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Unexpected formation of a "flyover-bridged" complex by reaction of a "ferrole" derivative with $Ph_2PCH_2PPh_2$ (dppm) and Me_3NO. Crystal structure of $[Fe_2(CO)_5(P\text{-dppm})\{C_2Et_2(CO)C_2Et_2\}]$

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Abstract

The reaction of the "ferrole" complex $[Fe_2(CO)_6(C_2Et_2)_2]$ with $Ph_2PCH_2PPh_2$ (dppm), in the presence of Me_3NO, affords as major product the "flyover-bridged" derivative $[Fe_2(CO)_5(P\text{-dppm})\{C_2Et_2(CO)C_2Et_2\}]$, apparently produced via CO insertion into the central carbon–carbon single bond of the original ligand. Its structure has been determined by an X-ray diffraction study. Simple CO substitution on the intact ferrole also occurs, as a minor process.

Chemically promoted displacement of a carbonyl ligand under mild conditions is much used for substitution reactions in metal carbonyl and cluster chemistry. Halide-promoted ruthenium clusters [1], and mono- or dinuclear platinum [2], nickel [3], iron [4], molybdenum [5], cobalt [6] and palladium [7] complexes have been used as promoters, and in most of these reactions there is evidence for electron transfer catalysis. Best known and more widely used are, however, the system Na/benzophenone ketyl [8] and trimethylamine *N*-oxide [9].

As a part of a study of the role of metalla-cyclopentadiene complexes as intermediates in homogeneous catalytic processes [10] we attempted CO substitution reactions on the "sawhorse-ferrole" [11] derivative $[Fe_2(CO)_6(C_2Et_2)_2]$ (1) [12,13] with PPh_2R (R = Ph or H) and Ph_2PXEPh_2 (E = P, X = CH_2, CH_2CH_2 or NH; E = As, X = CH_2), using Me_3NO as a CO-displacement promoter. Unexpectedly, in all the reactions but for those involving PPh_2H, which gave only substitution, we obtained CO-insertion derivatives, in yields similar to or higher than those of simple CO substitution products.

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Treatment of $[Fe_2(CO)_6(C_2Et_2)_2]$ (**1**) (1 g, 2.25 mmol) with $Ph_2PCH_2PPh_2$ (dppm, 0.75 g, 1.95 mmol) and Me_3NO (100 mg, 1.33 mmol) under N_2, in refluxing heptane, for 2–4 min gave a limpid cherry red solution; this was reduced to small volume *in vacuo* and purified by preparative TLC (Kieselgel P.F. Merck; diethyl ether and light petroleum 20/80 by volume as eluent) to give unchanged **1** (trace amounts), the red diferracycloheptadiene or "flyover-bridged" complex $[Fe_2(CO)_5(P\text{-dppm})\{C_2Et_2(CO)C_2Et_2\}]$ (**2**) [14*] (60%), and a red-purple band probably containing a mixture of the monosubstituted and disubstituted (chelate) "ferrole" derivatives $[Fe_2(CO)_5(P\text{-dppm})(C_2Et_2)_2]$ and $[Fe_2(CO)_4(\mu\text{-dppm})(C_2Et_2)_2]$.

The nature of **2** was fully elucidated by an X-ray diffraction study [15*]. In the structure of **2**, which is the first reported for a substituted flyover derivative (structures of some unsubstituted complexes have been previously reported [16]), the –(Et)C=CEtC(=O)CEt=C(Et)– pentadienone ligand, obtained by insertion of a CO molecule into the two C_2Et_2 alkynes, interacts with both Fe atoms, forming two σ-bonds through the terminal carbon atoms C(6) and C(10) and two π-bonds through the double bonds. The distance between the two Fe atoms is 2.545(2) Å, consistent with a metal–metal bond. The coordination around Fe(2) is completed by three terminal carbonyl groups and that around Fe(1) by two terminal carbonyl groups and the P((1) atom from a monodentate dppm ligand. The entering dppm acts as a two-electron donor, and is in a pseudo-axial (or *trans*) position with respect to the Fe–Fe bond: this arrangement has been previously suggested for substituted flyover complexes obtained by stereospecific photochemical activation of the parent $[Fe_2(CO)_6\{(C_2RR')_2CO\}]$ derivatives [17]. The reaction described here provides a new and general method for the synthesis of substituted flyover-bridged derivatives in good yields.

To our knowledge, this is also the first example of the direct transformation of a ferrole into a flyover derivative. Hübel reported that these complexes are formed independently starting from a common mono-alkyne intermediate, and attempts to release the organic moiety from the ferroles, under a variety of thermal and photochemical conditions, did not give flyover complexes [18]. In an electrochemical study on $[Fe_2(CO)_6(C_2Ph_2)_2]$ no flyover complexes were found in the solutions after electrolysis [19]. Recently, the formation of the flyover $[Fe_2(CO)_6(MeC_2NEt_2)(CO)\text{-}MeC_2NEt_2\}]$ has been explained in terms of separate coordination of two alkynes, insertion of CO into a M–C bond, and migration of the C_3 unit to the other alkyne in intramolecular processes; formation of ferroles also occurs, and is attributed to a different rearrangement in the intermediate having two alkynes coordinated independently. The flyover and ferrole derivatives do not undergo interconversion [20]. Moreover, reaction of the ferrole complexes $[Fe_2(CO)_6(C_2R_2)_2]$ with triphenylphosphine in refluxing toluene for several hours was shown to give high yields of monosubstituted products (R = H [20b]; R = Ph [20c]), and no mention was made of the formation of flyover complexes.

Nevertheless, complex **1**, in the presence of Me_3NO and dppm, apparently undergoes, as the main process, insertion of CO into the carbon–carbon single bond of the metallacyclopentadiene ring, along with the expected phosphine substitution,

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

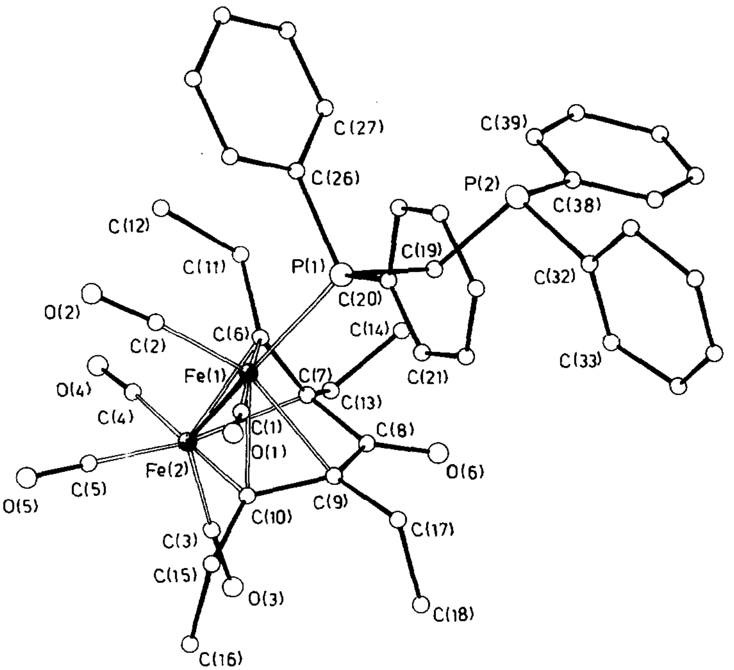
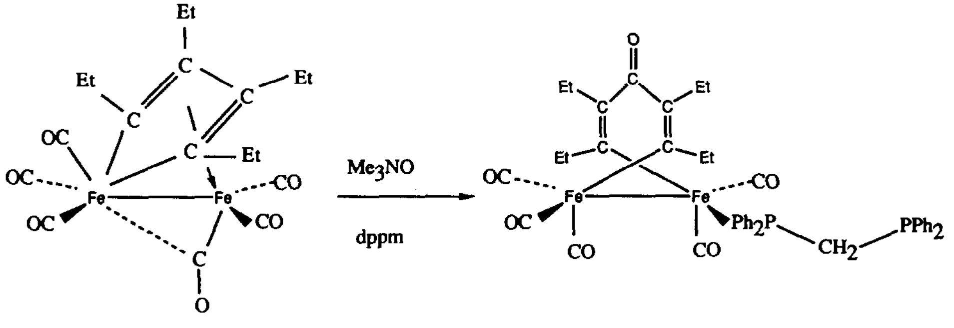


Fig. 1. View of the molecular structure of **2** with the atomic labelling scheme. Selected bond distances (Å) and angles (°): Fe(1)-Fe(2) 2.545(2), Fe(1)-P(1) 2.251(3), Fe(1)-C(6) 1.995(9), Fe(1)-C(9) 2.229(9), Fe(1)-C(10) 2.058(10), Fe(2)-C(6) 2.078(9), Fe(2)-C(7) 2.160(8), Fe(2)-C(10) 2.003(9), C(6)-C(7) 1.410(13), C(7)-C(8) 1.500(12), C(8)-C(9) 1.453(13), C(9)-C(10) 1.436(13), C(8)-O(6) 1.212(11); Fe(1)-Fe(2)-C(10) 52.2(3), Fe(2)-C(10)-C(9) 111.5(6), C(8)-C(9)-C(10) 115.9(8), C(7)-C(8)-C(9) 116.4(8), C(6)-C(7)-C(8) 113.4(8), Fe(1)-C(6)-C(7) 110.8(6).

to give, within a few minutes, the monosubstituted diferracycloheptadiene complex **2**, in good yield (Scheme 1).

The same product is obtained in the absence of Me_3NO, but the yield is reduced to 10% and a longer reaction time is necessary (30 min). This indicates that, in certain instances, Me_3NO may promote processes other than simple oxidation of the coordinated CO to CO_2 or, in other words, that, in this reaction pathway, there is an intermediate step in which "promoted" CO is still available for the insertion



Scheme 1.

reaction. The amine oxide and the entering ligand dppm could bring about insertion of a molecule of CO into an iron–carbon bond, followed by the formation of a cyclopentadienone-metal derivative [18,21], which would then turn into the flyover-bridged complex.

Recently, stepwise formation of di-iron flyover and tropone complexes has been reported; but the reaction sequence, starting from $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$, involves photochemically induced insertion of alkynes into a M–CO bond, followed by insertion of a second alkyne and release of CO, and finally photochemical insertion of a third alkyne [22].

We also found that the process leading to the flyover-bridged complex is inhibited by the presence of CO; thus, upon treatment of **1** with CO, Me_3NO and dppm in a sealed vial for 3 h, at 110 ° C, no complex **2** was formed.

We cannot at present exclude the possibility that the formation of **2** occurs through a more complex process involving, for example, intermediates with two independently coordinated alkynes.

Formation of flyover-like structures by reaction of $[Cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}RC{\equiv}CR')(\mu\text{-}CF_3C{\equiv}CCF_3)]$ involving formation of new C–O bonds is known [23]. Furthermore, intramolecular conversion of hetero-bimetallic complexes contains two separately co-ordinated alkynes into ferrole derivatives (in the presence of external CO) has been reported [24]. The reverse reaction, insertion of CO into two separate alkynes obtained from a ferrole, has not yet been observed.

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14 Complex **2**. Found (ca.c)%: C 62.5 (62.3), Fe 12.8 (13.5), H 5.3 (5.1), P 7.1 (7.5). IR (heptane): 2049vs, 1998vs, 1987sh, 1946s, 1648s cm^{-1}. ^{31}P NMR, δ ppm, ($CDCl_3$, H_3PO_4 as external reference): 47.6 d, −29.0 d (J(P,P) 19 Hz). ^{13}C NMR in the carbonyl region, δ ppm ($CDCl_3$, TMS): 205.2 (C8); 208.6 s, 210.5 s, 212.4 s (C3,4, 5); 211.6 d (C1 or 2, J(P,C) 15.2 Hz); 212.9 d (C2 or 1, J(P,C) 9.1 Hz).

15 *Crystal data* for **2**, $C_{43}H_{42}O_6P_2Fe_2$, $M = 828.48$, monoclinic, space group $P2_1/n$, $a = 38.045(11)$, $b = 9.700(5)$, $c = 10.876(6)$ Å, $\beta = 91.14(2)°$, $V = 4013(3)$ Å^3, $Z = 4$, $D_c = 1.371$ g cm^{-3}, $F(000) =$

1720, niobium-filtered Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu = 8.45$ cm^{-1}. The intensity data were collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 7524 Unique reflections were measured, with θ in the range 3–25°, 3122 having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions and introduced in the final structure factor calculations. The R and R_w values were 0.0582 and 0.0638, respectively. Tables of atomic coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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