Substituted Metal Carbonyls.
Part 5. Convenient Syntheses of some Group 6 Phosphine and Pyridine Substituted Penta- and Tetra-carbonyls and Isolation of the Singly Bridging 1,2-Bis(4-pyridyl)ethylene Dimetal Decacarbonyl Complexes

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The use of trimethylamine *N*-oxide (TMNO) in many reagent-promoted decarbonylation reactions of the mono-, di- and poly-nuclear metal carbonyls has been developing into a viable alternative to the classical photolytic and thermolytic techniques [1–6]. This substitution methodology has been recently extended to the diphosphine-bridged decacarbonyls and mixed-ligand tricarbonyls of the Group 6 metals [7–9]. In our continued effort to demonstrate the synthetic versatility of this technique and to synthesize the novel molecules which are not easily assessible via the conventional strategies, the present paper reports the one-pot synthesis of the mononuclear $M(CO)_5(L)$ (M = Cr, Mo, W; L = PPh_3, C_5H_5N), and $M(CO)_4(P{-}P)$(P–P = $Ph_2PCH_2PPh_2$, $Ph_2PC_3H_6PPh_2$); dinuclear $Mo_2(CO)_{10}(\mu$-dppe) (dppe = $Ph_2PC_2H_4PPh_2$) and, more interestingly, the novel singly bridging *trans*-1,2-bis(4-pyridyl)ethylene (BPE) decacarbonyls of Cr and Mo.

Experimental

General Procedures

All reactions were routinely performed under an atmosphere of pure dry dinitrogen by using standard Schlenk techniques. Proton and phosphorus-31 NMR spectra were recorded on a JOEL 90Q instrument. Infrared spectra were run on a Perkin-Elmer 1310 or FT-IR Perkin-Elmer 1710 Infrared spectrometer. Chemical reagents were supplied from commercial source.

Reactions

The preparation of $Mo_2(CO)_{10}$(dppe) represents a typical procedure and is described here.

Upon addition of TMNO dihydrate (0.2144 g; 1.93 mmol) to a suspension of $Mo(CO)_6$ (0.5071 g; 1.92 mmol) in CH_3CN (30 ml) at 0 °C, a yellow colour steadily developed. After 10 min of vigorous stirring, solid dppe (0.3820 g; 0.96 mmol) was introduced into the reaction mixture. The resultant light brown solution was stirred and kept at 0 °C for 21 h before evaporation to *ca.* 5 ml under vacuum. Filtration followed by recrystallisation from CH_2Cl_2/CH_3OH led to the isolation of the stable white microcrystals of $Mo_2(CO)_{10}$(dppe) (0.46 g; 56%).

All the other products followed similar preparative procedures the details of which are specified in Table I. The complexes may be purified by recrystallisation from CH_2Cl_2/CH_3OH or CH_2Cl_2/hexane.

Results and Discussion

All the syntheses, $Cr(CO)_4(Ph_2PCH_2PPh_2)$ excepted, were carried out in ambient or depressed temperature. Such a mild condition is necessary in order to subdue the product decomposition and occurrence of side reactions and hence simplifies the procedures in purification. Selectivity in these one-pot syntheses is achieved by the stoichiometrically controlled condition. The synthetic data and properties of the complexes are listed in Table I. Identity of the known compounds are confirmed by their infrared, proton- and, whenever applicable, ^{31}P NMR analyses. The chromium and molybdenum BPE-bridged complexes are novel whilst the others represent an improved facile synthesis via the TMNO-induced oxidative decarbonylation.

Thermolytic synthesis of the Mo analogue of the BPE-bridged dimer has been reported by Gaus *et al.* [10]. Photosubstitution and electron transfer reactions of these highly-conjugated bridged systems are currently a subject of research activity [11–14]. Of particular interest to us is a comparative study of the thermal stability and redox behaviour of these species.

Under the present preparation of $M_2(CO)_{10}(\mu$-bpe), there is no evidence for the formation of the higher substituted products such as the polymeric $[M(CO)_4(\mu\text{-bpe})]_n$ or the doubly bridged dimer $M_2(CO)_8(\mu\text{-bpe})_2$ [12]. It is however possible that the title singly bridged dimetal decacarbonyl complex be used as a precursor for preparing the latter complexes.

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TABLE I. Preparative and Infrared Data

Complexes[e] (colour, melting point (°C))	Substrates	Reaction temperature (°C); duration (h); solvent	Yield (%)	Elemental analyses (%)	ν(CO) (cm^{-1})	Reference
$\mathrm{Cr(CO)_5(PPh_3)}$ (pale yellow; 127–129)	$\mathrm{Cr(CO)_6}$ + TMNO + $\mathrm{PPh_3}$ (1:1:1)	0; 16; $\mathrm{CH_3CN}$	65	C, 60.54(60.80) H, 3.10(3.32)	2080m, 1990w, 1945vs, 1916sh[a]	15
$\mathrm{Mo(CO)_5(PPh_3)}$ (white; 131–133)	$\mathrm{Mo(CO)_6}$ + TMNO + $\mathrm{PPh_3}$ (1:1:1)	0; 16; $\mathrm{CH_3CN}$	42	C, 55.29(55.44) H, 2.73(3.03)	2080w, 1990vw, 1950vs[a]	15
$\mathrm{W(CO)_5(PPh_3)}$ (pale yellow; 143–144)	$\mathrm{W(CO)_6}$ + TMNO + $\mathrm{PPh_3}$ (1:1:1)	0; 16; $\mathrm{CH_3CN}$	45	C, 47.23(47.13) H, 2.50(2.58)	2080w, 1990vw, 1940vs, 1890sh[a]	16
$\mathrm{Cr(CO)_5(py)}$ (pale yellow; 95–96)	$\mathrm{Cr(CO)_6}$ + TMNO + py (1:1:1)	28; 3; THF	45	C, 44.19(44.30) H, 1.59(1.86)	2080w, 1980w, 1940vs, 1900sh[a]	18
$\mathrm{Mo(CO)_5(py)}$ (yellow; 84–85)	$\mathrm{Mo(CO)_6}$ + TMNO + py (1:1:1)	28; 3; THF	42	C, 38.78(38.12) H, 1.54(1.60)	2080vw, 1990w, 1945vs, 1910sh[a]	17
$\mathrm{W(CO)_5(py)}$ (yellow; 115–117)	$\mathrm{W(CO)_6}$ + TMNO + py (1:1:1)	28; 3; THF	52	C, 29.70(29.80) H, 1.09(1.25)	2078w, 1933vs, 1902m[a]	19
$\mathrm{Cr(CO)_4(dppm)}$ (orange; 159)	$\mathrm{Cr(CO)_6}$ + TMNO + dppm (1:2:1)	82; 18; $\mathrm{CH_3CN}$	40	C, 63.91(63.50) H, 3.79(4.01)	2006m, 1902vs, 1874m[b]	21
$\mathrm{Mo(CO)_4(dppm)}$ (pale yellow; 180–189)	$\mathrm{Mo(CO)_6}$ + TMNO + dppm (1:2:1)	28; 2; $\mathrm{CH_3CN}$	61	C, 58.92(58.78) H, 3.71(3.71)	2021m, 1915vs, 1871m[b]	20
$\mathrm{W(CO)_4(dppm)}$ (pale yellow; 197)	$\mathrm{W(CO)_6}$ + TMNO + dppm (1:2:1)	28; 18; $\mathrm{CH_3CN}$	35	C, 51.72(51.77) H, 3.25(3.24)	2021m, 1906vs, 1884m[b]	20
$\mathrm{Cr(CO)_4(dppp)}$ (yellow; 169–170)	$\mathrm{Cr(CO)_6}$ + TMNO + dppp (1:2:1)	28; 21; $\mathrm{CH_3CN}$	11	C, 64.28(64.53) H, 4.50(4.51)	2010m, 1929m, 1908s, 1890s[b]	21
$\mathrm{Mo_2(CO)_{10}(dppe)}$ (white; 187 dec.)	$\mathrm{Mo(CO)_6}$ + TMNO + dppe (1:1:½)	0; 21; $\mathrm{CH_3CN}$	56	C, 50.19(49.90) H, 2.76(2.73)	2072m, 1995m, 1928vs(br)[c]	22
$\mathrm{Cr_2(CO)_{10}(bpe)}$ (brown; 263)	$\mathrm{Cr(CO)_6}$ + TMNO + BPE (1:1:½)	28; 9; $\mathrm{CH_3CN}$	58	C, 46.32(46.64) H, 1.83(1.76)	2071w, 1934s(br), 1894w[d]	
$\mathrm{Mo_2(CO)_{10}(bpe)}$ (reddish-brown; >300)	$\mathrm{Mo(CO)_6}$ + TMNO + BPE (1:1:½)	28; 9; THF	64	C, 40.77(40.37) H, 1.54(1.53)	2074w, 1941s, 1901m[d]	
$\mathrm{W_2(CO)_{10}(bpe)}$ (orange; 154 dec.)	$\mathrm{W(CO)_6}$ + TMNO + BPE (1:1:½)	28; 9; $\mathrm{CH_3CN}$	43	C, 32.03(31.80) H, 1.25(1.20)	2072w, 1931s, 1907m(br)[d]	10

[a] $\mathrm{CHCl_3}$. [b] $\mathrm{CH_3CN}$. [c] KBr. [d] $\mathrm{CH_2Cl_2}$. [e] py: pyridine; dppm: bis(diphenylphosphino)methane; dppp: 1,3-bis(diphenylphosphino)propane; dppe: 1,2-bis(diphenylphosphino)ethane.

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