

## Substituted metal carbonyls

### XII \*. Synthesis of $\text{Fe}(\text{CO})_4(\eta^1\text{-dppf})$ ( $\text{dppf} = (\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Fe}$ ) and its conversion into $\text{Fe}_2(\text{CO})_8(\mu\text{-dppf})$ and $(\text{CO})_4\text{Fe}(\mu\text{-dppf})\text{Mo}(\text{CO})_5$

T.S. Andy Hor \*\* and Lai-Tee Phang

*Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 0511 (Singapore)*

(Received April 6th, 1989)

#### Abstract

Carbonyl substitution of  $\text{Fe}(\text{CO})_5$  by 1,1'-bis(diphenylphosphino)ferrocene (dppf) at 25°C with the aid of trimethylamine *N*-oxide (TMNO) gives  $\text{Fe}(\text{CO})_4(\eta^1\text{-dppf})$ , **1**, and the dinuclear triiron phosphine-bridged complex,  $\text{Fe}_2(\text{CO})_8(\mu\text{-dppf})$ , **2**. Like dppf itself, complex **1** is a good precursor for heterometallic species, as exemplified in the synthesis of  $(\text{CO})_4\text{Fe}(\mu\text{-dppf})\text{Mo}(\text{CO})_5$ . Conversion of **1** into **2** is facile in the presence of  $\text{Fe}(\text{CO})_5$  and TMNO. The chelate,  $\text{Fe}(\text{CO})_3(\eta^2\text{-dppf})$  is accessible by reaction of  $\text{Fe}(\text{CO})_5$  with dppf and  $\text{NaBH}_4$  in *n*-butyl alcohol under reflux. The structures have been determined by IR, NMR ( $^1\text{H}$  and  $^{31}\text{P}$ ) and elemental analyses.

#### Introduction

Diphosphine ligands often form chelates or bridges in substituted iron carbonyl complexes [1-4]. The unidentate ligation mode is uncommon. In diphosphine ligands of the type  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ , only dpmm and dppe ( $n = 1$  and 2, respectively) form of complexes in this coordination mode [4-10].

Ligand substitution of group 6 metal hexacarbonyls by 1,1'-bis(diphenylphosphino)ferrocene (dppf) in the presence of trimethylamine *N*-oxide to form a range of mono- and dinuclear phosphine complexes in the chelating, bridging or unidentate ligation mode has recently been reported [11]. As a comparison, this reagent-induced substitution has been extended to the iron carbonyl system which is more challenging owing to (i) technical difficulties in purification, (ii) complication by possible cluster formation as well as (iii) the long-standing interest in the stereo-

\* For part XI see ref. 11

\*\* To whom correspondence should be addressed.

chemistry of pentacoordinate iron complexes. The ligating ability of  $\text{Fe}(\text{CO})_4(\eta^1\text{-dppf})$ , similar to dppf, for various binary carbonyls, e.g.  $\text{Fe}(\text{CO})_5$  and  $\text{Mo}(\text{CO})_6$  to form homo- and heterometallic species respectively, is also demonstrated.

## Results and discussion

Reaction of 1,1'-bis(diphenylphosphino)ferrocene (dppf) with  $\text{Fe}(\text{CO})_5$  at  $25^\circ\text{C}$  in the presence of trimethylamine *N*-oxide (TMNO) in a ratio of 1.2/1.0/2.0 yields the major product  $\text{Fe}(\text{CO})_4(\text{dppf})$ , **1**, which is one of the few examples of unidentate diphosphines in an iron carbonyl coordination sphere. The dimer  $\text{Fe}_2(\text{CO})_8(\text{dppf})$ , **2**, can be isolated when the ligand is restricted to the ratio 0.4/1.0/0.8.

Both complexes can be isolated analytically pure and have been characterized by IR and NMR ( $^1\text{H}$  and  $^{31}\text{P}$ ) spectroscopy. The stereochemistry of these systems is of considerable interest. The presence of three carbonyl absorptions indicates an approximate  $C_{3v}$  symmetry [12] in both complexes. In the diiron complex **1**, the ligand is axially substituted, whereas the triiron complex **2**, shows apical-apical substitution. Though the determination of axial vs. equatorial substitution in  $\text{Fe}(\text{CO})_4\text{L}$  is complicated by the splitting of the E mode if ligand shows dissymmetry in L [1], this problem is not apparent in our complexes.

Unlike the chelates of group 6 metal carbonyls which can be readily synthesized by TMNO decarbonylation [11], the iron chelate *cis*- $\text{Fe}(\text{CO})_3(\eta^2\text{-dppf})$ , **3**, is not readily accessible by this route. This complex can be conveniently prepared by reaction of  $\text{Fe}(\text{CO})_5$ , dppf and  $\text{NaBH}_4$  in *n*-butyl alcohol under reflux, similar to that used by Keiter in the preparation of *trans*- $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$  [13].

The presence of three IR-active bands in the spectrum of **3** leads to ambiguity in the identification of the coordination geometry [12], which may be a trigonal bipyramid (tbp) or square pyramid (sp) or their intermediates. Cotton's X-ray crystallographic examination of an analogous dppm chelate revealed a coordination geometry intermediate between tbp and sp [3]. The greater steric requirement and larger bite size of dppf [14] compared to those of other common diphosphines probably cause greater distortion in **3** from the normal geometries of tbp and sp. In contrast to **1** and **2** but similar to other group 6 dppf chelates [11,15], this complex shows the typical ring reversal fluxionality of the Cp protons in these systems.

In the reaction of **1** with  $\text{Fe}(\text{CO})_5$  and TMNO, the phosphine-bridged complex **2** is formed in which **1**, like dppf in a similar reaction, is ligated to an  $\text{Fe}(\text{CO})_4$  moiety. This conversion suggests that in the preparation above, **2** is a secondary product arising from **1**. Complex **3**, in contrast, cannot be obtained from the decarbonylation of **1**. The ability of **1** to act as a precursor for homo- or heterometallic species is further manifested in the formation of the novel heterobimetallic complex  $(\text{CO})_4\text{Fe}(\mu\text{-dppf})\text{Mo}(\text{CO})_5$ , **4**, at ambient temperature ( $25^\circ\text{C}$ ) in the TMNO-induced decarbonylation of  $\text{Mo}(\text{CO})_6$  with **1**.

The IR spectrum of **4** shows four  $\nu(\text{CO})$  bands, two of which occur above  $2000\text{ cm}^{-1}$  (Table 1). These two high-energy bands of **4** are characteristic of the combined presence of  $\text{Fe}(\text{CO})_4$  and  $\text{Mo}(\text{CO})_5$  moieties. A comparison of the carbonyl stretching frequencies of **4** with those of **1** and  $\text{Mo}(\text{CO})_5(\text{dppf})$  also reveals the additive effect of the latter two complexes in **4**. This phenomenon has also been observed by Shaw and coworkers [10] in a related complex with bridging dppm; the spectral data of which are similar to those for **4**.

Table 1

## Spectroscopic data

Complex	$\nu(\text{CO})(\text{cm}^{-1})^a$	$\delta(^1\text{H})(\text{ppm})^{a,b}$	$\delta(^{31}\text{P})(\text{ppm})^a$
1	2049s, 1975m, 1941vs(br)	7.11–7.57[m, 20H], 4.45[m, br, 2H <sub>b</sub> ], 4.40[q, 2H <sub>a</sub> ], 3.86[t, 2H' <sub>b</sub> ], 3.68[q, 2H' <sub>a</sub> ] <sup>c</sup>	66.77(s, –Ph <sub>2</sub> P), –17.10(s, –Ph <sub>2</sub> P')
2	2050s, 1976m, 1943vs(br)	7.25–7.45[m, 20H], 4.21[q, 4H <sub>a</sub> ], 3.92[m, br, 4H <sub>b</sub> ]	67.04(s)
3	1989s, 1916m, 1883s	7.15–7.76[m, 20H], 4.22[s, br, 8H]	62.06(s)
4	2073m, 2050m, 1980w, 1945s	7.26–7.44[m, 20H], 4.35[m, br, 2H <sub>b</sub> <sup>Mo</sup> ], 4.28[q, 2H <sub>a</sub> <sup>Fe</sup> ], 3.92[m, br, 2H <sub>a</sub> <sup>Mo</sup> + 2H <sub>b</sub> <sup>Fe</sup> ] <sup>d</sup>	67.04(s, –Ph <sub>2</sub> PFe) 28.40(s, –Ph <sub>2</sub> PMo)

<sup>a</sup> CDCl<sub>3</sub>, <sup>b</sup> H<sub>a</sub> and H<sub>b</sub> refer to the external and internal cyclopentadienyl protons respectively. The primed H' and P' represent the protons and phosphorus on the uncoordinated phosphinocyclopentadienyl ring. <sup>c</sup> Spectra assignment is assisted by <sup>1</sup>H–<sup>1</sup>H decoupling experiments. <sup>d</sup> H<sup>Mo</sup> and H<sup>Fe</sup> denote the protons of the Mo- and Fe-coordinated phosphinocyclopentadienyl rings.

Two broad multiplets and a quartet are observed in the <sup>1</sup>H NMR spectrum of **4** (Table 1). By comparing the shift values and coupling patterns with those of the relevant Fe or Mo dimers [11], the higher field multiplet at 3.92 ppm can be assigned to the overlapping resonances of the internal and external Cp protons adjacent to the Fe(CO)<sub>4</sub> and Mo(CO)<sub>5</sub> coordination spheres, respectively. The lower field multiplet at 4.35 ppm belongs to the internal protons on the Cp ring proximal to the Mo centre whereas the external protons adjacent to the Fe carbonyl sphere show a typical quartet at 4.28 ppm.

Further substantiation of the identity of the Fe–Mo phosphine-bridged complex is provided by <sup>31</sup>P NMR spectra in which two singlets are present at 67.04 and 28.40 ppm. These shift values are remarkably close to those found in **2** (67.04 ppm) and (CO)<sub>5</sub>Mo(μ-dppf)Mo(CO)<sub>5</sub> (28.53 ppm). These results would suggest that in these dimeric systems, there is little interaction between the two metal centres across the bridge.

## Conclusion

Fe(CO)<sub>4</sub>(dppf) is expected to play an important role in the immediate future of iron carbonyl chemistry. This is not only attributable to its ligating ability, which makes it an ideal building block for heterometallic species, but also to the possible activation of the Fe centre in close proximity to its neighbouring metal centre. The success of Fe(CO)<sub>4</sub>(dppm) as the synthon in the synthesis of a variety of novel heterobimetallic complexes [9,10,16–18], indicates that Fe(CO)<sub>4</sub>(dppf) will assume an equally significant role in the syntheses of heterometallic complexes having two or more different metal centres. The role of dppf ligand in some proven catalytically active complexes is a subject of vigorous research interest [19–23]. The possible

development of these novel complexes, **1** in particular, in this direction provides an added incentive for our studies.

## Experimental

### General Procedure

All reactions were performed under dry dinitrogen by standard Schlenk techniques. Chemical reagents were commercial products and were used without further purification. Precoated silica plates of layer thickness 0.25 mm were purchased from Merck and Baker. All the solvents were reagent-grade and 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.). Proton NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.55 MHz using  $(\text{CH}_3)_4\text{Si}$  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%  $\text{H}_3\text{PO}_4$ . Infrared spectra were recorded as  $\text{CHCl}_3$  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 the solvent of crystallisation was confirmed by NMR spectroscopy. The NMR and IR data are listed in Table 1. The overlapping of some resonances and their complications owing to some observed long-range couplings preclude an accurate analysis of the  $J(\text{H}-\text{P})$  and  $J(\text{H}-\text{H})$  values.

### Preparations

#### $\text{Fe}(\text{CO})_4(\eta^1\text{-dppf})$ and $\text{Fe}_2(\text{CO})_8(\mu\text{-dppf})$

$\text{Fe}(\text{CO})_5$  (0.2  $\text{cm}^3$ , 1.52 mmol) was added to a solution of dppf (1.0 g, 1.80 mmol) and TMNO dihydrate (0.34 g, 3.04 mmol) in THF (60  $\text{cm}^3$ ). The resulting orange-brown solution was stirred at 25 °C for 4 h, after which the reaction mixture was filtered and the solvent removed in vacuo. The residue was extracted with a minimum quantity of  $\text{CH}_2\text{Cl}_2$  to give an orange solution that was applied to silica TLC plates. Elution with 20%  $\text{CH}_2\text{Cl}_2$  in hexane solution followed by further recrystallisation from  $\text{CH}_2\text{Cl}_2$ /hexane mixture gave  $[\text{Fe}(\text{CO})_4(\text{dppf})] \cdot 1/3\text{C}_6\text{H}_{14}$ , **1**, (0.130 g, 11%) (Found: C, 64.02; H, 4.08;  $\text{C}_{40}\text{H}_{33}\text{Fe}_2\text{O}_4\text{P}_2$ , calcd.: C, 63.97; H, 4.38%) [Mol. Wt. (benzene). Found: 729, calcd.: 722], traces of  $\text{Fe}_2(\text{CO})_8(\text{dppf})$  (2%) and  $\text{Fe}(\text{CO})_3(\text{dppf})$  which decomposed during elution. However, elution with 30% benzene in hexane solution followed by further recrystallisation, resulted in a cleaner separation and a higher yield of **1** (24%).

With a stoichiometric ratio of 1/0.4/0.8 for  $\text{Fe}(\text{CO})_5$ /dppf/TMNO and a reaction time of 1.75 h,  $[\text{Fe}_2(\text{CO})_8(\text{dppf})] \cdot \text{C}_6\text{H}_{14}$ , **2**, (10%) (Found: C, 59.64; H, 4.26;  $\text{C}_{48}\text{H}_{42}\text{Fe}_3\text{O}_8\text{P}_2$  calcd.: C, 59.04; H, 4.34%) and **1** (4%) were the major isolable products instead.

Reaction of **1** with TMNO and  $\text{Fe}(\text{CO})_5$  (1/1.3/1.7) in THF for 5 h at 25 °C gave **2** (16%) which was isolated by preparative TLC and recrystallised as above.

$\text{Fe}(\text{CO})_3(\eta^2\text{-dppf})$ .  $\text{Fe}(\text{CO})_5$  (0.50  $\text{cm}^3$ , 3.80 mmol) was added to a stirred mixture of dppf (0.42 g, 0.76 mmol) and  $\text{NaBH}_4$  (0.06 g, 1.53 mmol) in 50  $\text{cm}^3$  of n-butyl alcohol. The orange reaction mixture was refluxed for 26–29 h, cooled to room temperature, and kept at –20 °C for ca. 12 h. The orange-yellow precipitate

that formed, was collected by filtration and washed with several portions of methanol to remove the excess borate. It was then further recrystallised from  $\text{CH}_2\text{Cl}_2$ /methanol, to give 0.176 g (33%) of  $\text{Fe}(\text{CO})_3(\text{dppf})$ , **3** (Found: C, 64.07; H, 4.13;  $\text{C}_{37}\text{H}_{28}\text{Fe}_2\text{O}_3\text{P}_2$  calcd.: C, 64.01; H, 4.07%).

$\text{FeMo}(\text{CO})_9(\mu\text{-dppf})$ . When **1** (0.20 g, 0.28 mmol) was added to a stirred mixture of  $\text{Mo}(\text{CO})_6$  (0.10 g, 0.39 mmol) and TMNO (0.04 g, 0.36 mmol) in THF, an orange-yellow solution was obtained which was then stirred for 3 h. Separation by preparative TLC with 20%  $\text{CH}_2\text{Cl}_2$  in hexane solution as eluent, followed by further recrystallisation with  $\text{CH}_2\text{Cl}_2$ /hexane mixture gave the orange  $[\text{Fe}(\text{CO})_4(\mu\text{-dppf})\text{Mo}(\text{CO})_5] \cdot 1/3\text{C}_6\text{H}_{14}$ , **4**, (0.089 g, 33%) (Anal. Found: C, 54.48; H, 3.45;  $\text{C}_{45}\text{H}_{33}\text{Fe}_2\text{MoO}_9\text{P}_2$  calcd.: C, 54.76; H, 3.37%) as the major product. An unidentified orange-brown side product (0.007 g) was also obtained.

## Acknowledgements

The authors express their appreciation to Y.P. Leong for technical assistance and the National University of Singapore for financial support (Grant No. RP 850030) and a scholarship to L.T. Phang.

## References

- 1 W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, *Inorg. Chem.*, **8** (1969) 1464.
- 2 W.R. Cullen and D.A. Harbourne, *Can. J. Chem.*, **47** (1969) 3371.
- 3 F.A. Cotton, K.I. Hardcastle and G.A. Rusholme, *J. Coord. Chem.*, **2** (1973) 217.
- 4 P.A. Wegner, L.F. Evans and J. Haddock, *Inorg. Chem.*, **14** (1975) 192.
- 5 S.D. Ittel, C.A. Tolman, P.J. Krusic, A.D. English and J.P. Jesson, *Inorg. Chem.*, **17** (1978) 3432.
- 6 R.L. Keiter, A.L. Rheingold, J.J. Hamerski and C.K. Castle, *Organometallics*, **2** (1983) 1635.
- 7 A.S. Goldman and D.R. Tyler, *Inorg. Chim. Acta*, **98** (1985) L47.
- 8 S. Cartwright, J.A. Clucas, R.H. Dawson, D.F. Foster, M.M. Harding and A.K. Smith, *J. Organomet. Chem.*, **302** (1986) 403.
- 9 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, (1986) 13.
- 10 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1987) 1509.
- 11 T.S.A. Hor and L.-T. Phang, *J. Organomet. Chem.*, **373** (1989) 319.
- 12 F.A. Cotton and R.V. Parish, *J. Chem. Soc.*, (1960) 1440.
- 13 R.L. Keiter, E.A. Keiter, K.H. Hecker and C.A. Boecker, *Organometallics*, **7** (1988) 2466.
- 14 A.W. Rudie, D.W. Lichtenberg, M.L. Katcher and A. Davison, *Inorg. Chem.*, **17** (1978) 2859.
- 15 I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, *Organometallics*, **4** (1985) 972.
- 16 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, **11** (1987) 2751.
- 17 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, **12** (1987) 3079.
- 18 X.L.R. Fontaine, G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.* **9** (1987) 662.
- 19 P. Kalck, M. Ridmy and A. Thorez, *C. R. Acad. Sci., Ser. 2*, **305** (1987) 953.
- 20 R.O. Hughes, *United States Pat. US 4169861* (Date 791002).
- 21 J.D. Unruh and W.J. Wells, *Germany Offen. Pat. DE 2617306* (Date 761104).
- 22 R.O. Hughes and J.D. Unruh, *J. Mol. Catal.*, **12** (1981) 71.
- 23 R.O. Hughes and D.A. Young, *J. Am. Chem. Soc.*, **103** (1981) 6636.