Novel synthesis of two *tert*-butyl ketenyl phosphinidine ligands on a trinuclear ruthenium framework. X-Ray structure determination of $[Ru_3(\mu\text{-dppm})(CO)_7\{\mu_3\text{-PC(=C=O)Bu}^t\}_2]$

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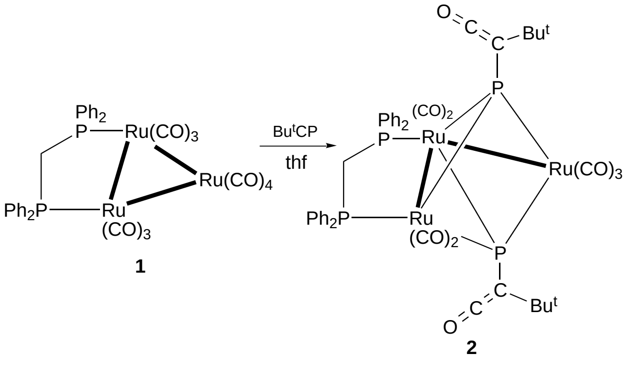
The reaction of an excess of $Bu^tC{\equiv}P$ with $[Ru_3(\mu\text{-dppm})(CO)_{10}]$ 1 in refluxing thf gives $[Ru_3(\mu\text{-dppm})(CO)_7\{\mu_3\text{-P(C=C=O)Bu}^t\}_2]$ 2 with two bridging phosphinidine ligands as the major product after chromatography.

The considerable attention focussed on the chemistry of phosphaalkynes has been manifested in a sharp increase in numbers of papers dealing with the subject over the last ten years. This work is described in several excellent reviews which deal with both organometallic[1–3] and organic aspects.[4,5]

The chemistry of $[Ru_3(\mu\text{-dppm})(CO)_{10}]$ **1** [dppm = 1,2-bis(diphenylphosphino)methane], is characterised by its enhanced reactivity over that of the unsubstituted carbonyl $[Ru_3(CO)_{12}]$. Pyrolysis results in the elimination of benzene from dppm and metallation of one of the remaining phenyl groups.[6] Phosphines readily add to the unsubstituted Ru atom[7–9] and internal and terminal alkynes add readily to the ruthenium triangle.[10] As part of a continuing study of the reactivity of the activated cluster **1**, the reaction with 2-*tert*-butyl-1-phosphaalkyne was examined and the results are reported herein.

The reaction (Scheme 1)† in refluxing thf gave a mixture of products that are readily separated by thin layer chromatography, the major yellow band providing a moderate yield (*ca.* 27%) of $[Ru_3(\mu\text{-dppm})(CO)_7\{\mu_3\text{-PC(=C=O)Bu}^t\}_2]$ **2**, a 50-electron cluster. The compound remarkably contains two μ_3-Bu^t ketenyl phosphinidine ligands and is noteworthy for the lack of oligomerisation normally exhibited in the reactions of several equivalents of Bu^tCP on transition-metal centres.

The FABMS of **2** showed a molecular ion M^+ at *m/z* 1141 that appeared to indicate the incorporation of two Bu^tCP units and the sequential loss of nine CO groups. This latter fact is normally a reliable indication of the number of metal bound carbonyl groups and the fact that **1** readily adds substrates at the unsubstituted ruthenium[9] suggested a localised dimer at that atom occupying one coordination site. This formulation was at odds with the spectroscopic data which indicated the presence of four inequivalent phosphorus atoms. The fact that the phosphinidine ligands were found to be inequivalent was puzzling and seemingly at odds with the solid-state structure. The ^{31}P NMR spectrum of **2** contained four resonances that remained essentially unchanged within the temperature range 190 to 360 K indicating that the complex was rigid on the NMR timescale. The ^{31}P NMR spectrum was reproducible from a number of different samples and in different solvents. This suggests that the possibility of impurities or other structural isomers can be discounted.



Scheme 1

The results of the room-temperature single-crystal X-ray structure study‡ are consistent with the stoichiometry and connectivity as expressed in **2** above and Fig. 1, a pair of substrate carbonyl ligands having been incorporated by the Bu^tCP reactants to form a pair of $Bu^tC(CO)P$ phosphinidine entities. The phosphorus atoms of the latter approach the Ru_3 triangle from above and below the plane with approximately equivalent distances to the ruthenium atoms, much more precisely so about P(4). Notwithstanding, the phosphorus atoms are displaced from above the centroid of the triangle (and from

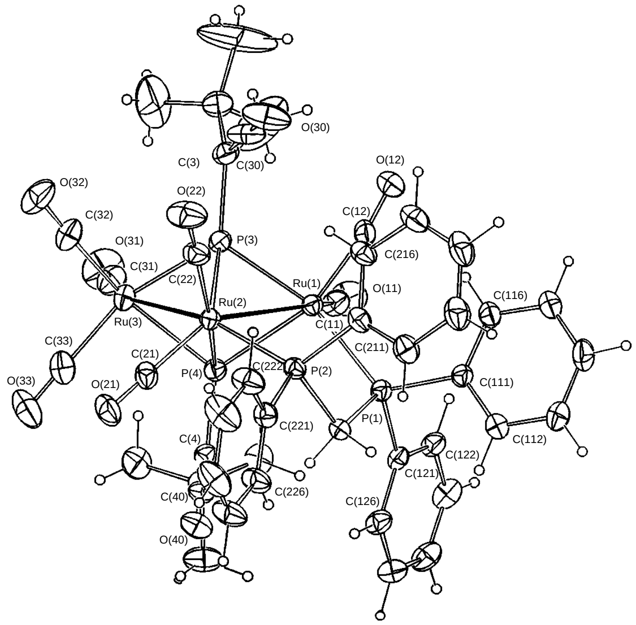
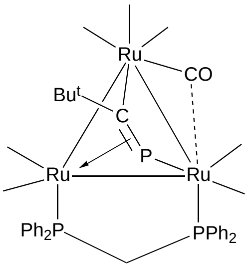


Fig. 1 Projection of **2** approximately through the Ru_3 plane. 20% thermal ellipsoids are shown for non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.916(1), Ru(2)–Ru(3) 2.831(1), P(3)–Ru(1–3), 2.296(2), 2.381(2), 2.330(2), P(4)–Ru(1–3) 2.380(2), 2.378(2), 2.377(2), Ru(1)–P(1) 2.386(2), Ru(2)–P(2) 2.306(2), P(3)–C(3) 1.807(7), C(3)–C(30) 1.27(1), C(30)–O(30) 1.19(1), P(4)–C(4) 1.809(7), C(4)–C(40) 1.293(9), C(40)–O(40) 1.176(8), Ru(3)–Ru(2)–Ru(1) 83.80(3), P(3)–C(3)–C(30) 114.7(6), P(4)–C(4)–C(40) 113.6(5), C(3)–C(30)–O(30) 179(1), C(4)–C(40)–O(40) 180(1), P(1)–C(0)–P(2) 110.4(3), C(3)–P(3)–Ru(1–3) 121.6(7), 126.9(2), 125.0(3), C(4)–P(4)–Ru(1–3) 129.6(3), 127.3(2), 121.4(3).



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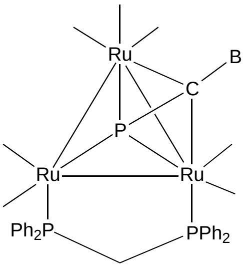

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the dppm) so that they bridge one pair of ruthenium atoms, with the associated Ru···Ru distance lengthened to 3.839(1) Å, and with an unsymmetrical dppm disposition. The major difference observed lies in the Ru(1)–P(*n*)–Ru(3) angles [for $n = 3$, 112.14(7)°; $n = 4$, 107.59(6)°] and this possibly affects the observed ^{31}P NMR resonances for these nuclei. It is of note that the ^{31}P NMR shifts of μ-phosphido ligands in a series of structurally characterised compounds were greatly affected by small variations in Ru–P–Ru angle.[11] In the dppm ligand the two now inequivalent phosphorus atoms, bound to a pair of inequivalent ruthenium atoms, with inequivalent Ru–P [2.386(2), 2.306(2) Å], lie necessarily to one side of the Ru_3 plane so that the molecule's incipient *m* symmetry is lost. Despite this, the pair of phosphinidine ligands are almost eclipsed in projection, with the ketenyl moieties in surprisingly close proximity to other moieties in the coordination sphere [O(30)···O(22), H(216) 2.951(8), 2.6_9; O(40)···H(0a) 2.6_6 Å] and adjacent molecules [O(30)···H(0b) 2.5_0 Å]. The geometries of the Bu^t ketenyl phosphinidine ligands are similar to those observed in $[Re_2Pt(CO)_8(dppe)\{\mu_3\text{-}PC(=C=O)(Bu^t)\}]$[12] and $[Fe_3(CO)_7(Se)(PBu^t)(Bu^tC_2H)\{\mu_3\text{-}PC(=C=O)Bu^t\}]$.[13]

In the absence of oligomerisation it is likely that the formation of **2** results from the stepwise addition of Bu^tCP (which can act as either a four- or six-electron donor) units with cleavage of a Ru–Ru bond. Further work is required to determine the mechanism operating in this reaction but a likely sequence of events would involve addition of Bu^tCP presumably through the labile equatorial site on the unsubstituted Ru atom, which adopts initially a μ_3-η^2 (‖) **3** or (⊥) **4** ligating mode followed by addition of the liberated or metal-bound CO to the CP bond, the process being repeated to give the other ligand.

Work is in progress to identify the minor products from this reaction in the belief that they will shed further light on the course of this reaction.

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Footnotes

† *Synthesis of* **2**: an excess of Bu^tCP (0.05 ml) was added to a solution of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (0.104 g, 0.107 mmol) in thf (20 ml) and heated to reflux for 40 min. After cooling the solvent was removed *in vacuo*, and the residue was dissolved in the minimum amount of CH_2Cl_2 and chromatographed (TLC, silica GF_{254} 0.5 mm; 3 : 1 hexanes–CH_2Cl_2). Three bands were resolved but only the major yellow band (R_f 0.6) was isolated, being crystallised from CH_2Cl_2–MeOH to give **2** (0.033 g, 27%). [Found: C, 46.44; H, 3.39; M(FAB MS) 1141 (M^+). $C_{44}H_{40}O_9P_4Ru_3$ requires C, 46.35; H, 3.54; M, 1141.] IR(C_6H_{12}) ν(CO) 2092m, 2077m 2055s, 2002s, 1973w, 1949w cm^{-1}. ^{31}P NMR (C_6D_6, 202.48 MHz) δ 14.8 (ddd, $Ph_2P^1CH_2$, $^2J_{P1P3}$ 163, $^2J_{P1P2}$ 73, $^2J_{P1P4}$ 18 Hz), 30.0 ($Ph_2P^2CH_2$, $^2J_{P2P3}$ 22, $^2J_{P2P4}$ 5 Hz), 111.2 [ddd, $P^3(Bu^t)(CCO)$, $^2J_{P3P4}$ 172 Hz], 236.8 [ddd, $P^4(Bu^t)(CCO)$].

‡ *Crystal/refinement data* for **2**: $C_{44}H_{40}O_9P_4Ru_3$, $M = 1139.9$, monoclinic, space group $P2_1/c$, $a = 15.001(5)$, $b = 17.930(4)$, $c = 20.131(6)$ Å, $\beta = 116.43(3)$°, $U = 4849$ Å^3, D_c ($Z = 4$) 1.56 g cm^{-3}, 4727 independent, absorption corrected, 'observed' [$I > 3\sigma(I)$], diffractometer data being refined by full-matrix least squares to $R = 0.035$, $R_w = 0.030$ (statistical weights). Monochromatic Mo-Kα radiation, $\lambda = 0.710\,7_3$ Å, $T = 295$ K; anisotropic thermal parameter refinement for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ included constrained. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/333.

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