# Substituted Metal Carbonyls.
# Part 7. Direct Route to Group 6 Tricarbonyl Complexes with Tris(2-chloroethyl)phosphite as Ligand

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Group 6 metal carbonyl complexes of phosphite esters such as $P(OEt)_3$ are well-documented for their electronic, electrochemical and spectroscopic properties [1–6]. The influence on these properties of an electron withdrawing substituent on the alkyl chain of the phosphite remains a subject of current interest [1, 7–11]. In an attempt to supplement our recent study on Group 6 $M(CO)_3(N\text{-}N)[P(OEt)_3]$ (M = Cr, Mo, W; N-N = 1,10-phen, 2,2'-bipy) [12], we herein report the isolation of the analogous complexes with ligating tris(2-chloroethyl)phosphite, *viz.* $M(CO)_3(N\text{-}N)[P(OCH_2CH_2Cl)_3]$.

## Experimental

### General Procedures

All reactions were performed under an atmosphere of pure dry dinitrogen 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 FT-IR 1710 spectrometer. All the other instruments are the same as that cited in the earlier reports [12–14]. Chemical reagents were supplied from commercial sources.

### Reactions

The preparation of $Cr(CO)_3(bipy)[P(OCH_2CH_2Cl)_3]$ represents a typical procedure and is described here.

$Cr(CO)_6$ (0.5019 g; 2.28 mmol), 2,2'-bipyridyl (0.4268 g; 2.74 mmol), trimethylamine *N*-oxide dihydrate (1.5185 g; 13.68 mmol) and $P(OCH_2CH_2Cl)_3$ (0.56 ml; 2.74 mmol) were added in sequence to benzene (60 ml) and the mixture was vigorously stirred for 5 min at 28 °C and then gently refluxed for 1 h. The purplish brown solution thus formed was filtered and the solid discarded. The filtrate was reduced to low volume under vacuum followed by slow addition of excess hexane. The precipitate thus isolated was repeatedly recrystallised from benzene/hexane to give dark brown microcrystals (0.21 g; 17%). Found: C, 40.68; H, 3.46; N, 5.19. Calc. for $C_{19}H_{20}Cl_3CrN_2O_6P$: C, 40.59; H, 3.56; N, 4.98%.

All the other products followed similar preparative procedures the details of which are specified in Table I. All the samples are analytically pure.

## Results and Discussion

All the six tricarbonyls are novel in the literature. Their syntheses are based on a strategy we recently adopted and modified—oxidative decarbonylation

TABLE I. Preparative Data

| Complexes[a] (colour, melting point (°C)) | Substrates[a] | Reaction temperature (°C); duration (h); solvent | Yield (%) |
|---|---|---|---|
| $Cr(CO)_3(bipy)(P)$ (1)<br>(dark brown; 125–128 dec) | $Cr(CO)_6$ + TMNO + bipy + P<br>(1:6:1.2:1.2) | 80; 1; benzene | 17 |
| $Cr(CO)_3(phen)(P)$ (2)<br>(dark brown; 119–122 dec) | $Cr(CO)_6$ + TMNO + phen + P<br>(1:6:1.2:1.2) | 110; 1; toluene | 30 |
| $Mo(CO)_3(bipy)(P)$ (3)<br>(red; 150–154 dec) | $Mo(CO)_6$ + TMNO + bipy + P<br>(1:4:1.2:1.2) | 80; 4; benzene | 33 |
| $Mo(CO)_3(phen)(P)$ (4)<br>(dark red; 135–137 dec) | $Mo(CO)_6$ + TMNO + phen + P<br>(1:6:1.2:1.2) | 110; 1; toluene | 32 |
| $W(CO)_3(bipy)(P)$ (5)<br>(brown; 230 dec) | $W(CO)_6$ + TMNO + bipy + P<br>(1:6:1.2:1.5) | 137–144; 4; xylenes | 8 |
| $W(CO)_3(phen)(P)$ (6)<br>(dark brown; 182–185 dec) | $W(CO)_6$ + TMNO + phen + P<br>(1:4:1.2:1.2) | 137–144; 4; xylenes | 19 |

[a] bipy: 2,2'-bipyridyl; phen: 1,10-phenanthroline; P: tris(2-chloroethyl)phosphite; TMNO: trimethylamine *N*-oxide.

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TABLE II. Spectroscopic Data

| Complexes | $\nu$(CO) (cm$^{-1}$)$^a$ | $\delta$($^1$H, $P(OCH_2CH_2Cl)_3$) (ppm)$^b$ | $\delta$($^{31}$P) (ppm)$^b$ |
|---|---|---|---|
| 1 | 1928vs, 1835s, 1791s | 4.03(dt, $-OCH_2-$), 3.41(t, $-CH_2Cl$);<br>$J$(HH) = 5.62 Hz, $J$(PH) = 7.08 Hz | 169.5 (s) |
| 2 | 1928vs, 1838s, 1795s | 3.96(dt, $-OCH_2-$), 3.31(t, $-CH_2Cl$);<br>$J$(HH) = 5.62 Hz, $J$(PH) = 7.08 Hz | 169.5 (s) |
| 3 | 1934vs, 1839s, 1796s | 3.74(dt, $-OCH_2-$), 3.42(t, $-CH_2Cl$);<br>$J$(HH) = 5.62 Hz, $J$(PH) = 7.57 Hz | 154.7 (s) |
| 4 | 1934vs, 1839s, 1796s | 3.96(dt, $-OCH_2-$), 3.31(t, $-CH_2Cl$);<br>$J$(HH) = 5.62 Hz, $J$(PH) = 7.32 Hz | 154.8 (s) |
| 5 | 1926vs, 1832s, 1791s | 4.03(dt, $-OCH_2-$), 3.43(t, $-CH_2Cl$);<br>$J$(HH) = 5.50 Hz, $J$(PH) = 7.57 Hz | 142.6 (t);<br>$J$(WP) = 386 Hz |
| 6 | 1926vs, 1832s, 1791s | 3.97(dt, $-OCH_2-$), 3.32(t, $-CH_2Cl$);<br>$J$(HH) = 5.62 Hz, $J$(PH) = 7.57 Hz | 142.7 (t);<br>$J$(WP) = 385 Hz |

$^a$$CH_2Cl_2$. $^b$$CDCl_3$.

of the hexacarbonyls by amine oxide in a one-pot reaction mixture [13–16]. The relevant synthetic data are listed in Table I. Formation of the Mo complexes is considerably more facile. Accordingly, side reactions such as ligand scrambling are much less severe than their Cr and W counterparts. The products isolated are predominantly the thermodynamically stable *fac*-isomers. The melting points of these $P(OCH_2CH_2Cl)_3$ complexes are generally lower than that of the $P(OEt)_3$ analogues. We have recently initiated a program on the thermogravimetric analysis of some metal carbonyls [17, 18]; thermal properties of the present complexes are being studied.

Characterisations of the titled complexes are similar to that reported for the triethylphosphite species [12]. The FT-IR and NMR ($^1$H and $^{31}$P) data are summarised in Table II. Substitution of chloride on the alkyl chains of the phosphite ligand imposes an insignificant impact on the carbonyl stretching frequencies. Its effect on the $^{31}$P resonances is however more substantial, with an average of *ca.* 2 ppm downfield shift to higher frequency.

Continued studies in the Group 6 mixed-ligand tricarbonyls, especially those with strong $\pi$-acids such as $P(OCH_2CH_2Cl)_3$, would enable a better understanding of the kinetics of ligand substitution [19] and redox properties [20–25] of the related systems which are of recent interest.

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