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Preliminary communication

Cluster bound phosphinovinylidenes and phosphinitovinylidenes from alkynylphosphines and their oxides: synthesis and structures of $[Ru_3(CO)_9\{\mu_3\text{-}\sigma,\sigma,\eta^3\text{-}C{=}\overline{CCHMe_2(P}Ph_2)\}]$ and $[Fe_3(CO)_9\{\mu_3\text{-}\sigma,\sigma,\eta^3\text{-}C{=}\overline{CCHMe_2(Ph_2PO}\mathrm{)}\}]$

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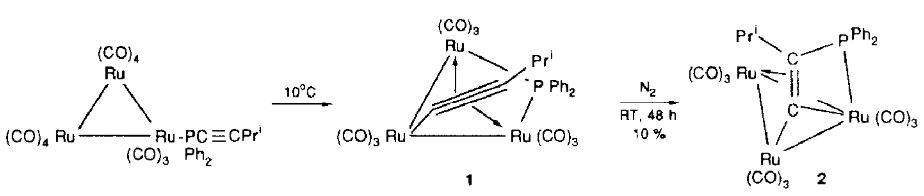
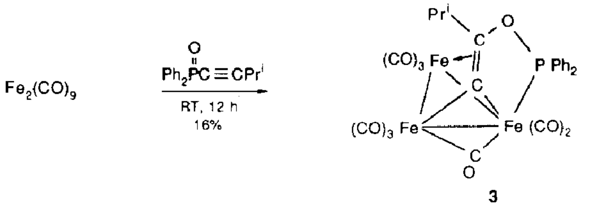
Abstract

The alkynylphosphine $Ph_2PC{\equiv}CCHMe_2$ can be converted via the phosphido-acetylide complex $Ru_3(CO)_9\{\mu_3\text{-}\sigma,\eta^2\text{-}C{\equiv}\underline{C(CHMe_2)}\}(\mu\text{-}PPh_2)$ to the isomeric vinylidene cluster $[Ru_3(CO)_9\{\mu_3\text{-}\sigma,\sigma,\eta^3\text{-}C{=}\overline{CCHMe_2(P}Ph_2)\}]$ whose structure has been determined by X-ray analysis; the oxide $Ph_2P(O)C{\equiv}CCHMe_2$ with $Fe_2(CO)_9$ afforded a structurally related cluster $[Fe_3(CO)_9\{\mu_3\text{-}\sigma,\sigma,\eta^3\text{-}C{=}\overline{CCHMe_2(Ph_2PO}\mathrm{)}\}]$.

Vinylidenes (:C=CRR′) are valence isomers of acetylenes RC≡CR′ and the interrelationships between these two carbon ligands in organometallic chemistry are the focus of current attention [1,2]. Coordinated terminal alkynes have been converted to vinylidenes [2] and in some cases hydrido acetylides have been implicated as intermediates [2a,b]. There are however few examples in the literature [1,3] of the facile conversion of a disubstituted acetylene to a coordinated vinylidene, in large part because such a transformation requires the activation of a normally strong $R{-}C_{sp}$ bond. We report herein two new examples of acetylene–vinylidene transformations involving the net conversion of the phosphinoalkyne $Ph_2PC{\equiv}CCHMe_2$ and its oxide $Ph_2P(O)C{\equiv}CCHMe_2$ to coordinated 6-electron vinylidene ligands, $[C{=}CCHMe_2(PPh_2)]$ and $[C{=}CCHMe_2(Ph_2PO)]$ via reactions with iron group carbonyls. Cluster bound μ_3- and μ_4-vinylidenes are still uncommon [4] although chemistry at binuclear centres is now undergoing extensive investigation [5].

The μ-phosphido, μ-acetylide complex $Ru_3(CO)_9\{\mu_3\text{-}\sigma,\eta^2\text{-}C{\equiv}CCHMe_2\}(\mu\text{-}PPh_2)$ (**1**) [6] is the major product of $P{-}C_{sp}$ bond cleavage at 283 K in the coordinated phosphinoalkyne complex $Ru_3(CO)_{11}(Ph_2PC{\equiv}CCHMe_2)$. Passage of a stream of N_2





through a solution of **1** (0.5 g, 0.62 mmol) in toluene (20 ml) and hexane (80 ml) for 48 h at 297 K followed by chromatography on Florisil (hexane eluant) gave a trace of $Ru_3(CO)_{12}$, pale yellow $Ru_2(CO)_6(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CCHMe_2)(\mu\text{-}PPh_2)$ followed by a greenish-brown band of **2** * (10%) and subsequently (heptane/benzene eluant) blue, green and red bands of products characterised elsewhere [6,7]. The binuclear product is apparently not the precursor of **2** since reaction of $Ru_3(CO)_{12}$ with $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CCHMe_2)(\mu\text{-}PPh_2)$ does not give the trinuclear species. In contrast with the behaviour of $Ph_2PC{\equiv}CCHMe_2$ with $Fe_2(CO)_9$ which yields predominantly mono and binuclear products, reaction of $Ph_2P(O)C{\equiv}CCHMe_2$ (0.5 g, 1.86 mmol) with $Fe_2(CO)_9$ (2 equiv) in C_6H_6 (30 ml) under N_2 for 12 h at 297 K gave phosphinitovinylidene complex **3**. Column chromatography (eluant hexane) afforded brown-green **3** * (16%), followed (eluant benzene) by a red band of $Fe_2(CO)_6\{\mu\text{-}\sigma,\eta^4\text{-}Ph_2P(O)CH{=}C{=}CMe_2\}$ [8].

Crystals of **2** were grown from pentane and of **3** from hexane/toluene **. The molecular structures of **2** and **3** are illustrated in Figs. 1 and 2. In both molecules a two-carbon vinylidene unit is coordinated on the face of a closed M_3 triangle with the α-carbon atom C(10) interacting asymmetrically with all three metals and the double bond (C(10)–C(11) 1.408(7) Å in **2**; 1.388(5) Å in **3**) η^2-bound to M(2).

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* Selected spectroscopic data for **2**: ν(CO) (C_6H_{12}) 2079s, 2042vs, 2030vs, 2010s, 1994m, 1988m, 1982m, 1968w; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −70.9 (s); ^1H (C_6D_6) 7.6, 7.1 (m, 10H, Ph), 2.3 (dh, J(P–H) 16.7, J(H–H) 6.7 Hz, 1H, $CHMe_2$), 1.0 (d, J 6.7 Hz, 3H, $CHMe_2$), 0.8 (d, J 6.7 Hz, 3H, $CHMe_2$); $^{13}C\{^1H\}$ ($CDCl_3$) (297 K); 254.9(d, ^2J(P–C) 26.1 Hz, C_α); 196.2 (d, ^2J(P–C) 3.2 Hz, CO); 137.7 (d, ^1J(P–C) 39.2 Hz, C_i); 133.9 (d, ^2J(P–C) 11.7 Hz, C_o'); 131.8 (d, ^2J(P–C) 11.0 Hz, C_o); 131.8 (d, ^4J(P–C) 2.9 Hz, C_p); 130.4 (d, J(P–C) 2.9 Hz, C_p'); 128.8 (d, ^3J(P–C) 4.6 Hz, C_m); 128.5 (d, ^3J(P–C) 5.9 Hz, C_m'); 127.9 (d, ^1J(P–C) 42.9 Hz, C_i'); 100.3 (d, ^1J(P–C) 33.5 Hz, C_β); 38.6 (s, $\mathit{C}H_3$); 24.9 (s, $\mathit{C}H_3'$); 20.9 (d, ^2J(P–C) 5.7 Hz, $\mathit{C}HMe_2$). {253 K, CO region, 202.3 (s); 201.3 (d, ^2J(P–C) 56.3 Hz); 199.7 (s); 197.3 (s); 196.7 (s, 2 CO); 196.1 (d, ^2J(P–C) 29.8 Hz); 192.6 (s); 188.2 (s)}.

Compound **3**: ν(CO) (C_6H_{12}) 2068m, 2024vs, 2008s, 1998m, 1976m, 1958w, 1902w br; $^{31}P\{^1H\}$ NMR (C_6D_6) δ +177.9 (s); ^1H ($CDCl_3$) 7.3–7.6 (m, 10H, Ph); 2.6 (h, J(H–H) 6.7 Hz, 1H, $CHMe_2$), 1.3 (d, J(H–H) 6.7 Hz, 6H, $CHMe_2$); $^{13}C\{^1H\}$ (C_6D_6) 264.2 (d, ^2J(P–C) 15.8 Hz, C_α); 210.9 (s, CO); 145.4 (d, ^1J(P–C) 4.1 Hz, C_β); 132.5–127.8 (7 peaks, C-Ph); 39.9 (d), ^2J(P–C) 9.9 Hz, $\mathit{C}HMe_2$); 21.9 (s, $CH\mathit{Me}_2$).

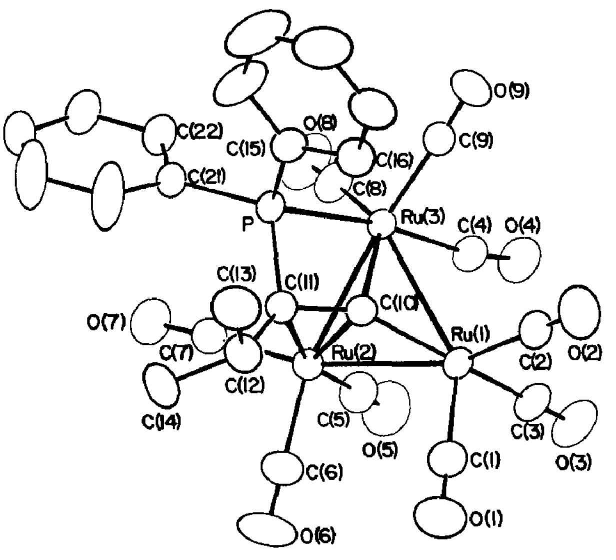

Fig. 1. An ORTEP II plot of the molecular structure of $[Ru_3(CO)_9\{\mu_3\text{-}\sigma,\sigma,\eta^3\text{-C=CCHMe}_2(PPh_2)\}]$ (**2**), showing the atomic numbering. Important bond lengths (Å) and angles (°) not mentioned in the text include: Ru(1)–Ru(2) 2.8007(6), Ru(1)–Ru(3) 2.9140(6), Ru(2)–C(10) 2.126(5), Ru(2)-C(11) 2.340(5), Ru(3)–C(10) 2.182(5), Ru(3)–P 2.375(1), P–C(11) 1.809(5); Ru(1)–Ru(2)–Ru(3) 63.54(1), Ru(1)–Ru(3)–Ru(2) 59.36(1), Ru(2)–Ru(1)–Ru(3) 57.11(1), Ru(1)–C(10)–Ru(3) 90.3(1), Ru(3)–P–C(11) 88.5(1), P–C(11)–C(10) 93.6(2), Ru(3)–C(10)–C(11) 108.5(2), P–Ru(3)–C(10) 62.2(1), C(10)–C(11)–C(12) 126.5(3), Ru(2)–C(10)–Ru(3) 78.7(1).

Complexes **2** and **3** are thus members of a small class of clusters [4a,e,f,h] in which a vinylidene fragment is μ_3-σ,σ,η^2-bound on a triangular face.

The β-carbon atom of the vinylidene group is attached to a diphenylphosphino ligand which functions as a 2-electron donor to Ru(3) in **2** thus forming a strained 4-membered $\overline{\text{Ru(2)–Ru(3)–P–C(11)}}$ ring. In **3** the substituent attached to C(11) is a Ph_2PO group giving a 5-membered $\overline{\text{Fe(2)-Fe(3)-P-O-C(11)}}$ ring. The smaller ring size in **2** results in a distortion of the metal triangle with the Ru(2)–Ru(3) distance (2.7332(5) Å) 0.12 Å shorter than the average of the two remaining bond lengths. A correspondingly greater degree of asymmetry is apparent in the M–C(10) distances

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** *Crystal data for 2*: $C_{26}H_{17}O_9PRu_3$, $M = 807.60$, triclinic, space group $P\bar{1}$, a 8.772(1), b 11.129(1), c 15.706(2) Å, α 80.34(1), β 75.84(1), γ 78.19(1)°, U 1443.9(4) $Å^3$, $Z = 2$, D_c 1.857 g cm^{-3}, $F(000) = 784$, graphite-monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 16.17 cm^{-1}. Intensity data were collected on a Syntex $P2_1$ diffractometer at 294 ± 1 K (θ–2θ scans out to $2\theta = 50°$). Structure solution (Patterson, Fourier methods) and least-squares refinement (full matrix) based on 4381 observed ($I > 3\sigma(I)$) intensities gave R and R_w values of 0.033 and 0.040 respectively.

Crystal data for 3: $C_{26}H_{17}Fe_3PO_{10}$, $M = 687.93$, monoclinic, space group $P2_1/n$, a 9.848(1), b 18.890(3), c 15.317(1) Å, β 96.03(1)°, U 2833.6(6) $Å^3$, $Z = 4$, D_c 1.612 g cm^{-3}, $F(000) = 1384$, graphite monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 16.66 cm^{-1}, Syntex $P2_1$ diffractometer (294 ± 1 K, θ–2θ scans out to $2\theta > 45°$). The intensities of 2878 observed ($I > 3\sigma(I)$) reflections were used to solve (heavy-atom methods) and refine (full matrix, all non-hydrogen atoms anisotropic) the structure to R and R_w values of 0.026 and 0.029.

The atomic coordinates (Tables I and II), thermal parameters (Tables III and IV) and full listings of bond lengths and angles (Tables V and VI) for **2** and **3** are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation.

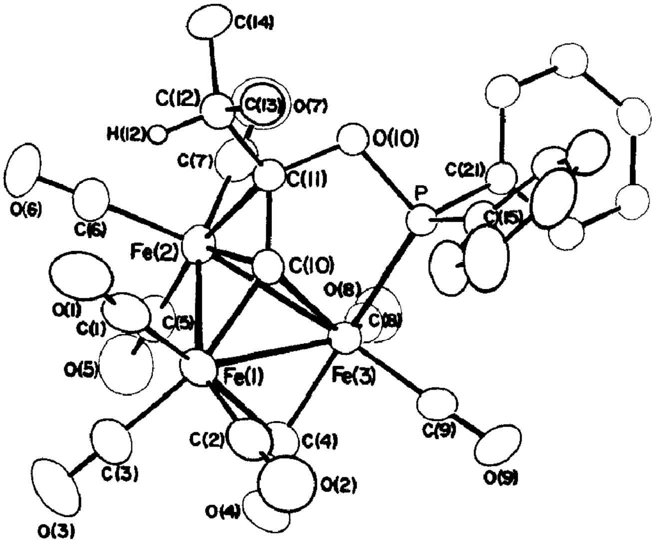

Fig. 2. A perspective view of the structure of [$Fe_3(CO)_9\{\mu_3$-σ,σ,η^3-C=CCHMe$_2$(Ph$_2$PO)$\}$] (3). Important bond lengths (Å) and angles (°) are: Fe(1)–Fe(2) 2.6096(8), Fe(1)–Fe(3) 2.5862(7), Fe(2)–Fe(3) 2.6186(7), Fe(2)–C(10) 1.982(3), Fe(2)–C(11) 2.230(3), Fe(3)–C(10) 1.945(3), Fe(3)–P 2.1954(9), P–O(10) 1.631(2), C(11)–O(10) 1.429(4); Fe(1)–Fe(2)–Fe(3) 59.29(1), Fe(1)–Fe(3)–Fe(2) 60.18(1), Fe(2)–Fe(1)–Fe(3) 60.53(1), Fe(1)–C(10)–Fe(3) 85.8(1), Fe(3)–P–O(10) 108.07(7), P–O(10)–C(11) 106.5(1), C(10)–C(11)–O(10) 113.7(1), Fe(3)–C(10)–C(11) 123.1(1), P–Fe(3)–C(10) 73.1(1), C(10)–C(11)–C(12) 130.2(2), Fe(2)–C(10)–Fe(3) 83.7(1).

in **2** but in both complexes the shortest metal–vinylidene interaction is M(1)–C(10) (1.921(5) Å in **2**, 1.853(3) Å in **3**). Although both molecules are 48-electron species, on a localised electron count basis M(3) has 19 electrons and M(1) 17 electrons suggesting a donor–acceptor bond from M(3) to M(1). In fact a carbonyl group C(4)–O(4) in **2** which interacts only very weakly, if at all, with Ru(1) (Ru(3)–C(4)–O(4) 167.9(2)°; Ru(1)— — —C(4) 2.881(7) Å) becomes distinctly semi-bridging in **3** (Fe(3)–C(4)–O(4) 155.2(2)°; Fe(1)— — —C(4) 2.291(4) Å).

The synthesis of **3** from $Ph_2P(O)C{\equiv}CCHMe_2$ and $Fe_2(CO)_9$ effectively involves isomerisation of the disubstituted alkyne to the vinylidene [C=CCHMe$_2$(Ph$_2$PO)]. For **2** the overall transformation is similar but the cluster $Ru_3(CO)_9(\mu_3$-σ,η^2-$C{\equiv}CCHMe_2)(\mu$-$PPh_2)$ is an intermediate. Since μ-phosphido, μ-acetylide complexes are products of oxidative insertion into the P–C_{sp} bonds of phosphinoalkynes it is likely that the $Ph_2PC{\equiv}CR$ to C=C(R)PPh$_2$ isomerisation occurs via an oxidative addition-reductive intramolecular coupling mechanism. We are currently examining the potential of other heteroatom functionalised acetylenes for access to polynuclear vinylidene complexes.

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References

1 (a) M.I. Bruce and A.G. Swincer, Adv. Organomet. Chem., 22 (1983) 59; (b) J. Holton, M.F. Lappert, R. Pearce and P.I.W. Yarrow, Chem. Rev., 83 (1983) 135.

2 (a) J. Wolf, H. Werner, O. Serhadli and M.L. Ziegler, Angew. Chem. Int. Ed. Engl., 22 (1983) 414; (b) F.J.G. Alonso, A. Hohn, J. Wolf, H. Otto and H. Werner, Angew. Chem. Int. Ed. Engl., 24 (1985) 406; (c) W. Bernhardt and H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 23 (1984) 141; (d) J.G. Jeffrey, B.F.G. Johnson, J. Lewis, P.R. Raithby and D.A. Welch, J. Chem. Soc., Chem. Commun., (1986) 318; (e) A.J.L. Pombeiro, J.C. Jeffery, C.J. Pickett and R.L. Richards, J. Organomet. Chem., 277 (1984) C7; (f) K.R. Birdwhistell, S.J. Nieter Burgmayer and J.L. Templeton, J. Am. Chem. Soc., 105 (1983) 7789.

3 (a) I.T. Horvath, G. Palyi, L. Marko and G.D. Andreetti, Inorg. Chem., 22 (1983) 1049; (b) A.B. Antonova, N.E. Kolobova, P.V. Petrovsky, B.V. Lokshin and N.S. Obezyuk, J. Organomet. Chem., 137 (1977) 55.

4 (a) A.J. Deeming, S. Hasso and M. Underhill, J. Chem. Soc., Dalton Trans., (1975) 1614; (b) A.J. Carty, S.A. MacLaughlin and N.J. Taylor, J. Chem. Soc., Chem. Commun., (1981) 476; (c) P. Brun, G.M. Dawkins, M. Green, R.M. Mills, J.Y. Salaun, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1981) 966; (d) A.J. Carty, N.J. Taylor, E. Sappa and A. Tiripicchio, Inorg. Chem., 22 (1983) 1871; (e) C.J. Cooksey, A.J. Deeming and I.P. Rothwell, J. Chem. Soc., Dalton Trans., (1981) 1718; (f) S. Aime, A.J. Deeming, M.B. Hursthouse and J.D.J. Backer-Dirks, J. Chem. Soc., Dalton Trans., (1982) 1625; (g) R.D. Adams and S. Wang, Organometallics, 4 (1985) 1902; (h) E. Roland, W. Bernhardt and H. Vahrenkamp, Chem. Ber., 118 (1985) 2858.

5 (a) S.F.T. Froom, M. Green, R.J. Mercer, K.R. Nagle, A.G. Orpen and S. Schwiegk, J. Chem. Soc., Chem. Commun., (1986) 1666; (b) N.M. Doherty, M.J. Fildes, N.J. Forrow, S.A.R. Knox, K.A. Macpherson and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1986) 1355; (c) R.J. Mercer, M. Green and A.G. Orpen, J. Chem. Commun., (1986) 567; (d) H. Werner, J. Wolf, G. Muller and C. Kruger, Angew. Chem. Int. Ed. Engl., 23 (1984) 431; (e) D.H. Berry and R. Eisenberg, J. Am. Chem. Soc., 107 (1985) 7181; (f) S.P. Deraniyagala and K.R. Grundy, Organometallics, 4 (1985) 424.

6 A.J. Carty, S.A. MacLaughlin and N.J. Taylor, J. Organomet. Chem., 204 (1981) C27.

7 (a) S.A. MacLaughlin, N.J. Taylor and A.J. Carty, Organometallics, 2 (1983) 1194; (b) A.A. Cherkas, S.A. MacLaughlin, L.H. Randall, G.N. Mott, N.J. Taylor and A.J. Carty, Organometallics, 7 (1988) 696.

8 D.E. Fogg, W.F. Smith and A.J. Carty, to be published.