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Substituted metal carbonyls

XIII *. $Fe(CO)_4(\eta^1\text{-dppf})$ [where dppf = $(Ph_2PC_5H_4)_2Fe$]: a convenient building block for heterometallic complexes

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Abstract

The potential of $Fe(CO)_4(\eta^1\text{-dppf})$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) as a precursor for heterometallic species is fully expanded in the synthesis of $(OC)_4Fe(\mu\text{-dppf})Cr(CO)_5$, $(OC)_4Fe(\mu\text{-dppf})W(CO)_5$, and $(OC)_4Fe(\mu\text{-dppf})Mn_2(CO)_9$, all of which have been characterized by IR, NMR (^1H and ^{31}P) and elemental analyses. The low energy requirement of TMNO ($Me_3NO \cdot 2H_2O$)-decarbonylation allows the formation of monosubstituted $Mn_2(CO)_{10}$ as the major product. This aspect is further substantiated by the isolation of $Mn_4(CO)_{18}(\mu\text{-dppf})$ in which the single bridging of a diphosphine group between two $Mn_2(CO)_9$ moieties is unprecedented.

Introduction

The paucity of heterometallic carbonyl complexes which contain a singly bridging diphosphine ligand is partly due to the lack of convenient precursors for such designed syntheses. The few notable examples include $(OC)_4Fe(\mu\text{-dppm})RhCl(CO)$ (dppm = $Ph_2PCH_2PPh_2$) [1,2], $(OC)_4Fe(\mu\text{-P–P})Mn(CO)_nBr$ (P–P = dppm, n = 3, 4; P–P = $CH_2{=}C(PPh_2)_2$, n = 3), $(OC)_4Fe(\mu\text{-dppm})Mo(CO)_n$ (n = 4, 5) [3] by Shaw and coworkers, and $(OC)_5M(\mu\text{-dppe})M'(CO)_5$ (M, M′ = Cr, Mo, W, M ≠ M′; dppe = $Ph_2PCH_2CH_2PPh_2$) by Keiter et al. [4]. For the intriguing ligand complex 1,1′-bis(diphenylphosphino)ferrocene (dppf) [5–8], we have illustrated the feasibility of the formation of such complexes by the synthesis of $(OC)_4Fe(\mu\text{-dppf})Mo(CO)_5$

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from $Fe(CO)_4(dppf)$ in a previous paper [9]. In this report we further extend the reactive functionality of $Fe(CO)_4(dppf)$ to the other group 6 binary carbonyls, viz. Cr and W.

Monosubstitution of $Mn_2(CO)_{10}$ by ligands such as tertiary phosphines is often complicated by higher substitution, scission of the Mn–Mn bond, hydrogen abstraction, and valence disproportionation reactions [10]. When a diphosphine is used, disubstitution invariably results; the ligand inevitably prefers intramolecular to intermolecular bridging [11–13]. These competing reactions and secondary products occur because of the stringent synthetic conditions [10–15]. The diversity and complexity of this type of substitution chemistry, led us to examine the TMNO-assisted interaction between $Mn_2(CO)_{10}$ and $Fe(CO)_4(dppf)$ and, for comparison, that between $Mn_2(CO)_{10}$ and dppf.

Results and discussion

At ambient temperature, $(OC)_4Fe(\mu\text{-dppf})M(CO)_5$ (M = Cr, W) is isolated as the major product in the reaction of $Fe(CO)_4(dppf)$ with $M(CO)_6$ and $Me_3NO \cdot 2H_2O$ (TMNO) in a stoichiometric ratio of 1 : 1.4 : 1.3. These novel bimetallics are also accessible from the related Cr and W complexes $M(CO)_5(\eta^1\text{-dppf})$ with $Fe(CO)_5$. The IR spectra of these heterometallic complexes show a common pattern of four bands in the carbonyl stretching region, two of which are found above 2000 cm^{-1}. The absorption at 2050 cm^{-1} belongs characteristically to the $Fe(CO)_4$ moiety while the remaining high-energy A_1 band corresponds to the $M(CO)_5$ fragment.

The additive effect of the homonuclear analogues in the mixed-metal dimers is also evident in the NMR (^1H and ^{31}P) spectra (Table 1). In the proton spectra, the overlapping substituted cyclopentadienyl (Cp) signals of the respective homometallic dimers render the splitting patterns of the Cp resonances indiscernible. The ^{31}P NMR spectra show typical plots of a single resonance at 67.04 ppm (Ph_2PFe)

Table 1

Spectroscopic data

Complex	$\nu(CO)$ (cm^{-1}) [a]	$\delta(^1H)$ (ppm) [b,c]	$\delta(^{31}P)$ (ppm) [b]
$(OC)_4Fe(\mu\text{-dppf})\text{-}Cr(CO)_5 \cdot \frac{3}{4}C_6H_{14}$	2063m, 2050m, 1977w, 1941s	7.25–7.60(m, 20H) 4.30(m, br, $2H_b^{Cr} + 2H_a^{Fe}$) 3.93(m, br, $2H_a^{Cr} + 2H_b^{Fe}$)	67.04(s, Ph_2PFe) 47.39(s, Ph_2PCr)
$(OC)_4Fe(\mu\text{-dppf})\text{-}W(CO)_5$	2072m, 2050m, 1978w, 1940s	7.26–7.59(m, 20H) 4.35(m, br, $2H_b^{W}$) 4.28(m, br, $2H_a^{Fe}$) 3.94(m, $2H_a^{W} + 2H_b^{Fe}$)	67.04(s, Ph_2PFe) 11.17(t, Ph_2PW) *J*(PW) 244Hz
$(OC)_4Fe(\mu\text{-dppf})\text{-}Mn_2(CO)_9 \cdot C_6H_{14}$	2091m, 2050m, 2009w, 1994s, 1934s	7.24–7.45(m, 20H) 4.29(m, br, $2H_b^{Mn} + 2H_a^{Fe}$) 3.94(m, br, $2H_a^{Mn} + 2H_b^{Fe}$)	67.11(s, Ph_2PFe) 66.30(s, br, Ph_2PMn)
$Mn_4(CO)_{18}(dppf) \cdot \frac{1}{4}C_6H_{14}$	2091m, 2001w, 1995s, 1934s	7.26–7.44(m, 20H) 4.28(m, br, $4H_b$) 4.03(q, $4H_a$)	66.37(s, br)

[a] $CHCl_3$. [b] $CDCl_3$. [c] H_a and H_b refer to the external and internal cyclopentadienyl protons, respectively. H^M denotes the proton of the M (M = Cr, Fe, Mn, Mo, W)-coordinated phosphinocyclopentadienyl ring.

with another resonance at higher field bearing the identity of a P atom adjacent to a group 6 metal (Cr or W). Since these shift values compare favourably with those of $M(CO)_5$(dppf), $M_2(CO)_{10}$(dppf) [16], $Fe(CO)_4$(dppf) and $Fe_2(CO)_8$(dppf) [9], little interaction between the two metal centres across the bridge is predicted. Structural data published recently show that there are no M–M bonds on the two related complexes, $Fe_2(CO)_8$(dppf) having staggered conformation of the Cp rings [9,17] and $Mo_2(CO)_{10}$(dpppropane) [18,19]. Though it is uncertain if the mixed-metal and mixed-geometry complexes would adopt the same configuration, it is clear that the newly synthesized compounds could be useful examples for comparative reactivity studies of the Fe/(Cr,Mo,W) coordination spheres. These heterometallics are related to the recently reported dppm-bridged $(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4$ which has an Fe→Mo donor–acceptor bond and $(OC)_4Fe(\mu\text{-dppm})Mo(CO)_5$ [3] which has not been isolated. The absence of reinforcing metal–metal bonds, and the use of a versatile bridging ligand, should give our title complexes a flexible and more open structure. It remains to be seen if these features will have any influence on their reactivities.

Reaction of $Mn_2(CO)_{10}$, with $Fe(CO)_4$(dppf) also gives the heterometallic complex. The presence of a $Mn_2(CO)_9$ fragment is supported by IR, microanalytical and mass susceptibility data. Five carbonyl stretching frequencies are observed in the IR spectrum. Except for the absorption at 2050 cm^{-1} that is associated with the $Fe(CO)_4$ moiety, the other found frequencies agree fairly well with those of axial $Mn_2(CO)_9L$ (L = monodentate ligand) complexes [20–23]. The mass susceptibility ($\chi_g = -0.401 \times 10^{-6}$ cgs) reveals the diamagnetic nature of the complex and together with the microanalytical data and molecular weight preclude the existence of a 17-electron monomeric Mn fragment.

In the ^{31}P NMR spectrum, two singlets are seen with the signal at 67.11 ppm corresponding to the phosphorus atom bonded to iron. The higher field resonance at 66.30 ppm is assigned to the phosphorus atom on manganese and is significantly broadened by the quadrupolar effect of the ^{55}Mn nucleus (100%, $I = 5/2$).

Likewise, no cleavage of the Mn–Mn binuclear bond is observed in the TMNO-induced decarbonylation reaction of $Mn_2(CO)_{10}$ with dppf. As in $(OC)_4Fe(\mu\text{-dppf})Mn_2(CO)_9$, the molecular weight, IR, NMR, microanalytical and mass susceptibility data ($\chi_g = -0.407 \times 10^{-5}$ cgs) point to the formulation $Mn_4(CO)_{18}$-(dppf), in which the two $Mn_2(CO)_9$ moieties are linked by a symmetrical diphosphine bridge. The unidentate diphosphine ligation mode is eliminated by the absence of a high field ^{31}P signal close to that of free dppf molecule. The chemical equivalence of the two phosphorus nuclei is confirmed by the appearance of a single ^{31}P resonance at 66.37 ppm. The quadrupolar effect of the ^{55}Mn nucleus on the phosphorus atom is again observed.

Similar to the spectra of group 6 dimers $M_2(CO)_{10}$(dppf), the ^1H NMR spectrum consists of a broad multiplet and a higher-field quartet attributable to the internal and external Cp protons, respectively, in the Cp proton-signal region [16].

Unlike classical thermolytic and photochemical methods, the mild reaction conditions afforded by TMNO-decarbonylation avoid the cleavage of the Mn–Mn bond [24,25] and hence render the synthesis of $(OC)_4Fe(\mu\text{-dppf})Mn_2(CO)_9$ and $Mn_4(CO)_{18}(\mu\text{-dppf})$ feasible. To our knowledge, these are the first examples of a diphosphine group linking $Fe(CO)_4$ to $Mn_2(CO)_9$ or of linking two of the $Mn_2(CO)_9$ moieties.

Under our experimental conditions, the formation of the usual intramolecular-bridged complexes $Mn_2(CO)_8(\mu\text{-P-P})$ [10–13] or the reactive $(OC)_5Mn\text{-}Mn(CO)_4(\eta^1\text{-dppf})$ is not observed. There is also no evidence for any primary or secondary products arising from the dimerization of the hypothetical radical $Mn(CO)_4(\eta^1\text{-dppf})$. Though it is commonly accepted that carbonyl substitution of the parent decacarbonyl occurs by fission of the Mn–Mn bond [26], we are skeptical whether this is necessarily the dominant mechanism here. The presence of TMNO may simply promote a documented nucleophilic attack which is followed by oxygen transfer [24,25,27,28], which in the process keeps the Mn–Mn bond intact.

Conclusion

The ease of synthesis of $Fe(CO)_4(dppf)$, its stability and yet ready complexation to a substitution-labile fragment make it an attractive substrate for iron-based heterometallic studies. Of great interest is the difference in reactivities of different metal sites in such complexes towards further substitution. This aspect will be explored in future, together with the utility of the Fe/unidentate as a ligand in other chemical reactions.

The isolation of the novel complex $Mn_4(CO)_{18}(\mu\text{-dppf})$, which consists of a large molecule linking five metal centres in a row, supported or unsupported by metal–metal bonds, is likely to spark off academic interest and open up new initiatives in the research of manganese carbonyl chemistry.

Experimental

General procedure

All reactions were performed under dry dinitrogen by use of standard Schlenk techniques. Chemical reagents were supplied from commercial sources and were used without further purification. Precoated silica plates of layer thickness 0.25 mm were obtained from Merck and Baker. The reagent-grade solvents were freshly distilled and degassed before use. Molecular weight determinations were carried out by vapour pressure osmometry in a Knauer-Dampfdruck Osmometer by Galbraith Laboratories, Inc. in Knoxville U.S.A. Mass susceptibility was measured by use of a Johnson Matthey Magnetic Susceptibility balance. Proton NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.55 MHz using $(CH_3)_4Si$ as internal standard. Phosphorus-31 NMR spectra were recorded on the same instrument at 36.23 MHz. Chemical shifts are in ppm to high frequency of external 85% H_3PO_4. Infrared spectra were recorded as $CHCl_3$ solutions on a FT–IR Perkin-Elmer 1710 spectrometer. Elemental analyses were performed by the Analytical Service of this department. The presence of hexane as a solvent of crystallization was confirmed by NMR analysis. Spectroscopic (NMR and IR) data are listed in Table 1. The overlapping of some resonances and their complications because of long range couplings preclude accurate analysis of the J(HP) and J(HH) values.

Preparations

$Fe(CO)_4(dppf)$ was prepared as previously described [9].

$FeM(CO)_9(\mu\text{-dppf})$ (M = Cr, W). The addition of $Fe(CO)_4(dppf)$ (0.200 g, 0.28 mmol) to a previously stirred (15 min) mixture of $M(CO)_6$ (0.39 mmol) and TMNO

(0.36 mmol) in THF (40 cm^3) at 25°C, gave an orange-yellow solution. After $4\frac{1}{2}$–5 h of vigorous stirring, the reaction mixture was filtered and the solvent was removed in vacuo. The residue was extracted with a minimum quantity of CH_2Cl_2 to give an orange solution that was applied to the silica TLC plates. Elution with 20% CH_2Cl_2 in hexane solution followed by further recrystallization from CH_2Cl_2/hexane mixture yielded the required orange product, together with an unidentified orange side product.

$[(OC)_4Fe(\mu\text{-dppf})Cr(CO)_5] \cdot \frac{3}{4}C_6H_{14}$, yield 0.116 g (42%), Found: C, 58.44; H, 3.38. $C_{48}H_{39}CrFe_2O_9P_2$ calcd.: C, 58.28; H, 3.96%.

$[(OC)_4Fe(\mu\text{-dppf})W(CO)_5]$, yield 0.064 g (22%), Found: C, 48.77; H, 2.98. $C_{43}H_{28}Fe_2O_9P_2W$ calcd.: C, 49.37; H, 2.70%.

FeMn$_2$(CO)$_{13}$(μ-dppf). An orange-red solution was obtained by stirring $Mn_2(CO)_{10}$ (0.380 g, 0.97 mmol) and TMNO (0.102 g, 0.90 mmol) in THF (50 cm^3) for 15 min. $Fe(CO)_4(dppf)$ (0.500 g, 0.69 mmol) was then added and the mixture was stirred for a further 2 h. Separation by preparative TLC as before, followed by recrystallization from pure hexane gave the orange-yellow $(OC)_4Fe(\mu\text{-dppf})Mn_2(CO)_9 \cdot C_6H_{14}$ (0.539 g, 67%). Found: C, 54.32; H, 3.43. $C_{53}H_{42}Fe_2Mn_2O_{13}P_2$ calcd.: C, 54.38; H, 3.62%. Mol. Wt.(benzene)—Found: 1088, calcd.: 1084.

Mn$_4$(CO)$_{18}$(μ-dppf). The 3 h reaction of $Mn_2(CO)_{10}$ (1.000 g, 2.57 mmol) with dppf (0.712 g, 1.28 mmol) and TMNO (0.287 g, 2.58 mmol) in THF (50 cm^3) at 25°C followed by purification with preparative TLC and hexane/CH_2Cl_2, gave deep orange $(OC)_9Mn_2(\mu\text{-dppf})Mn_2(CO)_9 \cdot \frac{1}{4}C_6H_{14}$ as the major product. Yield 1.002 g (68%), Found: C, 49.31; H, 2.43. $C_{54}H_{32}FeMn_4O_{18}P_2$ calcd.: C, 49.39; H, 2.42%. Mol. Wt.(benzene)—Found: 1276, calcd.: 1278.

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References

1 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1987) 2751.
2 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1986) 13.
3 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1987) 1509.
4 R.L. Keiter, S.L. Kaiser, N.P. Hansen, J.W. Brodack and L.W. Cary, Inorg. Chem., 20 (1981) 283.
5 T. Hayashi, M. Konishi and M. Kumada, J. Organomet. Chem., 186 (1980) C1.
6 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, J. Am. Chem. Soc., 106 (1984) 158.
7 I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, Organometallics, 4 (1985) 972.
8 T.S.A. Hor and L.-T. Phang, Chemistry International-3rd Asian Chemical Congress Proceedings, Brisbane, Australia, August 1989, submitted for publication.
9 T.S.A. Hor and L.-T. Phang, J. Organomet. Chem., 381 (1990) 121.
10 P.M. Treichel, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982, Ch. 29.
11 W. Hieber and W. Freyer, Chem. Ber., 93 (1960) 462.
12 C.J. Commons and B.F. Hoskins, Aust. J. Chem., 28 (1975) 1663.
13 R. Colton and C.J. Commons, Aust. J. Chem., 28 (1975) 1673.
14 A. Sacco, Gazz. Chim. Ital., 93 (1963) 698.
15 R.H. Reimann and E. Singleton, J. Organomet. Chem., 38 (1972) 113.

16 T.S.A. Hor and L.-T. Phang, J. Organomet. Chem., 373 (1989) 319.
17 L.-K. Liu, private communication.
18 T.S.A. Hor, J. Organomet. Chem., 340 (1988) 51.
19 R.A. Gossage, private communication.
20 M.L. Ziegler, H. Haas and R.K. Sheline, Chem. Ber., 98 (1965) 2454.
21 H. Wawersik and F. Basolo, Chem. Commun., (1966) 366.
22 C.U. Pittman, Jr. and G.O. Evans, J. Organomet. Chem., 43 (1972) 361.
23 R.H. Reimann and E. Singleton, J. Chem. Soc., Dalton Trans., (1976) 2109.
24 M.O. Albers and N.J. Coville, Coord. Chem. Rev., 53 (1984) 227.
25 T.-Y. Luh, Coord. Chem. Rev., 60 (1984) 255.
26 D.R. Kidd, C.P. Cheng and T.L. Brown, J. Amer. Chem. Soc., 100 (1978) 4103.
27 Y.-L. Shi, Y.-C. Gao, Q.-Z. Shi, D.L. Kershner and F. Basolo, Organometallics, 6 (1987) 1528.
28 J.-K. Shen, Y.-C. Gao, Q.-Z. Shi and F. Basolo, Organometallics, 8 (1989) 2144.