, (ring CH)]. **6**: $\delta^{31}P$: −63.0; $\delta^{13}C$: 116.7 [J_{PC} 62.7 (ring C)], 78.8 [J_{PC} 4.7 (ring CH)]; δ^1H: 4.57 [J_{PH} 5.1 (ring CH)]. **7**: $\delta^{31}P$: 48.4.

‡ *Crystal data*: colourless crystals of **6**, $C_{22}H_{35}PRu$ were grown from a methanol solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallises in space group $P2_1$ (No. 4), a = 10.521(1), b = 9.337(1), c = 12.034(1) Å, β = 113.52(1) °; U = 1083.92(4) Å^3; $Z = 2$; $D_c = 1.322\ \text{g cm}^{-3}$; $\mu = 7.8\ \text{cm}^{-1}$; $F(000) = 452$. A total of 3503 unique reflections were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 1003 were considered as unobserved [$F^2 < 3.0\theta\sigma(F^2)$], leaving 2500 for solution and refinement. The position of the ruthenium atom was obtained from a Patterson map. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.05. The final agreement factors were $R = 0.025$, $R_w = 0.034$, GOF = 1.00.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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