

Co-ordinative activation of phosphalkynes: methyl neopentylidene phosphorane complexes of ruthenium(II); crystal structure of $[\text{Ru}(\text{MeP}=\text{CHBu}^t)\text{Cl}(\text{I})(\text{CO})(\text{PPh}_3)_2]$

Robin B. Bedford,^a Anthony F. Hill,^{*†,a} Cameron Jones,^{*‡,b} Andrew J. P. White^c and James D. E. T. Wilton-Ely^a

^a Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

^b Department of Chemistry, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK

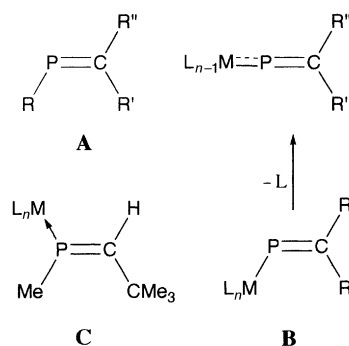
^c Chemical Crystallography Laboratory, Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

The reactions of $[\text{Ru}(\text{P}=\text{CHBu}^t)\text{Cl}(\text{CA})(\text{PPh}_3)_2]$ ($\text{A} = \text{O}$ or S) with iodomethane provided the phosphalkene complexes $[\text{Ru}(\text{PMe}=\text{CHBu}^t)\text{Cl}(\text{I})(\text{CA})(\text{PPh}_3)_2]$ (I *trans* to phosphalkene), with one example ($\text{A} = \text{O}$) having been crystallographically characterised.

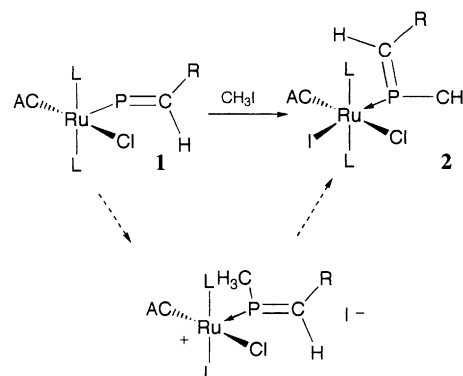
Phosphalkenes (**A**)¹ (Scheme 1) are generally difficult to isolate unless they bear kinetically stabilising substituents capable of protecting the reactive unsaturated $\text{P}=\text{C}$ linkage. One class of phosphorus substituent which has been shown to confer remarkable stability, both thermodynamic 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 phosphalkynes.² Thus the complex $[\text{Ru}(\text{P}=\text{CHBu}^t)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **1a**² and its thiocarbonyl analogue $[\text{Ru}(\text{P}=\text{CHBu}^t)\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ **1b**³ result in high yield from the reaction of $\text{P}=\text{CBu}^t$ with the hydride complexes $[\text{RuH}(\text{Cl})(\text{CA})(\text{PPh}_3)_3]$ ($\text{A} = \text{O}$ or S). The nucleophilicity of the phosphorus atom of the phosphalkenyl ligand has been demonstrated in reactions with Brønsted acids⁴ 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 $[\text{Ru}(\text{P}=\text{CHBu}^t)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ **1a** in dichloromethane with an excess of methyl iodide leads to slow decolourisation and formation of a pale yellow complex which is formulated as $[\text{Ru}(\text{PMe}=\text{CHBu}^t)\text{Cl}(\text{I})(\text{CO})(\text{PPh}_3)_2]$ **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 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **2a**. Alkylation of **1a** is accompanied by a dramatic shift in the resonance due to the phosphalkenyl ligand and 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' phosphalkene complex $[\text{Ru}(\text{HP}=\text{CHBu}^t)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ **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

§ Data for **2a**. Yield 79% (0.20 mmol scale) IR: (Nujol) 1978 $[\nu(\text{CO})]$, 1717, 1259, 899, 853 cm^{-1} ; (CH_2Cl_2) 1976 $[\nu(\text{CO})]$ cm^{-1} . NMR (CD_2Cl_2 , 25 °C): ^1H , δ 0.90 (s, 9 H, CMe_3), 2.95 [br d, 3 H, PMe , $J(\text{PH}) = 12.9$], 6.35 [d, 1 H, $\text{P}=\text{CH}$, $J(\text{PH}) = 7.6$ Hz], 7.28–8.03 (m, 30 H, PC_6H_5), $^{13}\text{C}\{-^1\text{H}\}$, δ 197.4 (m, CO), 165.3 [d, $\text{P}=\text{C}$, $J(\text{PC}) = 55.4$], 135.3–126.8 (PC_6H_5), 118.8 [d, PMe , $J(\text{PC}) = 89.3$], 40.4 [d, CCH_3 , $J(\text{PC}) = 16.1$], 31.0 [d, CCH_3 , $J(\text{PC}) = 12.5$ Hz]; $^{31}\text{P}\{-^1\text{H}\}$, δ 225.1 [t, $J(\text{PP}) = 39.0$], 10.4 [d, $J(\text{PP}) = 40.7$ Hz]. FAB-MS: m/z 897 $[\text{M} - \text{Cl}]^+$, 820 $[\text{M} + \text{H}_2\text{O} - \text{I}]^+$, 805 $[\text{M} - \text{I}]^+$, 780 $[\text{RuI}(\text{CO})(\text{PPh}_3)_2]^+$, 689 $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]^+$, 654 $[\text{RuCl}(\text{PPh}_3)_2]^+$, 625 $[\text{Ru}(\text{PPh}_3)_2]^+$, 363 $[\text{RuPPh}_3]^+$. Data for **2b**. Yield 74% (20 mmol scale) IR: (Nujol) 1290 $[\nu(\text{CS})]$, 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 , $J(\text{PH}) = 13.2$ Hz], 6.63 [br d, 1 H, $\text{P}=\text{CH}$, $J(\text{PH})$ not resolved], 7.16–8.04 (m, 30 H, PC_6H_5), $^{13}\text{C}\{-^1\text{H}\}$, δ 295.5 [dt, CS, $J(\text{P}_2\text{P}) \approx J(\text{PP}) \approx 12.5$], 161.8 [d, $\text{P}=\text{C}$, $J(\text{PC}) = 57.1$], 119.0 [d, PMe , $J(\text{PC}) = 91.1$], 39.6 [d, CCH_3 , $J(\text{PC}) = 17.8$], 31.1 [d, CCH_3 , $J(\text{PC}) = 12.5$ Hz]; $^{31}\text{P}\{-^1\text{H}\}$, δ 219.5 [t, $J(\text{PP}) = 37$], 11.6 [d, $J(\text{PP}) = 41$ Hz]. FAB-MS: m/z 913 $[\text{M} - \text{Cl}]^+$, 821 $[\text{M} - \text{I}]^+$, 780 $[\text{RuI}(\text{CS})(\text{PPh}_3)_2]^+$, 705 $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]^+$, 669 $[\text{RuCl}(\text{PPh}_3)_2]^+$, 651 $[\text{M} - \text{Cl} - \text{PPh}_3]^+$, 625 $[\text{Ru}(\text{PPh}_3)_2]^+$, 363 $[\text{RuPPh}_3]^+$.

† E-Mail: a.hill@ic.ac.uk

‡ E-Mail: c.a.jones@swansea.ac.uk

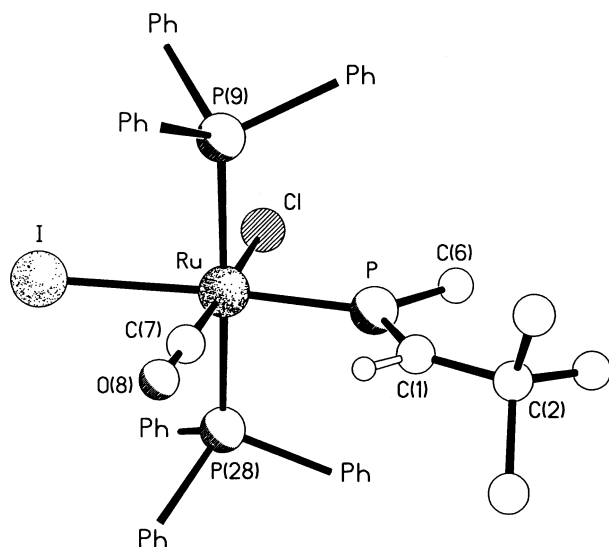


Fig. 1 Molecular geometry for complex **2a**. Hydrogen atoms and phenyl groups omitted

ruthenium. The ligand of primary interest is the phosphalkene which has trigonal geometry at phosphorus [intersubstituent angles in the range $114.8(4)$ – $123.4(3)^\circ$], 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 \AA by C(6)]. The P–C(1) bond length of $1.657(8) \text{ \AA}$ is clearly multiple in nature, and significantly shorter than the single bond of $1.803(8) \text{ \AA}$ to C(6), and that of the π -bound phosphalkene ligand in, e.g. $[\text{Rh}(\eta^2\text{-CH}_2\text{PPh})(\text{CO})(\eta\text{-C}_5\text{Me}_5)]$ [$1.740(4) \text{ \AA}$].⁵ Indeed this value lies marginally below the range 1.68 – 1.72 \AA associated with free phosphalkenes.⁶ The Ru–P separation is substantially shorter [$2.280(2) \text{ \AA}$] than those to the phosphines [P(28), $2.417(2)$; P(9), $2.412(2) \text{ \AA}$]. This may be interpreted as indicating a pronounced π -acceptor role for the phosphalkene ligand, a feature presumably enhanced by the π -donative capacity of the iodide, and reflected in the $\nu(\text{CO})$ value (1978 cm^{-1}) which is comparatively high for neutral divalent ruthenium.

The *trans* arrangement of the iodide and MeP=CHBu^t ligands suggests that the mechanism is in fact a two-step

process, presumably involving initial nucleophilic displacement of iodide from **1a** by **1a** to provide the 16-electron complex $[\text{Ru}(\text{MeP=CHBu}^t)\text{Cl}(\text{CO})(\text{PPh}_3)_2]^+$. 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 phosphalkenyl phosphorus in **1a** is itself noteworthy, in that phosphalkenyl ligands bound to 15-electron metal centres typically show electrophilic behaviour at phosphorus as a result of the linear M=P=CR_2 linkage. In the case of **1a**, as with formally isoelectronic nitrosyls of the late transition metals, e.g. $[\text{OsCl}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$, 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 phosphalkenyl 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 $[\text{Ru}(\text{P=CHBu}^t)\text{Cl}(\text{I})(\text{CS})(\text{PPh}_3)_2]$ **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 , $[\text{Et}_3\text{O}]\text{BF}_4$, $\text{N=N=CHCO}_2\text{Et}$, PhCH_2Cl and $\text{Me}_2\text{NC(=S)Cl}$. 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 Me_3SnCl or 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 $[\text{Ru}(\text{P=CHBu}^t)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ which must have a bent (and accordingly nucleophilic) Ru-P=CHBu^t linkage.

Although the range of carbon electrophiles to which **1a** and **1b** are susceptible 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

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References

- 1 L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 271 and refs. therein.
- 2 R. B. Bedford, A. F. Hill and C. Jones, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 547.
- 3 R. B. Bedford, A. F. Hill, C. Jones, J. D. E. T. Wilton-Ely, A. J. P. White and D. J. Williams, *Chem. Commun.*, in the press.
- 4 R. B. Bedford, D. E. Hibbs, A. F. Hill, M. B. Hursthouse, K. M. A. Malik and C. Jones, *Chem. Commun.*, 1996, 1985.
- 5 H. Werner, W. Paul, J. Wolf, M. Steinmetz, R. Zolk, G. Müller, O. Steigelmann and J. Riede, *Chem. Ber.*, 1989, **122**, 1061.
- 6 R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731; A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter and H.-M. Zhang, *J. Am. Chem. Soc.*, 1984, **106**, 7015.

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† Crystal data for **2a**. $\text{C}_{43}\text{H}_{43}\text{ClIOP}_3\text{Ru}\cdot 0.75\text{CH}_2\text{Cl}_2\cdot 0.5\text{Et}_2\text{O}$, $M = 1032.9$, monoclinic, space group $P2_1/c$, $a = 12.168(2)$, $b = 16.728(2)$, $c = 22.585(3) \text{ \AA}$, $\beta = 101.00(1)^\circ$, $U = 4513(1) \text{ \AA}^3$, $Z = 4$, $D_c = 1.520 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 13.2 \text{ cm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, $F(000) = 2082$. A yellow cube with dimensions $0.44 \times 0.33 \times 0.27 \text{ mm}$ was used. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-K α radiation (ω scans). 7947 Independent reflections were measured ($2\theta \leq 50^\circ$) 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.