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Substituted metal carbonyls

IV *. Studies of the synthesis and decomposition of singly-bridging 1,3-bis(diphenylphosphino)propanedimetal decacarbonyls of chromium, molybdenum and tungsten

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Abstract

Singly-bridging diphosphine complexes $M_2(CO)_{10}(\mu\text{-dppp})$ (M = Cr, W; dppp = $Ph_2P(CH_2)_3PPh_2$) have been isolated in a facile synthesis via an oxidative decarbonylation of $M(CO)_6$ using trimethylamine-*N*-oxide as the initiator. The thermal decomposition of these complexes, together with the molybdenum analogue, have been studied in refluxing acetonitrile, benzene or toluene under N_2 or CO. The characterisations and thermal stabilities of these species are described and discussed. Conversion of the 1,3-bis(diphenylphosphino)propanedimetal decacarbonyl complexes of chromium, molybdenum and tungsten into the chelate $M(CO)_4(\eta^2\text{-dppp})$ is promoted by free dppp but inhibited by CO gas.

Introduction

Substitution reactions of Group 6 metal hexacarbonyls are well-documented, but complex [4–8]. When a diphosphine ligand (P–P) such as dppm, dppe or dppp ** is involved, several possibilities may result, which include $M(CO)_5(\eta^1\text{-P–P})$ [1,9,10], $M_2(CO)_{10}(\mu\text{-P–P})$ [1,11,12], $M(CO)_4(\eta^2\text{-P–P})$ [13,14] and $M_2(CO)_8(\mu\text{-P–P})_2$ [15]. Conventional thermolytic and photolytic techniques [16–19] are non-selective and hence unsatisfactory for designed syntheses of these species. After our recent success in isolating a singly-bridged dimolybdenum complex $Mo_2(CO)_{10}(\mu\text{-dppp})$ from the trimethylamine *N*-oxide (TMNO)-initiated decarbonylation of $Mo(CO)_6$ [1], we

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* For parts I–III see ref. 1–3.

** dppm = bis(diphenylphosphine)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppe = 1,3-bis(diphenylphosphino)propane.

hereby reinforce the utility of this strategy by reporting the syntheses of the chromium and tungsten analogues and describe the decomposition of these dppp-bridged complexes.

Results and discussion

$Cr_2(CO)_{10}(\mu$-dppp) (**1**) and $W_2(CO)_{10}(\mu$-dppp) (**2**) form readily upon mixing $M(CO)_6$, dppp and TMNO in a stoichiometric ratio in acetonitrile at ambient temperature. Formation of side products such as the monomeric chelate $M(CO)_4(\eta^2$-dppp) is inhibited by the stoichiometry-controlled condition.

The identity of **1** and **2** is evident from their IR and NMR (^1H and ^{31}P) spectra (Table 1). These spectra indicate that there is a single and symmetrical diphosphine bridge linking two $M(CO)_5$ moieties. The complexes have an approximate C_{4v} symmetry [1,20] which is reflected in a strong and broad (E and A_1), and two weak-medium (A_1 and B_1), carbonyl bands in the IR spectra. Absence of a high field ^{31}P NMR resonance close to that of free dppp molecule precludes the existence of a unidentate diphosphine ligation mode such as in $M(CO)_5(\eta^1$-dppp) [21]. Both complexes show a single ^{31}P resonance, as expected for two chemically equivalent phosphorus nuclei in a symmetrical bridge. The ^{183}W satellites (ca. 7% each) are clearly discernible in the spectrum of **2**. The ^1H NMR spectra are, not surprisingly, uninformative [18] with broad multiplets attributable to the methylene protons of the dppp bridge.

The thermal decomposition of complex **1** was studied and compared with that of the analogous $Mo_2(CO)_{10}(\mu$-dppp) (**3**) [1]. Both complexes are remarkably stable in boiling benzene. IR and ^{31}P NMR spectra suggest insignificant changes in the solution despite prolonged heating (24 h). As anticipated, such kinetic inertness of the diphosphine-bridged complexes contrasts with those which bear a dangling phosphine, e.g., $M(CO)_5(\eta^1$-dppe) [22,23], but is comparable with the chelates, e.g., $M(CO)_4(\eta^2$-dppe) [13,14,22,23], and the doubly-bridged dimetal compounds with a 10-membered ring, e.g., $Mo_2(CO)_8(\mu$-dppe$)_2$ [15]. More interestingly, complexes **1** and **3** exhibit no reaction with a two-fold excess of TMNO at 28 ° C. Approx. 90% of the decacarbonyl remains intact even after 6 h in benzene at reflux. Only after

Table 1

Analytical and spectroscopic data

Complex (M.p. (° C))	Microanalyses (Found (calc) (%))		$\nu(CO)$ (cm^{-1}) [a]	$\delta(^1H)$ (ppm)	$\delta(^{31}P)$ (ppm)
	C	H			
$Cr_2(CO)_{10}$(dppp) (**1**) (171, dec)	55.54 (55.78)	3.54 (3.27)	2080m, 1990vw, 1940vs(br).	7.11–7.39(m,20H) 2.28(br)(m,4H) 1.22(br)(m,2H)	46.58(s,2P)
$W_2(CO)_{10}$(dppp) (**2**) (196, dec)	41.92 (41.89)	2.35 (2.45)	2071m, 1982w, 1941vs(br).	7.13–7.41(m,20H) 2.47(m,4H) 1.29(br)(m,2H)	9.29(t,2P); J(WP) 240 Hz

[a] KBr disc.

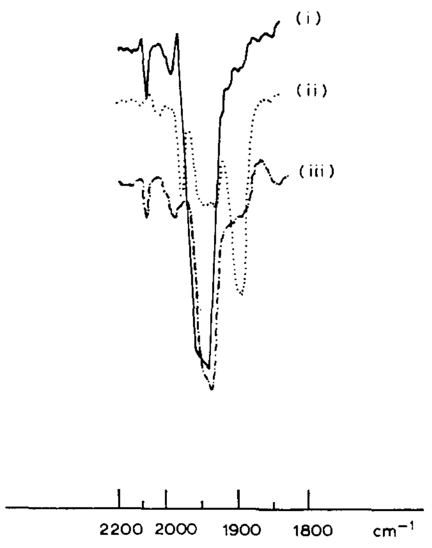

Fig. 1. Infrared spectra of $Cr_2(CO)_{10}$(dppp) in toluene (i) at 25 °C, (ii) 24 h reflux under N_2 and (iii) 24 h reflux under CO.

prolonged heating (24 h) does $M(CO)_4(\eta^2$-dppp) appear, as indicated by its IR and ^{31}P NMR spectra. These observations further emphasize the importance of the proximity of an uncoordinated phosphorus to the metal centre for facile chelation to occur. Both **1** and **3**, however, decompose readily to $M(CO)_4(\eta^2$-dppp) [17,18,24] under N_2 in refluxing toluene. The bridge-cleavage reaction is monitored hourly by IR spectral changes. The spectra of the sample before, and after, heating for 24 h are depicted in Figs. 1 and 2. Complete decomposition after 24 h occurs for the Mo but not for the Cr complex. This observation is consistent with the results of Werner et al. [12] that $Mo_2(CO)_{10}(\mu$-dppe) decarbonylates faster than its Cr analogue in toluene.

More intriguingly, decomposition in refluxing toluene is inhibited by the presence of CO gas. When the heating is carried out under 1 atm of CO, insignificant changes in the IR (Figs. 1 and 2) and ^{31}P NMR spectra are observed after 24 h of reflux. The resultant spectra also show no evidence of $M(CO)_5(\eta^1$-dppp). The effect of dppp is opposite to that of CO gas on the decarbonylative decomposition reaction. Complexes **1** and **3** both gradually yield their respective chelates $M(CO)_4(\eta^2$-dppp) when mixed with a two-fold excess of dppp in refluxing benzene and the reaction is virtually complete within 24 h. The conversion is rapid in refluxing toluene and in the case of **3** particularly is complete within 1 h. These observations infer that the rate-determining decomposition step for these diphosphine-bridged species involves M–CO bond scission, instead of the M–P bond scission suggested by Werner et al. [12] in a brief report on $Mo_2(CO)_{10}(\mu$-dppe).

To further test the resistivity of complex **3** to decarbonylation, the decomposition was carried out under N_2 in a five-fold excess of TMNO. Similarly, negligible changes occur in refluxing hexane. But, when the temperature is elevated to 110 °C (toluene), rapid and complete decarbonylations occur within 2 h, as observed in the IR spectrum.

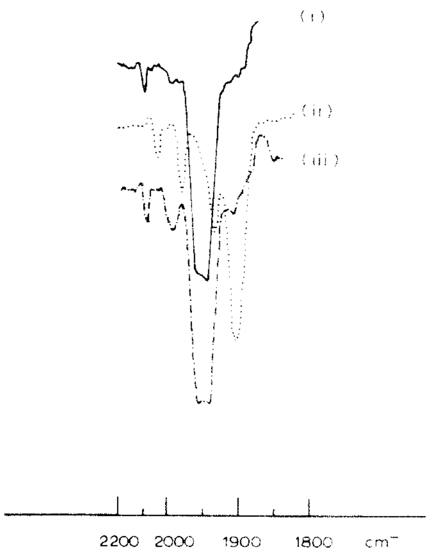

Fig. 2. Infrared spectra of $Mo_2(CO)_{10}$(dppp) in toluene (i) at 25 °C, (ii) 24 h reflux under N_2 and (iii) 24 h reflux under CO.

The behaviour of complex **2** is similar to that of its Cr and Mo analogues except that its stability is even more pronounced. The IR spectra of the complexes after 24 h under N_2 or CO in benzene or toluene at reflux show that there is no generation of the tetracarbonyl species. Addition of two molar equivalents of dppp ligand fails to break down the complex even in refluxing toluene. Decomposition commences only after 3 h in boiling xylenes (137–144 °C) under N_2 and is complete within 24 h with or without the introduction of free dppp.

Polar and donor solvents such as acetonitrile are known to promote decarbonylations in many carbonyl complexes. Though such solvent effect (CH_3CN) is not observed in complexes **1** and **2**, the Mo dimer **3** readily transforms under CO or N_2 into the tetracarbonyl in refluxing CH_3CN; such conversion is complete within 4 h. Our observations support the common conception that ease of decarbonylation undergone by Group 6 metal carbonyls follows the order Mo > Cr > W [8].

For the experiments which demonstrate the accelerating effects of free dppp on the decomposition of the decacarbonyl complexes, there is no evidence of the formation of bridging-carbonyl or doubly-bridged $\{\mu_2\text{-dppp}\}_2$ intermediate. Hence it is more likely that the rate-determining step involves a nucleophilic attack of the diphosphine on one of the metal centres, followed by cleavage of the M–CO bond or the M(μ-dppp)M bridge. Either mechanism can be terminated by the cyclisation of the dangling phosphine to give a 6-membered chelate.

Conclusion

As manifested by the isolation of $M_2(CO)_{10}(\mu\text{-dppp})$, TMNO is further proved to be effective in governing the degree of substitution in metal hexacarbonyls. This leads to the formation of a stable entity in which two $M(CO)_5$ entities are linked by a diphosphine ligand. Whereas the current literature is abundant in systematic substitution and decompositional studies on the homonuclear metal pentacarbonyls $M(CO)_5(L)$ [4,8,25], analogous studies on their dinuclear counterparts $M_2(CO)_{10}(\mu\text{-}L\text{-}L)$ [4,12] are surprisingly sketchy. This report reaffirms the stability of singly-bridging diphosphine dinuclear decacarbonyl metal complexes. However, the effect of chain length on the stability and reactivity of the complex, and the relationship between these singly-bridged and doubly-bridged metal carbonyls have yet to be fully understood. A thorough analysis of these concepts will no doubt contribute significantly to our knowledge of metal carbonyl syntheses and substitution reactions. Further work is in progress in our laboratory towards this end.

Experimental

General procedures

All reactions were performed under pure dry dinitrogen using standard Schlenk techniques. Solvents were reagent grade and degassed before use. Proton NMR spectra were recorded on a JEOL FX 90Q at 89.55 MHz by using $(CH_3)_4Si$ as internal standard. ^{31}P NMR spectra were recorded on the same spectrometer at 36.23 MHz. Chemical shifts are reported in ppm to high frequency of external 85% phosphoric acid. The samples were run in deuterated chloroform. Infrared spectra were run on a Perkin–Elmer 1310 or FT-IR Perkin–Elmer 1710 IR spectrometer. Melting points were recorded by using a Thomas Hoover Uni-melt capillary melting point apparatus without calibration. Elemental analyses were performed by the Analytical Service of this Department. Analysis and spectroscopic (NMR and IR) data are given in Table 1 together with the melting points. $M(CO)_6$ (M = Cr, Mo and W), dppp and TMNO dihydrate were supplied by Aldrich Chemical Co. and used without further purification. The phosphine, however, was checked for purity by ^{13}C and ^{31}P NMR spectroscopy before use. Pure dry carbon monoxide was supplied by Soxal (Singapore) and used as purchased.

Preparation

$Cr_2(CO)_{10}(dppp)$. A mixture of $Cr(CO)_6$ (0.5032 g, 2.29 mmol), TMNO (0.2517 g, 2.27 mmol) and dppp (0.4700 g, 1.14 mmol) in CH_3CN (80 ml) was stirred for 4.5 h, which gave a green solution. The solvent was removed under vacuum and the residue dissolved in CH_2Cl_2. Addition of CH_3OH followed by concentration under vacuum precipitated a yellow product, which was isolated by filtration. The solid was recrystallised from CH_2Cl_2/CH_3OH to afford fine yellow crystals. Yield: 0.48 g (53%).

$W_2(CO)_{10}(dppp)$. $W(CO)_6$ (0.5029 g, 1.43 mmol), TMNO (0.1626 g, 1.46 mmol) and dppp (0.2936 g, 0.71 mmol) in CH_3CN (30 ml) was stirred for 20 h until a yellow suspension had formed. The yellow solid was isolated by filtration and recrystallised from CH_2Cl_2/CH_3OH to yield the microcrystals. A second crop was obtained by adding CH_3OH (50 ml) to the CH_3CN filtrate, the mixture was reduced in volume under vacuum, and then filtered. Yield: 0.38 g (50%).

$Mo_2(CO)_{10}(dppp)$. The procedure used is outlined in Ref. 1, and is similar to that for the Cr and W analogues.

Reactions

(a) Reflux under N_2 or CO. $Mo_2(CO)_{10}$(dppp) (0.0528 g, 5.97 × 10^{-2} mmol) in benzene (25 ml) was refluxed under N_2 for 24 h. The IR spectrum of the solution was taken hourly. The resultant mixture was evaporated to dryness, redissolved in $CDCl_3$ and submitted to ^{31}P NMR analysis. The procedure was repeated in acetonitrile and toluene, and in benzene and toluene under a 1 atm. pressure of CO gas.

Similar procedures were carried out on $W_2(CO)_{10}$(dppp) and $Cr_2(CO)_{10}$(dppp). $W_2(CO)_{10}$(dppp) (0.0498, 4.70 × 10^{-2} mmol) was also decomposed similarly in xylene (25 ml) under N_2.

(b) Reflux in the presence of TMNO. A mixture of $Mo_2(CO)_{10}$(dppp) (0.0980 g, 0.11 mmol) and TMNO (0.0159 g, 0.14 mmol) in hexane (25 ml) was refluxed under N_2 for 24 h. The IR spectrum of the solution mixture was checked hourly. The procedure was repeated using two-fold excess of TMNO (0.0341 g, 0.31 mmol) in benzene, and five-fold excess (0.0773 g, 0.70 mmol) of TMNO in hexane and toluene.

Similar procedures were carried out on $Cr_2(CO)_{10}$(dppp) (0.1250 g, 0.16 mmol) and TMNO (0.0362 g, 0.33 mmol) in benzene.

(c) Reflux in the presence of dppp. A mixture of $Mo_2(CO)_{10}$(dppp) (0.1235 g, 0.14 mmol) and dppp (0.1277 g, 0.31 mmol) were mixed in benzene (30 ml) and refluxed under N_2 for 24 h. The IR was monitored hourly. The reflux was repeated in toluene. Similar procedures were carried out on $Cr_2(CO)_{10}$(dppp) and $W_2(CO)_{10}$(dppp).

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