Tris(alkynyl)phosphines $(RC{\equiv}C)_3P$ as a Source of Functionalized Phosphido and Phosphinidene Clusters: A Complete Triad of $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)\{\mu_2\text{-}P(C{\equiv}CBu^t)_2\}]$ Complexes and the X-Ray Structure of a Novel Square-planar Alkynylphosphinidene Cluster $[Ru_4(CO)_{10}(\mu_4\text{-}\eta^4\text{-}Bu^tC{\equiv}C\text{-}C{\equiv}CBu^t)\{\mu_4\text{-}P(C{\equiv}CBu^t)\}]$

Bradley J. Bobbie, Nicholas J. Taylor and Arthur J. Carty*

Guelph-Waterloo Center for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Polyunsaturated, alkynyl functionalized phosphido and phosphinidene clusters are readily accessible from tris(alkynyl)phosphines $(RC{\equiv}C)_3P$: a complete triad of isostructural clusters $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)\{\mu_2\text{-}P(C{\equiv}CBu^t)_2\}]$ (M = Fe, Ru, Os) and a novel square-planar alkynylphosphinidene cluster $[Ru_4(CO)_{10}(\mu_4\text{-}\eta^4\text{-}Bu^tC{\equiv}C\text{–}C{\equiv}CBu^t)\{\mu_4\text{-}P(C{\equiv}CBu^t)\}]$ have been structurally characterized.

The polyunsaturated phosphines $P(C{\equiv}CR)_3$ are potentially valuable precursors to a family of phosphido and phosphinidene complexes bearing pendent alkynyl groups and strongly bound edge- or face-bridging μ-PR_2 or μ-PR ligands. Such functionality is useful for the incorporation of polymetallic fragments into macromolecules.[1] In this communication we describe the facile synthesis of $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)\{\mu_2\text{-}P(C{\equiv}CBu^t)_2\}]$ [M = Fe, **1**; M = Ru, **2**; M = Os, **3** under mild conditions from $[M_3(CO)_{12}]$ and $P(C{\equiv}CBu^t)_3$ and the conversion of **2** to the novel alkynylphosphinidene cluster

$[Ru_4(CO)_{10}(\mu_4$-η^4-Bu^{t}C≡CC≡CBu^t){μ_4-P(C≡CBu^t)}] **4**. The square-planar cluster **4** is the first example, to our knowledge, where an eight-electron donor diacetylene, formed by linking two acetylides, is bound to a single square face.

The trinuclear clusters **1–3** were obtained in high yields from the monosubstituted carbonyl compounds $[M_3(CO)_{11}$P-(C≡CBu$^t)_3]$ as follows: **1**, hexane, 50 °C, 30 min, 94%; **2**, tetrahydrofuran (THF), 60 °C, 1 h, 97%; **3**, toluene, 110 °C, 24 h, 62%. The structures of these molecules were determined by IR, ^{31}P and ^{13}C NMR spectroscopy,† and for **1** by a single-crystal X-ray diffraction experiment.‡ The molecular structure of **1** is illustrated in Fig. 1. The three unsaturated hydrocarbyl units are inequivalent: one acetylide bound to the Fe_3 triangle, as a five-electron donor, has a remarkably short carbene-like Fe (3)–C(10) bond (1.824 Å); the other two alkynyl groups on the phosphorus atom have *syn*- and *anti*-orientation with respect to the M_3 triangle. Relatively few μ_3-η^2-acetylides of the iron group are known[2] and a complete series of isostructural molecules such as **1–3** has not yet been reported. The facility with which P–C$_{sp}$ bonds can be cleaved has been noted,[3] but the essentially quantitative conversion of a tertiary phosphine to a phosphido ligand as in Scheme 1 is without precedent. An interesting feature of the ^{31}P{^{1}H} NMR spectra of **1–3** is the high-field ^{31}P chemical shifts [δ ^{31}P{^{1}H}, **1** −125.2; **2** −178.1; **3** −278.5 relative to 85% H_3PO_4]. These values, while consistent with the presence of a μ-phosphido group bridging an open metal–metal edge, are more than 100 ppm upfield of the corresponding μ-PPh$_2$ shifts indicating a substantial shielding effect at the phosphorus by the alkynyl groups.

Removal of a second alkynyl group from phosphorus and conversion of **2** to the phosphinidene cluster $[Ru_4(CO)_{10}(\mu_4$-η^4-Bu^{t}C≡C–C≡CBu^t){μ_4-P(C≡CBu^t)}] **4** was accomplished by refluxing **2** in *o*-xylene for 18 h, followed by column chromatography on Florisil. The first band eluted afforded red crystals of **4** in 31% yield.§ The low-field ^{31}P{^{1}H} shift (δ 216.5) indicated the presence of an alkynylphosphinidene group, the first of its kind to be reported. A single-crystal X-ray analysis‡ revealed the structure illustrated in Fig. 2.

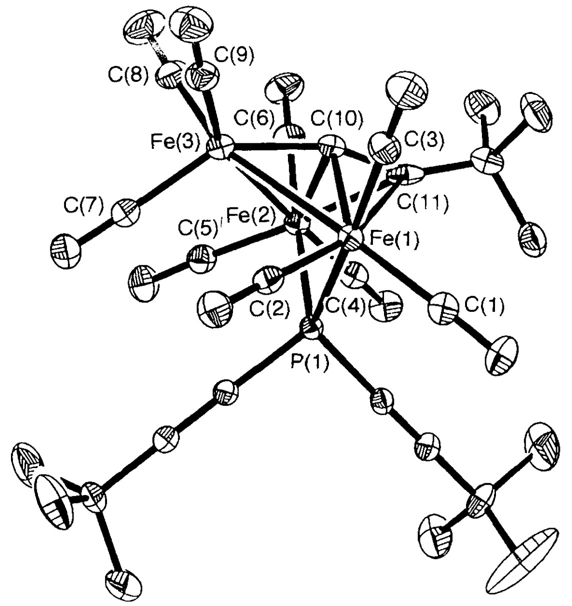
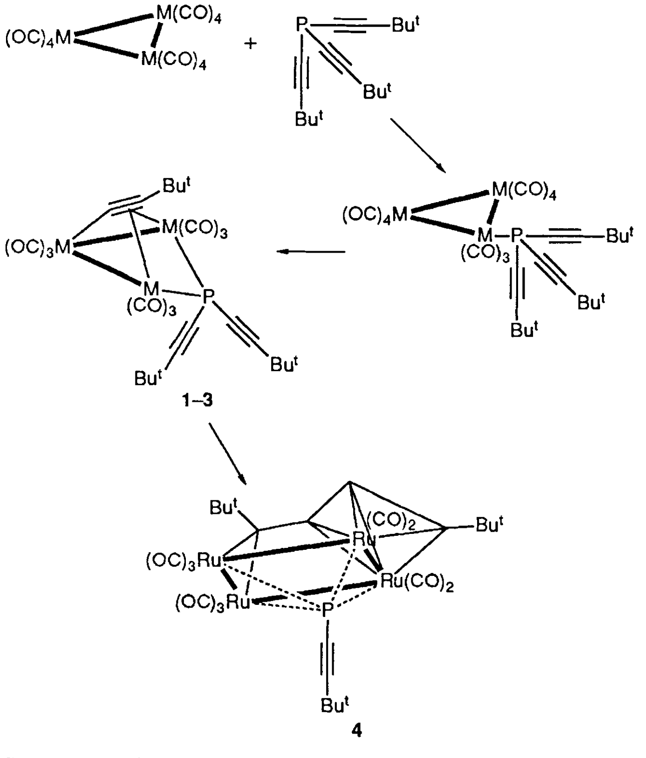


Fig. 1 A perspective view of the molecular structure of **1** showing the atomic numbering



Scheme 1 The synthesis of the $[M_3(CO)_9(\mu_3$-η^2-C≡CBu^t){μ_2-P(C≡CBu$^t)_2$}]{(M = Fe, Ru, Os) complexes from their parent carbonyls $[M_3(CO)_{12}]$ and P(C≡CBu$^t)_3$

---

† Selected spectroscopic data for **1**: IR (C_6H_{12}): ν/cm^{-1} 2208br, 2163br ν(C≡C); 2076m, 2044vs, 2035w, 2024s, 2006s, 1991m, 1975m, 1970w, ν(CO); NMR, ^{31}P{^{1}H} δ −125.2; ^{13}C{^{1}H} 146.7 [d, C(10), J_{PC} 10.2 Hz], 114.9 [d, C(17 or 23), J_{PC} 5.4 Hz], 110.2 [d, C(17 or 23), J_{PC} 3.3 Hz], 78.4 [d, C(16 or 22), J_{PC} 73.0 Hz], 74.5 [d, C(16 or 22), J_{PC} 79.0] and 74.2 [d, C(11), J_{PC} 13 Hz]. **2**: IR (C_6H_{12}): ν/cm^{-1} 2210vw, 2165br ν(C≡C); 2084w, 2062vs, 2041s, 2014vs, 2003m, 1981w, 1978w, ν(CO). NMR, ^{31}P{^{1}H} δ −178.1; ^{113}C{^{1}H} 134.5 [d, C(10), J_{PC} 9.6 Hz], 112.5 [d, C(17 or 23), J_{PC} 10.8 Hz], 107.0 [d, C(17 or 23), J_{PC} 7.9 Hz], 79.6 [d, C(16 or 22), J_{PC} 68.2 Hz] and 75.1 [d, C(16 or 22), J_{PC} 91 Hz]; **3**: IR (C_6H_{12}): ν/cm^{-1} 2210vw, 2164br ν(C≡C); 2086w, 2062vs, 2041s, 2008vs, 1997m, 1979m, 1971vw, ν(CO); NMR, ^{31}P{^{1}H} δ −278.5 s; ^{13}C{^{1}H} 116.5 [d, C(10), J_{PC} 14.5 Hz], 111.2 [d, C(17 or 23), J_{PC} 13.0 Hz], 107.0 [d, C(17 or 23), J_{PC} 10.9 Hz], 77.2 [d, C(16 or 22), J_{PC} 131.5 Hz], 73.5 [d, C(16 or 22), J_{PC} 137.5 Hz] and 65.1 [d, C(11), J_{PC} 7.4 Hz].

‡ *Crystal data* for **1**: red plates from hexane; $C_{27}H_{27}Fe_3O_9P$, M = 694.0; monoclinic, space group $P2_1/n$, a = 11.529(1), b = 18.992(2), c = 14.684(2) Å, β = 100.05(1)°, U = 3166.0(6) Å^3, Z = 4, D_c = 1.456 g cm^{-3}, F(000) = 1416. The structure was solved (Patterson, Fourier methods) and refined (full-matrix least-squares, all non-hydrogen atoms anisotropic) on the basis of 5428 observed [$F > 6.0\sigma(F)$] reflections measured at 180 K using Mo-Kα (λ = 0.71073 Å) radiation on a Nicolet R3m/V diffractometer. The final R and R_w values were 0.0499 and 0.0534 respectively.

Crystal data for **4**: dark-red prism from hexane; $C_{28}H_{27}O_{10}PRu_4$, M = 958.77; monoclinic, space group $P2_1/n$, a = 17.610(3), b = 11.168(2), c = 18.209 Å, β = 107.99(1)°, U = 3406.0(9) Å^3, Z = 4, D_c = 1.870 g cm^{-3} F(000) = 1864. The structure was solved (Patterson, Fourier methods) and refined (full-matrix least-squares, all non-hydrogen atoms anisotropic) on the basis of 4470 observed [$I > 3.0\sigma(I)$] reflections measured at 298 K using Mo-Kα (λ = 0.71073 Å) radiation on a Nicolet R3m/V diffractometer. The final R and R_w values were 0.031 and 0.038 respectively.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Selected spectroscopic data for **4**: IR (C_6H_{12}): ν/cm^{-1} 2211vw, 2164br, ν(C≡C); 2077w, 2052s, 2023s, 2012s, 2010s, 1968w, ν(CO); NMR ^{31}P{^{1}H}, 216.5s; ^{13}C{^{1}H}, 154.6 [d, C(12) or C(18), J_{PC} 13.6 Hz], 135.5 [d, C(12) or C(18), J_{PC} 5.1 Hz], 95.0 [d, C(24), J_{PC} 3.9 Hz], 79.6 [d, C(23), J_{PC} 63.8 Hz], 79.5 [d, C(11) or C(17), J_{PC} 5.6 Hz], 42.1 [s, C(13) or C(19)], 37.5 [s, C(13) or C(19)] and 4.18 [d, C(11) or C(17), J_{PC} 18.8 Hz].

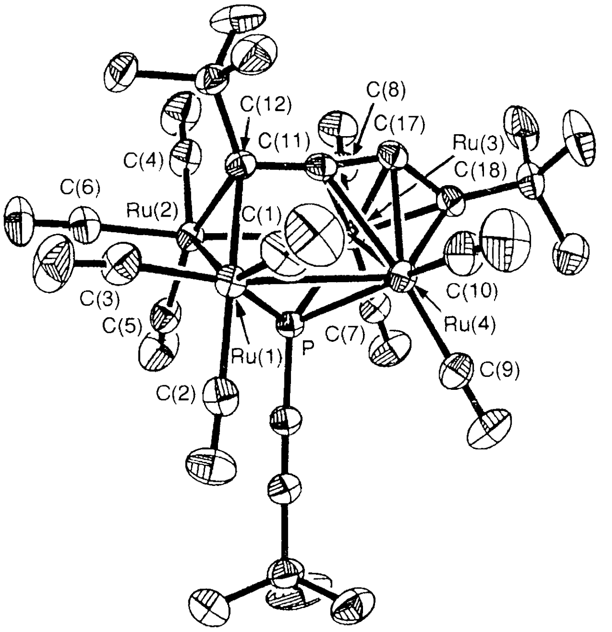


Fig. 2 An ORTEP drawing of the molecular structure of **4** showing the atomic numbering

The cluster consists of an approximately square planar-array of four ruthenium atoms bridged on one face by a capping μ_4-P(C$\equiv$CBu^t) ligand and on the other by a diacetylene, Bu^{t}C$\equiv$C–C$\equiv$CBu^t, derived from the tail-to-tail coupling of two acetylide groups. The shortest Ru–Ru bond [Ru(3)–Ru(4) 2.6673(5) Å] is between the two metal atoms bound to the three carbon atoms C(11), C(17) and C(18) of the diacetylene unit. The opposite edge of the Ru$_4$ framework [Ru(1)–Ru(2) 2.8291(6) Å] is bound only to C(12) of the diacetylene. The remaining Ru–Ru bond distances [Ru(2)–Ru(3) 2.9481(6) Å and Ru(1)–Ru(4) 3.0034(6) Å] are somewhat elongated and approach the Ru–Ru bond lengths in some electron-rich planar Ru$_4$ systems.[4] Of particular interest is the bonding mode of the diacetylene. Although complexes containing diacetylenes are known,[5] there are no examples where all four alkyne carbon atoms interact with a single M$_4$ face as an eight-electron donor. The stereochemistry of the nonlinear C$_6$ fragment is best described as *cis,trans* about the two formal triple bonds C(11)–C(12) and C(17)–C(18), but the bond lengths within the C(12)–C(11)–C(17)–C(18) unit [C(11)–C(12) 1.417(7), C(11)–C(17) 1.304, C(17)–C(18) 1.400(8) Å] suggest that the central C(11)–C(17) bond exhibits the greatest multiple bond character. These bond lengths contrast sharply with values in the free diacetylene [–C$\equiv$C– 1.272(4); $\equiv$C–C$\equiv$ 1.421(4) Å] indicating that in **4** the alkyne carbon atoms have undergone considerable rehybridization. A description of **4** as a bis(alkylidyne) dicarbide cluster is not inappropriate.

Although many bis(acetylide) cluster complexes are known,[6] examples of the coupling of two acetylide fragments to generate a dialkyne are rare. One of the few instances is the conversion of [{(η^5-C$_5$H$_4$Me)$_2$Ti(C$\equiv$CPh)}$_2$] to [{(η^5-C$_5$H$_4$Me)Ti}$_2$(PhC$\equiv$C–C$\equiv$CPh)].[7] Molecular orbital calculations[8] suggest that such coupling may be facilitated by bending of the bridging acetylides from linearity, causing –C$\equiv$C– bond lengthening and initiating weak interacetylide C···C interactions. In this regard coupling in bis σ–π-acetylide complexes may be particularly favourable. We are currently exploring this aspect and the generation of other alkynylphosphinidenes and phosphides from tris(alkynyl)phosphines.

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Received, 12th July 1991; Com. 1/03562B

References

1 *Inorganic and Organometallic Polymers*, ed. M. Zeldin, K. J. Wayne and H. R. Allcock, ACS Symposium Series 360, American Chemical Society, Washington, DC. 1988; *Metal Containing Polymer Systems*, ed. J. E. Sheats, C. E. Carraher, Jr. and C. U. Pittman, Jr., Plenum Press, New York, 1985.

2 A. J. Carty, N. J. Taylor, E. Sappa, A. Tiripicchio and M. Tiripicchio Camelini, *Organometallics*, 1991, **10**, 1907; D. Seyferth, J. B. Hoke, A. L. Rheingold, M. Cowie and A. D. Hunter, *Organometallics*, 1988, **7**, 2163; J. Suades, F. Dahan and R. Mathieu, *Organometallics*, 1988, **7**, 47; A. J. Deeming, M. S. Felix, P. A. Bates and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1987, 461.

3 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113.

4 G. Hogarth, N. Hadj-Bagheri, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1990, 1352; G. Hogarth, J. A. Phillips, F. van Gastel, N. J. Taylor, T. B. Marder and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1988, 1570.

5 W. Bonrath, K. R. Roschke, G. Wilke, K. Angermund and C. Kruger, *Angew. Chem.*, 1988, **100**, 853.

6 A. A. Cherkas, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1990, 394.

7 D. G. Sekutowski and G. D. Stucky, *J. Am. Chem. Soc.*, 1976, **98**, 1376.

8 P. N. Pavan-Kumar and E. D. Jemmis, *J. Am. Chem. Soc.*, 1988, **110**, 125.