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STUDIES OF CHELATION

II. PHOSPHINE COMPLEXES OF MOLYBDENUM AND MANGANESE

J.A. CONNOR and G.A. HUDSON
Department of Chemistry, The University, Manchester, M13 9PL (Great Britain)

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Summary

Activation parameters have been obtained for the chelation of $Mo(CO)_5dpe$ (dpe = $Ph_2PCH_2CH_2PPh_2$) and of $Mo(CO)_5dmpe$ (dmpe = $Me_2PCH_2CH_2PMe_2$) to give *cis*-$Mo(CO)_4dpe$ and *cis*-$Mo(CO)_4dmpe$ respectively. The results are compared with those for the analogous chromium complexes and show that the enthalpy contribution determines the more rapid chelation in the molybdenum complexes. The preparation and properties of the chelate-bridged hetero-metallic complex $(CO)_5ModmpeMn(CO)_4Br$ are reported. The reaction between $Et_4N[Mn(CO)_4X_2]$ (X = Cl, Br) and bidentate ligands dpe, dmpe and ape (ape = $Ph_2PCH_2CH_2AsPh_2$) in the presence of either silver(I) tetrafluoroborate or Et_3OBF_4 produces *cis*-$Mn(CO)_4X$(bidentate) which is identified by infrared and mass spectrometry. At room temperature the $Mn(CO)_4X$(bidentate) complex is rapidly converted to the chelated *fac*-$Mn(CO)_3X$(bidentate) complex. The chelation process is approximately 10^4 times more rapid than in the isoelectronic chromium(0) complexes. The preparation and characterisation of *fac*-$Mn(CO)_3Br$(dmpe), *cis*-$Mn(CO)_4Br(PMe_3)$ and *fac*-$Mn(CO)_3Br(PMe_3)_2$ are reported.

Introduction

A specific synthesis of monosubstituted derivatives of Group VI metal carbonyls, $M(CO)_5L$ (M = Cr, Mo, W), which permitted extension to the case where L is a multidentate ligand has been developed [1]. The availability of compounds in which L is a potentially bidentate ligand has facilitated a study of the mechanism by which they are converted into chelate complexes *cis*-$M(CO)_4L$. It was shown that a concerted process is involved in which enthalpy makes the largest contribution to the overall free energy of chelation. The entropy contribution largely discriminates between the rates of chelation of ligands containing similar donor atoms. The effects of the metal centre could not be defined exactly although it was observed that the rate of chelation of $M(CO)_5L$ decreases in the order M = Mo > Cr > W [2]. In an attempt to explain the position of molybdenum in this order, we report the determination of the activation parameters for chelation of $Mo(CO)_5$dpe and $Mo(CO)_5$dmpe.

We also report the extension of the synthetic method to Group VII metal carbonyls in that the tetraethylammonium salts $Et_4N[Mn(CO)_4X_2]$ (X = Cl, Br) are shown to react with mono- and bi-dentate ligands, L, in the presence of Lewis acids to give *cis*-$Mn(CO)_4LX$. When L is bidentate, the resulting complex is rapidly converted to *fac*-$Mn(CO)_3LX$.

Results and discussion

a. Chelation at a molybdenum centre

The preparation and characterisation of $Mo(CO)_5$dmpe was reported earlier. The dpe analogue was obtained as a white microcrystalline solid (76% yield) from the reaction between $Et_4N[Mo(CO)_5I]$ and dpe in methylene chloride solution on the addition of Et_3OBF_4. The infrared and mass spectra of the complex are similar to those of the chromium and tungsten analogues [2].

The rate of chelation of $Mo(CO)_5$dmpe and of $Mo(CO)_5$dpe to give *cis*-$Mo(CO)_4$dmpe and *cis*-$Mo(CO)_4$dpe respectively has been measured by infrared spectrophotometry in the frequency range 2100—1850 cm^{-1} using high boiling hydrocarbon solvents (n-octane, n-nonane) in the manner previously described [2]. Several determinations were made on each compound at each of four temperatures in the range 360—400 K. The activation parameters were calculated from the standard equations [3] by the method of least squares. The average values of the rate constants, k, and the computed activation parameters, $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ for these molybdenum complexes together with similar data for their chromium analogues are presented in Table 1.

The results confirm and extend the single observation [2] on $Mo(CO)_5$dmpe

TABLE 1

RATE CONSTANTS AND ACTIVATION PARAMETERS

(a) Rate constants for chelation of $Mo(CO)_5LL$, $k \times 10^5$ (sec^{-1})

T(K)	LL = dpe	T(K)	LL = dmpe
363	5.01	362	2.67
374	16.77	372	7.35
383	38.54	382	20.70
399	186.9	393	63.45

(b) Activation parameters for chelation of $M(CO)_5LL$ at 400 K

M	LL	ΔH(kJ mol^{-1})	TΔS(kJ mol^{-1})
Cr	dpe	135	10.8
Mo	dpe	120	5.7
Cr	dmpe	132	2.4
Mo	dmpe	118	−2.8

(c) Rate constants for chelation of $M(CO)_5LL$ at ca. 397 K

M	LL	k × 10^5 (sec^{-1})	LL	k × 10^5 (sec^{-1})
Cr	dpe	34	dmpe	7.5
Mo	dpe	155	dmpe	93.3

(now corrected) that chelation in a molybdenum complex is more rapid than in its chromium analogue. We note that when the chelating ligand is dpe the relative rate, $k(\mathrm{Mo})/k(\mathrm{Cr})$ is approximately 5 but when the chelating ligand is dmpe the relative rate is increased to approximately 12. An explanation of these relative rates comes from a consideration of the activation parameters. The enthalpy of activation is by far the more important contributor to the overall free energy. Whereas the mean Mo—CO bond energy in $Mo(CO)_6$ (152 kJ mol^{-1}) is substantially greater than the mean Cr—CO bond energy in $Cr(CO)_6$ (107 kJ mol^{-1}) [4] the enthalpy of activation for chelation, $\Delta H^{\ddagger}$ in both of the molybdenum complexes is significantly less than that in their chromium analogues. Further, we note that the enthalpy of activation in the case of both of the chromium complexes is greater than the mean Cr—CO bond energy whereas the reverse is true for the molybdenum analogues. These observations may suggest that, although the mechanism of the chelation reaction is concerted in both cases, there is more dissociative or S_N1 character in this process in the case of chromium than there is in the case of molybdenum. This may reflect the larger size of molybdenum [$r(Mo^0)$ 162; $r(Cr^0)$ 148 pm] [5] which reduces the need for the metal—CO bond to stretch in order to accomodate the incoming donor atom (phosphorus) in the transition state.

The earlier observation that dpe chelates to chromium more rapidly than does dmpe is confirmed in the case of molybdenum, where dpe chelation is approximately twice as rapid as dmpe chelation. The conclusion that the dpe is favoured by a more positive entropy of activation than dmpe is reinforced by the results in the molybdenum system. The argument based on the assumption of greater steric hinderance at the donor atom of dpe compared with that of dmpe may, perhaps, be ill founded.

It was shown that the Lewis acid assisted nucleophilic displacement reaction could be applied to the synthesis of bridged homonuclear complexes such as $(CO)_5MR_2P(CH_2)_2PR_2M(CO)_5$ (M = Cr, Mo, W; R = Me, Ph). When R = Me, the bridged product decomposes very easily in solution whereas when R = Ph the product is readily isolated. We have extended this concept to heteronuclear systems [2]. When $Mo(CO)_5$dpe is added to $Et_4N[Mn(CO)_4Br_2]$ in the presence of silver(I) salts the complex $(CO)_5$ModpeMn$(CO)_4$Br can be isolated. In contrast to the previous experience, the use of $Mo(CO)_5$dmpe in the same type of reaction gave $(CO)_5$ModmpeMn$(CO)_4$Br as fine yellow-orange crystals which dissolve to form solutions which are stable and from which the solid complex can be recovered easily.

b. Chelation at manganese(I)

Monosubstituted manganese carbonyl halide complexes are usually prepared from the reaction between $MnX(CO)_5$ and the ligand L in a solvent such as chloroform [6]. Addition of a second mole of a monodentate ligand gives $MnX(CO)_3L_2$. If a bidentate ligand LL is employed, the product is *fac*-$MnX(CO)_3$-LL which is thought to be formed via the corresponding monosubstituted complex *cis*-$MnX(CO)_4$LL, although evidence for this is lacking [7].

Infrared spectroscopic evidence has indicated that a monosubstituted intermediate is formed in the reaction between $ReX(CO)_5$ and dpe, but the subsequent chelation step was too rapid to allow the isolation of *cis*-$ReX(CO)_4$dpe.

The results of kinetic studies indicate that the overall rate of reaction between $MnX(CO)_5$ and dpe is approximately 100 times faster than in the case of ReX(CO) [8]. The reaction between $ReX(CO)_5$ and $(Ph_2As)_2CH_2$ (dam) in heptane solution at reflux permitted in isolation of *cis*-$ReX(CO)_4$dam which gave the chelated product *fac*-$ReX(CO)_3$dam on further heating in solution [9]. It was to be expected that the Lewis acid assisted reaction between the anions *cis*-$[MnX_2(CO)_4]^-$ and bidentate ligands LL in solution at or below ambient temperature might permit the isolation of the corresponding *cis*-$MnX(CO)_4$LL complex.

The manganese-containing products of reaction between $Et_4N[MnX_2(CO)_4]$ (X = Cl, Br) and the bidentate ligands dpe, dmpe and ape (LL) in the presence of either $AgBF_4$ or of Et_3OBF_4 in methylene chloride solution at 273—283 K consist of a mixture of both the chelated and the unchelated species $MnX(CO)_3$LL and $MnX(CO)_4$LL respectively. The composition of the mixture depends upon the temperature at which the reaction is conducted, the halogen, the ligand LL and the reaction time. Infrared spectroscopic evidence indicated that under the most favourable conditions we could devise (low temperature, short reaction time), the ratio of chelated to unchelated material formed in the reaction approached 3. All our attempts to isolate the pure unchelated complex $MnX(CO)_4$LL by fractional crystallisation at low temperature were unsuccessful. Moreover, by monitoring the infrared spectrum it was found that the conversion of *cis*-$MnX(CO)_4$LL to *fac*-$MnX(CO)_3$LL was fairly rapid even at 273 K.

Evidence that the tetracarbonyl complex is indeed formed in these reactions comes principally from the infrared spectra of the product mixture. In order to obtain more detailed information on the spectra of complexes of both types of product we have prepared pure samples of *fac*-$MnBr(CO)_3$LL (LL is dpe, dmpe, ape, $2PMe_3$) and *cis*-$MnX(CO)_4$L (X = Br, L = PMe_3, PPh_3; X = Cl, L = PMe_3).

The infrared spectra of the mixture of manganese containing products from the reaction show five bands in the 2100—1850 cm^{-1} region (Table 2), two of

TABLE 2

INFRARED SPECTRA OF $MnX(CO)_3LL$ and $MnX(CO)_4L$ COMPLEXES

X	L or LL	$\nu(CO)$ cm^{-1} [a]				
(a) MnX (CO)₄L						
Cl	PMe_3	2092s	2020m(sh)	2004vs	1955s	
Br	PMe_3	2093s	2020m(sh)	2006vs	1958s	
Br	PPh_3	2093s	2018m(sh)	2010vs	1963s	
(b) MnX (CO)₃LL						
Br	dpe		2027s		1960m	1919m
Br	dmpe		2028s		1958s	1909s
Cl	dmpe		2021s		1950s	1908s
Br	ape		2029s		1957s	1918m
Br	$2PMe_3$		2030s		1954s	1910s
(c) Product mixture MnX (CO)₄LL + MnX (CO)₃LL						
Br	dpe	2093m	2025vs	2011m(sh)	1957s	1917s
Cl	dpe	2088w	2021vs	2005w(sh)	1950s	1908s
Br	dmpe	2092w	2028vs	2004m(sh)	1956s	1904s
Cl	dmpe	2091w	2025vs	2005m(sh)	1954s	1904s
Br	ape	2093m	2026vs	2009s(sh)	1957s	1918m

[a] CH_2Cl_2 solution.

which (ca. 2090 and ca. 2005 cm^{-1}) decrease in intensity with time. Comparison of these spectra with those obtained under comparable conditions from pure *cis*-$MnX(CO)_4L$ and *fac*-$MnX(CO)_3LL$ complexes indicates strongly that the unchelated complex *cis*-$MnX(CO)_4LL$ is first formed and is then converted to the chelated complex *fac*-$MnX(CO)_3LL$. Qualitatively the rate of chelation increases in the order LL is dmpe(slowest) < ape < dpe(fastest) as was found for the analogous Group VI compounds, $M(CO)_5LL$.

The mass spectra of a range of manganese carbonyl halide complexes have been measured. These spectra were obtained only with difficulty as high source temperatures were necessary to obtain sufficient ion intensity. The relative abundance data for selected ions from a series of bromo-compounds $MnBr(CO)_nQ$ ($n = 3$, Q = LL; $n = 4$, Q = L) are summarised in Table 3. This shows that $MnBr(CO)_4L$ forms a parent ion and that the ion $[Mn(CO)_4L]^+$, formed by loss of bromine, is present. Both of these ions are absent from the spectra of the tricarbonyl complexes. Mass spectra of the mixture of products resulting from the Lewis acid assisted nucleophilic substitution reaction of bidentate ligands reported here contain ions at *m/e* values which correspond to the unchelated species $MnBr(CO)_4LL$ (LL = dmpe, dpe). In each case the intensity of the molecular ion and $[Mn(CO)_4LL]^+$ ion diminished very rapidly (minutes) after which the spectrum corresponded to that of the pure chelated material, $MnBr(CO)_3LL$. This may explain why the molecular ion of $MnBr(CO)_4ape$ is not observed although the formation of the complex is indicated by infrared spectroscopy.

Although unchelated complexes $MnX(CO)_4LL$ have not been isolated in a pure form, the results of these experiments provide the first substantial evidence that such compounds are formed as labile intermediates in the production of the chelated complexes $Mn(CO)_3LL$ from $MnX(CO)_5$. It is possible to compare the relative rates of chelation of the same ligand on different metals in the isoelectronic systems $Cr(CO)_5LL$ and $MnX(CO)_4LL$, on the basis of a qualitative estimate of the rate in the latter system as indicated by the disappearence of the band at ca. 2090 cm^{-1} in the infrared spectrum. [$MnBr(CO)_4(dmpe)$ ca. 2×10^{-3} sec^{-1} at 300 K; $MnBr(CO)_4(dpe)$ ca. 10^{-2} sec^{-1} at 300 K]. This comparison sug-

TABLE 3

MASS SPECTRA OF $MnBr(CO)_xQ$ COMPLEXES

Ion	Relative abundance (%)							
	x =	4	4	3	3	3,4	3,4	3,4
	Q = LL or L =	PMe_3	PPh_3	dpe	dmpe	dpe	dmpe	ape
$MnBr(CO)_4Q^+$		18	1			5	4	
$MnBr(CO)_3Q^+$				0.4	216	4	25	5
$MnBr(CO)_2Q^+$		6				4	3	
$MnBr(CO)Q^+$		19			5	1	22	
$MnBrQ^+$		167	13	4	608	71	93	8
$Mn(CO)_4Q^+$		5	30			13		
$Mn(CO)_3Q^+$			13	3	3	12	11	15
$Mn(CO)_2Q^+$		2	7		2	5	2	8
$Mn(CO)Q^+$		3	5	0.1	3	8	8	5
MnQ^+		100	100	100	100	100	100	100

gests that at the same temperature, chelation in the manganese(I) system is approximately 10^4 times faster than in the chromium(0) system. This may be seen as an index of the labilising influence of the halogen, X, upon the three *cis* carbonyl groups in the pseudo-octahedral $MnX(CO)_4LL$ complex with the concommittant strengthening of the Mn—CO (*trans*) bond so that only the *fac*-isomer of the $MnX(CO)_3LL$ product is isolated.

Experimental

All preparations and kinetic studies were carried out in an atmosphere of oxygen-free dry nitrogen, products being similarly handled and stored. Solvents were purified and dried in the usual manner and then purged with nitrogen at reflux prior to use. Melting points were recorded on a hot stage block and are uncorrected. Infrared spectra were recorded in hydrocarbon or halocarbon solution on a Perkin Elmer PE 257 grating spectrometer using either 0.5 or 1.0 mm cells. Mass spectra were recorded on an AE1 MS12 spectrometer with a nominal beam energy of 70 eV. Microanalyses were carried out by Mr. M. Hart and his staff, Manchester University. The following starting materials were prepared by standard methods $Et_4N[Mo(CO)_5I]$ [10], dpe [11], $Mo(CO)_5$dmpe [2], dmpe [12], Et_3OBF_4 [13], $Mn_2(CO)_{10}$ [14], $Et_4N[Mn(CO)_4X_2]$ (X = Cl, Br) [15]. The purity of these materials was established by microanalysis and spectroscopy. The ligand ape and $Mo(CO)_6$ were purchased from Strem Chemicals Inc., Danvers, Massachusetts, and $AgBF_4$ was purchased from Alpha Inorganics, Beverly, Massachusetts.

Preparation of $Mo(CO)_5$dpe

The ligand dpe (0.81 g, 2.04 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added to a solution of $Et_4N[Mo(CO)_5I]$ (1.0 g, 2.04 mmol) in the solvent (5 cm^3) at room temperature. A solution of Et_3OBF_4 (0.39 g, 2.04 mmol) in CH_2Cl_2 (5 cm^3) was added immediately to the stirred mixture. The initial orange coloration disappeared within a few seconds to leave a pale yellow solution. All volatile components were removed under reduced pressure (water pump) and the residue was extracted with ether/hexane (3/1 v/v). Crystallisation of this solution at —20° gave the complex as a white powder (0.97 g, 1.64 mmol, 76%) m.p. 95—96°. Found: C, 58.9; H, 4.1; P, 9.4. $C_{26}H_{24}MoO_5P_2$ calcd.: C, 58.7; H, 3.8; P, 9.8%. ν_{max} 2072m, 1986w, 1954s, 1946vs (hexane) cm^{-1}. *m/e* (*I*, %) 606(20), 578(33), 550(14), 522(36), 494(100).

Kinetic studies of chelation

A freshly filtered (G4) solution of the complex in a hydrocarbon solvent was place in a clean, dry Schenk tube in a pre-heated thermostat (temperature constant to within ± 1°). The chelation reaction was followed by monitoring the disappearance of the strong band at ca. 1946 cm^{-1} and the appearance of the strong band at ca. 1920 cm^{-1}. Activation parameters were calculated from the usual equations by the method of least squares using the Fortran programme Arrhenius-4 on the ICL 1906A computer at the University of Manchester Regional Computer Centre. The error in the enthalpy of activation (2 kJ mol^{-1}) and in the entropy of activation (6 J mol^{-1} K^{-1}) was estimated in the usual manner.

Preparation of $Mo(CO)_5dmpeMnBr(CO)_4$

The complex $Mo(CO)_5$dmpe (0.39 g, 1 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of $Et_4N[Mn(CO)_4Br_2]$ (0.46 g, 1 mmol) in the same solvent (5 cm^3) at room temperature. A solution of Et_3OBF_4 (0.19 g, 1 mmol) in CH_2Cl_2 (5 cm^3) was added to the stirred mixture. The mixture was elaborated in the usual manner to give the complex as an orange powder (0.42 g, 65%) m.p. 106° (dec.). Found: C, 29.2; H, 3.1. $C_{15}H_{16}BrMnMoO_9$ calcd.: C, 28.6; H, 2.6%. ν_{max} 2092w, 2074w, 2050vw, 2023m, 2009m, 1942s(br), 1918m(sh) (CH_2Cl_2) cm^{-1}. *m/e* (*I*%) 633(9)M^+, 605(3), 577(9), 549(22), 521(7), 493(60), 465(50), 437(40), 409(54), 381(100), 301(11).

Reaction between $Et_4N[MnBr_2(CO)_4]$ and dpe in the presence of Et_3OBF_4

The ligand dpe (1.33 g, 3.3 mmol) dissolved in CH_2Cl_2 (25 cm^3) was added to the salt $Et_4N[MnBr_2(CO)_4]$ (1.5 g, 3.3 mmol) dissolved in the same solvent (20 cm^3). A solution of Et_3OBF_4 (0.63 g, 3.3 mmol) in CH_2Cl_2 (10 cm^3) was added immediately to the stirred mixture, after which the intensely orange solution became slightly paler. Volatile components were removed under reduced pressure. The residue was extracted with ether to give a pale yellow powder which was recrystallised from hexane/CH_2Cl_2 (2/1 v/v) at 0° to give bright orange microcrystals. M.p. 166—168°. Found: C, 55.8; H, 3.6; Br, 13.7; P, 9.7. $C_{29}H_{24}BrMnO_3P_2$ calcd.: C, 56.4; H, 3.9; Br, 13.0; P, 10.0 and $C_{30}H_{24}BrMnO_4P_2$ calcd.: C, 55.8; H, 3.7; Br, 12.4; P, 9.6%.

The following were obtained in a similar manner *(a)* $MnCl(CO)_x$dpe (x = 3, 4) m.p. 154—156°. Found: C, 59.6; H, 4.2; Cl, 6.9; P, 11.0%. *(b)* $MnBr(CO)_x$dmpe (x = 3, 4) m.p. 132—134°. Found: C, 30.2; H, 4.7; Br, 21.2; P, 16.1%. *(c)* $MnBr(CO)_x$ape (x = 3, 4) m.p. 140—142°. Found: C, 51.6; H, 4.0; Br, 12.5; P, 4.7%. Spectroscopic results for these complexes are given in Tables 2 and 3.

Preparation of $MnBr(CO)_3dmpe$

The ligand dmpe (0.22 g, 1.4 mmol) in chloroform (10 cm^3) was added to a stirred solution of $MnBr(CO)_5$ (0.38 g, 1.4 mmol) in the same solvent. The mixture was heated at reflux for 1 h after which reaction was complete. The complex was recrystallised from hot chloroform and obtained as orange needles (0.45 g, 86%) m.p. 134—135°. Found: C, 29.7; H, 4.6; Br, 21.5; P, 16.4. $C_9H_{16}BrMnO_3P_2$ calcd.: C, 29.3; H, 4.4; Br, 21.7; P, 16.7%.

Preparation of $MnBr(CO)_4(PMe_3)$ and $MnBr(CO)_3(PMe_3)_2$

The ligand in the form of Me_3PAgNO_3 (0.4 g, 1.6 mmol) was added to a stirred solution of $Et_4N[MnBr_2(CO)_4]$ (0.75 g, 1.6 mmol) in CH_2Cl_2 (25 cm^3). Reaction was apparently immediate. The solution was filtered (G3) to remove silver(I) bromide and volatile materials were then removed under reduced pressure. The residue was extracted with ether (5 × 10 cm^3) and the solution was allowed to crystallise at low temperature. This gave bright yellow crystals of the substituted complex *fac*-$MnBr(CO)_3(PMe_3)_2$ m.p. 61—62°. Found: C, 30.0; H, 5.1; P, 16.5. $C_9H_{18}BrMnO_3P_2$ calcd.: C, 29.4; H, 4.9; P, 16.7%. *m/e* (*I*, %) 372(76), 291(0.4), 288(500), 263(0.3), 235(0.4), 212(117), 207(3), 192(7), 164(2), 136(25), 131(100). Yield ca. 10%. The mother liquor was concentrated to an orange oil. The oil was mixed with warm hexane (30 cm^3) and the solution left to crystallise at 0°. Orange crystals of *cis*-$MnBr(CO)_4(PMe_3)$ were deposited from the solution. M.p. 56—57°. Found: C, 26.1; H, 3.1. $C_7H_9BrMnO_4P$ calcd.: C, 26.0; H, 2.8%. Yield ca. 50%. Other spectroscopic results are in Tables 2 and 3.

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