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Substituted Metal Carbonyls.
Part 8. Group 6 Dimetal Decacarbonyls with Singly Bridging Long-backbone Diphosphines

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Chelating and bridging diphosphines play an important role in the stabilisation of many carbonyl complexes [1–10]. The fact that these difunctional ligands generally prefer the η^2-chelating to the bridging coordination mode is reflected in the overwhelming abundance of the metal chelates in the literature [11–20]. In this correspondence, we present the synthesis and characterisation of the monobridged $M_2(CO)_{10}(\mu\text{-P-P})$ (M = Cr, Mo, W; P-P = dppb, dppp, dpph*). Using a diphosphine with a long alkyl chain as backbone and under a stoichiometrically controlled and low-energy decarbonylation pathway, we demonstrate that the singly bridged dinuclear carbonyls can be isolated as major products.

Experimental

General Procedures

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Precoated silica plates of layer thickness 0.5 mm were obtained from Merck. IR spectra were recorded as $CDCl_3$ solutions on a Perkin-Elmer 1710 FT–IR spectrophotometer. Details of the other instruments and techniques used are specified in our earlier report [21].

Preparation

A typical procedure is described for $Mo_2(CO)_{10}$-(dppb). A mixture of $Mo(CO)_6$ (0.1689 g; 1.90 mmol), dppb (0.3241 g; 0.76 mmol) and trimethylamine *N*-oxide dihydrate (TMNO) (0.1689 g; 1.52 mmol) in CH_3CN (100 ml) was stirred for 80 min at 28 °C. Completion of the reaction was indicated by the disappearance of the phosphine ligand from the TLC check. The resultant yellow solution was evaporated to dryness under vacuum. The product was extracted by CH_2Cl_2 and precipitated by addition of excess CH_3OH. The solid was purified by recrystallisation from CH_2Cl_2/CH_3OH followed by TLC. A concentrated sample solution in CH_2Cl_2 was applied to silica TLC plates. Elution with CH_2Cl_2/hexane (20:80) led to the isolation of the product as yellow microcrystals (0.36 g; yield 53% based on dppb). *Anal.* Found: C, 50.76; H, 3.27; P, 7.41. Calc. for $C_{38}H_{28}Mo_2O_{10}P_2$: C, 50.78; H, 3.12; P, 6.90%.

With the use of different $M(CO)_6$ and diphosphines, all the other complexes were prepared in a similar manner. The reaction solvents and yields are listed in Table 1. All the samples are analytically pure.

Results and Discussion

TMNO-induced oxidative decarbonylation of group 6 hexacarbonyls in the presence of a restricted quantity of dppb, dppp or dpph led to the isolation of nine dinuclear complexes. The Mo dimers have been briefly reported [22] but the Cr and W analogues are novel. Characterisations of these systems follow that of our earlier report on $M_2(CO)_{10}(\mu\text{-}Ph_2PC_3H_6PPh_2)$ [23] and are listed in Table 1. The reaction solvents and yields are also listed in the table. Analytically pure samples can be obtained as pale yellow microcrystals by repeated recrystallisations or preparative TLC technique. The complexes are air-stable when pure and resist decomposition under N_2 in refluxing hexane.

Though the coordination shift (Δ) is strongly dependent on the nature of the metal (see Table 1), it is insensitive to the chain-length of the diphosphine bridge. Similarly, *J*(WP) is virtually independent of the diphosphine length. These results indicate that minimum strain is exerted on the bridging group and that there is little correlation between the M–P bond strength and the chain-length of these systems.

Formation of the products is facile at room temperature. While there is no evidence for the generation of the doubly bridged dimer, *viz.* $M_2(CO)_8(\mu\text{-P-P})_2$, only the Cr reactions show a higher degree of substitution and, in such a case, $Cr(CO)_4(\eta^2\text{-P-P})$ is the chief contaminant. The mechanistic relationship between the chelate and the doubly bridged dimer is unclear but the former is likely to be a direct product of the bridge cleavage reaction of the titled monobridged complexes.

Metal carbonyls with chelating diphosphines are generally most stable for five- and six-membered ring systems. Consequently, chelates with bigger ring sizes, which are potential probes for isomer and conformational studies [10, 24–27], are poorly established in the literature whilst complexes like $M(CO)_4$-(dpph) are hitherto unknown. The feasibility for the generation of such high-membered chelates from the title dimers is a subject of our current investigations.

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*dppb = 1,4-bis(diphenylphosphino)butane; dppp = 1,5-bis(diphenylphosphino)pentane; dpph = 1,6-bis(diphenylphosphino)hexane.

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TABLE 1. Synthetic and Spectroscopic Data

Complex (Melting point, °C)	Solvent/yield (%)	ν(CO) (cm^{-1})	δ(^{31}P) (ppm)	Δ (ppm)^a
$Cr_2CO)_{10}$(dppb) (254–257, dec)	CH_2Cl_2 + THF (1:1)/32	2063m, 1983vw, 1937vs(br)	46.17(s,2P)	61.65
$Cr_2(CO)_{10}$(dppp) (140–132)	THF/58	2062m, 1982vw, 1937vs(br)	46.58(s,2P)	62.20
$Cr_2(CO)_{10}$(dpph) (89–92)	THF/56	2062m, 1982vw, 1942vs(br)	46.31(s,2P)	61.79
$Mo_2(CO)_{10}$(dppb) (139–142, dec)	CH_3CN/53	2072m, 1990vw, 1953vs(br)	27.86(s,2P)	43.34
$Mo_2(CO)_{10}$(dppp) (126–129, dec)	CH_3CN/22	2072m, 1990vw, 1952vs(br)	28.00(s,2P)	43.62
$Mo_2(CO)_{10}$(dpph) (162–165, dec)	THF + CH_3CN (1:1)/88	2072m, 1990vw, 1952vs(br)	27.87(s,2P)	43.35
$W_2(CO)_{10}$(dppb) (122–125)	CH_3CN/32	2071m, 1980vw, 1935vs(br)	9.56(t,2P); J(WP) 239 Hz	25.04
$W_2(CO)_{10}$(dppp) (138–141)	THF/71	2071m, 1980vw, 1943vs(br)	9.96(t,2P); J(WP) 239 Hz	25.58
$W_2(CO)_{10}$(dpph) (191–193, dec)	THF/76	2071m, 1979vw, 1947vs(br)	9.69(t,2P); J(WP) 239 Hz	25.17

$^a\delta$(complex) − δ(free ligand).

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