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Substituted Metal Carbonyls.
Part 2.* Facile Syntheses of Mixed-ligand Tricarbonyl Complexes of Chromium, Molybdenum and Tungsten

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Reports on 1,10-phenanthroline (phen) substituted tetracarbonyls, $M(CO)_4(phen)$ (where M = Cr, Mo and W) [2–7] and tricarbonyl phosphines, $M(CO)_3(phen)(P)$ (where P = monophosphines) [4, 8, 9] emerged in the literature nearly a couple of decades ago. Among the latter compounds, the synthetic methods utilised are generally not feasible for diphosphines owing to the complications caused from side reactions such as chelation, bridge formation and ligand displacement. Using trimethylamine *N*-oxide (TMNO) as an initiator [10, 11], it is found that the mixed-ligand complexes, $M(CO)_3(phen)(\eta^1\text{-dppm})$ (where M = Cr, Mo and W and dppm = bis(diphenylphosphino)methane) can be conveniently synthesized.

Experimental

(1) General Procedures

All reactions were routinely performed under an atmosphere of pure dry dinitrogen using standard Schlenk techniques. Proton NMR spectra were recorded on a JOEL 90Q at 89.55 MHz using TMS as internal standard. Phosphorus-31 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 as $CHCl_3$ solutions were run on a FT-IR Perkin Elmer 1710 IR spectrometer.

Chemical reagents were supplied from commercial sources.

(2) Reactions

$(CH_3)_3NO\cdot 2H_2O$ (TMNO) (0.5151 g; 4.64 mmol) was added to a benzene solution (20 ml) of $Cr(CO)_6$ (0.5021 g; 2.28 mmol) to give a pale yellow solution. After stirring for 15 min, phen (0.4554 g; 2.29 mmol) was introduced and the mixture was further stirred for 18 h at room temperature. The resultant red precipitate of $Cr(CO)_4(phen)$ was isolated by filtration and recrystallised from CH_2Cl_2/hexane to give a yield of 75%. $Mo(CO)_4(phen)$ (yield: 93%) and $W(CO)_4(phen)$ (yield: 81%) were prepared similarly.

Preparation of $Mo(CO)_3(phen)(dppm)$ adopted similar procedures from a mixture of $Mo(CO)_4(phen)$:TMNO:dppm (1:1:1) in acetonitrile. Recrystallisation was performed in CH_2Cl_2/CH_3OH (yield: >95%). $Cr(CO)_3(phen)(dppm)$ was isolated similarly, except that the molar ratio of TMNO was increased to 1.5 (yield: 83%). $W(CO)_3(phen)(dppm)$ (yield: 50%) required 6 h of reflux after 18 h of stirring at room temperature in CH_3CN.

Results and Discussion

TMNO-induced oxidative decarbonylation of Gp VI metal hexacarbonyls at ambient temperature in the presence of stoichiometric quantities of phen readily generated the tetracarbonyl substitution products, $M(CO)_4(phen)$. The use of the more arduous conventional thermolytic or photolytic route [8, 9, 12] can be avoided.

Behrens *et al.* [13] reported the synthesis of $Mo(CO)_4(phen)(\eta^1\text{-dppm})$ (**1**) from the carbonyl-bridged dimer $Mo_2(CO)_4(\mu\text{-}CO)_2(phen)_2$ which in turn could be prepared from $Mo(CO)_3(C_7H_8)$ [14, 15]. NMR characterisations of **1** however are lacking. Analogous complexes $Cr(CO)_3(phen)(\eta^1\text{-dppm})$ (**2**) and $W(CO)_3(phen)(\eta^1\text{-dppm})$ (**3**) have not been isolated. Using the same chemically induced synthetic strategy, the present study offers a convenient synthesis of $M(CO)_4(phen)$ and **1**, **2** and **3**, all of which, **3** excepted, give products in yields higher than 75%. Spectroscopic data (IR, ^1H and ^{31}P NMR) are summarised in Table 1.

The presence of three strong absorptions (a_1 + 2e) in **1**, **2** and **3** suggested a *fac*-configuration** of the complexes [5, 16–19]. The unidentate coordination mode of the dppm ligand is inferred from the presence of two mutually coupled non-equivalent phosphorus NMR resonances and that the high field signal has a chemical shift very similar to that of the free dppm molecule [1]. The downfield resonance due to the coordinated phosphorus demonstrated

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*For Part 1, see ref. 1.

**Slight ambiguities however exist in the literature in the differentiation of the *fac* and *mer* isomers from IR spectral analysis. While Stone *et al.* [19] proposed 3 strong absorptions and Isaacs and Graham [20] suggested 2 strong bands (presumably due to the degenerate e mode) for the *fac* isomer, Shaw *et al.* [21] related three strong carbonyl bands to the *mer* configuration in $Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})$.

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TABLE I. Spectroscopic Data

Complexes	ν (cm^{-1})	$\delta(^1H)(CH_2$ in dppm) (ppm)	$\delta(^{31}P)$ (ppm)
$Cr(CO)_3(phen)(\eta^1$-dppm)	1910s, 1822m, 1785m	2.47(br)	46.51(d, 1P), −27.19 (d, 1P); $J(PP)$ = 51.27 Hz
$Mo(CO)_3(phen)(\eta^1$-dppm)	1916s, 1822m, 1789m	2.49(dd); $J(HP_a)$ = 4.89 Hz, $J(HP_b)$ = 2.20 Hz	29.28(d, 1P), −26.99 (d, 1P); $J(PP)$ = 63.48 Hz
$W(CO)_3(phen)(\eta^1$-dppm)	1907s, 1820m, 1790m	2.57(dd); $J(HP_a)$ = 6.37 Hz, $J(HP_b)$ = 3.18 Hz	20.75(dt, 1P), −27.24 (d, 1P); $J(PP)$ = 62.26 Hz, $^1J(WP)$ = 224.61 Hz

a decrease in coordination shift, defined as $\delta_{complex} - \delta_{free ligand}$, in the anticipated order of Cr (68.18 ppm) > Mo (50.95 ppm) > W (42.42 ppm) [22–24].

It is interesting to compare the present tricarbonyl complexes with the well-documented dppm-substituted tricarbonyls, $M(CO)_3(\eta^2$-dppm)(η^1-dppm) [25, 26], which, owing to the poorer pi-accepting ability of the phosphines, are more susceptible to oxidation. Electrochemical redox reactions [21, 27–29] and the kinetics and mechanism of the ligand substitutions [4, 30–33] in these octahedral species have always attracted attention among the organometallic researchers. It is hoped that, by studying similar complexes of varying ligands and metals, the chemistry of the above processes can be better understood. The generality of this chemically induced synthetic pathway and the reactivities of these newly synthesized compounds are currently a subject of investigations.

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