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Substituted metal carbonyls

XI *. 1,1′-Bis(diphenylphosphino)ferrocene — a bridging, chelating and unidentate ligand in the synthesis of $M_2(CO)_{10}(\mu\text{-P-P})$, $M(CO)_4(\eta^2\text{-P-P})$ and $M(CO)_5(\eta^1\text{-P-P})$ (where M = Cr, Mo, W and $P\text{-}P = Fe(C_5H_4PPh_2)_2$)

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Abstract

Trimethylamine *N*-oxide-initiated decarbonylation of $M(CO)_6$ (M = Cr, Mo, W) followed by nucleophilic attack by 1,1′-bis(diphenylphosphino)ferrocene (dppf) affords a mixture of heterometallic products which consists mainly of a chelate with a bidentate diphosphine, $M(CO)_4$(dppf), and a dinuclear phosphine-bridged complex $M_2(CO)_{10}$(dppf) at ambient temperature (28 °C). The corresponding unidentate diphosphine, $M(CO)_5$(dppf), is obtained as the major isolable product at 10 °C. The IR and NMR (^1H and ^{31}P) spectral data and the structural properties of these complexes are presented and discussed.

Introduction

Ever since the synthesis of 1,1′-bis(diphenylphosphino)ferrocene (dppf) more than two decades ago [1–3], this intriguing diphosphine ligand, which is a complex by itself, has often been used as a ligand in organometallic syntheses [4–9]. Its use as a precursor for heterometallic carbonyl complexes is exemplified in a recent report by Baker and coworkers on the synthesis of a range of ferrocenylphosphine complexes of the type $[MX_2(CO)_x(\text{dppf})_y]$ (M = Mo, W; X = Cl, I; $x = 2$, 3 and $y = 1$, 2) [10]. Similar reports on the synthesis of other low-valent Group 6 transition metal carbonyl complexes containing dppf as an auxiliary ligand are however

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surprisingly rare [9,11,12]. The pentacarbonyls $M(CO)_5(\eta^1\text{-dppf})$ (M = Cr, W) and the dinuclear compounds, $M_2(CO)_{10}(\mu\text{-dppf})$ (M = Cr, Mo, W), are hitherto unknown, though the tetracarbonyls $M(CO)_4(\eta^2\text{-dppf})$ were synthesised as much as a decade ago [9], and the analogous cobaltocenylphosphine-bridged dimer $Mo_2(CO)_{10}\{\mu\text{-}Co(C_5H_4PPh_2)_2\}$ was recently isolated [13]. While most of the attention is centred on the dppf ligand in its chelating or bridging mode, a rare example of the ligand in its unidentate state has been studied recently by use of ^{95}Mo NMR spectroscopy [11].

The recent success in isolating some novel Group 6 carbonyls substituted with diphosphine ligands such as $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–3) by using trimethylamine *N*-oxide (TMNO) as an initiator opens up a suitable synthetic route that proceeds at ambient or low temperatures [14–18]. In this paper, we report a similar approach in the synthesis of the aforementioned systems. We also demonstrate unequivocally that dppf is a highly versatile ligand which can coordinate in a bridging, chelating, or unidentate fashion.

Results and discussion

A mixture of $Mo(CO)_6$, dppf, and TMNO in a stoichiometric ratio of 1 : 0.4 : 0.8 at ambient temperature yields several products, three of which in appreciable quantity. Two of the products are the tetracarbonyl $Mo(CO)_4(dppf)$ (**1**) and the dinuclear complex $Mo_2(CO)_{10}(dppf)$ (**2**), but the third component has yet to be characterised. Despite the stoichiometry-controlled conditions, formation of the chelate **1** and other side products is not inhibited.

The identity of **1** and **2** is evident from their IR and NMR (^1H and ^{31}P) data (Table 1). Compound **1** has been briefly described [9], and our IR and ^1H NMR data are fairly consistent with the published values. The presence of three IR absorptions, viz., a very strong and broad band ($B_1 + B_2$), a strong peak (A_1), and a medium peak (A_1), in the carbonyl region supports the formation of a *cis*-coordinated tetracarbonyl complex that has C_{2v} symmetry. This is further substantiated by the ^{31}P NMR spectrum which shows a single resonance at 33.92 ppm, thus indicating the chemical equivalence of the phosphorus nuclei. For the ^1H NMR spectrum, the presence of a single broad peak at 4.28 ppm in addition to the multiplets shown by the phenyl protons suggests a fluxional nature of the cyclopentadienyl (Cp) protons.

Compound **2** is novel. Its IR and NMR (^1H and ^{31}P) spectra infer a single and symmetrical diphosphine bridge that links the two $Mo(CO)_5$ moieties. The complex possesses an approximate C_{4v} symmetry which is inferred from the strong and broad ($E + A_1$) and two medium weak (A_1 and B_1) carbonyl absorption bands. The symmetry of this molecule, though similar to that of the cobaltocenylphosphine analogue $Mo_2(CO)_{10}\{Co(C_5H_4PPh_2)_2\}$, is likely to be slightly higher, as five carbonyl absorptions have been observed in the latter [13]. Absence of a high field ^{31}P resonance close to that of the free dppf molecule precludes the existence of a unidentate diphosphine ligation mode. The complex shows a single ^{31}P resonance, as expected for two chemically equivalent phosphorus nuclei in a symmetrical bridge. Unlike the ^1H NMR spectra of $Mo_2(CO)_{10}\{Ph_2P(CH_2)_nPPh_2\}$ ($n = 2$, 3) which give broad multiplets for the protons in the diphosphine backbone [14], the protons of the Cp ring of **2** are well resolved. Two signals are observed — a broad multiplet

Table 1

Spectroscopic data

Complex [a]	ν(CO) (cm^{-1})	δ(^{1}H) (ppm) [b]	δ(^{31}P) (ppm)
$Mo(CO)_4$(dppf) (**1**)	2020m, 1921s, 1901 vs	7.26–7.71(m, 20H), 4.28(s, 8H)	33.92(s)
$Mo_2(CO)_{10}$(dppf)]·C_6H_{14} (**2**)	2073m, 1991m, 1957vs	7.22–7.40(m, 20H), 4.31(m,br, $4H_b$), 4.01(q, $4H_a$)	28.53(s)
$Mo(CO)_5$(dppf), (**3**)	2072m, 1991m, 1947vs	7.14–7.41(m, 20H), 4.40(m, $2H_b$), 4.19(t,$2H'_b$), 4.14(q, $2H_a$), 3.82(q, $2H'_a$)	28.27(s), −17.10(s)
$Cr(CO)_4$(dppf) (**4**)	2007m, 1916m, 1889vs	7.25–7.74(m, 20H), 4.31(s, 8H)	52.63(s)
[$Cr_2(CO)_{10}$(dppf)]·$\frac{1}{2}C_6H_{14}$ (**5**)	2063m, 1985m, 1953vs	7.25–7.42(m, 20H), 4.27(m,br, 4Hb), 4.02(q, $4H_a$)	47.50(s)
[$Cr(CO)_5$(dppf)]·$\frac{1}{2}C_6H_{14}$ (**6**)	2063m, 1984m, 1940vs	7.14–7.43(m, 20H), 4.39(m,br, $2H_b$), 4.16(t, $2H_a + 2H'_b$), 3.82(q, $2H'_a$)	47.25(s), −17.23(s)
$W(CO)_4$(dppf) (**7**)	2016m, 1915s, 1891vs	7.25–7.71(m, 20H), 4.29(s, 8H)	18.44(t); J(PW) 239 Hz
[$W_2(CO)_{10}$(dppf)]·$\frac{1}{3}C_6H_{14}$ (**8**)	2071m, 1983m, 1939vs	7.26–7.41(m, 20H), 4.34(m,br, $4H_b$), 4.01(q, $4H_a$)	11.31(t); J(PW) 244 Hz
$W(CO)_5$(dppf) (**9**)	2071m, 1982m, 1943vs	7.14–7.50(m, 20H), 4.43(dt, $2H_b$), 4.20 (t,$2H'_b$), 4.14 (q, $2H_a$), 3.82 (q, $2H'_a$).	11.31(t); J(PW) 249 Hz, −17.10(s)

[a] dppf: 1,1′-bis(diphenylphosphino)ferrocene. [b] H_a and H_b refer to the α (adjacent to the phosphine group) and β cyclopentadienyl protons respectively. The superscripted H′ represents the protons on the uncoordinated phosphinocyclopentadienyl ring.

and a quartet. The appearance of the quartet, attributable to the two protons adjacent to the phosphorus atom, suggests that the ^{1}H–^{31}P coupling is of the same magnitude as that of ^{1}H–^{1}H.

The pentacarbonyl $Mo(CO)_5$(dppf) (**3**), which is a major product at lower temperature (10 °C) but is isolated only in trace quantity at 28 °C, has been similarly characterised. Like all the other monosubstituted carbonyls, the compound possesses C_{4v} symmetry [19], as judged from its IR spectrum. The ^{31}P NMR spectrum indicates a low field shift for the coordinated phosphorus (28.27 ppm) with the high field resonance at −17.10 ppm representing the dangling phosphine. The NMR data of the free dppf ligand, despite their slight incongruity in the literature, have been reported [3,5]. In the ^{1}H NMR spectrum of **3**, four sets of multiplets due to the non-equivalent Cp protons are observed. The triplet at 4.19 ppm and the quartet at 3.82 ppm can be attributed to the protons of the Cp ring, that has the uncoordinated phosphine, as they have shift values comparable to that of the free dppf. The other quartet at 4.14 ppm, which partially overlaps the signal at 4.19 ppm and appears as a sextuplet, is comparable to that found in the spectrum of dimer **2** and is thought to arise from the protons adjacent to the coordinated phosphorus. The most deshielding of the four signals is assigned to the other pair of protons in the same Cp ring. Such a downfield shift of the ligand resonance which occurs upon complexation is inherent in all the dppf complexes in our study and is in accord with those found in other similar systems [12]. The $^1H-^{31}P$ coupling though not well-resolved is clearly discernible which is in contrast to that found in the spectrum of the free ligand.

Likewise, $Cr(CO)_6$ gives a mixture of products similar to that of $Mo(CO)_6$ under similar conditions. The identities of the tetracarbonyl complex $Cr(CO)_4$(dppf), the dimer $Cr_2(CO)_{10}$(dppf) and the unidentate $Cr(CO)_5$(dppf) are consistent with that discussed above for their Mo analogues.

Though the corresponding tungsten reactions follow a similar pattern, the pentacarbonyl $W(CO)_5$(dppf) is obtained as a major product at ambient or low temperatures. The higher stability of this tungsten complex is also reflected in the relatively low yields of the corresponding chelate and dimer which presumably are secondary products formed from $W(CO)_5$(dppf).

The similarity in the ^{31}P shift values of the unidentate and bridged complexes and the larger downfield shift of the chelates can be explained on the basis of ring strain. It is of no surprise that for all the complexes the coordination shift falls in the order Cr > Mo > W. It is however noteworthy to compare the chelation shift ($\delta_{chelate}$-$\delta_{unidentate}$) of the W complexes with that of the other two metals. The trend, which decreases in the order W (7.13 ppm) > Mo (5.65 ppm) ≥ Cr (5.38 ppm), lends further support to the seemingly unusual higher stability, and hence its high yield, of $W(CO)_5$(dppf) compared to that of $W(CO)_4$(dppf).

Conclusion

The chelating and bridging nature of dppf is well documented in the literature, but its unidentate property has rarely been found. The present complexes $M(CO)_5$(dppf) represent the few reported heterometallic complexes which are possible phosphine ligands. We are currently exploring its ligating properties in the hope of isolating more heterometallic complexes with two or more differing metal centres. The versatility of the ligand dppf in different coordination modes is clearly illustrated in the bimetallic complexes reported in this paper. It is this flexibility in its geometry that ensures the high hydroformylation activity of many catalytic dppf complexes [20–24]. The proximity effect of two or more metal centres locked by the dppf ligand is likely to attact further attention in the forseeable future.

Experimental

General procedure

All reactions were performed under pure 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. Solvents were reagent-grade and were freshly distilled and degassed before use. Proton NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.55 MHz with $(CH_3)_4Si$ as internal standard. Phosphorus-31 NMR spectra were recorded on the same instrument at 36.23 MHz. Chemical shifts are reported in ppm to high frequency of external 85% H_3PO_4. Infrared spectra were recorded as $CDCl_3$ 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 analysis. The solvent inclusion property of these compounds has been reported [7,10,12]. In all the low-temperature reactions, some of the unreacted dppf ligand was recovered; hence the experimental yields are based on amount of ligand consumed. Spectroscopic (NMR and IR) data are listed in Table 1. The overlapping of some resonances and their complication because of some observed long-range couplings preclude an accurate analysis of the J(HP) and J(HH) values.

Preparations

TMNO dihydrate (0.165 g, 1.52 mmol) was added to a solution of $Mo(CO)_6$ (0.501 g, 1.89 mmol) and dppf (0.425 g, 0.76 mmol) in a mixture of CH_2Cl_2 (15 ml) and THF (40 ml). The resultant orange solution was stirred at room temperature (28 °C) for $3\frac{1}{2}$ h after which 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 silica TLC plates. Elution with 20% CH_2Cl_2 in hexane solution followed by further recrystallisation from CH_2Cl_2/hexane mixture led to the isolation of compounds $Mo(CO)_4$(dppf) (**1**), (0.105 g, 18%) (Found: C, 59.36; H, 3.47. $C_{38}H_{28}FeMoO_4P_2$ calcd.: C, 59.81; H, 3.67%), $[Mo_2(CO)_{10}(dppf)] \cdot C_6H_{14}$ (**2**), (0.109 g, 13%) (Found: C, 54.39; H, 3.36. $C_{50}H_{42}FeMo_2O_{10}P_2$ calcd.: C, 53.98; H, 3.81%), $Mo(CO)_5$(dppf) (**3**), (0.018 g, 3%) (Found: C, 59.34; H, 3.47. $C_{39}H_{28}FeMoO_5P_2$ calcd.: C, 59.27; H, 3.57%.) and an unidentified orange-yellow compound (0.089 g).

The low temperature reaction was carried out similarly at ca. 10 °C during 4 h. The yields of **1**, **2**, and **3** were 5, 5, and 14% respectively.

A similar procedure was adopted for the Cr analogue at ambient and at low temperatures with reaction times of 3 and $3\frac{1}{2}$ h, respectively. Three major products, of which two were identified as $Cr(CO)_4$(dppf) (**4**) (22%) (Found: C, 63.29; H, 3.95. $C_{38}H_{28}CrFeO_4P_2$ calcd.: C, 63.53; H, 3.93%) and $[Cr_2(CO)_{10}(dppf)] \cdot \frac{1}{2}C_6H_{14}$ (**5**) (15%) (Found: C, 57.31; H, 3.12. $C_{47}H_{35}Cr_2FeO_{10}P_2$ calcd.: C, 57.31; H, 3.59%), and a trace quantity of $[Cr(CO)_5(dppf)] \cdot \frac{1}{2}C_6H_{14}$ (**6**) (3%) (Found: C, 63.58; H, 3.93. $C_{42}H_{35}CrFeO_5P_2$ calcd.: C, 63.89; H, 4.47%) were isolated. At 10 °C, compound **6** was isolated as the major product (13%) together with **4** (11%) and **5** (7%).

Under similar conditions at ambient temperature, the W analogue gave only two identifiable compounds, $W(CO)_4$(dppf) (**7**) (8%) (Found: C, 53.19; H, 3.11. $C_{38}H_{28}FeO_4P_2W$ calcd.: C, 53.68; H, 3.32%) and $W(CO)_5$(dppf) (**9**) (27%) (Found: C, 53.39; H, 3.14. $C_{39}H_{28}FeO_5P_2W$ calcd.: C, 53.34; H, 3.21%). At 10 °C, **7** and **9** were isolated in trace amounts ($< 2\%$) and 28% respectively. The dimer $[W_2(CO)_{10}(dppf)] \cdot 1/3C_6H_{14}$ (**8**), which formed only in trace amounts, was best synthesised under similar reaction conditions with 4-h stirring at room temperature in pure THF as solvent. Yield: 14%. (Found: C, 44.77; H, 2.43. $C_{46}H_{33}FeO_{10}P_2W_2$ calcd.: C, 44.89; H, 2.68%). The other products in this preparation were compound **9** (18%), a trace amount of **7** and an unidentified bright yellow compound which was a common by-product in all the tungsten reactions.

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