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Substituted metal carbonyls

VI. Convenient syntheses and characterizations of group 6 metal tricarbonyls with ligating α-diimine and triethyl phosphite

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Abstract

Syntheses of group 6 mixed-ligand tricarbonyls $M(CO)_3(N-N)[P(OC_2H_5)_3]$ (M = Cr, Mo, W; N–N = 2,2′-bipyridyl and 1,10-phenanthroline) have been reinvestigated, simplified and the complexes spectroscopically characterized. The Cr and Mo complexes can be prepared conveniently from the tetracarbonyls $M(CO)_4(N-N)$ at ambient temperature via a trimethylamine *N*-oxide-initiated decarbonylation pathway. All the tricarbonyls can also be satisfactorily prepared by refluxing a mixture of $M(CO)_6$, $(CH_3)_3NO$, $P(OC_2H_5)_3$ and the α-diimine ligand in a one-pot reaction. FT-IR, ^1H and ^{31}P NMR spectroscopic data are presented and discussed.

Introduction

Chemically induced decarbonylation reaction has become an active area of research in recent years [1–9]; this is understandable when one considers the close association of unsaturated metal carbonyls with a variety of catalytic processes [1,10–12]. The successful use of trimethylamine *N*-oxide (TMNO) in various carbonyl substitution reactions covering those of mononuclear [9,13] dinuclear [14,15] and cluster species [8,16,17] has been noted. Group 6 metal carbonyls are among the most extensively investigated [18–24].

Mixed derivatives like $M(CO)_3(N-N)[P(OEt)_3]$ (M = Cr, Mo and W; N–N = 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen)) were among the first reported group 6 substituted metal carbonyls [25,26]. These complexes were prepared by the direct action of excess triethylphosphite on the tetracarbonyl counterpart

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$M(CO)_4(N-N)$ in refluxing toluene or xylene [26,27]. In view of the undesirable occurrence of ligand scramblings under such stringent conditions, the lack of detailed spectroscopic data on our complexes, and their relevance to many kinetic and mechanistic studies, we report here an improved synthesis under mild conditions and give a full characterization of these complexes.

Results and discussion

The carbonyl displacement reaction of $M(CO)_4(N-N)$ by $P(OEt)_3$ is found to proceed smoothly at 28 °C when carried out in the presence of a molar equivalent of TMNO in CH_3CN. The *cis* labilizing effect of the α-diimine ligands [28,29] probably contributes to the ease of this substitution. Formation of the Cr and Mo tricarbonyls is virtually complete after stirring overnight but the W counterparts are heavily contaminated by the tetracarbonyl substrate. The latter reactions however can be driven to completion under reflux in toluene. All of these syntheses can be simplified further by use of a one-pot strategy represented by eq. 1.

$$M(CO)_6 + N\text{-}N + 3\ Me_3NO + P(OEt)_3 \rightarrow$$
$$M(CO)_3(N\text{-}N)[P(OEt)_3] + 3\ CO_2 + 3\ Me_3N \qquad (1)$$

Maximum yields are obtained in refluxing tetrahydrofuran for the Cr and Mo tricarbonyls and xylenes for the W analogues. The preparative data are summarised in Table 1.

Table 1

Preparative data

Complex (Colour; M.p. (°C))	Substrate [a]	Reaction temperature (°C)/time (h) solvent	Yield (%)
$Cr(CO)_3(bipy)(P(OEt)_3)$ (**1**) (dark brown; 157–160)	$Cr(CO)_4(bipy) + TMNO + P(OEt)_3$ (1/1/1)	28/18/CH_3CN	25
	$Cr(CO)_6 + bipy + TMNO + P(OEt)_3$ (1/1/4/1.5)	66/3/THF	18
$Cr(CO)_3(phen)(P(OEt)_3)$ (**2**) (dark purple; 93–96, dec)	$Cr(CO)_4(phen) + TMNO + P(OEt)_3$ (1/1/1)	28/18/CH_3CN	71
	$Cr(CO)_6 + phen + TMNO + P(OEt)_3$ (1/1/4/1.5)	66/3/THF	51
$Mo(CO)_3(bipy)(P(OEt)_3)$ (**3**) (reddish brown; 189–190)	$Mo(CO)_4(bipy) + TMNO + P(OEt)_3$ (1/1/1)	28/18/CH_3CN	40
	$Mo(CO)_6 + bipy + TMNO + P(OEt)_3$ (1/1/4/1.5)	66/3/THF	31
$Mo(CO)_3(phen)(P(OEt)_3)$ (**4**) (dark brown; 179–180)	$Mo(CO)_4(phen) + TMNO + P(OEt)_3$ (1/1/1)	28/18/CH_3CN	60
	$Mo(CO)_6 + phen + TMNO + P(OEt)_3$ (1/1/4/1.5)	66/3/THF	74
$W(CO)_3(bipy)(P(OEt)_3)$ (**5**) (dark brown; 206–211)	$W(CO)_6 + bipy + TMNO + P(OEt)_3$ (1/1/7/3)	137–144/5/xylenes	17
$W(CO)_3(phen)(P(OEt)_3)$ (**6**) (purplish black; 200, dec)	$W(CO)_6 + phen + TMNO + P(OEt)_3$ (1/1/7/3)	137–144/5/xylenes	70

[a] TMNO = trimethylamine *N*-oxide; bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline.

Table 2

Spectroscopic data

Complex	ν(CO) (cm^{-1}) [a]	δ(^{1}H,P(OEt)$_3$) (ppm) [b]	δ(^{31}P) (ppm) [b]
1	1924vs, 1839s, 1800s	3.75[dq [c], CH$_2$], 0.96[t, CH$_3$]; J(HH) 6.96 Hz, J(PH) 6.84 Hz	166.5(s)
2	1923vs, 1839s, 1801s	*fac*-: 3.66[dq, CH$_2$], 0.84 [t, CH$_3$]; J(HH) 7.08 Hz, J(PH) 6.83 Hz *mer*-: ca. 3.8 [d][dq, CH$_2$], 1.27[t, CH$_3$]; J(HH) 7.08 Hz, J(PH) ca. 6.7 Hz [d]	*fac*-: 166.7(s) *mer*-: 139.2(s)
3	1930vs, 1839s, 1805s	3.76[dq, CH$_2$], 0.96[t, CH$_3$]; J(HH) 6.96 Hz, J(PH) 7.21 Hz	152.3(s)
4	1929vs, 1839s, 1806s	3.67[dq, CH$_2$], 0.83[t, CH$_3$]; J(HH) 6.96 Hz, J(PH) 7.08 Hz	152.0(s)
5	1923vs, 1834s, 1800s	3.76[dq, CH$_2$], 0.96[t, CH$_3$]; J(HH) 7.08 Hz, J(PH) 7.09 Hz	141.4(t); J(WP) 366 Hz
6	1922vs, 1834s, 1801s	3.67[dq, CH$_2$], 0.83[t, CH$_3$]; J(HH) 6.96 Hz, J(PH) 7.20 Hz	141.2(3) J(WP) 366 Hz

[a] Benzene. [b] CDCl$_3$. [c] Doublets of a quartet. [d] Signals partially obscured.

The six complexes have been characterised by FT-IR, the data of which agree fairly well with the literature values [26], and by ^{1}H and ^{31}P NMR spectroscopy (see Table 2). A common feature of three strong carbonyl absorption bands implies the formation of the *fac* isomer of the mixed ligand tricarbonyls (C_s) [25,30]. A similar pattern was observed for the analogous bis(diphenylphosphino)methane (dppm) complexes M(CO)$_3$(N–N)(η^1-dppm) [21,22] except that the observed carbonyl stretching frequencies in the present cases are generally ca. 15 cm^{-1} higher. This is consistent with the strong π-accepting ability of the P(OEt)$_3$ ligand as compared to the unidentate dppm.

The ^{1}H NMR spectra of the six complexes display similar chemical shifts, J(HH) and J(PH) for the coordinated phosphite. A minor quantity of the *mer* isomer, for Cr(CO)$_3$(phen)[P(OEt)$_3$], which is the most sterically demanding complex of the six studied, was detected in its NMR spectrum. The ^{31}P signals show the expected shifts in the order Cr > Mo > W [31–33]. For each metal system, values for δ(^{31}P) of the bipy and phen complexes differ by only 0.2–0.3 ppm. The ^{183}W satellites in the W complexes are clearly discernible; the ^{183}W–^{31}P coupling of 366 Hz is within the expected range (200–500 Hz) for WP(OEt)$_3$ complexes [34,35].

Conclusion

Isolation of group 6 M(CO)$_3$(N–N)[P(OEt)$_3$] (N–N = bipy and phen) at ambient temperature by a TMNO-induced decarbonylation pathway could pave the way for the synthesis of other highly substituted metal carbonyls. A distinct advantage is the suppression of ligand scrambling a phenomenon which would be particularly severe in systems with many hetero ligands. The introduction of strong π-acceptors as incoming ligands may facilitate carbonyl substitution, to enhance the ligand stability and so reveal some interesting redox behaviour for these species. Current work in our laboratory is directed towards these objectives.

Experimental

General procedure

All reactions were carried out under pure dry dinitrogen using standard Schlenk techniques. Infrared spectra were recorded as benzene solutions on a FT-IR Perkin–Elmer 1710 spectrometer. The other instruments used are the same as those described previously [22–24]. Preparative data and the melting points are listed in Table 1. Spectroscopic (NMR and IR) data are given in Table 2. $M(CO)_4(N-N)$ (M = Cr, Mo and W; N–N = bipy and phen) were prepared by published procedures [21,22].

Decarbonylation of $M(CO)_4(N-N)$

$Cr(CO)_3(phen)[P(OEt)_3]$. $Cr(CO)_4(phen)$ (0.1755 g, 0.51 mmol) and TMNO (0.0700 g, 0.63 mmol) were mixed in CH_3CN (20 ml) to give a red suspension. After it had been stirred for 10 min, $P(OEt)_3$ (0.09 ml, 0.52 mmol) was injected slowly into the reaction mixture which gradually turned dark purple. Stirring for 18 h at 28 ° C yielded a purple solution which was evaporated to dryness. The dark purple crude product was recrystallised from benzene/hexane to give an analytically pure crystalline sample. Yield: 0.17 g (71%). Found: C, 52.29; H, 4.69; N, 5.89. $C_{21}H_{23}CrN_2O_6P$ calcd.: C, 52.29; H, 4.80; N, 5.81%.

Similar preparative procedures were adopted for the phen and the analogous Mo complexes; detailed reaction conditions are in Table 1.

One-pot syntheses from $M(CO)_6$

Reactions were carried out similar to the above procedures except that the four substrates were mixed and refluxed as a one-pot mixture. The stoichiometries and yields are listed in Table 1.

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