Novel P–O Bond Forming Reactions *via* Coupling of Phosphinidene and Phosphidoxo Groups on a Tetranuclear Ruthenium Cluster: Face Capping Ph_2POPR Ligands and the X-Ray Structure of $Ru_4(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)[\mu_3\text{-}\eta^2\text{-}PPh_2(OPPh)]$

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Reaction of the alkynylphosphine oxide $Ph_2P(O)C{\equiv}CBu^t$ with square-pyramidal *nido*-$Ru_4(CO)_{13}(\mu_3\text{-}PR)$ (**1a**, R = Ph; **1b**, R = NPr^i_2) affords a novel example of P–O bond synthesis to yield the ligands Ph_2POPR, coordinated on a triangular face of the clusters $Ru_4(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)[\mu_3\text{-}\eta^2\text{-}PPh_2(OPPh)]$ (**2a**, R = Ph; **2b**, R = NPr^i_2).

Although the synthesis and reactivity of both phosphido (PR_2) and phosphinidene (PR) ligands in bi- and poly-nuclear transition metal complexes are thoroughly documented,[1] the roles of their corresponding oxides (R_2PO, RPO) in supporting and enhancing cluster reactivity have only recently become the focus of increased attention.[2] The presence of both hard (oxygen) and soft (phosphorus) donor atoms in transition metal complexes bearing these ligands offers an opportunity to compare and contrast site reactivities in homometallic systems[3] and also has considerable potential for bridge assisted early/late transition metal cluster synthesis.[4,5]

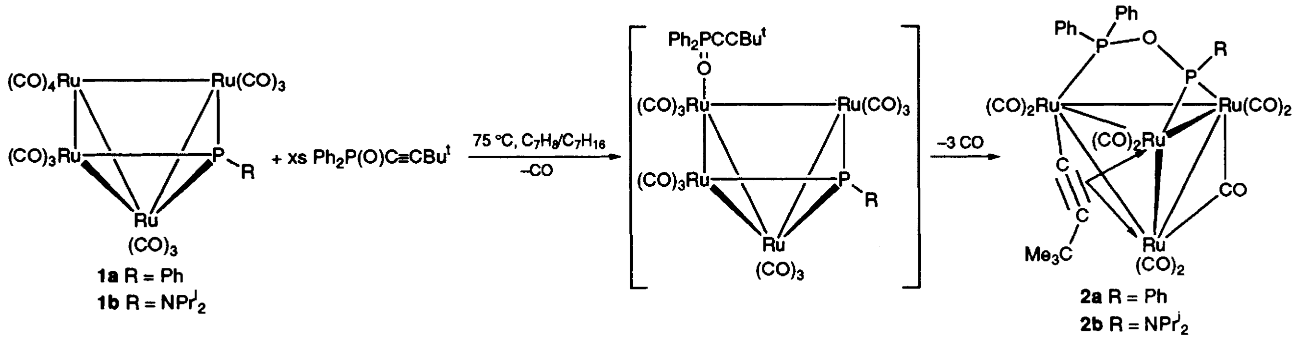
Recent studies of square pyramidal *nido*-$Ru_4(CO)_{13}(\mu_3\text{-}PR)$[6] (**1a**, R = Ph; **1b**, R = $PNPr^i_2$) illustrated that the main group atom behaves as an integral part of the skeletal framework when reacted with unsaturated organic molecules, undergoing facile P–C bond forming reactions. This suggests the possibility of generating other novel ligands *via* P–X coupling at PR skeletal sites. A recent report of P–O coupling of a phosphido bridge and a CO ligand at a binuclear iron centre[7] prompts us to describe an example of P–O bond synthesis in the formation of the $Ph_2P\text{–}O\text{–}PR$ supported clusters $Ru_4(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)[\mu_3\text{-}\eta^2\text{-}PPh_2(OPR)]$ (**2a**, R = Ph; **2b**, R = NPr^i_2) from the reaction of **1** with the alkynylphosphine oxide $Ph_2P(O)C{\equiv}CBu^t$.[8] Noteworthy features of the formation of **2** are: (*i*) the unprecedented P–O coupling reaction of phosphinidene (PR) and phosphidoxo ($R_2P{=}O$) ligands. This bond forming reaction contrasts with the facile P–O cleavage observed by Riera *et al.*[9a] using the ligand $(EtO)_2POP(OEt)_2$. Cleavage of P–OR bonds has also been noted in the reaction of phosphites with metal carbonyl compounds under forcing conditions;[9b] by-products isolated include pentanuclear clusters with $\mu_3\text{-}\eta^3\text{-}OP(OR)OP(OR)_2$ ligands.[9c] (*ii*) Conversion of a four-electron donor μ_3-PR group into a five-electron $\mu_3\text{-}PR(OPPh_2)$ ligand which bridges three metal centres. Although terminal or doubly bridging $R_2P\text{–}O\text{–}$ ligands have been generated *via* oxidation of coordinated phosphido groups,[10] face-bridging $RP\text{–}O\text{–}PR_2$ groups are unknown.

The reaction of **1** (0.075 g) with excess $Ph_2P(O)C{\equiv}CBu^t$ (0.145 g) in *n*-heptane–toluene (50 : 50, 75 °C) leads to the high yield formation of $Ru_4(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)[\mu_3\text{-}\eta^2\text{-}PPh_2(OPR)]$ (**2a**, R = Ph; **2b**, R = NPr^i_2) as the sole product after chromatographic workup and recrystallisation (Yield: **2a**, 0.067 g; **2b**, 0.053 g). Spectroscopic investigations† of **2** confirmed the presence of two inequivalent phosphorus nuclei and the formation of a coordinated acetylide ligand. The $^{31}P\{^1H\}$ NMR spectrum of **2** consisted of two resonances of equal intensity, one at high field [**2a**, δ 137.0(s); **2b**, δ 140.4(d), $^2J_{PP}$ = 13.8 Hz] the other to much lower field [**2a**, δ 339.0(s); **2b**, δ 309.2(d), $^2J_{PP}$ = 13.8 Hz]. The former signals lie in the region associated with $\mu\text{-}R_2P{=}O$ ligands[3] and this, together with the presence of acetylide signals in the $^{13}C\{^1H\}$ NMR spectra, suggested the formation of such a bridging species *via* the expected facile P–C alkyne cleavage reaction.

A single crystal X-ray analysis‡ provided full structural details. The molecular structure of **2a** is shown in Fig. 1. The most important and striking feature of **2a** is the unexpected formation of the $\mu_3\text{-}\eta^2\text{-}PPh_2(OPPh)$ ligand which lies above a closed Ru_3 face. The two phosphorus-oxygen bonding distances [P(1)–O(10) 1.653(2), P(2)–O(10) 1.652(2) Å] are identical and reflect the single bond nature of the P–O–P linkages between the two atoms. In contrast for example the P–O distances in $Fe_3(CO)_9[\mu\text{-}P(Ph_2){=}O](\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)$ [1.539(2) Å][3] and $[(\eta^5\text{-}Cp^*)_2Ni_2W(CO)_4(\mu_3\text{-}PO)_2]$ (Cp^* = $Pr^i_4C_5H$) [1.480(10) and 1.462(9) Å][11] are much shorter than those found in **2a**.

Atom P(1) is now best regarded as a phosphido [μ-PR(OR′)] ligand and thus acts as a three-electron donor to the metal framework. The ruthenium-phosphorus distances [Ru(1)–P(1) 2.285(1), Ru(4)–P(1) 2.220(1) Å] are typical for such systems. Conversely, atom P(2) serves as a simple two-electron terminal phosphine bonded to Ru(3) [P(2)–Ru(3) 2.278(1) Å]. The metal atom framework has closed up on converting from **1a** to **2a** with the formation of a sixth metal–metal bond to yield a tetrahedral array of ruthenium atoms. The 60-electron cluster valence electron count is satisfied with the acetylide ligand serving as a five electron donor. The metal–metal bond lengths [2.721(1)–2.869(1) Å] reflect the electron precise nature of the cluster famework with the shortest ruthenium–ruthenium contact between Ru(2) and Ru(4), this vector being unsymmetrically bridged by a carbonyl ligand.

Monitoring the reaction of **1a** with $Ph_2P(O)PC{\equiv}CBu^t$ *via* ^{31}P NMR spectroscopy provided evidence for the formation of an



Scheme 1

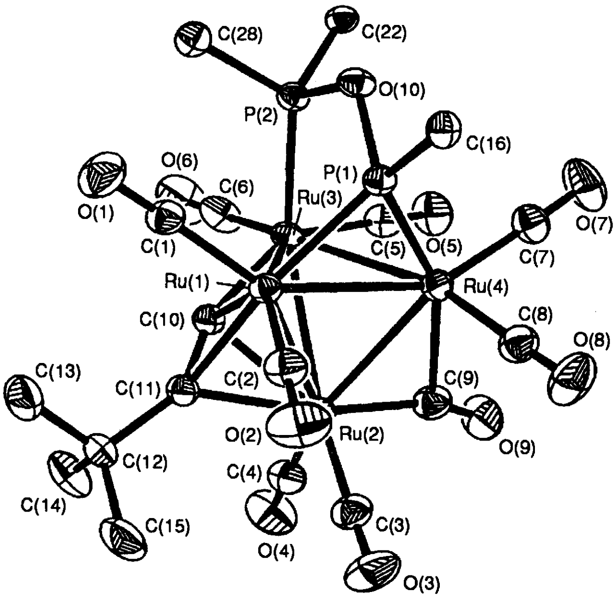


Fig. 1 The molecular structure of $Ru_4(CO)_8(\mu{-}CO)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)$-$[\mu_3\text{-}\eta^2\text{-}PPh_2(OPPh)]$ **2a** illustrating the coordinated Ph_2OPPh ligand. Phenyl rings are omitted for clarity. Important bond lengths (Å) and angles (°) not mentioned in the text: Ru(1)–Ru(2) 2.757(1), Ru(1)–Ru(3) 2.831(1), Ru(1)–Ru(4) 2.782(1), Ru(2)–Ru(3) 2.848(1), Ru(2)–Ru(4) 2.721(1), Ru(3)–Ru(4) 2.869(1), Ru(2)–C(9) 1.982(5), Ru(4)–C(9) 2.436(5), C(10)–C(11) 1.307(5); Ru(1)–P(1)–Ru(4) 76.3(1), Ru(1)–P(1)–O(10) 115.0(1), Ru(4)–P(1)–O(10) 115.0(1), Ru(3)–P(2)–O(10) 112.1(1), P(1)–O(10)–P(2) 114.8(2)

intermediate [δ 456.3(s), 54.8(s)] and suggests that the reaction proceeds *via* the displacement of a carbonyl ligand and the coordination of the alkynylphosphine ligand through the oxygen atom to a hinge ruthenium atom. This would parallel previous studies on the substitution chemistry of **1a** with phosphines.[12] Intramolecular coupling of proximate Ph_2PO and μ_3-PR ligands would then lead to **2**. Experiments are currently underway to confirm the mechanistic details and to explore the applicability of this coupling sequence to other phosphorus supported clusters.

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Footnotes

† *Selected spectroscopic data* for **2a**: IR ν(CO) (CH_2Cl_2) 2056w, 2020w, 2007sh, 2004s, 1962w, 1942vw, 1918vw. NMR $^{31}P\{^1H\}$ ($CDCl_3$, δ) 339.0(s), 137.0(s). $^{13}C\{^1H\}$ (C_4D_8O, δ) 206.5 (t, C_α or CO, J_{PC} = 13.0 Hz), 205.8 (d, CO, J_{PC} = 27.5 Hz), 205.6 (d, CO, J_{PC} = 20.0 Hz), 200.6 (s, CO), 198.1 (d, CO, J_{PC} = 12.2 Hz), 196.5 (t, C_α or CO, J_{PC} = 9.7 Hz), 195.6 (s, CO), 161.6 (d, C_β, $^2J_{PC}$ = 28.0 Hz), 144.6 (dd, C_i, $^1J_{PC}$ = 30.7 Hz, $^3J_{PC}$ = 7.5 Hz), 140.7 (dd, C_i, $^1J_{PC}$ = 58.9 Hz, $^3J_{PC}$ = 4.8 Hz), 133.3–128.8 (m, C_{phenyl}), 39.1 [s, $-C(CH_3)_3$], 35.0 (s, $-CH_3$). ^1H (CD_2Cl_2, δ) 7.98–7.40 (m, H_{phenyl}, 15 H), 1.71 (s, $-CH_3$, 9 H). Satisfactory microanalyses were obtained.

Selected spectroscopic data for **2b**: IR ν(CO) (C_6H_{12}) 2052m, 2013m, 2005vs, 1995s, 1966w, 1958w, 1941vw, 1925vw. NMR $^{31}P\{^1H\}$ ($CDCl_3$, δ) 309.2 (d, $^2J_{PP}$ = 13.8 Hz), 140.4 (d, $^2J_{PP}$ = 13.8 Hz) $^{13}C\{^1H\}$ ($CDCl_3$, δ) 206.5 (d, CO, J_{PC} = 5.7 Hz), 205.8 (t, C_α, J_{PC} = 7.6 Hz), 205.4 (d, CO, J_{PC} = 11.6 Hz), 201.5 (s, CO), 196.9 (d, CO, J_{PC} = 7.6 Hz), 195.7 (s, CO), 165.5 (d, C_β, $^2J_{PC}$ = 26.6 Hz), 140.4 (dd, C_i, $^1J_{PC}$ = 59.3 Hz, $^3J_{PC}$ = 5.5 Hz), 136.8 (d, C_i, $^1J_{PC}$ = 52.1 Hz), 133.6–127.9 (m, C_{phenyl}), 49.6 (d, $-CH-$, $^2J_{PC}$ = 8.7 Hz), 38.9 [s, $-C(CH_3)_3$], 34.8 [s, $-C(CH_3)_3$], 22.5 [d, $-CH(CH_3)$, $^3J_{PC}$ = 13.6 Hz]. ^1H ($CDCl_3$, δ) 7.55–7.23 (m, H_{phenyl}, 10 H), 1.78 (dspt, $-CH-$, $^3J_{PH}$ = 19.0 Hz, $^3J_{HH}$ = 6.7 Hz, 2H), 1.64 [s, $-C(CH_3)_3$, 9H], 1.39 (d, $-CH_3$, $^3J_{HH}$ = 6.7 Hz, 6 H), 1.13 (d, $-CH_3$, $^3J_{HH}$ = 6.7 Hz, 6 H). Satisfactory microanalyses were obtained.

‡ *Crystal data* for **2a**: red-brown needle prisms from CH_2Cl_2–*n*-hexane; $C_{33}H_{24}O_{10}P_2Ru_4$, M = 1046.7; triclinic, space group $P\bar{1}$, a = 8.969(2), b = 12.168(2), c = 17.162(3) Å, α = 99.17(2)°, β = 91.79(2)°, γ = 101.10(2)°, U = 1810.9(5) Å^3, Z = 2, D_c = 1.920 g cm^{-3}, $F(000)$ = 1016, μ(Mo-Kα) = 17.78 cm^{-1}. The structure was solved (Patterson, Fourier methods) and refined (full-matrix least squares, all non-hydrogen atoms anisotropic) on the basis of 5970 observed [$F > 6.0\,\sigma(F)$] reflections measured at 294 K using Mo-Kα (λ = 0.71073 Å) on a Siemens R3m/V diffractometer. The final R and R_w values were 0.0244 and 0.0278 respectively. 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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