Journal of Organometallic Chemistry, 156 (1978) 427—437

ANIONIC TRICARBONYL DERIVATIVES OF MOLYBDENUM AND TUNGSTEN AND THEIR REACTIONS WITH ALLYL HALIDES

BRIAN J.BRISDON, DENNIS A.EDWARDS
and JAMES W.WHITE

School of Chemistry, University of Bath,
Bath BA2 7AY (Great Britain)

(Received May 17th, 1978)

Summary

A series of carbonylmetallate anions fac-$[MX(CO)_3L_2]^-$, where M = Mo or W, X = Cl, Br or I and L_2 = 1,10-phenanthroline(phen) or 2,2'-bipyridine(bipy) have been prepared from the corresponding cis-$M(CO)_4L_2$ complexes. No evidence of fac-to mer-isomerisation was evident on dissolution, although in MeCN solvolysis occurred with the formation of fac-$M(CO)_3L_2(MeCN)$. Reaction of the anions with various allyl halides resulted in high yields of η^3-allyl complexes $[MX(CO)_2(\eta^3\text{-}RC_3H_4)L_2]$. The significance of these observations for the mechanism of the allyl oxidative-addition reaction are discussed.

Introduction

The use of highly reactive carbonylmetallate anions for the synthesis of organometallics of the early transition metals is now a well-established procedure [1,2]. Because of the mild conditions under which these nucleophiles react with allyl halides, many new η^3-allyl complexes of these elements have been prepared by this route [3-7], including some chromium analogues of the Group VI series *[$MX(CO)_2(\eta^3-C_3H_5)$bidentate], where M = Mo or W and X = halide* [8]. The starting materials for the facile synthesis of this series of allyl-complexes are the anions [$MX(CO)_3$bidentate]$^-$, first prepared by Behrens et al. [9] from $M(CO)_3$(cycloheptatriene) (eq.1). A more convenient route to these anions was subsequently found (eq.2), but full experimental details were not given [7].

$$M(CO)_3\text{cht} + \text{bidentate} + X^- \rightarrow [MX(CO)_3\text{bidentate}]^- + \text{cht} \qquad (1)$$

$$M(CO)_4\text{bidentate} + X^- \rightarrow [MX(CO)_3\text{bidentate}]^- + CO \qquad (2)$$

This paper reports the synthesis and spectroscopic properties of the molybdenum and tungsten anionic complexes, and illustrates their use in the preparation of several allyl derivatives of these elements.

Experimental

All solvents were purified and dried, and reactions were carried out in an atmosphere of dry nitrogen gas. The starting materials cis-$M(CO)_4L_2$, where M = Mo or W; L_2 = 2,2'-bipyridine or 1,10-phenanthroline, were prepared by literature methods [10]. Ph_4PI was precipitated from aqueous Ph_4PCl by a stoichiometric quantity of KI, while commercial samples of Ph_4PX (X = Cl or Br) and Et_4NX (X = Cl, Br or I) were warmed in vacuo before use.

^1H NMR spectra were recorded on a JEOL PS 100 spectrometer using tetramethylsilane as internal reference. Infrared spectra were recorded on a Hilger and Watts H 1200 Infrascan and on a Perkin-Elmer 237 spectrophotometer using Nujol mulls and solutions of complexes in MeCN or CH_2Cl_2. Far infrared studies were carried out on a Beckmann FS 720 interferometer with samples dispersed in pressed polythene discs.

Preparation of [$MX(CO)_3L_2$]$^-$ salts

These complexes were prepared by the direct reaction of cis-$M(CO)_4L_2$ with Ph_4PX or Et_4NX in MeCN /toluene or MeCN/xylene mixtures. Typical procedures are given for one molybdenum and one tungsten complex, and significant variations in experimental details are noted below.

$Ph_4P[MoCl(CO)_3phen]$. $Mo(CO)_4phen$ (1 mmol) was reacted with Ph_4PCl (1.5 mmol) in refluxing 4:1 toluene/acetonitrile (40 cm^3) for 1 h. On cooling, the product was filtered off, washed rapidly with a little cold methanol and dried _in vacuo_. Yield 97%. Complexes II, IV and V (Table 1) were prepared by similar procedures. For the synthesis of complexes XII and XIII a reaction time of 4 h. was necessary.

$Et_4N[WI(CO)_3bipy]$. $W(CO)_4bipy$ (1 mmol) was heated with finely divided Et_4NI (5 mmol) in refluxing 8:1 xylene/acetonitrile (40 cm^3) for 8 h. The product was filtered off, washed rapidly with ice-cold water, then methanol and dried _in vacuo_. Yield 93%. Complexes XIV-XVI were prepared in an analogous manner. The remaining complexes in Table 1 required a 16 h, reaction time and a $M(CO)_4L_2:R_4ZX$ ratio of 1:3 for the iodo-complex and 1:1.5 for the bromo- and chloro-analogues.

Preparation of $[MX(CO)_2(\eta\text{-}RC_3H_4)L_2]$

The complex $R_4Z[MX(CO)_3L_2]$ (1 mmol) was added to a stirred solution of allyl halide (10 mmol) in methanol (10 cm^3) at ambient temperatures. When the reaction was complete (0.2 h for Mo and 1.0 h for W compounds), the solid product was filtered off, washed with methanol and dried _in vacuo_. Complex XXIV (Table 2) crystallised only slowly and the reaction mixture was allowed to stand at $0^\circ C$ for 72 h prior to filtration.

The known complexes $[MX(CO)_2(\eta\text{-}C_3H_5)L_2]$, where L_2 = bipy, M = Mo, X = Cl or Br; L_2 = bipy or phen, M = W, X = Cl or I [11,12] were all isolated in over 80% yields by this procedure.

Preparation of $[MoBr(CO)_2(\eta^3\text{-cyclohexenyl})bipy]$

$Ph_4P[MoBr(CO)_3bipy]$ (0.5 mmol) was added to a deoxygenated solution of 3-bromocyclohexene (5 mmol) in $CHCl_3$ (5 cm^3) at $-15^\circ C$. The product (complex XXII, Table 2) was filtered off, washed with CH_2Cl_2 and dried _in vacuo_. Yield 42%. The corresponding phenanthroline anion reacted in an

TABLE 1

ANALYTICAL DATA FOR ANIONIC TRICARBONYL COMPLEXES

Complex	Yield (%)	Elemental analysis found (calcd.) (%)		
		C	H	N
$Ph_4P[MoCl(CO)_3phen]$(I)	97	61.5 (63.7)	4.0 (3.8)	4.0 (3.8)
$Ph_4P[MoBr(CO)_3phen]$ (II)	86	58.3 (60.1)	3.5 (3.6)	3.8 (4.0)
$Ph_4P[MoI(CO)_3phen]$ (III)[a]	~ 70			
$Ph_4P[MoCl(CO)_3bipy]$ (IV)	97	61.1 (62.5)	4.1 (4.0)	3.9 (3.9)
$Ph_4P[MoBr(CO)_3bipy]$ (V)	96	56.6 (58.8)	4.1 (3.7)	4.0 (3.7)
$Ph_4P[MoI(CO)_3bipy]$ (VI)[a]	~ 90			
$Ph_4P[WCl(CO)_3phen]$ (VII)	95	56.1 (56.9)	3.7 (3.4)	3.5 (3.4)
$Ph_4P[WBr(CO)_3phen]$ (VIII)	94	52.6 (54.0)	3.4 (3.3)	3.2 (3.2)
$Ph_4P[WI(CO)_3phen]$ (IX)[a]	~ 60			
$Ph_4P[WCl(CO)_3bipy]$ (X)	98	54.2 (55.6)	3.6 (3.5)	3.4 (3.5)
$Ph_4P[WBr(CO)_3bipy]$ (XI)	83	52.8 (52.7)	3.4 (3.4)	3.2 (3.3)
$Et_4N[MoCl(CO)_3phen]$ (XII)	86	52.0 (52.5)	5.2 (5.4)	7.9 (8.0)
$Et_4N[MoCl(CO)_3bipy]$ (XIII)[b]	66	49.7 (50.3)	5.7 (5.6)	8.2 (8.4)
$Et_4N[MoI(CO)_3phen]$ (XIV)	53	44.5 (44.8)	4.7 (4.6)	7.0 (6.8)
$Et_4N[MoI(CO)_3bipy]$ (XV)	58	41.3 (42.5)	4.3 (4.8)	6.8 (7.0)
$Et_4N[WI(CO)_3phen]$ (XVI)	90	38.2 (39.2)	3.8 (4.0)	5.8 (6.0)
$Et_4N[WI(CO)_3bipy]$ (XVII)	93	37.4 (37.0)	4.1 (4.1)	5.9 (6.2)

[a] Unstable and always contaminated with traces of decomposition products

[b] Readily forms a hydrate which is slowly desiccated over silica gel

analogous manner but the η^3-cyclohexenyl derivative so formed was easily oxidised and could not be obtained in an analytically pure state.

Results and discussion

Tricarbonyl anions $[MX(CO)_3L_2]^-$

The anionic complexes listed in Table 1 were all obtained in high yields as deep purple crystalline solids which slowly decomposed on standing to reform cis-$M(CO)_4L_2$ as one of the decomposition products. The complexes were at most sparingly soluble in non-coordinating solvents such as $CHCl_3$ and CH_2Cl_2 and were immediately solvolysed by coordinating solvents, consequently most of the spectroscopic data were confined to solid state measurements (Table 3).

Complexes of stoichiometry $[MX(CO)_3L_2]$, where L_2 is a bidentate chelating ligand, may exist in either of two isomeric forms, both of which should give rise to three infrared-active terminal carbonyl stretching vibrations. In general the fac-isomer may be distinguished from the mer-isomer by band intensity measurements, since in the former case three strong absorptions are predicted whereas one weak and two strong bands are expected for the latter [13]. The anions under discussion show three strong carbonyl absorptions in the solid state and in solution in non-coordinating solvents (Table 3), and are consequently assigned a fac-configuration. In coordinating solvents at room temperature the anions were quickly solvolysed. Thus infrared spectra of MeCN solutions of any of the complexes showed features characteristic of $[M(CO)_3(MeCN)L_2]$, where M = Mo or W and L_2 = bipy or phen [14]. In MeCN saturated with halide ion, this solvolytic reaction could be retarded and the carbonyl stretching frequencies of both the solvolysed and the anionic species were discernable. There was no evidence of fac-to mer-isomerisation of the anion in any of these complexes on dissolution in MeCN, as reported previously for $NMe_4[MoI(CO)_3bipy]$ and $[Ni(phen)_3][Mo(SH)(CO)_3bipy]$ [9].

Force constant data for the carbonyl anions were calculated by the Cotton-Kraihanzel method as modified by Dalton et al. [15]. In previous

(Continued on p.434)

TABLE 2

ANALYTICAL AND SELECTED INFRARED DATA FOR THE COMPLEXES $[MX(CO)_2(\eta\text{-allyl})L_2]$

Complex		Yield (%)	Elemental analysis found (calcd.) (%)			Infrared data (cm^{-1}) ν(C-O)[a]		ν(M-X)
			C	H	N	A_1	B_1	
$[MoCl(CO)_2(\eta\text{-2-MeC}_3H_4)phen]$	(XVIII)[b]	86				1923	1847	266
$[MoCl(CO)_2(\eta\text{-2-MeC}_3H_4)bipy]$	(XIX)	90	46.7 (48.2)	3.7 (3.8)	7.0 (7.0)	1925	1836	267
$[MoBr(CO)_2(\eta\text{-1-MeC}_3H_4)phen]$	(XX)[b]	83				1925	1838	168
$[MoBr(CO)_2(\eta\text{-1-MeC}_3H_4)bipy]$	(XXI)	82	42.2 (43.4)	3.4 (3.4)	5.7 (6.3)	1920	1831	164
$[MoBr(CO)_2(\eta\text{-C}_6H_9)bipy]$	(XXII)	42	47.1 (46.1)	3.6 (3.7)	5.7 (6.0)	1920	1838	166
$[MoBr(CO)_2(\eta\text{-2-MeC}_3H_4)bipy]$	(XXIII)	89	44.8 (43.4)	3.8 (3.4)	6.5 (6.3)	1928	1840	164
$[WCl(CO)_2(\eta\text{-2-MeC}_3H_4)bipy]$	(XXIV)	78	38.0 (39.5)	3.1 (3.1)	5.8 (5.8)	1918	1841	268

[a] Recorded on Nujol mulls, all bands are strong unless otherwise noted

[b] Known complexes

TABLE 3

SELECTED INFRARED AND FORCE CONSTANT DATA FOR CARBONYL ANIONS

Complex	ν(M-X) (cm^{-1})	ν(C-O)^{a}(cm^{-1})			Carbonyl force constants (mdyne Å^{-1})^{b}			
		A'	A'	A"	K_c	K_c'	K_1	K_2
I	227	1880	1765	1742	0.59	0.60	12.9	13.4
II	146	1886	1751br		0.50	0.70	12.9	13.4
III		1884	1764	1742	0.60	0.63	12.9	13.5
IV	227	1887	1769	1748	0.59	0.62	12.9	13.5
V	153	1886	1772	1751	0.57	0.60	13.0	13.5
VI		1884	1763	1740	0.61	0.63	12.8	13.5
VII	234	1874	1764	1743	0.55	0.57	12.8	13.4
		1880	1760	1743^{c}	0.56	0.62	12.8	13.4
VIII	147	1874	1743br		0.48	0.68	12.8	13.2
		1880	1766	1745^{c}	0.57	0.59	12.9	13.4
IX		1875	1746br		0.47	0.67	12.8	13.3
X	230	1877	1763	1743	0.56	0.59	12.8	13.4
XI	158	1867	1753	1736	0.54	0.60	12.7	13.3
		1879	1758	1742^{c}	0.56	0.63	12.8	13.4
XII	229	1879	1763	1719	0.53	0.75	13.0	13.5
XIII	222	1884	1766	1737	0.45	0.64	13.2	13.7
XIV	129	1900	1778br		0.59	0.63	13.0	13.6
		1892	1771	1751^{c}	0.60	0.64	12.6	13.2
XV	129	1899	1756br		0.51	0.72	12.7	13.2
XVI	127	1870	1747	1726	0.64	0.62	12.8	13.5
		1881	1762	1752^{c}	0.51	0.62	12.9	13.4
XVII	125	1877	1737br		0.74	0.60	12.7	13.4

[a] Recorded on Nujol mulls unless otherwise indicated

[b] Calculated by the procedure given in ref.15

[c] Solution data in CH_2Cl_2

studies of *cis*-$L_2YM(CO)_3$ derivatives, where L = bipy or phen, Y = monodentate Lewis base and M = Mo or W [14,15], the assignment A' > A' > A'' has been used in such calculations, resulting in axial CO stretching force constants K_2 greater than the equatorial CO stretching force constants K_1, as expected from simple π-bonding considerations. However, for some manganese complexes *cis*-$MnX(CO)_3L_2$ containing an electronegative halide ligand X, K_1 becomes larger than K_2 and the A'' mode has been assigned to the band at intermediate frequency [15-17]. Since the anionic Group VI complexes under consideration are isoelectronic with neutral Group VII derivatives of this stoichiometry, both assignments were considered possible and consequently force constants were also calculated based on the alternative band order A' > A'' > A'. These calculations yielded stretching force constants of a similar magnitude to those given in Table 3 with $K_2 > K_1$, but with widely divergent interaction constants($\delta = \frac{K_c}{K_c}$, as low as 0.33), and hence this second possible assignment seems less likely than that tabulated..

Neither K_1 nor K_2 varies significantly throughout the molybdenum or the tungsten series. Thus the marked effect of the halogen on the *cis* CO group found for the manganese pentacarbonyl halides [18] does not extend to these complexes, probably as a result of the increased covalent radii of these Group VI elements. The effect of back-donation of the increased charge on the central atom of the anions into C 2π orbitals results in a significant decrease of the CO stretching force constants compared with many neutral *fac*-$MY(CO)_3L_2$, where M = Mo or W, L_2 = bipy or phen and Y = monodentate Lewis base [14,15,19] and *fac*-$MX(CO)_3L_2$ where M = Mn or Re and X = halide, complexes [16].

In the far-infrared region only a single strong halogen-sensitive band was found for each of the anions (Table 3), at even lower wavenumbers than the M-X stretches of the corresponding halopentacarbonyl anions $[MX(CO)_5]^-$ [20]. On allyl oxidation, the M(II) derivatives so formed showed an increased complexity in their far-infrared spectra and M-X stretching frequencies were more difficult to assign with confidence. The most halogen sensitive bands in the entire infrared spectra of complexes XVIII – XXIV are given in Table 2 and are tentatively assigned as ν(M-X). These values are in good agreement with data on analogous ditertiary phosphine derivatives [21] and the ratio ν(M-Cl) : ν(M-Br) correlates closely with thatof the parent anions. $[WI(CO)_2(\eta\text{-}C_3H_5)bipy]$ and $[WI(CO)_2(\eta\text{-}C_3H_5)phen]$ were also examined to complete the series X = Cl, Br and I and show strong W-I stretching frequencies at 137 and 139 cm^{-1} respectively.

Allyl derivatives $[MX(CO)_2(\eta^3\text{-allyl})L_2]$

The carbonyl anions listed in Table 1 reacted readily with allyl halides at room temperature or below to give high yields of M(II)-η^3-allyl derivatives. This route is particularly useful for the tungsten analogues which are difficult to prepare by the procedure normally adopted for the molybdenum complexes [11,12] due to the slow kinetics and competing reactions of the tungsten intermediates. Only complexes XVIII and XIX were sufficiently soluble for NMR measurements. In SO_2 at −57°C the latter showed singlets at δ 1.01, 1.40 and 2.99 ppm with intensity ratios 3:2:2 due to the η^3-allyl group, and 2,2'-bipyridine absorptions at δ 8.79(d), 8.25(d), 8.06(t) and 7.61(t) ppm. The pronounced up-field shift of the allyl methyl group is no doubt caused by the shielding effects of the aromatic ring, and in the corresponding phenanthroline complex this shift is even greater (δ 0.70 ppm for the allyl methyl group). In the closely related complex $[Mo(NCS)(CO)_2(\eta\text{-}2\text{-}MeC_3H_4)phen]$ the allyl methyl group has been shown to lay over the plane of the aromatic ligand [22]. The low solubilities of the remaining complexes in Table 2 in suitable NMR solvents precluded their full characterisation, but the absence of an uncoordinated C=C stretch in their solid-state infrared spectra and their general spectroscopic similarity to complexes XVIII and XIX and to other complexes of this stoichiometry with known structures [22,23] indicated they were also members of the η^3-allyl series.

Various mechanisms have been proposed for the oxidative addition of allyl and related halides to low-valent transition metal complexes, including nucleophilic attack of the metal at the carbon atom bearing the halogen [24], a concerted insertion reaction [25], a radical chain process [26] and initial coordination of the C=C to the metal as the rate determining step [27]. Strong evidence that this last mechanism is operative in the allyl halide-$IrX(CO)(PR_3)_2$ systems has been presented recently [28]. A similar mechanism (A), or direct nucleophilic attack of the metal atom on the α-C atom of the allyl halide (B), would explain why the halogen in the anion is initially retained in the M(II)-allyl products, although subsequent exchange of halide occurs in some instances in solution on standing.

A

$$\begin{tikzcd} {[MX(CO)_3L_2]^-} + CH_2{=}CH{-}CH_2Y \arrow[r] & {[(YCH_2CH{=}CH_2MX(CO)_2L_2]^-} + CO \arrow[d, "fast"] \\ & {[(\eta^3{-}C_3H_5)MX(CO)_2L_2]} + Y^- \end{tikzcd}$$

B

$$\begin{tikzcd} {[MX(CO)_3L_2]^-} + CH_2{=}CH{-}CH_2Y \arrow[r] & {[(CH_2{=}CH{-}CH_2)MX(CO)_3L_2]} + Y^- \arrow[d, "fast"] \\ & {[(\eta^3{-}C_3H_5)MX\ (CO)_2L_2]} + CO \end{tikzcd}$$

Attempts to identify positively either of these reactive intermediates have proved unsuccessful so far.

Acknowledgement

We thank the S.R.C. for the award of a Research Studentship (to J.W.W.).

References

1. J.Ellis, J.Organometal.Chem., 86 (1975) 1
2. R.B.King, Acc.Chem.Res., 3 (1970) 417
3. G.Doyle, J.Organcmetal.Chem., 132 (1977) 243
4. J.Ellis and R.A.Faltynek, J.Organometal.Chem., 93 (1975) 205

5. M.Schneider and E.Weiss, J.Organometal.Chem., 73 (1974) C7

6. F.Hohmann, J.Organometal.Chem., 137 (1977) 315

7. B.J.Brisdon and G.F.Griffin, J.Chem.Soc.Dalton (1975) 1999

8. B.J.Brisdon and G.F.Griffin, J.Organometal.Chem., 76 (1974) C47

9. H.Behrens, E.Lindner and G.Lehnert, J.Organometal.Chem., 22 (1970) 665

10. M.B.H.Stiddard, J.Chem.Soc., (1962) 4712

11. C.G.Hull and M.B.H.Stiddard, J.Organometal.Chem., 9 (1969) 519

12. H. tom Dieck and H.Friedel, J.Organometal.Chem., 14 (1968) 375

13. L.E.Orgel, Inorg.Chem., 1 (1962) 25

14. L.W.Houk and G.R.Dobson, Inorg.Chem., 5 (1966) 2119

15. J.Dalton, I.Paul, J.G.Smith and F.G.A.Stone, J.Chem.Soc.A, (1968) 1208

16. L.F.Wuyts and G.P.Van der Kelen, Inorg.Chim.Acta 23 (1977) 19

17. R.J.Angelici, F.Basolo and A.J.Poe, J.Amer.Chem.Soc., 85 (1963) 2215

18. M.B.Hall and R.F.Fenske, Inorg.Chem., 11 (1972) 1619

19. L.W.Houk and G.R.Dobson, J.Chem.Soc.A, (1966) 317

20. R.J.H.Clark and B.C.Crosse, J.Chem.Soc.A, (1969) 224

21. B.J.Brisdon and K.E.Paddick, J.Organometal Chem., 149 (1978) 113

22. A.J.Graham and R.H.Fenn, J.Organometal.Chem., 25 (1970) 173

23. A.J.Graham and R.H.Fenn, J.Organometal.Chem., 17 (1969) 405

24. P.K.Wong, K.S.Y.Lau and J.K.Stille, J.Amer.Chem.Soc., 96 (1974) 5956

25. R.G.Pearson, Fortschu.Chem.Forsch., 41 (1973) 76

26. J.A.Labinger, A.V.Kramer and J.A.Osborn, J.Amer.Chem.Soc., 95 (1973) 7908

27. J.A.Osborn, in Y.Ishii and M.Tsutsui (Eds), Organo-transition Metal Chemistry, Plenum Publishing Corp., New York, 1975.

28. J.A.Kaduk, A.T.Poulos and J.A.Ibers, J.Organometal.Chem., 127 (1977) 245