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Preliminary Communication

A new route to complexes containing the tetracarbon (C_4) ligand

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Abstract

Pyrolysis of a solution of $\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})$ (bdpp = bis(diphenylphosphino)butadiyne) yielded the complex $\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_6\text{-}C_4)$, which contains a μ_6-C_4 ligand symmetrically bridging two $Ru_3(\mu\text{-}PPh_2)(CO)_9$ clusters. When the complex $\{Fe(CO)_4\}_2(\mu\text{-bdpp})$ was heated in the presence of $Fe_2(CO)_9$ another example of a C_4 complex, $\{Fe_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu\text{-}C_4)$, was obtained. Both complexes were characterised by X-ray structure determinations; the C_4 ligand behaves as a buta-1,3-diyne-1,4-diyl system.

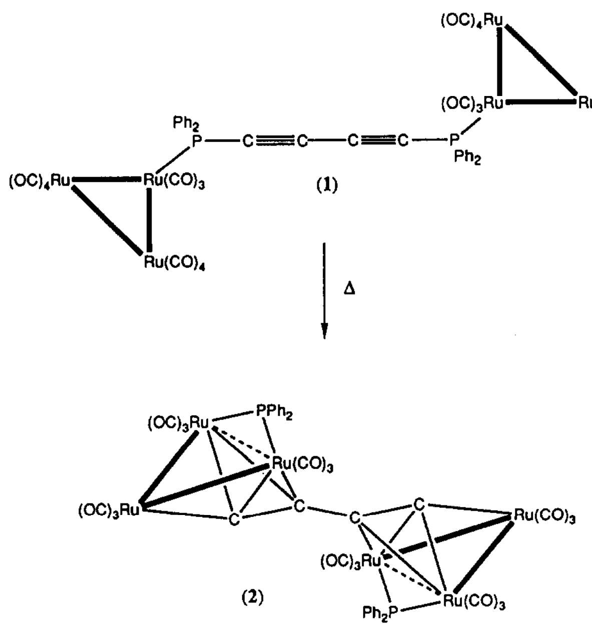
Current interest in complexes containing all-carbon ligands (C_n, $n = 1, 2, 3, \ldots, C_{60}, C_{70}$) prompts us to report a facile route to derivatives containing the tetracarbon (C_4) ligand. The C_4 ligand can, in principle, take up a number of different coordination modes, the extremes being the forms **A**, **B** and **C** illustrated below.

M-C≡C-C≡C-M (**A**) M=C=C=C=C=M (**B**) M≡C-C≡C-C≡M (**C**)

To our knowledge, apart from a few complexes containing C_4 bridging two mononuclear fragments, such as $M(CO)_2(L)(\eta\text{-}C_5H_5)$ (M = Mo, W; L = CO, PPh_3) [1], $Fe(CO)(L)(\eta\text{-}C_5H_5)$ (L = CO, PPh_3) [1], $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ [2] or $MCl(PBu_3)_2$ (M = Ni, Pd, Pt) (and related polymeric materials) [3], the only cluster complexes containing this ligand are $\{Co_3(CO)_{9-n}(L)_n\}_2(\mu_3 : \mu_3\text{-}C_4)$ (L = CO, PPh_3, PCy_3; n = 0–2) [4], which are, of course, members of the well-known $Co_3(\mu_3\text{-CR})(CO)_9$ series.

We have previously described the synthesis of complexes containing dicarbon, including $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$ [5], $Ru_5(\mu_5\text{-}C_2)(\mu\text{-SMe})_2(\mu\text{-}PPh_2)_2(CO)_n$ (n = 11 and 12) [6], and $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)(CO)_{11}(py)_2$ [7] from precursors derived from the acetylenic bis-tertiary phosphine, $C_2(PPh_2)_2$ (dppa). We have now extended this approach to the synthesis of complexes containing the C_4 ligand.

The complex $\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})$ (**1**, Scheme 1; bdpp = 1,4-bis(diphenylphosphino)buta-1,3-diyne, $PPh_2C{\equiv}CC{\equiv}CPPh_2$) was prepared by one of two methods: addition of bdpp to a solution of $Ru_3(CO)_{11}(NCMe)$ or addition of trimethylamine oxide to a solution containing a 2/1 mixture of $Ru_3(CO)_{12}$ and bdpp. In contrast to the outcome of the related reaction of $\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})$, when a solution of **1** is heated (CH_2Cl_2, reflux, 7 h) with a nitrogen purge, both C(sp)–P bonds are broken to give, as the major product, the yellow $\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3,\eta^2 : \mu_3,\eta^2\text{-}C_4)$ (**2**) [8*], obtained in good yield (*ca.* 70%). Similarly, when $\{Fe(CO)_4\}_2(\mu\text{-bdpp})$ (**3**) [9] was heated with $Fe_2(CO)_9$ (Carius tube, toluene, 100°C, 2.5 h), red $\{Fe_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu,\eta^2 : \mu,\eta^2\text{-}C_4)$ (**4**) [9] was produced in low (12%) yield. The chemistry is summarised in Schemes 1 and 2, respectively.



Scheme 1.

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

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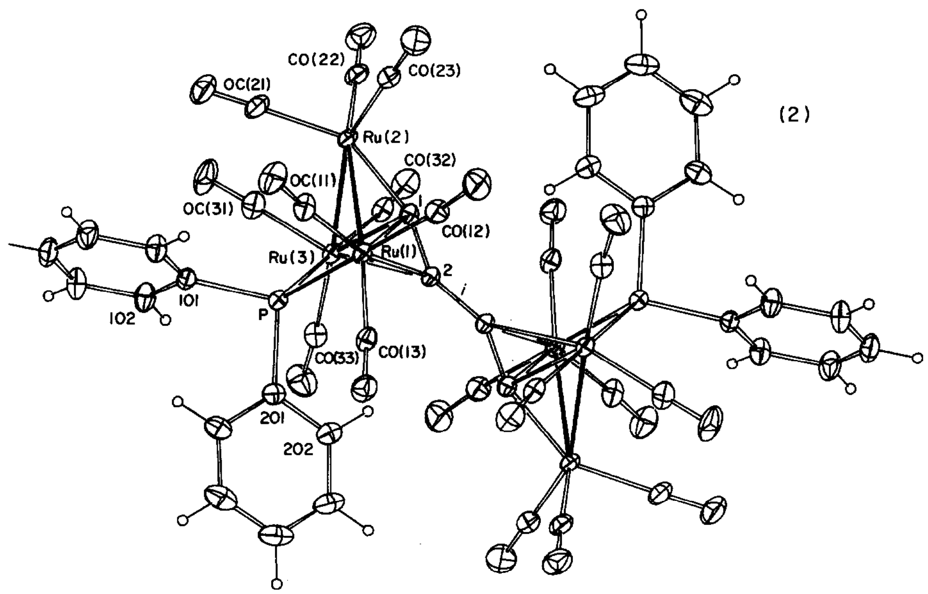


Fig. 1. Molecular structure of $\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_6\text{-}C_4)$ (2). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Bond distances (Å): Ru(1)–Ru(2) 2.841(1), Ru(2)–Ru(3) 2.846(1), Ru(1) ··· Ru(3) 3.452(1), Ru(1)–C(1) 2.277(4), Ru(1)–C(2) 2.444(4), Ru(2)–C(1) 1.936(6), Ru(3)–C(1) 2.254(4), Ru(3)–C(2) 2.450(5), Ru(1)–P 2.393(1), Ru(3)–P 2.385(1), C(1)–C(2) 1.302(9), C(2)–C(2′) 1.417(8). Bond angles (deg.): Ru(1)–Ru(2)–Ru(3) 74.74(3), Ru(2)–C(1)–C(2) 159.2(3), C(1)–C(2)–C(2′) 149.6(4).

Complexes **2** and **4** have been fully characterised by single-crystal X-ray studies [10*] and their molecular structures are shown in Figs. 1 and 2; significant bond parameters are given in the captions. As can be seen, the C_4 ligand behaves as a diacetylide, and interacts with the Ru_3 clusters in **2** in the familiar μ_3-σ, $2\pi(\perp)$ fashion. The Ru(1) ··· Ru(3) separation [3.452(1) Å] is essentially non-bonding, the geometry resembling that found in $Ru_3(\mu\text{-}PPh_2)(\mu_3\text{-}C_2{}^iPr)(CO)_9$, where the corresponding distance is 3.466(1) Å [11]. With the μ_3-C_2R ligands acting as 5e donors, both this complex and **2** are 50e clusters with only two Ru–Ru bonds.

In **4**, the $Fe_2(CO)_6$ fragments are similarly attached to the C_4 ligand in the σ,π-mode found previously in

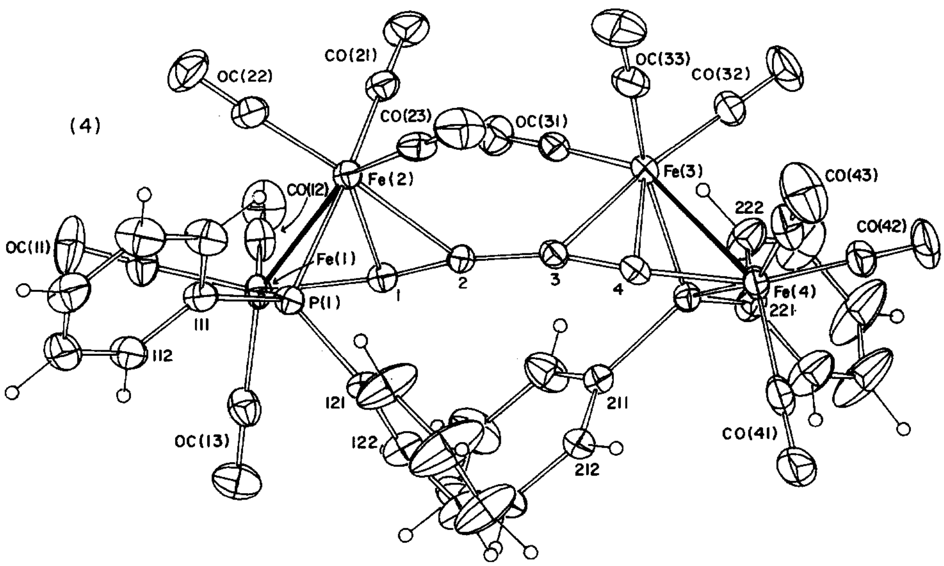
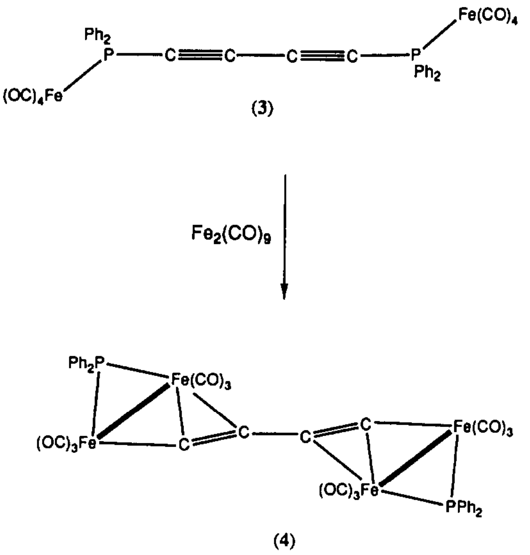


Fig. 2. Molecular structure of $\{Fe_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu_6\text{-}C_4)$ (4). Bond distances (Å): Fe(1)–Fe(2) 2.595(1), Fe(3)–Fe(4) 2.593(1), Fe(1)–C(1) 1.875(6), Fe(2)–C(1) 2.101(4), Fe(2)–C(2) 2.354(4), Fe(3)–C(3) 2.322(5), Fe(3)–C(4) 2.113(5), Fe(4)–C(4) 1.877(6), Fe(1)–P(1) 2.209(2), Fe(2)–P(1) 2.224(2), Fe(3)–P(2) 2.215(1), Fe(4)–P(2) 2.212(2), C(1)–C(2) 1.231(8), C(2)–C(3) 1.371(8), C(3)–C(4) 1.240(8). Bond angles (deg.): Fe(2)–Fe(1)–C(1) 53.1(1), Fe(1)–C(1)–C(2) 166.2(4), Fe(4)–C(4)–C(3) 161.6(5), C(1)–C(2)–C(3) 164.2(4), C(2)–C(3)–C(4) 165.8(5).



Scheme 2.

several related complexes, including $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}C_2{}^tBu)(CO)_6$ [12]. In these cases, an Fe–Fe bond is present (2.595(1) in **4**; 2.5959(6) Å in the $C_2{}^tBu$ complex [12]), the C_2R units acting as 3e donor ligands. That there is some interaction between the two C≡C units in **4** can be deduced from the central C–C distances of 1.371(8) Å; in **2**, this separation is somewhat longer [1.417(8) Å].

The likely course of these reactions has been discussed previously by Carty and coworkers [12], the initial product of the reaction between **3**, and $Fe_2(CO)_9$ probably being a cluster formed by interaction of an iron carbonyl unit with one of the C≡C triple bonds. A model for this stage is the crystallographically-characterised derivative $\{Fe(CO)_4\}_2\{\mu\text{-}P,\eta^2\text{-}PPh_2(C_2{}^tBu)\}$ [13].

The ready synthesis of these complexes makes them available for further studies of their chemical and physical properties, including in particular their propensity for forming extended cluster complexes, which we shall describe elsewhere.

Acknowledgements

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References and notes

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8 Selected spectroscopic data are as follows. For **2**: IR ν(CO) (CH_2Cl_2) 2078(sh), 2071vs, 2046m, 2024m, 2004m, 1985m cm^{-1}. FAB MS (m/z): 1530, M^+; 1502–1026, $[M-nCO]^+$ ($n=1$–18); 949, $[M-18CO-Ph]^+$. For **5**: IR: ν(CO) (cyclohexane) 2079m, 2066s, 2039vs, 2013vs, 1998(sh), 1902vs, 1977w cm^{-1}. FAB MS (m/z): 978, M^+; 950–642, $[M-nCO]^+$ ($n=1$–12).

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10 (**2**) $\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_4\text{-}C_4) \equiv C_{46}H_{20}O_{18}P_2Ru_6$, $M=$ 1529.0. Monoclinic, space group $P2_1/c$, $a=15.177(2)$, $b=$ 9.752(4), $c=19.622(7)$ Å, $\beta=121.55(2)°$, $V=2475$ Å^3, $Z=2$, ρ_c $=2.05$ g cm^{-3}. CAD4 diffractometer, $2\theta_{max}=50°$, μ(Mo Kα)= 19.2 cm^{-1}. Crystal dimensions $0.18\times0.27\times0.32$ mm. 3525 observed absorption-corrected data ($I\geq3\sigma(I)$) from 4343 data measured were refined to $R=0.028$, $R_w=0.033$ (statistical weights).
(**4**) $\{Fe_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu_6\text{-}C_4) \equiv C_{40}H_{20}Fe_4O_{12}P_2$, $M=978.0$. Triclinic, space group $P\bar{1}$, $a=16.168(4)$, $b=12.023(3)$, $c=$ 11.602(2) Å, $\alpha=94.58(2)$, $\beta=101.18(2)$, $\gamma=106.27(2)°$, $V=2102$ Å^3, $Z=2$, $\rho_c=1.55$ g cm^{-3}. CAD4 diffractometer, $2\theta_{max}=50°$, μ(Mo Kα)$=14.1$ cm^{-1}. Crystal dimensions $0.33\times0.07\times0.21$ mm. 4684 observed absorption-corrected data ($I\geq3\sigma(I)$) from 7375 data measured were refined to $R=0.041$, $R_w=0.040$ (statistical weights).
For both structures, tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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