Phospha-alkyne hydro-osmiation: synthesis of $[Os\{\kappa^1P,\kappa^1P'\text{-}P{=}CRP(=CHR)\}Cl(CO)(PPh_3)_2]$ (R = CMe_3)

Anthony F. Hill,*[a] Cameron Jones*[b] and James D. E. T. Wilton-Ely[a]

[a] *Centre for Chemical Synthesis, Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London, UK SW7 2AY. E-mail: a.hill@ic.ac.uk*

[b] *Department of Chemistry, Cardiff University, Cardiff, UK CF1 3TB. E-mail: jonesca6@cardiff.ac.uk*

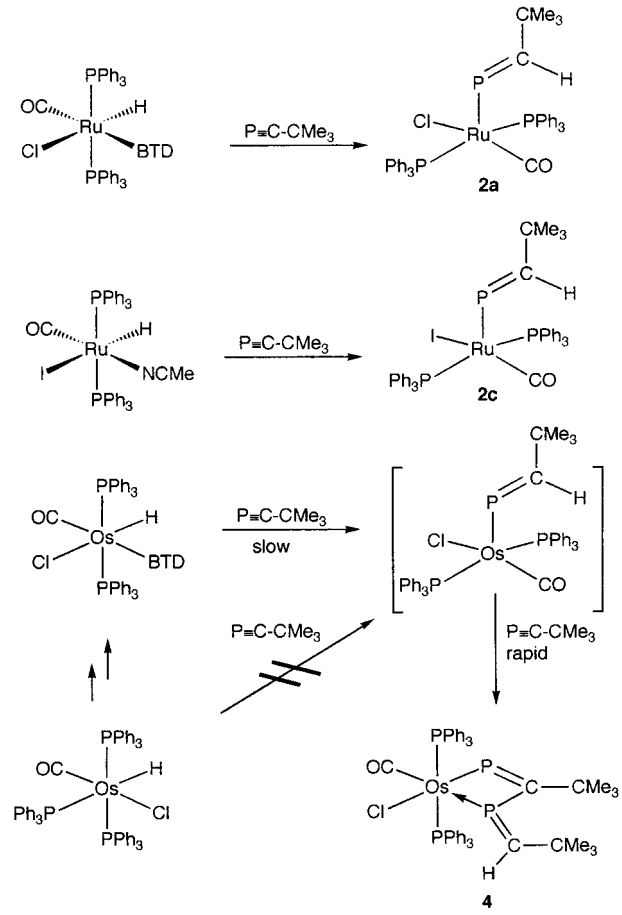
Received (in Cambridge, UK) 8th January 1999, Accepted 20th January 1999

The reaction of $[OsHCl(CO)(PPh_3)_2(BTD)]$ (BTD = 2,1,3-benzothiadiazole) with P≡$CCMe_3$ provides the novel complex $[Os\{\kappa^1P,\kappa^1P'\text{-}P{=}CRP(=CHR)Cl(CO)(PPh_3)_2]$ (R = CMe_3) which features both phospha-alkenyl and phospha-alkene donors within the same metallacycle.

We have recently described the facile hydroruthenation of phospha-alkynes by the ruthenium complexes $[RuHCl(CA)(PPh_3)_3]$ (A = O **1a**, S **1b**).[1] The phospha-alkenyl complexes $[Ru(P{=}CHCMe_3)Cl(CA)(PPh_3)_2]$ (A = O **2a**, S **2b**) which results are remarkable for a number of reasons. Firstly, the metal centre is coordinatively unsaturated, as a result of a non-linear Ru–P–C phospha-alkenyl spine. Secondly, the phospha-alkenyl ligand is unusually simple, in that it lacks the previously requisite kinetic or thermodynamic stabilisation conferred by bulky or π-dative substituents.[2] Finally but perhaps most significantly, the phospha-alkenyl ligand serves as a versatile precursor for the preparation of a range of novel complexes of otherwise inaccessible organophosphorus ligands including the unusual phospha-alkenes $XP{=}CHCMe_3$ (X = H, Me, ClHg, $AuPPh_3$, HgPh).[3] The successful synthesis and synthetic utility of the complexes **2a** and **2b** immediately raises the question of the generality of the phospha-alkyne hydrometallation strategy. Encouragingly, Nixon and coworkers have recently reported the hydrozirconation of a *coordinated* phospha-alkyne by the Schwarz' reagent to provide a synthetically useful P-zirconated phospha-alkene complex $[ZrPt(\mu\text{-}PCHCMe_3)Cl(dppe)(\eta\text{-}C_5H_5)_2]$.[4] Furthermore the hydrostannylation of phospha-alkynes has now been reported, although in this case the process lacks the regioselectivity offered by the two transition metal systems.[5] Herein we report the hydro-osmiation of a phospha-alkyne, leading to a novel osmacycle which includes both phospha-alkene and phospha-alkenyl donor components.

In contrast to the ruthenium complexes **2a** and **2b**, treating $[OsHCl(CO)(PPh_3)_3]$ **1c** with an excess of P≡$CCMe_3$ fails to result in any appreciable reaction. We have encountered a similar lack of reactivity of **1c** towards alkynes and attributed this to the lack of phosphine lability under mild conditions. However, prior conversion of **1c** to the more labile complex $[OsHCl(CO)(PPh_3)_2(BTD)]$ **3a** (BTD = 2,1,3-benzothiadiazole) provides a reagent capable of alkyne hydro-osmiation under ambient conditions providing convenient access to the complexes $[Os(CH{=}CHR)Cl(CO)(PPh_3)_2(BTD)]$.[6] It is noteworthy that whilst the analogous ruthenium complex $[RuHCl(CO)(PPh_3)_2(BTD)]$ **3b**[7] also hydrometallates alkynes to provide coordinatively saturated σ-alkenyl complexes $[Ru(CH{=}CHR)Cl(CO)(PPh_3)_2(BTD)]$,[8] we find that treating **3b** with an excess of P≡$CCMe_3$ results in the exclusive formation of *coordinatively unsaturated* **2a** with no indication of BTD coordination. In a similar manner the acetonitrile complex $[RuHI(CO)(NCMe)(PPh_3)_2]$ reacts with P≡$CCMe_3$ to provide the new phospha-alkenyl complex $[Ru(P{=}CHCMe_3)I(CO)(PPh_3)_2]$ **2c** which despite being coordinatively unsaturated, fails to recoordinate the liberated acetonitrile ligand (Scheme 1). The formulation of **2c** follows unambiguously from spectroscopic and microanalytical data,† amongst which the ^{31}P NMR data are particularly informative. The phospha-alkenyl ligand gives rise to a triplet resonance at δ 462.7 [$J(P_2P)$ 13.1 Hz] due to coupling to the two chemically equivalent phosphine phosphorus nuclei. This resonance is shifted slightly to higher field of that for **2a** [δ 450.4, $J(P_2P)$ 10.0 Hz]. Whilst **2a** is air stable both as a solid and in solution, solutions of the more electron rich complex **2c** are rapidly decomposed by air.

The reaction of **3a** with P≡$CCMe_3$ was then investigated and surprisingly *ultimately* found not to provide the analogous phospha-alkenyl complex $[Os(P{=}CHCMe_3)Cl(CO)(PPh_3)_2]$. Rather, the product **4** obtained after 18 h at room temperature was found to incorporate two equivalents of phospha-alkyne. Even when the reaction was performed with a deficiency of phospha-alkyne, no species other than **3a** and **4** could be spectroscopically observed to accumulate during the course of the reaction. In the absence of crystals suitable for an X-ray diffraction study, the complex **4** is formulated as the metallacyclic phospha-alkenyl–phospha-alkene complex



Scheme 1

$[Os\{\kappa^1P,\kappa^1P'\text{-}P{=}C(CMe_3)P(=CHCMe_3)\}Cl(CO)(PPh_3)_2]$ on the basis of spectroscopic, micro-analytical and FABMS data.† Characteristic data pertaining to the '$OsCl(CO)(PPh_3)_2$' unit are unremarkable, with interest focusing on those associated with the novel metallacycle: Two Bu^t chemical environments follow from the appearance of two singlet resonances in the ^{1}H NMR spectrum (δ 0.90, 0.70) in addition to a doublet resonance at δ 6.83 [^2J(PH) 12.6 Hz] corresponding to the vinylic (neopentylidene) proton. The ^{31}P NMR spectrum consists of three resonances: the two phosphine ligands give rise to a double-doublet resonance [δ −1.35, J(PP) 12, 18 Hz] confirming their mutually *trans* disposition, straddling the molecular symmetry plane; the phospha-alkenyl resonance appears as a slightly broadened singlet at δ 578.9 whilst the phospha-alkene phosphorus nucleus is manifest as an apparent triplet at δ 111.9 [J(PP) 19 Hz], indicating that the net coupling between the two phosphorus nuclei of the metallacycle is negligible. Only one isomer is formed with respect to the osmium stereochemistry, and since our recent structural studies of various σ-P phospha-alkene complexes suggest a moderate π-acidity,[3] it seems reasonable that it is the isomer shown (phospha-alkene *trans* to π-basic chloride) which is formed.

The metallacycle in **4** is unique in possessing both phospha-alkenyl and phospha-alkene ligating groups, although other metallacyclic phospha-alkenyl complexes have been reported, *viz*. $[Os\{P{=}C(CF_3)O\}(CO)_2(PPh_3)_2]$,[9] $[Rh\{P{=}C(CMe_3)\text{-}C{=}CH_2\}Cl(PPr^i_3)_2]$,[10] and the λ^5-phospha-alkenyl complex $[Ru\{P(=O){=}C(CMe_3)C(=O)\}(CNCMe_3)_2(PPh_3)_2]$,[11] (spectroscopic data of which support our formulation). The route by which **4** is formed presumably involves a slow insertion of one equivalent of $P{\equiv}CCMe_3$ into the osmium hydride bond to provide transiently the phospha-alkenyl complex $[Os(P{=}CHCMe_3)Cl(CO)(PPh_3)_2]$, followed by a rapid insertion of a second equivalent of phospha-alkyne into the Os–P bond and subsequent metallacyclisation. It is therefore noteworthy that treating the ruthenium complexes **2a** or **2c** with an excess of phospha-alkyne fails to result in any discernible reaction. Thus our very modest attempt to generalise what appears a simple reaction, phospha-alkyne hydrometallation, has highlighted the diversity of reactivity available to phospha-alkynes through coordinative activation by transition metals.

A. F. H. gratefully acknowledges the Leverhulme Trust and the Royal Society for the award of a Senior Research Fellowship. Osmium and ruthenium salts were generously provided by Johnson Matthey Chemicals Ltd.

Notes and references

† *Selected data* for new complexes. Satisfactory elemental microanalytical data obtained. **2c**: IR(CH_2Cl_2): 1936 [ν(CO)] cm^{-1}. (Nujol): 1925 [ν(CO)], 1660, 1247, 1157, 1119, 968, 862, 849 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.90 [d, 9H, CH_3, J(HP) 1.32 Hz], 6.41 [dt, 1H, PCH, J(HP) 4.48 J(HP_2) 0.75 Hz], 7.32–7.68 (m, 30H, PPh). ^{31}P{^{1}H}, δ 462.7 [t, P=C, 1 P, J(P_2P) 13 Hz], 33.1 [d, 2 P, PPh_3, J(PP_2) 14 Hz]. FABMS: *m/z* (%) = 883 (2) $[M]^+$, 853 (3) $[M - CO]^+$, 781 (19) $[M - PCHCMe_3]^+$, 755 (6) $[M - I]^+$, 654 (15) $[M - I - PCHCMe_3]^+$, 625 (14) $[M - CO - I - PCHCMe_3]^+$. **4**: IR ($CH_2Cl_2$): 1940 [$\nu$(CO)] cm^{-1}. (Nujol): 1934 [ν(CO)], 1718, 1311, 1263, 1089vs, 971, 931, 852 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.70, 0.90 (s × 2, 9H × 2, CH_3), 6.83 [br d, 1H, PCH, J(PH) 12.6 Hz], 7.33, 7.66 (m × 2, 30H, Ph). ^{31}P{^{1}H}, δ 578.9 (br s, 1 P), 111.9 [t, 1 P, J(PP) 19], −1.35 [dd, 2 P, J(PP) 12, 18 Hz] ^{13}C{^{1}H}: 226.1 [br d, P=CHR, J(PC) 68.0], 185.7 (m, OsCO), 134.6 [t, $C^{3,5}$ of Ph, J(P_2C) 4.4], 133.3 [t, C^1 of Ph, J(P_2C) 25.9], 129.9 (s, C^4 of Ph) 127.8 [t, $C^{2,6}$ of Ph, J(P_2C) 4.9], 48.0 (br s, P_2CCMe_3), 36.0 [d, $CHCMe_3$, J(PC) 4.3], 30.5 [d, CH_3, J(PC) 11.9 Hz], 29.8 (br s CH_3). NB: the neopentylidyne carbon resonance was not unambiguously identified and possibly lies beneath the phosphine resonances. FABMS: *m/z* (%) = 999 (7) $[M + H_2O]^+$, 979 (1) $[M]^+$, 779 (3) $[M - PCHCMe_3]^+$, 737 (6) $[M + H_2O - PPh_3]^+$, 707 (2) $[M + H_2O - CO - PPh_3]^+$.

1 R. B. Bedford, A. F. Hill and C. Jones, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 547; R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 1998, **17**, 4744.

2 For a recent review on the chemistry of phospha-alkenyl complexes, see: L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 271.

3 R. B. Bedford, D. E. Hibbs, A. F. Hill, M. B. Hursthouse, K. M. A. Malik and C. Jones, *Chem. Commun.*, 1996, 1895; R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1997, 139, 1113; R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1997, 179; A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1998, 1419.

4 M. H. A. Benvenutti, N. Cebac and J. Nixon, *Chem. Commun.*, 1997, 1327.

5 M. Schmidz, R. Göller, U. Bergsträßer, S. Leininger and M. Regitz, *Eur. J. Inorg. Chem.*, 1998, 227.

6 A. F. Hill and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1998, 3501.

7 N. W. Alcock, A. F. Hill and M. S. Roe, *J. Chem. Soc., Dalton Trans.*, 1990, 1737.

8 M. C. J. Harris and A. F. Hill, *J. Organomet. Chem.*, 1992, **438**, 209; M. C. J. Harris and A. F. Hill, *Organometallics*, 1991, **10**, 3903.

9 D. S. Bohle, G. R. Clark, C. E. F. Rickard and W. R. Roper, *J. Organomet. Chem.*, 1988, **353**, 355; D. S. Bohle, C. E. F. Rickard and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1985, 1594.

10 P. Binger, J. Haas, A. T. Herrmann, F. Langhauser and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 310.

11 A. F. Hill, C. Jones, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1998, 367.

Communication 9/00257J