

Reactions of the ‘ferrole’ complex $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)_2]$ with Group 15 donor ligands and with alkynes. Stepwise formation and disengagement of tropones. Crystal and molecular structure of $[\text{Fe}_2(\text{CO})_5\{(\text{CEt})_2\text{CO}(\text{CEt})_2\text{CHCPh}\}]$

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Received 15 August 1995

Abstract

The reactions of $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)_2]$ (complex A) with phosphorus donors in the presence of Me_3NO results in an unexpected CO insertion to give ‘flyover-bridged’ dinuclear compounds. The same reaction also takes place with nitriles giving similar, though less stable, complexes. The reactions of A with terminal alkynes give rise again to CO insertion into the ferrole ring and, in addition, the entering alkyne forms C–C bonds with the flyover moiety. The structure of $[\text{Fe}_2(\text{CO})_5\{(\text{CEt})_2\text{CO}(\text{CEt})_2\text{CHCPh}\}]$ has been fully elucidated by an X-ray study. Several organic products, including tropones, are produced by displacement reactions of the organic moieties from the ferrole and flyover derivatives, under thermal conditions.

Keywords: Iron; Ferrole complexes; Reactions with alkynes; Reaction mechanisms; X-ray structures; Phosphine complexes

1. Introduction

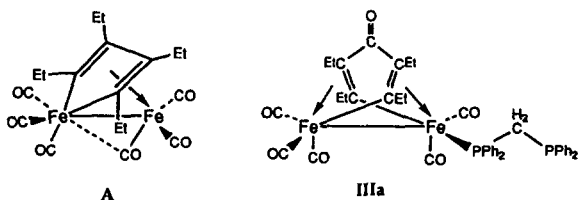
The di(ferracyclopentadienyl), or ‘iron ferrole’, complexes $[\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R}')_2]$ were among the first iron–acetylene derivatives discovered. A large number of these complexes is known [1] and several X-ray studies have been reported [2]. Since their discovery the ‘ferrole’ compounds have been considered as intermediates in the stoichiometric synthesis of organic compounds starting from alkynes [3]. In particular, Hübel [3a] hypothesized for these complexes (and for the ‘flyover’ derivatives discussed below) a role in the synthesis of quinones and tropones. Ferrole-like structures have also been invoked as intermediates in several other processes [4].

As part of a study on the role of metallacyclopentadienyl derivatives of cobalt, iron and ruthenium [5] in the synthesis of organic heterocycles from functionalized

alkynes and dialkynes, we decided to carry out a re-examination of the chemistry of the ferrole derivative $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)_2]$ (complex A, Scheme 1) obtained in good yield in the reaction of C_2Et_2 with $[\text{Fe}_3(\text{CO})_{12}]$ [6].

The displacement of the organic moieties formed upon reaction of coordinated acetylenes is easy for cobalt and difficult for iron [5]. It generally requires drastic conditions that cause the cleavage of dimetallic derivatives. In order to enhance the stability of the ferrole A we attempted the substitution of phosphorus donors for COs, in the presence of Me_3NO . Chemically promoted displacement of coordinated carbonyls is a common process for inducing substitution reactions in di- and polymetallic carbonyl compounds, metal complexes [7], Na-benzophenone ketyl [8] and, in particular, Me_3NO [9] currently being used. Unexpectedly, we found that when complex A reacts with dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$), Me_3NO promotes CO insertion into a C–C bond, affording a diferracycloheptadienone (‘flyover-bridged’) derivative (IIIa) (Scheme 1) [10].

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Scheme 1.

This paper deals with the reactions of **A** with a variety of Group 15 donors, such as PPh_3 , PPh_2H , dppm , dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), $\text{PPh}_2\text{C}\equiv\text{CPh}$, MeCN and PhCN , as well as with terminal alkynes in the presence of Me_3NO . Phosphines and nitriles form substituted ‘flyover’ derivatives (rather unstable in the case of nitriles), whereas alkynes insert into an Fe–C bond give stable complexes $[\text{Fe}_2(\text{CO})_5\{(\text{CEt})_2\text{CO}(\text{CEt})_2\text{CHCR}\}]$ with a seven-carbon-atom chain. By thermal treatment, these compounds afford the corresponding tropones, again in the presence of Me_3NO , which is effective in the displacement of the organic moieties, as previously reported for mononuclear iron complexes [11]. Also the ‘ferrole’ complex $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)_2]$ (**B**) and the unsubstituted ‘flyover’ $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)\text{CO}]$ (**C**) were subjected to some of these reactions for comparison.

In a previous paper, we described the HPLC-MS behaviour of the substituted ‘flyover’ derivatives $[\text{Fe}_2\{(\text{C}_2\text{Et}_2)\text{CO}\}(\text{CO})_5\{\text{PPh}_2(\text{CH}_2)_n\text{EPh}_2\}]$ ($\text{E} = \text{P}$, or As ; $n = 1$ or 2) [12].

2. Experimental

2.1. Materials and general experimental procedures

Complexes **A**, **B** and **C** were obtained following literature procedures [3,6]; phosphines, nitriles and alkynes were commercial products and were used as received; $\text{PPh}_2\text{C}_2\text{Ph}$ was supplied by Professor A.J. Carty, University of Waterloo, Ont., Canada. Anhydrous Me_3NO was obtained upon sublimation in vacuo of commercial $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$.

All the reactions were performed in three-necked flasks equipped with gas inlet, cooler, mercury check valve and magnetic stirrer. The reaction solutions, brought to small volume under reduced pressure, were purified on TLC preparative plates (Kieselgel PF Merck, eluant mixtures of diethyl ether and light petroleum 40–70°C); when possible the products were crystallized before the analyses.

Elemental analyses were performed by F. Pascher Lab. (Germany). The IR spectra were registered on a Perkin-Elmer 580 B instrument; the ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained from CDCl_3 solutions on JEOL JNM GX 270 FT, EX-400 FT and Bruker CXP 200 FT instruments. TMS was used as

internal standard for the ^1H and ^{13}C , and 85% H_3PO_4 for the ^{31}P spectra.

2.2. Reactions of complex **A** with Group 15 donor ligands

All the reactions were performed under dry N_2 in heptane or toluene, distilled and dried over sodium, and in the presence of anhydrous Me_3NO (100 or 200 mg in each run, 1.33 or 2.66 mmol).

2.2.1. Reaction I (PPh_3)

Treatment of **A** (1.0 g, 2.25 mmol) with 0.5 g (1.91 mmol) of PPh_3 for 1 min in *N*-heptane at reflux gave a dark red clear solution, which, upon TLC purification, yielded about 30% of unreacted **A**, 25% each of red $[\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\text{C}_2\text{Et}_2)_2\text{CO}]$ (**Ia**) and $[\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\text{C}_2\text{Et}_2)_2]$ (**Ib**), and some decomposition. Complex **Ia** (calculated values in parentheses): C, 61.0 (61.2); H, 5.1 (5.0)%. IR (νCO , cm^{-1}): 2046vs, 1996vs, 1986sh, 1943s, 1933 sh, 1650s. ^1H NMR, δ : 7.42–7.24 m (15H, Ph); 3.14 q, 2.34 q, 2.06q, 1.90q (8H, CH_2); 1.53 t, 1.47 t, 1.27 t, 1.06 t (12 H, CH_3). ^{31}P NMR, δ : 51.8 s. ^{13}C NMR, δ (CO region): 206.4 s, 208.1 s, 209.2 s, 210.5 d, 211.9 d, 212.2 s. Complex **Ib**: C, 62.1(61.9); H, 5.3(5.2); P, 4.4(4.6)%. IR (cm^{-1}): 2047vs, 1997vs, 1985s, 1947ms. ^1H NMR, δ : 7.51–7.23 m (15 H, Ph); 3.07 q, 2.89 q, 2.42 q, 1.96 q (8 H, CH_2); 1.52 t, 1.48 t, 1.14 t, 1.07 t (12 H, CH_3). ^{31}P NMR, δ : 21.06 s.

2.2.2. Reaction II (PPh_2H)

Treatment of **A** (1.0 g) with 0.5 ml of PPh_2H (2.68 mmol) for 30 s reflux yielded a cherry red solution containing about 30% unreacted **A**, 40% of red $[\text{Fe}_2(\text{CO})_5(\text{PPh}_2\text{H})(\text{C}_2\text{Et}_2)_2]$ (**Iib**) and an unstable red–violet derivative not identified. Complex **Iib**: C, 54.3(54.2); H, 5.8(5.6); P, 5.4(5.6)%. IR (cm^{-1}): 2050vs, 1997vs, 1979vs, 1947ms. ^{31}P NMR, δ : 51.5 s, 48.3 s, 48.5 s (relative intensities 100:50:35). The ^{31}P NMR spectrum suggested that complex **Iib** was present in solution as a mixture of isomers. **Iib** was collected on the TLC plates as a unique deep red band which gives, in CDCl_3 solution at room temperature, the same three ^{31}P resonances. TLC purification of the solution, after NMR, resulted again in a single red band. Careful crystallization of a freshly prepared sample (from heptane/ CHCl_3 mixture, 80/20 in volume, under N_2 at -20°C for some days) gave well-formed crystals. These were dissolved in CDCl_3 and again the three-resonance pattern was observed.

2.2.3. Reaction III (dppm)

Treatment of **A** (1.0 g) with 0.75 g of dppm (1.95 mmol) for 3 min under reflux gave a clear cherry red

solution containing traces of unreacted **A**, about 60% of $[\text{Fe}_2(\text{CO})_5(\text{dppm}-\text{P})(\text{C}_2\text{Et}_2)_2\text{CO}]$ (red, **IIIa**) and 30% of $[\text{Fe}_2(\text{CO})_5(\text{dppm}-\text{P})(\text{C}_2\text{Et}_2)_2]$ (reddish violet, **IIIb**) and some decomposition [10]. Treatment of **A** with a 4:1 molar excess of dppm in heptane under reflux for 30 min, in the absence of Me_3NO , yielded about 60% unreacted **A**, about 20% of **IIIa** and about 25% of **IIIb**. Characterization data for **IIIa** are reported in Ref. [10]. Complex **IIIb**: C, 63.3(63.0); Fe, 13.9(13.9); H, 5.4(5.3); P, 7.5(7.7)%. IR (cm^{-1}): 2048vs, 2026vs, 1997vs, 1978sh, 1945s. ^{31}P NMR, δ : 51.3 d, -26.1 d ($J_{\text{pp}} = 4$ Hz)

2.2.4. Reaction IV (dppe)

Treatment of **A** (0.5 g, 1.12 mmol) with dppe (0.4 g, 1.0 mmol) for 3 min, reflux gave a clear red solution containing unreacted **A** (30%), $[\text{Fe}_2(\text{CO})_5(\text{dppe}-\text{P})(\text{C}_2\text{Et}_2)_2\text{CO}]$ (25%, red, **IVa**) and $[\text{Fe}_2(\text{CO})_4(\text{dppe})(\text{C}_2\text{Et}_2)_2\text{CO}]$ (25%, red, **IVa'**). Complex **IVa**: IR (cm^{-1}): 1650ms. ^{31}P NMR, δ : 48.5 d, -13.4 d ($J_{\text{pp}} = 26$ Hz). Other data are reported in Ref. [12]. Complex **IVa'**: C, 63.6(63.4); H, 5.6(5.4); P, 7.4(7.6)%. IR (cm^{-1}): 2046vs, 1996vs, 1986sh, 1946vs, 1645s. ^{31}P NMR, δ : $+51.5$ br, $+47.0$ br.

2.2.5. Reaction V ($\text{Ph}_2\text{PC}\equiv\text{CH}$)

Treatment of **A** (1.0 g) with 0.6 g (2.85 mmol) of $\text{Ph}_2\text{PC}\equiv\text{CH}$ in refluxing toluene for 2 min yielded unreacted **A** (40%), $[\text{Fe}_2(\text{CO})_5(\text{Ph}_2\text{PC}\equiv\text{CH})(\text{C}_2\text{Et}_2)_2\text{CO}]$ (40%, purple, **Va**), trace amounts of three unidentified derivatives and some decomposition. Complex **Va**: C, 54.9(54.6); Fe, 19.0(19.5); H, 4.2(3.7); P, 5.7(5.4)%. IR (cm^{-1}): 2051vs, 1996vs, 1988sh, 1945s, 1670s. ^{13}C NMR, δ : 204 s (ketonic), 208.3 s, 210.6 s, 212.1 s (unsubstituted iron), 210.8 d, 213.4 d (substituted iron). ^{31}P NMR, δ : $+36.85$ s(100), $+33.7$ b(9), $+32.5$ s(16).

2.2.6. Reaction VI (MeCN)

Treatment of 1.0 g of **A** with an excess of liquid MeCN (5.0 ml) in toluene, under N_2 till incipient reflux (6 min) resulted in a change of colour from orange to purple. The solution was purified on TLC plates. Unreacted **A** (about 40%) and a purple band (tentative formulation as complex **VIa**, 25%) were found, together with some decomposition. Attempts at crystallization resulted in decomposition of **VIa** into **A** and insoluble materials. This type of decomposition was also observed during the registration of the NMR spectra. Complex **VIa**: IR (cm^{-1}): 2062s, 2055sh, 2040s, 2020sh, 2008vs, 2002sh, 1962s, 1670s.

2.2.7. Reaction VII (PhCN)

Treatment of **A** with an excess of liquid PhCN and Me_3NO in toluene under N_2 for 10 min (incipient reflux) gave a clear, dark purple solution, which upon

TLC purification showed the presence of unreacted **A** (30%) and red $[\text{Fe}_2(\text{CO})_5(\text{PhCN})(\text{C}_2\text{Et}_2)_2\text{CO}]$ (complex **VIIa**) (45%) and small amounts of decomposition. Complex **VIIa** was collected as a liquid contaminated by PhCN; after 36 h of drying under vacuum an oily solid was formed. This was dissolved in the minimum amount of heptane and left at -30°C for one night: An orange solution (containing **A**) and a dark red sticky precipitate were observed. The precipitate was further dried for 2 h under a N_2 stream. Finally, a dry, solid microcrystalline compound was obtained. Complex **VIIa**: C, 60.2(54.9); Fe, 19.7(20.4); H, 4.9(4.6); N, 2.4(2.6)%. IR (cm^{-1}): 2046sh, 2041s, 2006vs, 1987s, 1975s, 1670m. ^1H NMR, δ : 7.68–7.28 mm (Ph); 2.95 m, 2.70 m, 2.10 m, 1.84 m (Et, CH_2); 1.43 t, 1.35 t, 1.17 t, 1.10 t (Et, CH_3).

2.3. Reactions of complex A with alkynes

2.3.1. Reaction VIII (C_2Ph_2)

Treatment of 1.0 g of complex **A** with 0.5 g (2.81 mmol) of C_2Ph_2 and 0.2 g of Me_3NO in refluxing heptane for 3–4 min yielded 80% of unreacted **A**, a brown–purple complex, tentatively identified as $[\text{Fe}_2(\text{CO})_5(\text{C}_2\text{Ph}_2)(\text{C}_2\text{Et}_2)_2\text{CO}]$ (**VIIIa**, 5%), a red unidentified complex, and some decomposition. Complex **VIIIa**: IR (cm^{-1}): 2064vs, 2021sh, 2010vs, 2002sh, 1960s, 1670m.

2.3.2. Reaction IX ($\text{HC}\equiv\text{CPh}$)

Treatment of 1.0 g of complex **A** with 2 ml of $\text{HC}\equiv\text{CPh}$ (18.2 mmol) and 0.2 g of Me_3NO in refluxing heptane for 2 min yielded 50% of unreacted **A**, 30% of purple $\text{Fe}_2(\text{CO})_5\{(\text{C}_2\text{Et}_2)_2(\text{CO})(\text{HC}\equiv\text{CPh})\}$ (**IX**), and small amounts of decomposition products. Complex **IX**: C, 57.8(57.2); Fe, 20.7(20.4); H, 5.2(4.8)%. IR (cm^{-1}): 2066vs, 2021vs, 2011vs, 1999s, 1961vs, 1670s. ^1H NMR, δ : 7.81 d ($J = 4.8$ Hz) ($\text{HC}\equiv\text{CPh}$), 7.51–7.20 m, 6.71, 6.00 m (Ph), 3.79 m, 3.64 m, 2.92 m, 2.76 q, 2.70 q, 2.68 q (CH_2), 2.30 m, 2.15 m, 1.80 m, 1.61 t, 1.45 t, 1.30 t, 1.24 m, 0.90 t, 0.77 t (CH_3). ^{13}C NMR, δ : 68.97 s, 91.37 s, 97.15 s, 107.19 s, 122.14 s (C alkynes); 124.7–129.1 m (Ph); 139.8 s, 140.2 s, 142.2 s, 148.7 s, 151.7 (C alkynes); 200.2 s, 200.9 s, 205.7 s, 209.2 s, 211.2 s, 211.5 s, 214.0 s (terminal and ketonic COs).

2.3.3. Reaction X ($\text{HC}\equiv\text{C}^i\text{Bu}$)

Treatment of 1.0 g of complex **A** with 2.0 ml of $\text{HC}\equiv\text{C}^i\text{Bu}$ (16.2 mmol) and 0.2 g of Me_3NO in refluxing toluene for 4 min yielded an unidentified pale yellow derivative, 40% of unreacted **A**, 25% of **X** (whose IR spectrum has the same pattern as that of **IX**), and considerable decomposition. Complex **X**: C, 55.0 (54.9); Fe, 21.6 (21.1); H, 0.59 (0.57)%. IR (cm^{-1}): 2062vs, 2015vs, 2008vs, 1995vs, 1958vs, 1670s. ^1H

NMR, δ : 4.95 q, 4.80 q, 4.28 m, 3.60 m, 3.34 m (CH_2), 3.10 s (^1Bu), 2.85 t, 2.65 t, 2.55 t, 2.05 t (CH_3). ^{13}C NMR, δ : 65.6 s, 67.8 s (C, ^1Bu); 90.9 s, 95.6 s, 107.6 s (C alkynes); 201.6 s, 206.3 s, 209.6 s, 210.0 s, 211.05 s, 211.6 s, 224.8 s (terminal and ketonic COs).

2.4. Reaction XI: $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)_2]$ (**B**) with dppm

Treatment of 0.5 g of **B** (0.78 mmol) with 0.5 g of dppm (1.41 mmol), in the presence of Me_3NO in refluxing heptane under N_2 for 4 min yielded about 25% of unreacted parent ferrole, about 30% of purple $[\text{Fe}_2(\text{CO})_5(\text{dppm})(\text{C}_2\text{Ph}_2)_2]$ (**XIb**) [13], 15% of a red complex, tentatively identified as the complex $[\text{Fe}_2(\text{CO})_4(\text{dppm})(\text{C}_2\text{Ph}_2)_2]$ (**XIb'**) in which the diphosphine probably chelates, and considerable decomposition. Complex **XI**: C, 70.3 (70.2); H, 4.5(4.3); P, 6.1(6.2)%. IR (cm^{-1}): 2052vs, 1998vs, br, 1988sh, 1943m. ^{31}P NMR: +49.45 br, -32.15 br (relative intensities 1:1). Complex **XIb'**: C, 71.3 (71.0); H, 4.6 (4.4)%. IR (cm^{-1}): 2053vs, 1991vs, br, 1974s, 1940m, br. ^{31}P NMR, δ : +49.6 s.

2.5. Reactions of the unsubstituted flyover complex $[\text{Fe}_2(\text{CO})_6\{(\text{C}_2\text{Et}_2)\text{CO}\}]$ (**C**) in the presence of Me_3NO

Treatment of **C** (1.0 g, 2.12 mmol) with a considerable excess (1.0 g, 2.82 mmol) of dppm and of Me_3NO under N_2 in refluxing heptane for 10 min resulted in about 75% of unreacted **C**, very small amounts of two yellow and one purple derivatives, and some decomposition product. Neither complex **IIIa** nor ferrole **A** were detected.

Treatment of complex **C** with a 2:1 proportion of PPh_3 and Me_3NO under N_2 in refluxing heptane for 10 min gave about 70% of unreacted **C**, trace amounts of three unidentified yellow products and considerable decomposition product.

Treatment of complex **C** (1.0 g, 2.12 mmol) with 2.0 ml of $\text{HC}\equiv\text{C}^t\text{Bu}$ and 0.2 g Me_3NO in refluxing toluene for 2 min yielded about 5% of complex **A**, 75% of unreacted **C**, trace amounts of unidentified red and yellow derivatives and considerable decomposition products.

2.6. Ligand displacement reactions

All these reactions were performed in the presence of a considerable excess of Me_3NO , in anhydrous toluene distilled under dinitrogen. The reaction solutions were analyzed by GLC-MS (Carlo Erba 4200-Kratos MS-50) for the organic product and checked for organometallic compounds by TLC, IR and NMR spectroscopy. The structures of the organic products detected are depicted in Scheme 2.

2.6.1. Complex A

Treatment of **A** at reflux temperature for 2 min under N_2 yielded an orange suspension. Unreacted **A** (40%) and complex **C** (40%) were recovered. The organic compounds **K** and **J** (as major products) and traces of **W** were obtained. Treatment of **A** at reflux temperature under CO_2 for 1 min gave a brown solution containing **A** (15%), **C**(40%) and **K**, **J** (minor amounts). Heating under reflux for 2 min under a flow of C_2H_2 yielded a brown suspension and decomposition products, but no detectable complexes, and **Y**, **J** (minor amounts).

2.6.2. Complex C

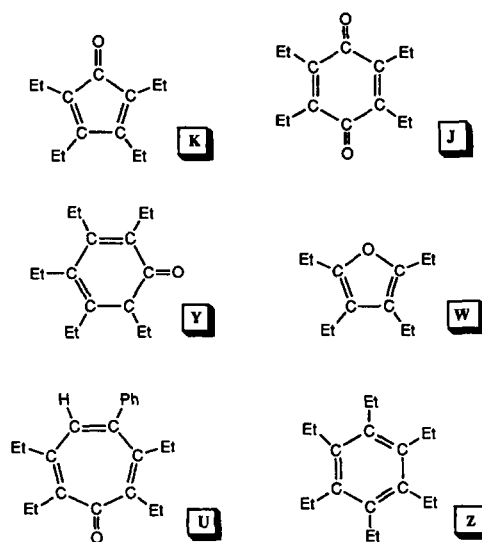
Treatment of **C** at incipient reflux under N_2 yielded an orange suspension containing **C** (20%) and the organic products **U** and **K** (minor). The same reaction for 2 min at reflux under a flow of C_2H_2 gave a yellow solution and evident decomposition: **C** (20%), **K** (very abundant), **Z** (minor). Heating under reflux in toluene for 5 min under a flow of CO_2 resulted in a purple solution containing **C** (80%) and **A**(10%) and **K**, **Z** (minor amounts).

2.6.3. Complex Ia

Treatment of **Ia** in refluxing toluene for 2 min under N_2 gave an orange–yellow solution containing **C** (80%), **K** (very abundant) and **J** (minor). Under C_2H_2 at reflux for 10 min gave a dark yellow suspension and decomposition: **Ia** (10%), **C** (10%), and **Y**. After 3 min at reflux under a flow of CO_2 a yellow solution containing **K** and **J** was obtained.

2.6.4. Complex IX

Treatment of the complex **IX** with Me_3NO under N_2 at reflux for 1 min yielded a purple suspension and decomposition products: unreacted **IX** (10%), **C** (10%),



Scheme 2.

and compound U, as the sole detectable organic product.

2.7. X-ray data collection, structure determination and refinement for complex IX

Deep red crystals of IX suitable for the X-ray analysis were obtained from a heptane–chloroform (70:30 v/v) solution kept under N₂ at –20°C for some days. The crystallographic data are summarized in Table 1. Data were collected at room temperature (22°C) on a Philips PW 1100 diffractometer, using graphite-monochromated Mo K α radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min⁻¹ and a scan width from $(\theta - 0.65)^\circ$ to $(\theta + 0.65 + 0.346 \tan \theta)^\circ$. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen [14]. Intensities were corrected for Lorentz and polarization effects. No correction for absorption was necessary. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms (except eight placed at their geometrically calculated positions) were clearly localized in the final ΔF map and refined isotropically. In the final cycles of refinement a weighting scheme, $w = [\sigma^2(F_o) + gF_o^{2-1}]^{-1}$ was used. At convergence the g value was 0.0065. The analytical scattering factors,

Table 1
Summary of crystallographic data for complex IX

| | |
|--|--|
| Formula | C ₂₆ H ₂₆ Fe ₂ O ₆ |
| Molecular weight | 546.18 |
| Crystal system | triclinic |
| Space group | P $\bar{1}$ |
| a (Å) | 16.128(8) |
| b (Å) | 9.455(5) |
| c (Å) | 9.173(4) |
| α (°) | 66.65(1) |
| β (°) | 73.23(1) |
| γ (°) | 72.80(1) |
| V (Å ³) | 1203(1) |
| Z | 2 |
| D_{calc} (g cm ⁻³) | 1.508 |
| $F(000)$ | 564 |
| Crystal size (mm ³) | 0.17 × 0.22 × 0.25 |
| μ (Mo K α) (cm ⁻¹) | 12.43 |
| θ range (°) | 3–23 |
| Reflections measured | $\pm h, \pm k, l$ |
| Unique total data | 3190 |
| Unique observed data | 1997 [$I > 2\sigma(I)$] |
| $R = \sum \Delta F / \sum F_o $ | 0.0377 |
| $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$ | 0.0396 |

Table 2

Fractional atomic coordinates ($\times 10^4$) with ESDs in parentheses for the non-hydrogen atoms of complex IX

| | x | y | z |
|-------|----------|-----------|-----------|
| Fe(1) | 2091(1) | 461(1) | 3787(1) |
| Fe(2) | 2350(1) | 3205(1) | 2352(1) |
| O(1) | 469(4) | 709(8) | 6250(8) |
| O(2) | 1518(4) | –1394(7) | 2502(9) |
| O(3) | 3049(4) | –2225(7) | 6110(8) |
| O(4) | 3040(5) | 6058(7) | 461(7) |
| O(5) | 972(4) | 5198(7) | 3928(9) |
| O(6) | 4664(3) | –137(6) | 2839(7) |
| C(1) | 1083(5) | 642(9) | 5287(10) |
| C(2) | 1726(5) | –693(9) | 3009(11) |
| C(3) | 2673(5) | –1190(10) | 5230(10) |
| C(4) | 2787(5) | 4912(9) | 1185(9) |
| C(5) | 1494(5) | 4382(10) | 3318(11) |
| C(6) | 2661(5) | 1727(8) | 4436(9) |
| C(7) | 3508(4) | 1867(8) | 3509(9) |
| C(8) | 3910(4) | 615(8) | 2782(8) |
| C(9) | 3278(4) | 392(7) | 2015(9) |
| C(10) | 3087(4) | 1939(8) | 666(9) |
| C(11) | 2207(4) | 2627(8) | 481(9) |
| C(12) | 1555(4) | 2288(8) | 1894(9) |
| C(13) | 2341(7) | 2038(11) | 6038(10) |
| C(14) | 2712(8) | 677(11) | 7440(11) |
| C(15) | 4145(6) | 2591(11) | 3797(12) |
| C(16) | 4865(6) | 3183(11) | 2334(12) |
| C(17) | 3636(5) | –990(9) | 1386(10) |
| C(18) | 3804(7) | –2646(10) | 2649(13) |
| C(19) | 3856(5) | 2441(9) | –695(9) |
| C(20) | 3645(7) | 3871(11) | –2139(11) |
| C(21) | 606(4) | 2669(8) | 1767(10) |
| C(22) | –97(5) | 3228(9) | 2812(12) |
| C(23) | –961(5) | 3512(9) | 2632(13) |
| C(24) | –1142(6) | 3234(11) | 1432(13) |
| C(25) | –463(6) | 2695(11) | 375(11) |
| C(26) | 405(6) | 2404(11) | 541(11) |

corrected for the real and imaginary parts of anomalous dispersions, were taken from Ref. [15]. All calculations were carried out on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [16]. The final atomic coordinates for the non-hydrogen atoms are given in Table 2. Additional data (atomic coordinates of the hydrogen atoms, thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre or are available from the authors.

3. Results and discussion

3.1. Complexes with P-donors

With some exceptions, the major products of the reactions of A with P-donors are the monosubstituted 'flyover' complexes $[\text{Fe}_2(\text{CO})_5(\text{L})\{(\text{C}_2\text{Et}_2)_2\text{CO}\}]$ (I–Va), which were characterized by elemental analyses,

spectroscopic techniques and by comparison with the derivatives $[\text{Fe}_2(\text{CO})_5(\text{L})\{(\text{C}_2\text{Ph}_2)_2\text{CO}\}]$ ($\text{L} = \text{PPh}_3$, P-dppe) formed in photochemical reactions of $[\text{Fe}_2(\text{CO})_6\{(\text{C}_2\text{Ph}_2)_2\text{CO}\}]$ [17]. The IR spectra of complexes **a** are characterized by a ketonic absorption at about 1650 cm^{-1} . The bidentate ligands act as two-electron donors, as shown by the ^{31}P NMR spectra of **IIIa** and **IVa**, where two doublets are observed at very different chemical shifts. The X-ray structure of **IIIa** was previously reported [10] and is shown in Scheme 1. It confirms that the entering ligands are pseudo-axial.

The derivative with $\text{PPh}_2\text{C}\equiv\text{CPh}$ (**Va**) is noteworthy because of the possible competition between $\text{C}\equiv\text{C}$ and PPh_2 for the same metal. The spectroscopic data show that the PPh_2 group is a ligand. The C-P bond cleavage, which generally occurs under mild conditions [18], is not observed. Minor products of the above reactions are the monosubstituted ferroles **b**. Their formulation is supported by elemental analyses and spectroscopic data, as their IR spectra do not show ketonic absorptions. PPh_2H gives only the complex **IIb**, which exists in solution as a mixture of three isomers, as indicated by its ^{31}P NMR spectrum. Similar monosubstituted products have been obtained by direct reaction of PPh_3 with ferroles [19]. An X-ray structural study of $[\text{Fe}_2(\text{CO})_5(\text{C}_2\text{Ph}_2)_2(\text{PPh}_3)]$ shows that the phosphine replaces a carbonyl on the iron atom *trans* to the semi-bridging CO [13].

The bidentate ligand dppe also gives the flyover complexes **IVa'**, where a bridging (or more probably chelating) ligand replaces two carbonyls. The available NMR data do not allow a univocal identification. The occurrence of this type of isomer is strongly dependent on the nature of the bidentate ligand [20].

3.2. Complexes with nitriles

The spectroscopic data for the nitrile complexes **VIa** and **VIIa** show that these ligands also probably act as two-electron donors and do not insert into the M-C bonds. The proposed structures for these complexes are hence close to those of complexes **I-Va**. During attempts at crystallization, complexes **VIa** and **VIIa** undergo decomposition, giving **A** and insoluble products. Apparently, the formation of complexes **VIa** and **VIIa** from the 'ferrole' **A** is only reversible in part. Thus, of donors with a triple $\text{C}\equiv\text{X}$ bond, only terminal alkynes show a tendency to insert into an Fe-C bond of the substituted flyover derivatives. Nitriles may also insert into Co-C bonds of metallacyclopentadienyl derivatives [5b,c].

3.3. Complexes with acetylenes. X-ray structure of complex IX

The IR spectra of the complexes are comparable and similar to those of complexes **a** in the terminal CO

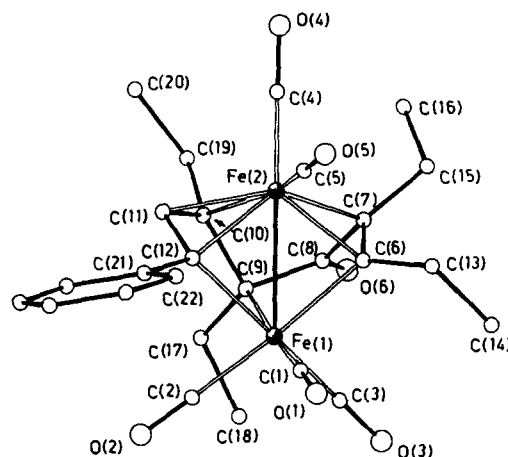


Fig. 1. View of the molecular structure of complex $[\text{Fe}_2(\text{CO})_5\{(\text{CEt})_2\text{CO}(\text{CEt})_2\text{CHCPh}\}]$ (**IX**) with the atomic labelling scheme.

region. All show an intense absorption in the region of ketonic carbonyls. The NMR spectra of **IX** and **X** show more signals than expected. This could indicate the presence of isomers in solution. The structure of complex **IX**, fully elucidated by an X-ray study, is shown in Fig. 1. Selected bond distances and angles are given in Table 3.

In the complex two iron atoms at a distance of $2.501(2)\text{ \AA}$, consistent with a metal-metal bond, are involved in complicated bonding with an organic moiety having a seven-carbon-atom chain, obtained upon insertion of a CO into the ferrole ring and coordination of a phenylacetylene. Three terminal carbonyls are bound to Fe(1) and two to Fe(2). In the organic ligand a diethylacetylene unit $[\text{C}(6)-\text{C}(7)]$ is σ -bonded to Fe(1) through C(6) [$\text{Fe}(1)-\text{C}(6) = 2.040(10)\text{ \AA}$] and π -bonded to Fe(2) [$\text{Fe}(2)-\text{C}(6) = 1.970(7)$ and $\text{Fe}(2)-\text{C}(7) = 2.212(7)\text{ \AA}$]. The second moiety, obtained by the interaction of a phenylacetylene $[\text{C}(11)-\text{C}(12)]$ via the $\text{HC}\equiv$ end with the other diethylacetylene unit $[\text{C}(9)-\text{C}(10)]$, chelates to Fe(1) forming two σ bonds through C(9) and C(12) [$\text{Fe}(1)-\text{C}(9) = 2.128(6)$ and $\text{Fe}(1)-\text{C}(12) = 2.087(6)\text{ \AA}$] and interacts with Fe(2) in an η^3 -allylic fashion [$\text{Fe}(2)-\text{C}(10) = 2.191(8)$, $\text{Fe}(2)-\text{C}(11) = 2.084(10)$ and $\text{Fe}(2)-\text{C}(12) = 1.957(9)\text{ \AA}$]. The $\text{C}(10)-\text{C}(11)$ and $\text{C}(11)-\text{C}(12)$ bonds [$1.404(9)$ and $1.405(9)\text{ \AA}$] are typical of an allylic system, which must be considered as a three-electron donor. In total, the organic ligand contributes eight electrons to the overall electron count. Both the iron atoms have an 18-electron configuration.

The phenylacetylene unit forms a new C-C bond $[\text{C}(10)-\text{C}(11)]$ with the organic moiety already coordinated by using the $\text{HC}\equiv$ carbon, presumably for steric reasons. Two X-ray structures of complexes similar to **IX** have been reported, but the complexes were obtained by direct reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with $\text{HC}\equiv\text{CPh}$ [21] or $\text{HC}\equiv\text{C}^t\text{Bu}$ [22] and therefore contained three

Table 3
Important interatomic distances (Å) and angles (°) for complex IX

| | | | |
|------------------|-----------|-------------------|-----------|
| Fe(1)–Fe(2) | 2.501(2) | Fe(2)–C(12) | 1.957(9) |
| Fe(1)–C(1) | 1.815(8) | C(6)–C(7) | 1.398(9) |
| Fe(1)–C(2) | 1.813(11) | C(7)–C(8) | 1.480(11) |
| Fe(1)–C(3) | 1.811(7) | C(8)–O(6) | 1.218(8) |
| Fe(1)–C(6) | 2.040(10) | C(8)–C(9) | 1.495(13) |
| Fe(1)–C(9) | 2.128(6) | C(9)–C(10) | 1.511(8) |
| Fe(1)–C(12) | 2.087(6) | C(10)–C(11) | 1.404(9) |
| Fe(2)–C(4) | 1.765(8) | C(11)–C(12) | 1.405(9) |
| Fe(2)–C(5) | 1.760(8) | C(1)–O(1) | 1.126(10) |
| Fe(2)–C(6) | 1.970(7) | C(2)–O(2) | 1.111(15) |
| Fe(2)–C(7) | 2.212(7) | C(3)–O(3) | 1.133(9) |
| Fe(2)–C(10) | 2.191(8) | C(4)–O(4) | 1.147(10) |
| Fe(2)–C(11) | 2.084(10) | C(5)–O(5) | 1.142(11) |
| Fe(2)–Fe(1)–C(1) | 104.8(3) | Fe(1)–C(6)–C(7) | 111.9(5) |
| Fe(2)–Fe(1)–C(2) | 127.3(3) | Fe(1)–C(6)–C(13) | 123.5(6) |
| Fe(2)–Fe(1)–C(3) | 129.7(3) | C(7)–C(6)–C(13) | 122.1(8) |
| Fe(2)–Fe(1)–C(9) | 71.7(2) | C(6)–C(7)–C(8) | 112.3(7) |
| C(1)–Fe(1)–C(2) | 94.5(4) | C(6)–C(7)–C(15) | 125.1(7) |
| C(1)–Fe(1)–C(3) | 93.2(4) | C(8)–C(7)–C(15) | 116.5(7) |
| C(1)–Fe(1)–C(6) | 93.4(4) | C(7)–C(8)–C(9) | 111.9(6) |
| C(1)–Fe(1)–C(12) | 94.0(3) | O(6)–C(8)–C(7) | 122.7(7) |
| C(2)–Fe(1)–C(3) | 96.5(4) | O(6)–C(8)–C(9) | 125.4(7) |
| C(2)–Fe(1)–C(9) | 88.5(3) | Fe(1)–C(9)–C(8) | 101.8(5) |
| C(2)–Fe(1)–C(12) | 81.2(3) | Fe(1)–C(9)–C(10) | 102.7(5) |
| C(3)–Fe(1)–C(6) | 82.8(4) | Fe(1)–C(9)–C(17) | 120.4(5) |
| C(3)–Fe(1)–C(9) | 88.4(3) | C(8)–C(9)–C(10) | 104.8(6) |
| C(6)–Fe(1)–C(9) | 83.6(3) | C(8)–C(9)–C(17) | 113.6(7) |
| C(6)–Fe(1)–C(12) | 98.4(3) | C(10)–C(9)–C(17) | 111.7(6) |
| C(9)–Fe(1)–C(12) | 84.5(3) | C(9)–C(10)–C(11) | 119.1(7) |
| Fe(1)–Fe(2)–C(5) | 105.6(3) | C(9)–C(10)–C(19) | 117.5(7) |
| C(4)–Fe(2)–C(5) | 87.2(4) | C(11)–C(10)–C(19) | 121.1(7) |
| Fe(1)–C(1)–O(1) | 177.8(8) | C(10)–C(11)–C(12) | 116.3(7) |
| Fe(1)–C(2)–O(2) | 178.4(8) | Fe(1)–C(12)–C(11) | 110.7(5) |
| Fe(1)–C(3)–O(3) | 178.7(8) | Fe(1)–C(12)–C(21) | 124.0(5) |
| Fe(2)–C(4)–O(4) | 177.0(8) | C(11)–C(12)–C(21) | 119.7(7) |
| Fe(2)–C(5)–O(5) | 176.1(8) | | |

identical alkynes. These alkynes were condensed head-to-tail and tail-to-tail respectively, giving rise to different isomers. Unfortunately, the presence of identical alkynes in each complex did not allow any hypothesis on the formation mechanism to be developed.

Complex IX is the first example in which evidence for formation of a new C–C bond upon insertion of CO into a ferrole ring followed by coordination of a third alkyne has been produced.

3.4. Formation pathways for the substituted ‘flyover’ derivatives a

The diferracycloheptadiene complexes (‘flyover-bridged’) Ia–VIIa are usually obtained, together with the ferroles, in the reactions of iron carbonyls with alkynes [1]. Direct formation of flyover-bridged complexes from ferroles has not been reported. Hübel [3a] proposed $[\text{Fe}_2(\text{CO})_7(\mu-\eta^2-\text{RC}\equiv\text{CR}')]]$ as a precursor of both ‘ferrole’ A (minor products) and ‘flyover’ C (major products). Attempts at releasing the organic moieties of

ferroles under thermal, chemical, or photochemical conditions [3a] did not result in the formation of complexes C. Moreover, after electrochemical studies on $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)_2]$ [23], no ‘flyover’ derivatives could be detected in the reaction mixtures. Finally, the formation of the ferrole $[\text{Fe}_2(\text{CO})_6\{\text{MeC}_2\text{NEt}_2\}_2]$ and of the ‘flyover’ $[\text{Fe}_2(\text{CO})_6\{\text{MeC}_2\text{NEt}_2(\text{CO})\text{MeC}_2\text{NEt}_2\}]$ was explained by invoking a common initial intermediate, which then gives different rearrangements. Once again the flyover and ferrole derivatives did not rearrange into each other [24].

As already mentioned, the formation of phosphine-substituted ‘flyover’ derivatives occurred only under photochemical conditions [17]. The formation of such substituted derivative is a key step for the synthesis of complexes such as IX, when alkynes are involved. Substituted ‘flyover’ derivatives are apparently formed upon addition of two-electron donors and migration and insertion of a CO into the C–C single bond of the parent ferrole. We observed that Me_3NO and/or the entering ligands do favour the formation of such complexes. In these reactions Me_3NO apparently plays the double role of promoting an unusual insertion of CO and release of the coordinated organic moieties (vide infra). The expected simple CO labilization is only a secondary process. The reactions described here represent a new and convenient method to obtain substituted flyover complexes and suggest new synthetic uses of Me_3NO .

The formation of the ‘flyover’ complex C also represents an example of the influence of the entering phosphines on the metal–ligand interactions [25]. In the reactions described here, the donor ability of the phosphines seems to exert a key role, since with PPh_2H only substitution occurs. Also the substituents on the ferrole ring affect the results. Indeed, the ‘ferrole’ $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)_2]$ reacts with dppm and Me_3NO to give only substitution products.

A possible reaction sequence which leads to substituted ‘flyover’ complexes could be the ‘addition’ of ligand with simultaneous CO displacement and insertion into an Fe–C σ bond of the ferrole. This could give rise to ferracyclopentadienone intermediates, which could subsequently rearrange into flyover derivatives.

A reaction sequence showing some analogies with that proposed here is the stepwise insertion of ethyne into a μ -CO under UV irradiation in the complex $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-dppm})]$ to give a flyover derivative and a diirontrone complex [26].

3.5. Formation of the tropone-precursor complexes IX and X and ligand disengagement reactions

The formation of these complexes is likely to occur as discussed for complexes a. Addition of alkynes together with CO migration would give substituted fly-

over complexes (not isolated). Ligand insertion into an Fe–C bond would then form complexes IX and X. The insertion of CO into the C–C bond of the tetraethylferrole ring appears to be a general reaction trend in the presence of Me_3NO and donors.

Examples of alkyne insertion into a cluster-coordinated cyclopentadienone, closely comparable with the processes leading to complexes IX and X, are known. $[\text{Os}_3(\text{CO})_9(\text{C}_2\text{Me}_2)_2\text{CO}]$ is formed by reaction of $[\text{Os}_3(\text{CO})_{10}(\text{CNMe})_2]$ with but-2-yne. Its derivative, $[\text{Os}_3(\text{CO})_8(\text{C}_2\text{Me}_2)_2\text{CO}(\text{CNMe})]$, inserts alkynes to give Os_3C_7 cluster units in which the incoming alkyne is bound to the already existing ligand in a way closely comparable with that found in IX [27].

Attempts at releasing organic molecules from complexes A, C, and from Ia and IX by thermal treatment, in the presence of Me_3NO [11] were made. Reactions under N_2 , CO_2 and C_2H_2 were explored. The nature of the displaced organic molecules was established on the basis of their fragmentation patterns (GLC-MS).

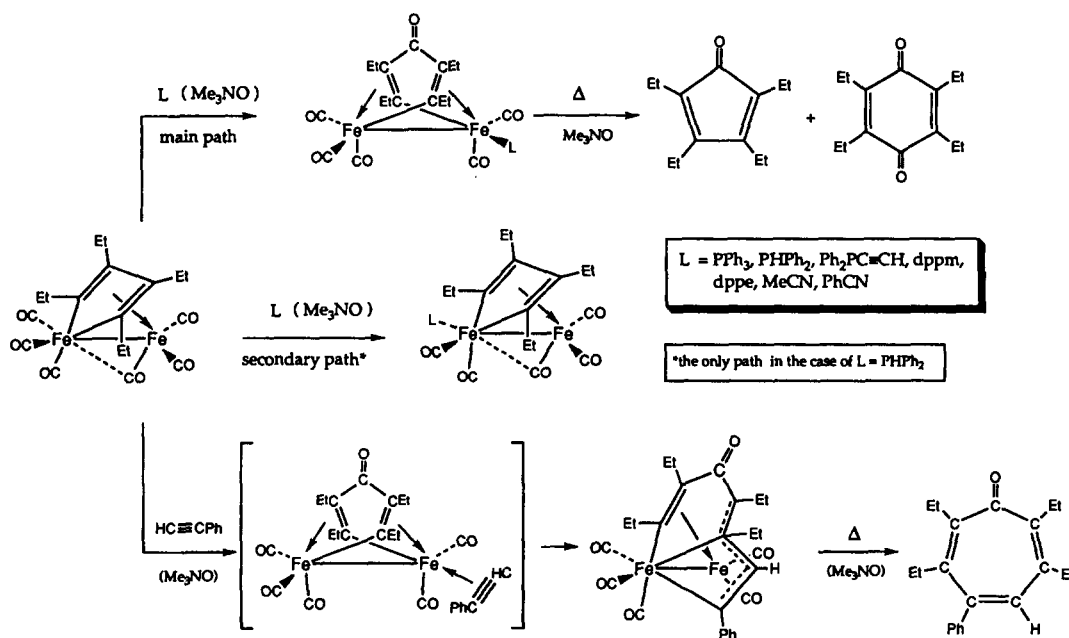
Complex A releases tetraethylcyclopentadienone and tetraethyl-*p*-quinone as the major organic products. This indicates insertion of CO into the ferrole ring, as observed in the above reactions. Complex C releases tetraethylcyclopentadienone and, unexpectedly, hexaethyltropone. In the presence of CO_2 and acetylene cyclooligomerization to hexaethylbenzene was also observed. However, in the presence of acetylene no tetraethyltropone was formed. Complex Ia releases mainly tetraethylcyclopentadienone and, as a minor product, tetraethyl-*p*-quinone. This indicates, once again, that the cyclopentadienone is formed "via" the intermediacy of a fly-

over structure. Finally, complex IX releases tetraethylphenyltropone.

The organic products observed are the same found by Hübner under photochemical conditions. However, in these reactions formation of tropone from the 'flyover' structures was not observed [1,3a]. The use of Me_3NO hence represents a valuable method for the displacement of a variety of organic molecules from the di-iron complexes, without using subsidiary reactants. CO_2 seems to prevent the incorporation of CO into the organic moieties, probably by inhibiting the effect of Me_3NO . Apparently acetylene plays the same role. However, tetraethylactone surprisingly is formed as the main product either from complex A or Ia in the presence of ethyne. This could indicate that the incorporation of CO_2 , formed in situ by reaction of the carbonyls with Me_3NO , is, to some extent, favoured.

Finally, in the reaction solutions of complex A (where CO could be present only as the result of substitution or decomposition reactions) relatively large amounts of the 'flyover' derivative C are found. In the reaction solutions of complex C, only small yields of complex A are found. This indicates that under our conditions interconversion between the two structures may occur, the 'flyover' structure being more stable [1,5a] than the other. The main reaction pathways involving complex A and its derivatives are shown in Scheme 3.

The reactions reported in this paper are, to our knowledge, the first evidence for the stepwise formation of tropones. Earlier reports on these processes [3a], although reaching the same conclusions, provided no evidence of the reaction pathways. The identification of



Scheme 3.

the key intermediates now allows some theorising concerning the reaction mechanisms.

Acknowledgement

Financial support for this work has been obtained from Consiglio Nazionale delle Ricerche (Rome).

References and notes

- [1] W.P. Fehlhammer and H. Stolzenberg, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds), *Comprehensive Organometallic Chemistry*, 1st edn., Vol. 4, Pergamon, Oxford, 1982, p. 548.
- [2] Recent X-ray studies include: (a) V. Crocq, J.-C. Daran and Y. Jeannin, *J. Organomet. Chem.*, **373** (1989) 85; (b) D. Seyferth, C.M. Archer and J.C. Dewan, *Organometallics*, **10** (1991) 3759 and references cited therein.
- [3] (a) W. Hübel, in I. Wender and P. Pino (eds.), *Organic Syntheses via Metal Carbonyls*, Vol. I, Wiley Interscience, New York, 1968, p. 273; (b) G. Palyi, G. Varadi and L. Markò, in I. Bernal (ed.), *Stereochemistry of Organometallic and Inorganic Compounds*, Vol. I, Elsevier, Amsterdam, 1986, p. 358.
- [4] See for example: (a) N. Calderon, J.P. Lawrence and F.A. Ofstead, *Adv. Organomet. Chem.*, **17** (1979) 449; (b) R.R. Schrock, *J. Organomet. Chem.*, **300** (1986) 249 and references cited therein; (c) M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem.*, **275** (1984) 119; (d) K.O. Bishop, *Chem. Rev.*, **76** (1976) 461; (e) G.K. Barker, M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, *J. Am. Chem. Soc.*, **93** (1973) 579; (f) F. Biagini, A.M. Caporusso, T. Funaioli and C. Fachinetti, *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 1009; (g) R.J. McKinney, *J. Chem. Soc., Chem. Commun.*, (1980) 490; (h) C. Otero Arean, E. Escalona Platero, G. Spoto and A. Zecchina, *J. Mol. Catal.*, **56** (1989) 211.
- [5] (a) G. Predieri, A. Tiripicchio, M. Tiripicchio Camellini, M. Costa and E. Sappa, *Organometallics*, **9** (1990) 1729. (b) M. Costa, G. Predieri, A. Tiripicchio and E. Sappa, *J. Organomet. Chem.*, **423** (1992) 129. (c) G. Gervasio, R. Giordano, E. Sappa, M. Costa, G. Predieri and A. Tiripicchio, *J. Cluster Sci.*, **4** (1993) 33.
- [6] S. Aime, L. Milone, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, (1979) 1155 and references cited therein.
- [7] See for example: (a) S. Rivomanana, G. Lavigne, N. Lugan, J.-J. Bonnet, R. Yanez and R. Mathieu, *J. Am. Chem. Soc.*, **111** (1989) 8959; (b) J.C. Bricker, C.C. Nagel and S.G. Shore, *J. Am. Chem. Soc.*, **107** (1985) 377; (c) D.S. Barratt and D.J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, (1985) 1559; (d) S.J. Wang and R. Angelici, *Inorg. Chem.*, **27** (1988) 3233; (e) M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem.*, **342** (1988) 97; (f) N.J. Coville, M.O. Albers, T.V. Ashworth and E. Singleton, *J. Chem. Soc., Chem. Commun.*, (1981) 408; (g) S. Aime, M. Botta, R. Gobetto and D. Osella, *Organometallics*, **4** (1985) 1475, *Inorg. Chim. Acta*, **115** (1986) 129.
- [8] M.I. Bruce, *Coord. Chem. Rev.*, **76** (1987) 1 and references cited therein.
- [9] G.A. Foulds, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, **296** (1985) 147.
- [10] R. Giordano, E. Sappa, D. Cauzzi, G. Predieri, A. Tiripicchio and M. Tiripicchio Camellini, *J. Organomet. Chem.*, **412** (1991) C14.
- [11] Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, (1974) 336.
- [12] M. Careri, A. Mangia, P. Manini, G. Predieri and E. Sappa, *J. Organomet. Chem.*, **476** (1994) 127.
- [13] L.J. Todd, J.P. Hickey, J.R. Wilkinson, J.C. Huffmann and K. Folting, *J. Organomet. Chem.*, **112** (1976) 167.
- [14] M.S. Lehmann and F.K. Larsen, *Acta Crystallogr.*, **A30** (1974) 580.
- [15] *International Tables for X-Ray Crystallography*; Vol IV, Kynoch, Birmingham, 1974.
- [16] G.M. Sheldrick, *SHELX-76 program for crystal structure determination*, University of Cambridge, 1976; *SHELXS-86 program for the solution of crystal structures*, University of Göttingen, 1986.
- [17] D. Osella, M. Botta, R. Gobetto, R. Amadelli and V. Carassiti *J. Chem. Soc., Dalton Trans.*, (1988) 2519.
- [18] A.J. Carty, *Pure and Appl. Chem.*, **54** (1982) 113.
- [19] (a) B.H. Nöth and L. Meinel, *Z. Anorg. Allg. Chem.*, **394** (1967) 225; (b) E. Weiss, W. Hübel and R. Merenyi, *Chem. Ber.*, **95** (1962) 1155.
- [20] (a) G. Predieri, A. Tiripicchio, C. Vignali and E. Sappa, *J. Organomet. Chem.*, **342** (1988) C 33; (b) E. Sappa, G. Predieri, A. Tiripicchio and C. Vignali, *J. Organomet. Chem.*, **378** (1989) 109.
- [21] J. Meunier-Piret, P. Piret and M. Van Meerssche, *Acta Crystallogr.*, **19** (1965) 85.
- [22] E. Sappa, L. Milone and G.D. Andreotti, *Inorg. Chim. Acta*, **13** (1975) 67.
- [23] (a) R.E. Dessy and R.L. Pohl, *J. Am. Chem. Soc.*, **90** (1968) 1995; (b) G. Zott, R.D. Rieke and J.S. McKennis, *J. Organomet. Chem.*, **228** (1982) 271; (c) D. Osella, G. Arman, M. Botta, R. Gobetto, F. Laschi and P. Zanello, *Organometallics*, **8** (1989) 620.
- [24] E. Cabrera, J.-C. Daran, Y. Jeannin and O. Kristiansson, *J. Organomet. Chem.*, **310** (1986) 367.
- [25] See for example: (a) D. Boccardo, M. Botta, R. Gobetto, D. Osella, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, (1988) 1249; (b) F.W.B. Einstein, K.G. Tyers, A.S. Tracey and D. Sutton, *Inorg. Chem.*, **25** (1986) 1631; (c) E. Rosenberg, J. Bracker-Novak, R.W. Gellert, S. Aime, R. Gobetto and D. Osella, *J. Organomet. Chem.*, **365** (1989) 163; (d) D. Nucciarone, N.J. Taylor, A.J. Carty, A. Tiripicchio, M. Tiripicchio Camellini and E. Sappa, *Organometallics*, **7** (1988) 118.
- [26] G. Hogarth, F. Kayser, S.A.R. Knox, D.A.V. Morton, A.G. Orpen and M.L. Turner, *J. Chem. Soc., Chem. Commun.*, (1988) 358.
- [27] B.F.G. Johnson, R. Khattar, J. Lewis, P.R. Raithby and D.N. Smit, *J. Chem. Soc., Dalton Trans.*, (1988) 1421.