DALTON COMMUNICATION

Co-ordinative activation of phosphaalkynes: methyl neopentylidene phosphorane complexes of ruthenium(II); crystal structure of $[Ru(MeP{=}CHBu^t)Cl(I)(CO)(PPh_3)_2]$

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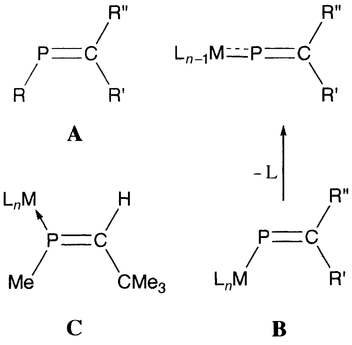
The reactions of $[Ru(P{=}CHBu^t)Cl(CA)(PPh_3)_2]$ (A = O or S) with iodomethane provided the phosphaalkene complexes $[Ru(PMe{=}CHBu^t)Cl(I)(CA)(PPh_3)_2]$ (I *trans* to phosphaalkene), with one example (A = O) having been crystallographically characterised.

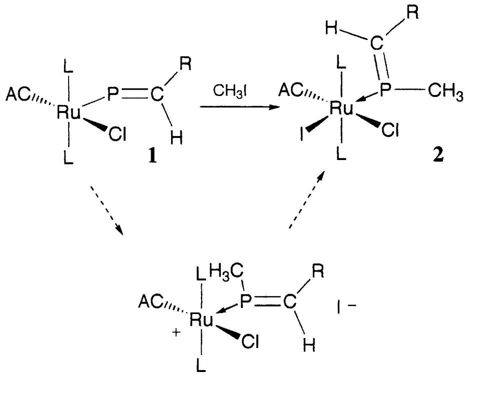
Phosphaalkenes (**A**)[1] (Scheme 1) are generally difficult to isolate unless they bear kinetically stabilising substituents capable of protecting the reactive unsaturated P=C linkage. One class of phosphorus substituent which has been shown to confer remarkable stability, both thermodynamic and kinetic, on such compounds are transition metals (**B**). Recently we have provided access to such compounds *via* a route of unprecedented simplicity, *viz* the hydrometallation of phosphaalkynes.[2] Thus the complex $[Ru(P{=}CHBu^t)Cl(CO)(PPh_3)_2]$ **1a**[2] and its thiocarbonyl analogue $[Ru(P{=}CHBu^t)Cl(CS)(PPh_3)_2]$ **1b**[3] result in high yield from the reaction of $P{\equiv}CBu^t$ with the hydride complexes $[RuH(Cl)(CA)(PPh_3)_3]$ (A = O or S). The nucleophilicity of the phosphorus atom of the phosphaalkenyl ligand has been demonstrated in reactions with Brønsted acids[4] and in this report we wish to discuss the reactions of these complexes with carbon-based electrophiles which lead to complexes of the otherwise unstable methyl neopentylidene phosphorane (**C**).

Treating a solution of $[Ru(P{=}CHBu^t)Cl(CO)(PPh_3)_2]$ **1a** in dichloromethane with an excess of methyl iodide leads to slow decolourisation and formation of a pale yellow complex which is formulated as $[Ru(PMe{=}CHBu^t)Cl(I)(CO)(PPh_3)_2]$ **2a** (Scheme 2) on the basis of spectroscopic data §. Most conspicuous and informative amongst the spectroscopic data is the clearly resolved AX_2 spin system apparent in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2a**. Alkylation of **1a** is accompanied by a dramatic shift in the resonance due to the phosphaalkenyl ligand from δ 450.4 in the precursor to δ 225.1 in **2a**. This latter datum may be compared with that observed at δ 187.9 for the 'parent' phosphaalkene complex $[Ru(HP{=}CHBu^t)Cl_2(CO)(PPh_3)_2]$ **3** obtained by addition of HCl to **1a**.[2]

The formulation was confirmed by single-crystal X-ray diffraction analysis,¶ the results of which are summarised in Fig. 1. The geometry at ruthenium is distorted octahedral with *cis* interligand angles in the range 80.7(2)–97.2(1)°, the angle between the *cis* co-ordinated chloride and iodide being noticeably enlarged. The bond lengths between ruthenium and the atoms I, Cl, P(28), P(9) and C(7) are unremarkable for divalent



Scheme 1



Scheme 2 L = PPh_3, R = Bu^t, A = O or S

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§ Data for **2a**. Yield 79% (0.20 mmol scale) IR: (Nujol) 1978 [ν(CO)], 1717, 1259, 899, 853 cm^{-1}; (CH_2Cl_2) 1976 [ν(CO)] cm^{-1}. NMR (CD_2Cl_2, 25 °C): ^1H, δ 0.90 (s, 9 H, CMe_3), 2.95 [br d, 3 H, PMe, *J*(PH) = 12.9], 6.35 [d, 1 H, P=CH, *J*(PH) = 7.6 Hz], 7.28–8.03 (m, 30 H, PC_6H_5), $^{13}C\text{-}\{H\}$, δ 197.4 (m, CO), 165.3 [d, P=C, *J*(PC) = 55.4], 135.3–126.8 (PC_6H_5), 118.8 [d, PMe, *J*(PC) = 89.3], 40.4 [d, $\mathit{C}CH_3$, *J*(PC) = 16.1], 31.0 [d, $C\mathit{C}H_3$, *J*(PC) = 12.5 Hz]; $^{31}P\text{-}\{^1H\}$, δ 225.1 [t, *J*(PP) = 39.0], 10.4 [d, *J*(PP) = 40.7 Hz]. FAB-MS: *m*/*z* 897 $[M - Cl]^+$, 820 $[M + H_2O - I]^+$, 805 $[M - I]^+$, 780 $[RuI(CO)(PPh_3)_2]^+$, 689 $[RuCl(CO)(PPh_3)_2]^+$, 654 $[RuCl(PPh_3)_2]^+$, 625 $[Ru(PPh_3)_2]^+$, 363 $[RuPPh_3]^+$. Data for **2b**. Yield 74% (20 mmol scale) IR: (Nujol) 1290 [ν(CS)], 894, 853 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 0.89 (s, 9 H, CMe_3), 3.18 [br d, 3 H, PMe, *J*(PH) = 13.2 Hz], 6.63 [br d, 1 H, P=CH, *J*(PH) = not resolved], 7.16–8.04 (m, 30 H, PC_6H_5), $^{13}C\text{-}\{H\}$, δ 295.5 [dt, CS, $J(P_2P) \approx J(PP) \approx 12.5$], 161.8 [d, P=C, *J*(PC) = 57.1], 119.0 [d, PMe, *J*(PC) = 91.1], 39.6 [d, $\mathit{C}CH_3$, *J*(PC) = 17.8], 31.1 (d, $C\mathit{C}H_3$, *J*(PC) = 12.5 Hz]; $^{31}P\text{-}\{^1H\}$, δ 219.5 [t, *J*(PP) = 37], 11.6 [d, *J*(PP) = 41 Hz]. FAB-MS: *m*/*z* 913 $[M - Cl]^+$, 821 $[M - I]^+$, 780 $[RuI(CS)[PPh_3)_2]^+$, 705 $[RuCl(CO)(PPh_3)_2]^+$, 669 $[RuCl(PPh_3]_2]^+$, 651 $[M - Cl - PPh_3]^+$, 625 $[Ru(PPh_3)_2]^+$, 363 $[RuPPh_3]^+$.

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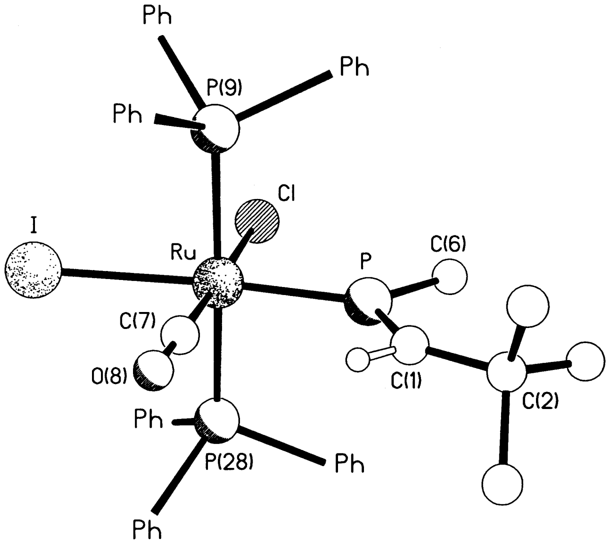

Fig. 1 Molecular geometry for complex **2a**. Hydrogen atoms and phenyl groups omitted

ruthenium. The ligand of primary interest is the phosphaalkene which has trigonal geometry at phosphorus [intersubstituent angles in the range 114.8(4)–123.4(3)°], the planarity of which extends to include C(2) and the remaining ligands in the equatorial ruthenium co-ordination plane [maximum deviation from planarity of 0.09 Å by C(6)]. The P–C(1) bond length of 1.657(8) Å is clearly multiple in nature, and significantly shorter than the single bond of 1.803(8) Å to C(6), and that of the π-bound phosphaalkene ligand in, *e.g.* $[\mathrm{Rh}(\eta^2\text{-}\mathrm{CH_2PPh})(\mathrm{CO})(\eta\text{-}\mathrm{C_5Me_5})]$ [1.740(4) Å].[5] Indeed this value lies marginally below the range 1.68–1.72 Å associated with free phosphaalkenes.[6] The Ru–P separation is substantially shorter [2.280(2) Å] than those to the phosphines [P(28), 2.417(2); P(9), 2.412(2) Å]. This may be interpreted as indicating a pronounced π-acceptor role for the phosphaalkene ligand, a feature presumably enhanced by the π-dative capacity of the iodide, and reflected in the ν(CO) value (1978 $\mathrm{cm^{-1}}$) which is comparatively high for neutral divalent ruthenium.

The *trans* arrangement of the iodide and $\mathrm{MeP{=}CHBu^t}$ ligands suggests that the mechanism is in fact a two-step process, presumably involving initial nucleophilic displacement of iodide from MeI by **1a** to provide the 16-electron complex $[\mathrm{Ru(MeP{=}CHBu^t)Cl(CO)(PPh_3)_2}]^+$. Notably, σ/π co-ordination (reminiscent of three-electron vinyl co-ordination) cannot be excluded as a means of temporarily stabilising the co-ordinative unsaturation in such an intermediate. The nucleophilicity of the phosphaalkenyl phosphorus in **1a** is itself noteworthy, in that phosphaalkenyl ligands bound to 15-electron metal centres typically show electrophilic behaviour at phosphorus as a result of the linear $\mathrm{M{=}P{=}CR_2}$ linkage. In the case of **1a**, as with formally isoelectronic nitrosyls of the late transition metals, *e.g.* $[\mathrm{OsCl(NO)(CO)(PPh_3)_2}]$, such a linear arrangement does not appear to be required, despite effective atomic number considerations. Thus despite formal co-ordinative unsaturation at the ruthenium centre of **1a**, the phosphaalkenyl ligand retains nucleophilic character.

Perhaps the most surprising feature of this approach is the apparent lack of generality. Whilst the thiocarbonyl complex **1b** reacts with methyl iodide in a similar manner to provide $[\mathrm{Ru(PMe{=}CHBu^t)Cl(I)(CS)(PPh_3)_2}]$ **2b**,§ attempts to broaden the range of carbon-based electrophiles have all met with failure. Thus **1a** fails to react cleanly with the carbon electrophiles EtI, $[\mathrm{Et_3O}]\mathrm{BF_4}$, $\mathrm{N{=}N{=}CHCO_2Et}$, $\mathrm{PhCH_2Cl}$ and $\mathrm{Me_2NC({=}S)Cl}$. Under more forcing conditions or with prolonged reaction times, the latter two reagents provide only traces of **3**, presumably due to hydrolysis of the organic halide by adventitious water. In a similar manner, **3** is the only product of the reactions of **1a** with $\mathrm{Me_3SnCl}$ or $\mathrm{Ph_3SiCl}$. Furthermore, treating **1a** with such electrophiles in the presence of carbon monoxide does not appear to induce reaction, even though (reversible) co-ordination of CO to **1a** results in $[\mathrm{Ru(P{=}CHBu^t)Cl(CO)_2(PPh_3)_2}]$ which must have a bent (and accordingly nucleophilic) $\mathrm{Ru{-}P{=}CHBu^t}$ linkage.

Although the range of carbon electrophiles to which **1a** and **1b** are succeptible appears to be very narrow, preliminary results indicate that metal-based electrophiles offer a much broader array of reagents for electrophilic attack, a subject on which we will report subsequently.[3]

Acknowledgements

We gratefully acknowledge the generous loan of ruthenium salts by Johnson Matthey Chemicals and the Engineering and Physical Sciences Research Council (UK), the Royal Society and the Nuffield Foundation for financial support.

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Received 14*th October* 1996; *Communication* 6/07016G

¶ Crystal data for **2a**. $\mathrm{C_{43}H_{43}ClIOP_3Ru{\cdot}0.75CH_2Cl_2{\cdot}0.5Et_2O}$, $M = 1032.9$, monoclinic, space group $P2_1/c$, $a = 12.168(2)$, $b = 16.728(2)$, $c = 22.585(3)$ Å, $\beta = 101.00(1)°$, $U = 4513(1)$ $\mathrm{Å^3}$, $Z = 4$, $D_c = 1.520$ g $\mathrm{cm^{-3}}$, $\mu(\mathrm{Mo\text{-}K\alpha}) = 13.2$ $\mathrm{cm^{-1}}$, $\lambda = 0.710\,73$ Å, $F(000) = 2082$. A yellow cube with dimensions 0.44 × 0.33 × 0.27 mm was used. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation (ω scans). 7947 Independent reflections were measured ($2\theta \leqslant 50°$) of which 5424 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by the heavy-atom method and the major occupancy non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2 using absorption-corrected data to give $R_1 = 0.055$, $wR_2 = 0.120$ for the observed data and 474 parameters. Atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 156/351.