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Preliminary communication

Complexes with functional phosphines

XVII *. Synthesis and characterization of ruthenium clusters with ketophosphine ligands. Crystal structure of the cluster $[Ru_3(\mu\text{-H})\{\mu\text{-}\eta^1(O):\eta^2(P,O)\text{-}O(=CPh)=CHPPh_2\}(CO)_9]$ containing a bridging phosphinoenolate ligand

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Abstract

Reactions of the ketophosphine $Ph_2PCH_2C(O)Ph$ (P–O) with $[Ru_3(CO)_{12}]$ afford the derivatives $[Ru_3(CO)_{11}(P\text{–}O)]$ (**1**) and $[Ru_3(CO)_{10}(P\text{–}O)_2]$ (**4**). In the presence of triphenylphosphiniminium acetate (PPN)(OAc), the former leads to the labile $[Ru_3(CO)_{10}\{\mu\text{-}(\widehat{P\ O})\}]$ (**2**), in which the functional phosphine acts as a (*P,O*) bridging ligand, whereas thermal activation of either **1** or **4** results in PC–H bond cleavage and formation of $[Ru_3(\mu\text{-H})\{\mu\text{-}\eta^1(O):\eta^2(P,O)\text{-}O(=CPh)=CHPPh_2\}(CO)_9]$ (**3**) whose crystal structure reveals an unprecedented bonding mode for the phosphinoenolate ligand, its oxygen atom bridging the Ru(1)–Ru(2) edge. Protonation of this complex occurs selectively at the enolato-carbon and $[Ru_3(\mu\text{-H})\{\mu\text{-}Ph_2PCH_2C(O)Ph\}(CO)_{10}]BF_4$ (**5**) and $[Ru_3(\mu\text{-H})\{\mu\text{-}Ph_2PCH_2C(O)Ph\}_2(CO)_8]BF_4$ (**7**) were characterized in which the $\widehat{P\ O}$ ligand(s) bridge between two Ru centres.

Despite increasing interest in the coordination chemistry and catalysis of complexes with hemilabile oxygen-phosphorus ligands, these studies have mostly focussed on mononuclear transition metal complexes [3]. We reasoned that it would be interesting to react such ligands with cluster molecules and see whether their multisite attachment would result in (i) an unprecedented bridging mode for

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* For Part 16, see ref. 1; Part 15, see ref. 2; Part 14, see ref. 4c.

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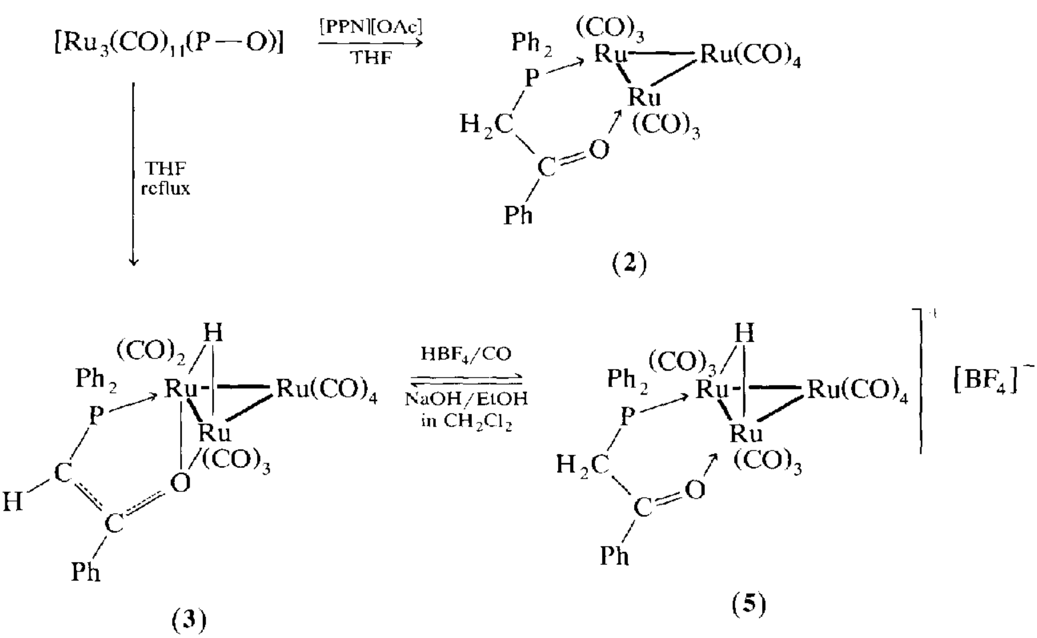

Scheme 1

the $\overset{\frown}{P\ O}$ ligand with a direct metal–oxygen interaction which furthermore might be cleaved reversibly, thus making available an empty coordination site, (ii) an easier ligand transformation, such as PC–*H* bond activation, leading to an interesting bonding mode for the resulting phosphinoenolate ligand. It has previously been found that the phosphinoenolate ligand $[Ph_2PCH{\cdots}C({\cdots}O)Ph]^-$, when (*P*,*O*) chelated to a M^{II} centre (M = Ni, Pd, or Pt), reacts with a range of electrophiles, such as heterocumulenes and alkynes, with carbon–carbon bond formation [4], and with chlorophosphines with phosphorus–oxygen coupling [5].

When $[Ru_3(CO)_{12}]$ (0.300 g, 0.469 mmol) reacted with $Ph_2PCH_2C(O)Ph$ (P–O, 0.150 g, 0.493 mmol) in tetrahydrofuran (THF) (100 ml) for 10 min in the presence of (PPN)(OAc) (0.012 g, 0.022 mmol), $[Ru_3(CO)_{11}(P–O)]$ (**1**) was isolated in 86% yield (chromatography on silica gel, toluene/pentane 1:2) [6*]. The ν(C=O) absorption in the IR spectrum at 1672 cm^{-1} is typical of an unco-ordinated ketone.

Addition of (PPN)(OAc) (0.012 g, 0.022 mmol) to a THF solution of **1** (0.046 g, 0.050 mmol) resulted in rapid formation of unstable **2**, as a result of CO loss and coordination of the ketone to an adjacent Ru centre (see Scheme 1) [6*]. Interestingly, heating a solution of **1** (0.078 g, 0.85 mmol) in THF (15 ml) under reflux for 3 h also led to loss of a CO and resulted in the formation of a new cluster **3** in 93% yield [6*]. This cluster was also obtained in 57% yield by heating under reflux (4 h) a THF solution of the disubstituted cluster $[Ru_3(CO)_{10}(P–O)_2]$ (**4**), which was obtained in 61% yield from the reaction of $[Ru_3(CO)_{12}]$ with 2

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* Reference number with asterisk indicates a note in the list of references.

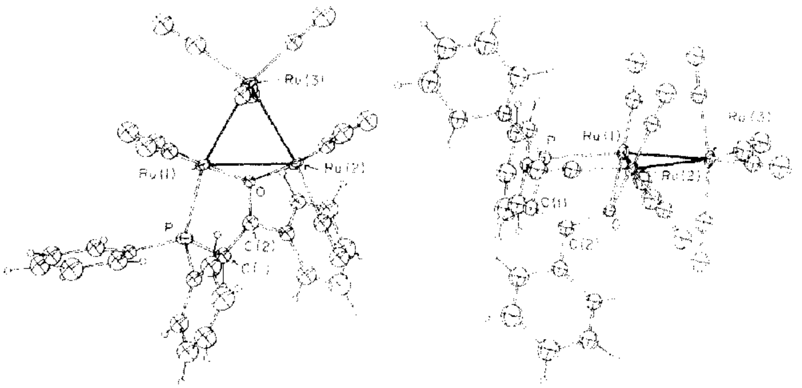


Fig. 1. Views of the molecular structure of $[Ru_3(\mu_2\text{-}H)\{\mu_2\text{-}O(=CPh)=CHPPh_2\}(CO)_9]$ (**3**). 20% thermal envelopes are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(2) 2.766(3), Ru(1)–Ru(3) 2.792(3), Ru(2)–Ru(3) 2.783(3), Ru(1)–P 2.301(8), Ru(1)–O 2.09(1), Ru(2)–O 2.12(1), P–C(1) 1.80(3), C(1)–C(2) 1.35(4), C(2)–O 1.34(3), C(2)–C(101) 1.50(4); Ru(2)–Ru(1)–Ru(3) 60.08(8), Ru(2)–Ru(1)–P 104.7(2), Ru(2)–Ru(1)–O 49.3(4), Ru(3)–Ru(1)–P 163.9(2), Ru(3)–Ru(1)–O 83.7(4), P–Ru(1)–O 81.9(5), Ru(1)–Ru(2)–Ru(3) 60.43(8), Ru(1)–Ru(2)–O 48.6(4), Ru(3)–Ru(2)–O 83.5(4), Ru(1)–Ru(3)–Ru(2) 59.49(8), Ru(1)–P–C(1) 100.8(9), P–C(1)–C(2) 115(2), C(1)–C(2)–O 123(2), Ru(1)–O–Ru(2) 82.1(5), Ru(1)–O–C(2) 120(2), Ru(2)–O–C(2) 118(1).

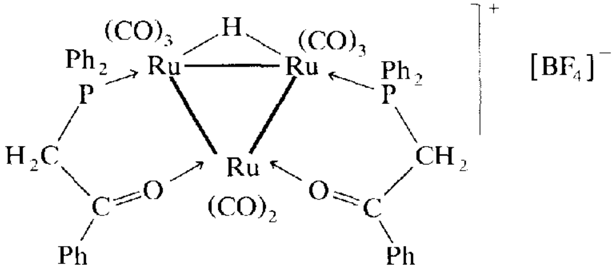
equivalents of P–O in the presence of $ONMe_3$ (THF, −78 to 25 °C, 2 h) [6*]. The IR spectrum of **3** showed an absorption at 1553 cm^{-1}, typical of the [ν(C=O) + ν(C=C)] absorption of the phosphinoenolate ligand [4,7], indicating that PC–H bond cleavage had occurred. This was confirmed by the ^1H NMR spectrum, which contained resonances at δ 5.38 for the remaining PC*H* proton (the ^2J(PH) coupling was not resolved) and at −11.77 (d, ^2J(PH) 7.43 Hz) which was assigned to a bridging hydride. In order to clarify the coordination mode of the phosphinoenolate ligand, an X-ray crystallographic analysis of **3** was undertaken [8*].

The molecular structure of **3** (Fig. 1) consists of a Ru_3 triangle of which the significantly shortened Ru(1)–Ru(2) edge is almost symmetrically bridged by the enolate oxygen. This unprecedented feature makes the phosphinoenolate ligand act as an anionic 6e donor toward the Ru_3 unit. The hydride ligand could not be located but the coordination geometry at Ru(1) and Ru(2) strongly suggests that it is bridging them. A bridging phosphine alkoxide ligand has recently been found in a dinuclear Rh complex [9].

In comparison with our thermally-induced enolate formation, thermal treatment of $[Ru_3(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{10}]$ was found to result in P–C instead of PC–H bond cleavage [10].

Protonation of **3** in the presence of CO ($HBF_4 \cdot Et_2O$, CH_2Cl_2, 1 h) occurred via a dark intermediate and afforded, in 70% yield, yellow-orange $[Ru_3(\mu\text{-}H)\{\mu\text{-}Ph_2PCH_2C(O)Ph\}(CO)_{10}]BF_4$ (**5**) in which the enolate carbon has been protonated [6*]. The ketonic vibration at 1558 cm^{-1} is consistent with bridging bonding for the $\widehat{P\ O}$ ligand. The presence in the ^1H NMR spectrum of an ABX pattern results from the disymmetry of the molecule. The presence of CO during the protonation reaction of **3** leading to **5** is necessary in order for Ru(1) to achieve a stable 18e configuration. Conversely, a PCH_2 proton of **5** in CH_2Cl_2 is instantaneously and selectively removed by NaOH/ethanol to regenerate **3**. The chemoselectivity of these transformations is reminiscent of related reactions performed with mononuclear complexes of this phosphinoenolate ligand [7].

When **3** was treated with one equivalent of $\overset{\frown}{P\ O}$ and $ONMe_3$ in THF at −78°C, an unstable complex **6** formed, the spectroscopic properties of which are consistent with an anionic, bis(phosphinoenolate)hydrido-cluster [6*]. When treated with $HBF_4 \cdot Et_2O$, it afforded the cationic, bis(ketophosphine) complex $[Ru_3(\mu_2\text{-}H)\{\mu_2\text{-}Ph_2PCH_2C(O)Ph\}_2(CO)_8]BF_4$ (**7**) [6*]. The ^1H NMR spectrum of **7** shows the expected ABX pattern for the PCH_AH_B protons [11]. It is interesting that both **2** and **7** contain slightly stabilized coordination sites that should prove of interest for reactivity studies.



(7)

The binding of the enolate oxygen to two metal centres in **3** should result in a decreased reactivity (nucleophilicity) of the enolate carbon centre. Accordingly, we have not yet been able to isolate reaction products with heterocumulenes or alkynes, although this may also be due to the lower reactivity of Ru compared to Ni, Pd or Pt complexes [4]. Further studies are in progress to evaluate the chemistry of such multisite-bound $\overset{\frown}{P\ O}$ ligands and their related phosphinoenolates in clusters.

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6 **1**: IR ν(CO) ($CHCl_3$) 2096 m, 2045 s, and 2014 s, ν(C=O) (KBr) 1672 cm^{-1}. ^1H NMR ($CDCl_3$, TMS as external reference): δ 4.28 (d, 2H, PCH_2, ^2J(PH) 8.36 Hz), 7.2–7.7 (m, 15H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 as external reference): δ 23.2 s. Anal. Found: C, 40.83; H, 1.93. $C_{31}H_{17}O_{12}PRu_3$ (M = 915.06) calc.: C, 40.65; H, 1.85. Mass spectrum (FAB): 916.8 (M^+). **2**: IR

(THF) ν(CO) 2077 w, 2058 w, 2032 m, 1995 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.29 (s, 2H, PCH_2), 7.15–7.70 (m, 15H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.6 s. Product too unstable for obtaining satisfactory elemental analyses. **3**: IR ν(CO) ($CHCl_3$) 2093 m, 2053 s, and 2009 sh; $\nu(C{=}O)+\nu(C{=}C)$ (KBr) 1553 mw cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −11.77 (d, 1H, ^2J(PH) 7.43 Hz, RuHRu), 5.38 (s, 1H, PCH), 7.38–7.76 (15 H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.5 s. Anal. Found: C, 40.23; H, 2.09. $C_{29}H_{17}O_{10}PRu_3$ (M = 859.05) calc.: C, 40.50; H, 1.97. Mass spectrum (FAB): 860.7 (M^+). **4**: IR ν(CO) (THF) 2069 m, 2019 s, and 1991 s, $\nu(C{=}O)$ (KBr) 1674 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.24 (d, 4H, PCH_2, ^2J(PH) 7.34 Hz), 7.25–7.67 (m, 30H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23 (s), 23.7 (s). Anal. Found: C, 50.51; H, 3.03. $C_{50}H_{34}O_{12}P_2Ru_3$ (M = 1191.03) calc.: C, 50.37; H, 2.85. Mass spectrum (FAB): 1191.8 (M^+). **5**: IR ν(CO) ($CHCl_3$) 2070 s, 2045 s, and 2009 s, $\nu(C{=}O)$ (KBr) 1558 m. ^{1}H NMR ($CDCl_3$): δ −15.20 (d, 1H, RuHRu, ^2J(PH) 11.9 Hz), δ_A 5.27, δ_B 4.89, ABX spin system (A = H, B = H, X = P) (J_{AB} = 19.1, J_{AX} = 11.1, J_{BX} = 11.4, 2H, PCH_AH_B), 7.26–8.29 (m, 15H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.7 (s). Anal. Found: C, 36.80; H, 2.19. $C_{30}H_{18}BF_4O_{11}PRu_3$ (M = 974.66) calc.: C, 36.93; H, 1.84. Mass spectrum (FAB): 889.5 (M^+). **6**: ^{1}H NMR ($CDCl_3$): δ −9.96 (t, 1H, RuHRu, ^2J(PH) 9.69 Hz), 5.40 (d, PCH, ^2J(PH) 3.62 Hz), 6.86–7.98 (m, 30H, aromatic). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 41.46 (s), 47.8 (s). **7**: IR ν(CO) (CH_2Cl_2) 2065 s, 2029 s, 2015 s, and 1999 s br, $\nu(C{=}O)$ (KBr) 1606 m and 1588 s. ^{1}H NMR ($CDCl_3$): δ −11.75 (t, 1H, RuHRu, ^2J(PH) 13.8 Hz), δ_B 2.97, δ_A 4.74, ABX spin system (A = H, B = H, X = P) (J_{AB} = 18.7, J_{AX} = 11.5, J_{BX} = 9.4, 4H, PCH_AH_B), 6.98–8.36 (m, 30H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.2 (s). Anal. Found: C, 46.96; H, 3.18. $C_{48}H_{35}BF_4O_{11}P_2Ru_3$ (M = 1222.77) calc.: C, 47.10; H, 2.86. Mass spectrum (FAB): 1137.6 (M^+).

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8 Crystal data: $C_{29}H_{17}O_{10}PRu_3$, M = 859.6, space group $P\bar{1}$, a = 14.882(4), b = 11.846(4), c = 8.973(6) Å, α = 88.83(5), β = 89.36(4), γ = 84.91(3)°, U = 1575 Å^3, Z = 2, $F(000)$ = 836, D_c = 1.81 g cm^{-3}, μ(Mo-K_α) = 13.5 cm^{-1}. The structure was solved by direct methods and refined to R = 0.107, R' = 0.127 (statistical weights) using 3260 unique absorption-corrected diffractometer reflections ($I \geq 3\sigma(I)$). Data were weak with broad linewidths: anisotropic thermal parameters were refined for Ru_3P only, the isotropic form being used for C, O. $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Atomic coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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