

CATIONIC CARBONYL COMPLEXES OF MANGANESE(I) WITH DIPHOSPHINES

G.A. CARRIEDO and V. RIERA *

Department of Inorganic Chemistry, University of Valladolid, Valladolid (Spain)

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Summary

The bromo-carbonyls *fac*-BrMn(CO)₃(diphos) (diphos = Ph₂P(CH₂)_nPPh₂ for *n* = 1(dpm), 2(dpe), 3(dpp) and 4(dbp)) react with AgClO₄ in dichloromethane solution to give the neutral *fac*-O₃ClOMn(CO)₃(diphos). The reaction of the latter complexes at room temperature with a variety of ligands L = phosphines (PR₃), phosphites P(OR)₃, pyridine (Py), acetonitrile (MeCN), tetrahydrothiophene (THT) or acetone (Me₂CO) leads to the cationic species *fac*-[Mn(CO)₃(diphos)L]ClO₄ (or to the [Mn(CO)₄(diphos)]ClO₄, when L = CO). When L is a phosphorus ligand, the cationic *fac*-tricarbonyls isomerize upon heating to the *mer* isomers, which could only be isolated by this method for diphos = dpm, the reaction being accompanied by decomposition in the other cases. UV irradiation of the *mer*-[Mn(CO)₃(diphos)L]ClO₄ in the presence of a large excess of L gives the corresponding *trans*-[Mn(CO)₂(diphos)L₂]ClO₄.

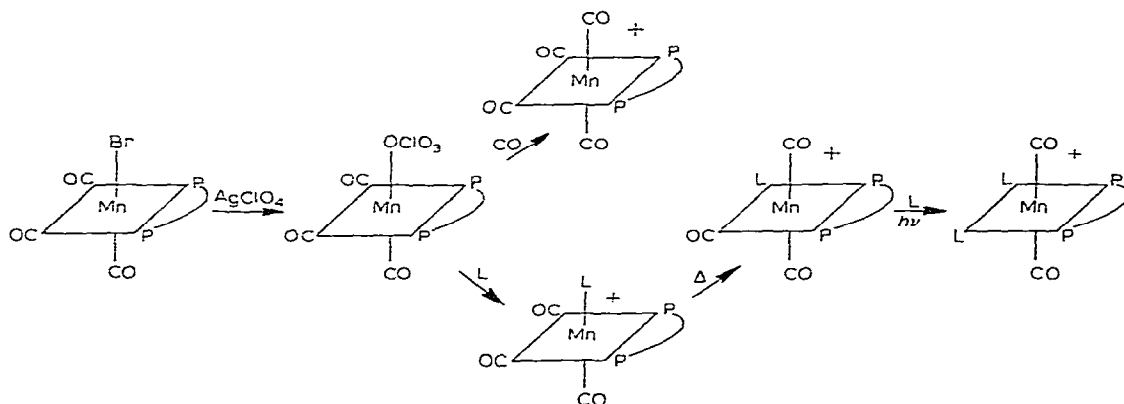
Introduction

Since the Abel and Tyfield review [1], many simple ways for synthesizing cationic carbonyl complexes have been developed. Among these, replacement of certain ligands, such as MeCN [2–4], Me₂CO [5] or H₂O [6] have received some attention, and recently the neutral complexes O₃ClOMn(CO)₃ [5], *fac*-O₃ClOMn(CO)₃(chel) (chel = bipy or phen) [7], and O₃ClOMn(CO)₃L₂ (L = PPh₃, P(OPh)₃, 1/2 bipy) [8] have been used as precursors of cationic manganese carbonyls, the perchlorate group being replaced by neutral ligands under mild conditions. The *fac*-[Mn(CO)₃(chel)L]ClO₄ (chel = bipy or phen) complexes obtained from *fac*-O₃ClOMn(CO)₃(chel) undergo replacement of CO by other ligands in boiling acetone or ethanol leading to *cis-trans*-[Mn(CO)₂(chel)L₂]ClO₄ [7], which reacts with L = P(OR)₃ under UV irradiation to give *mer*-[Mn(CO)(chel)L₃]ClO₄ [9]. It is likely that these reactions are favoured by

the *cis* labilizing effect of the two nitrogen atoms of the chelate ligand. *Fac* $\rightarrow$ *mer* isomerization in the cationic species $[\text{Mn}(\text{CO})_3\text{L}_3]^+$ and *cis* $\rightarrow$ *trans* in the $[\text{Mn}(\text{CO})_2\text{L}_4]^+$ have also recently been reported [5].

In this paper we described the preparation of *fac*- $\text{O}_3\text{ClOMn}(\text{CO})_3(\text{diphos})$ (diphos = dpm, dpe, dpp and dpb) complexes, and the synthesis from them of *fac*- $[\text{Mn}(\text{CO})_3(\text{diphos})\text{L}]\text{ClO}_3$ complexes. These cationic complexes isomerize to the corresponding *mer* isomers when heated in *n*-butanol in the presence of L, rather than undergoing CO substitution like the analogous *fac*- $[\text{Mn}(\text{CO})_3(\text{chel})\text{L}]\text{ClO}_4$ previously mentioned. The *mer* cationic tricarbonyls further react with L on UV irradiation to yield *trans*- $[\text{Mn}(\text{CO})_2(\text{diphos})\text{L}_2]\text{ClO}_4$ (see Scheme 1).

SCHEME 1



Results and discussion

It is well known that $\text{BrMn}(\text{CO})_5$ reacts with the diphosphines dpm and dpe under various conditions yielding the *fac*- $\text{BrMn}(\text{CO})_3(\text{diphos})$ [10–13]. We obtained these bromo-tricarbonyls for the diphosphines dpm, dpe, dpp and dpb, by refluxing a 1 : 1 molar mixture of $\text{BrMn}(\text{CO})_5$ and the diphosphine in toluene for a time varying from a minute for dpb to 20 minutes for dpm.

The complexes *fac*- $\text{BrMn}(\text{CO})_3(\text{diphos})$ react with silver perchlorate in dichloromethane at room temperature to give the neutral perchlorate complexes *fac*- $\text{O}_3\text{ClOMn}(\text{CO})_3(\text{diphos})$ which can easily be isolated. However it was observed that, if the reaction mixture is stirred for more than 1 or 2 hours, then depending on the diphosphine present on the complex various amounts of the tetracarbonyls $[\text{Mn}(\text{CO})_4(\text{diphos})]\text{ClO}_4$ are formed, as evidenced by the IR spectrum of the solution. This result is analogous to the reported formation of $\text{Mo}(\text{CO})_6$ in the decomposition of $\text{Mo}(\text{CO})_5(\text{amine})$ [14,15]. Thus, in the case of the diphosphine dpm, the mixture decomposes in ca. four hours and $[\text{Mn}(\text{CO})_4(\text{dpm})]\text{ClO}_4$ can be isolated. The pure *fac*- $\text{O}_3\text{ClOMn}(\text{CO})_3(\text{dpm})$ does not decompose during this time in the absence of AgClO_4 , showing that the latter must assist the decomposition, probably through the Ag^+ cation.

The cationic tetracarbonyl complexes $[\text{Mn}(\text{CO})_4(\text{diphos})]\text{ClO}_4$, for diphos =

dpm, dpe and dpb, can be prepared in relatively good yields by bubbling CO at atmospheric pressure through a dichloromethane solution of *fac*-O₃ClOMn(CO)₃(diphos) (Scheme 1). The reaction is, however, very slow in the case of the dpm and dpe, and when the rate was increased by irradiation, the corresponding tetracarbonyls were obtained in lower yields due to partial decomposition. The ion [Mn(CO)₄(dpe)]⁺ was previously obtained as the hexafluorophosphate salt, prepared from BrMn(CO)₃(dpe), AlCl₃ and CO at 1.5 atm [13].

The neutral *fac*-O₃ClOMn(CO)₃(diphos) complexes also react with N, O, S or P donor ligands in dichloromethane at room temperature, and the resulting *fac*-[Mn(CO)₃(diphos)L]ClO₄ can be isolated in practically quantitative yields. In this reaction, PPh₃ shows unusual behaviour in that when the diphosphine present in the perchlorate complex is dpm the resulting product is *mer*-[Mn(CO)₃(dpm)L]ClO₄, although the *fac* isomer is initially formed as shown by monitoring the reaction by infrared spectroscopy in the $\nu(\text{CO})$ region; when the diphosphine is dpe, the process leading to the *fac* isomer appears to be incomplete even with a 10 fold excess of PPh₃, and addition of AgClO₄ to the isolated *fac*-[Mn(CO)₃(dpe)(PPh₃)]ClO₄ regenerate the original *fac*-O₃ClOMn(CO)₃(dpe); finally, in the case of dpp no reaction takes place even when a large excess of PPh₃ is used. Me₂CO also replaces the perchlorate groups but the resulting *fac*-[Mn(CO)₃(diphos)(Me₂CO)]ClO₄ could not be isolated because it loses Me₂CO upon removal of the solvent. Both ligands, PPh₃ and Me₂CO, may be replaced by other ligands (N or P donors) under mild conditions.

The rate of replacement of the perchlorate group by the entering ligand L depends upon the number of methylene groups present in the diphosphine, the nature of the ligand, and the ligand concentration. The reaction is faster for the diphosphines with longer chains, e.g. the *fac*-O₃ClOMn(CO)₃(diphos) react at room temperature with a five-fold excess of P(OEt)₃ in 24 hours when diphos is dpm, while 3.5 hours is needed for dpe, 10 minutes for dpp and 1 minute for dpb. This result parallels the trends observed for the rate of CO exchange in Cr(CO)₄(diphos) [16]. On the other hand, the process is faster in the order:



which, except for MeCN, is that of decreasing π -acceptor ability (CO is not directly comparable with the others because its concentration was much lower). Finally, the rate was increased by increasing the ligand concentration, as was qualitatively demonstrated by monitoring the reaction between *fac*-O₃ClOMn(CO)₃(dpe) and varying amounts of P(OEt)₃.

The mechanism of the reaction must account for all these features, and because of the dependence of the concentration on the rate a simple D mechanism is not satisfactory, although, as in other cases where chelating ligands are present it operates alongside another mechanism, such as ring-opening [17] (as for example, in the reactions of Mo(CO)₄(H₂PCH₂CH₂PH₂) with phosphites [18]), or by an Id mechanism, like in the reactions of Mo(CO)₅(amine) with P-donor ligands [14]. A complete kinetic study would be necessary to establish the actual mechanism(s).

In an attempt to promote further CO substitution in the *fac*-[Mn(CO)₃(diphos)L]ClO₄, in order to give di- or monocarbonyl complexes (as in the case of the related *fac*-[Mn(CO)₃(chel)L]ClO₄, chel = bipy or phen [7]), the *fac*

TABLE 1
MELTING POINTS, CONDUCTIVITY AND ANALYTICAL DATA FOR COMPLEXES PREPARED

Compound	m.p.(°C)	Δ_M^a	Analysis found (calcd.) (%)		
			C	H	N
I <i>fac</i> -BrMn(CO) ₃ (dpp)	204(d)	2	57.3 (57.1)	4.17 (4.11)	
II <i>fac</i> -BrMn(CO) ₃ (dpb)	165	2	58.0 (57.7)	4.39 (4.34)	
III <i>fac</i> -O ₃ ClOMn(CO) ₃ (dpm)	153	123 ^b	53.1 (53.9)	4.47 (3.53)	
IV <i>fac</i> -O ₃ ClOMn(CO) ₃ (dpe)	154(d)	134 ^b	55.1 (54.7)	3.89 (3.81)	
V <i>fac</i> -O ₃ ClOMn(CO) ₃ (dpp)	148(d)	140 ^b	56.4 (55.3)	4.17 (4.00)	
VI <i>fac</i> -O ₃ ClOMn(CO) ₃ (dpb)	165(d)	130 ^b	56.0 (55.9)	4.35 (4.21)	
VII <i>cis</i> -[Mn(CO) ₄ (dpm)]ClO ₄	250(d)	120	53.2 (53.5)	3.52 (3.38)	
VIII <i>cis</i> -[Mn(CO) ₄ (dpe)]ClO ₄	218(d)	132	53.9 (54.1)	4.22 (3.61)	
IX <i>cis</i> -[Mn(CO) ₄ (dpb)]ClO ₄	168(d)	134	55.7 (55.5)	4.16 (4.04)	
X <i>fac</i> -[Mn(CO) ₃ (dpm)(Py)]ClO ₄	162(d)	124	56.6 (56.5)	3.90 (3.85)	2.25 (2.00)
XI <i>fac</i> -[Mn(CO) ₃ (dpm)(MeCN)]ClO ₄	183(d)	141	54.7 (54.3)	3.86 (3.76)	1.88 (2.11)
XII <i>fac</i> -[Mn(CO) ₃ (dpm)(P(OEt) ₃)]ClO ₄	187	148	52.7 (51.7)	4.85 (4.69)	
XIII <i>fac</i> -[Mn(CO) ₃ (dpe)(Py)]ClO ₄	164	120	56.4 (57.0)	4.00 (4.09)	1.88 (1.95)
XIV <i>fac</i> -[Mn(CO) ₃ (dpe)(MeCN)]ClO ₄	135(d)	140	54.9 (54.9)	4.58 (4.01)	1.67 (2.06)
XV <i>fac</i> -[Mn(CO) ₃ (dpe)(THT)]ClO ₄	165(d)	123	53.9 (54.6)	5.26 (4.41)	
XVI <i>fac</i> -[Mn(CO) ₃ (dpe)(PEt ₃)]ClO ₄	198	134	55.5 (55.6)	5.04 (5.17)	
XVII <i>fac</i> -[Mn(CO) ₃ (dpe)(P(OMe) ₃)]ClO ₄	195(d)	142	50.2 (50.5)	4.54 (4.37)	
XVIII <i>fac</i> -[Mn(CO) ₃ (dpe)(POEt ₃)]ClO ₄	179	119	52.9 (52.3)	5.15 (4.86)	
XIX <i>fac</i> -[Mn(CO) ₃ (dpe)(P(OPh) ₃)]ClO ₄	189(d)	134	60.0 (59.5)	4.68 (4.12)	
XX <i>fac</i> -[Mn(CO) ₃ (dpp)(P(OEt) ₃)]ClO ₄	135	122	53.3 (52.9)	5.60 (5.01)	
XXI <i>fac</i> -[Mn(CO) ₃ (dpb)(P(OEt) ₃)]ClO ₄	192	137	53.9 (53.5)	5.11 (5.17)	
XXII <i>mer</i> -[Mn(CO) ₃ (dpm)(PPh ₃)]ClO ₄	130(d)	120	62.1 (62.4)	4.80 (4.18)	
XXIII <i>mer</i> -[Mn(CO) ₃ (dpm)(P(OEt) ₃)]ClO ₄	209(d)	134	59.1 (59.2)	3.93 (4.00)	
XXIV <i>mer</i> -[Mn(CO) ₃ (dpm)(P(OPh) ₃)]ClO ₄	188(d)	140	51.6 (51.7)	5.10 (4.89)	
XXV <i>trans</i> -[Mn(CO) ₂ (dpm)(P(OEt) ₃) ₂]ClO ₄	180(d)	150	50.6 (51.1)	6.30 (5.60)	
XXVI <i>trans</i> -[Mn(CO) ₂ (dpm)(P(OPh) ₃) ₂]ClO ₄	189(d)	128	62.2 (62.3)	4.53 (4.31)	

^a Molar conductivity in S cm² mol⁻¹ of a 5 × 10⁻⁴ M acetone solution at 25°C.

^b Corresponds to *fac*-[Mn(CO)₃(diphos)(Me₂CO)]ClO₄.

tricarbonyls were heated in n-butanol in the presence of L. Only decomposition was observed for L = N donor ligands, but for L = PR₃ or P(OR)₃, isomerization to the corresponding *mer* species occurred. However, for diphos = dpp or dpb, this isomerization was accompanied by rapid decomposition, and for diphos = dpe, there was concomitant formation of *trans*-[Mn(CO)₂(dpe)₂]ClO₄, and so only the *mer*-[Mn(CO)₃(dpm)L]ClO₄ complexes could be prepared from the *fac* isomers. It was also observed that *fac*-O₃ClOMn(CO)₃(dpm) reacts with PPh₃ in dichloromethane at room temperature to give *mer*-[Mn(CO)₃(dpm)-(PPh₃)]ClO₄ directly, although monitoring of the reaction in the ν(CO) region clearly showed the slow isomerization of the initially formed *fac*-[Mn(CO)₃(dpm)(PPh₃)]ClO₄, as mentioned earlier.

A qualitative study revealed that the rate of *fac* → *mer* isomerization in boiling n-butanol is independent of the ligand concentration, a result which parallels that recently described for the neutral molybdenum analogue *fac*-Mo(CO)₃(dpe)(P(Oi-Pr)₃) [19], and the mechanism proposed for the latter may also operate in our case. As for the molybdenum tricarbonyl, the *fac* → *mer* isomerization of the [Mn(CO)₃(dpm)L]ClO₄ species for L = P(OR)₃ occurs at about 120°C, but for L = PPh₃ it takes place even at room temperature. Thus, although a kinetic study would be necessary to give a clear answer, the reason why the isomerization occurs at room temperature may be because of the easier dissociation of the Mn—PPh₃ bond (probably due to the larger steric hindrance of the PPh₃). This effect may influence both the equilibrium constant of the first step (see figure in ref. 19) and the lifetime of the intermediate [Mn(CO)₃(dpm)]⁺. It is noteworthy that the *fac*-[Mn(CO)₃(diphos)L]ClO₄ complexes which are formed most slowly isomerize most readily to the *mer* isomers.

When a solution of the *mer*-[Mn(CO)₃(diphos)L]ClO₄ was irradiated with UV light in the presence of a large excess of L, formation of the *trans*-[Mn(CO)₂(diphos)L₂]ClO₄ was demonstrated by monitoring the infrared spectrum of the reaction mixture. As in other cases above mentioned, for diphos = dpe, the *trans*-[Mn(CO)₂(dpe)₂]ClO₄ was also found among the products, and only those *trans* dicarbonyls containing dpm could be isolated pure.

In Table 1 are presented the analytical, melting point, and conductivity data for all the compounds prepared.

IR spectra

In addition to the expected bands due to the CO groups and the ligands, all the neutral perchlorate complexes show the characteristic pattern of the coordinated O₃ClO⁻ group (1060s, 1020s, 870m and 600–630m (br) cm⁻¹), while the cationic derivatives show bands at 1090s (br) and 630m cm⁻¹ characteristic of free ClO₄⁻.

Table 2 shows the observed ν(CO) frequencies and the corresponding Cotton-Kraihanzel parameters (CK) [20–22], for the *fac*-Mn(CO)₃(diphos)X (X = O₃ClO⁻ or Br, are neutral, X = L are cationic); K₁ refers to the CO *trans* to X. ν(CO) frequencies and CK parameters for the *mer*-[Mn(CO)₃(dpm)L]ClO₄ are given in Table 3; K₂ is that of the CO *trans* to another CO. In the case of the [Mn(CO)₄(diphos)]ClO₄, the CO force constants were calculated both by Cotton and Kraihanzel's method and that described by Van der Kelen et al.

TABLE 2

$\nu(\text{CO})$ FREQUENCIES (IN cm^{-1}), AND CK PARAMETERS (Nm^{-1}) FOR *fac*- $\text{Mn}(\text{CO})_3(\text{diphos})\text{X}$ IN DICHLOROMETHANE SOLUTION ^a

Compound	A	A'	A''	E	A'	K ₁	K	K ₂	K _i
<i>fac</i> -BrMn(CO) ₃ (dpm)	2025		1958		1917	1508		1590	42
<i>fac</i> -BrMn(CO) ₃ (dpe)	2029		1957		1919	1514		1591	44
I	2032		1962		1912	1500		1599	45
II	2028		1955		1905	1490		1590	46
III ^b	2049		1975		1937	1543		1621	46
IV ^b	2044		1975		1933	1534		1619	44
V ^b	2049		1977		1924	1519		1623	46
VI ^b	2044		1975		1927	1523		1619	44
X	2036		1963		1953	1575		1598	42
XI	2044		1972		1957	1579		1612	42
XII	2051		1965		1982	1647		1599	40
XIII	2040		1962		1950	1572		1599	45
XIV	2047		1975		1958	1580		1618	42
XV	2034			1954(br)			1585		43
XVI	2030			1955(br)			1583		40
<i>fac</i> -[Mn(CO) ₃ (dpe)(PPh ₃)] ⁺	2035			1965(br)			1597		38
XVII	2044	1961			1979	1642		1590	37
XVIII	2043	1959			1975	1633		1589	39
XIX	2050	1959			1984	imaginary roots			
XX	2045	1965			1975	1625		1599	40
XXI	2040	1957			1972	1626		1586	39

^a All bands are strong. ^b Recorded in Me₂CO solution, the spectra of these compounds showed bands at 2040s, 1967s, 1942s (III), and at 2035s, 1965s and 1943s (IV); corresponding to the cations [Mn(CO)₃(diphos)(Me₂CO)]⁺. Bands of the acetone complexes of V and VI could not be observed, because of the rapid reactions with the NaCl window cell which seemed to lead to *fac*-ClMn(CO)₃(diphos).

[23], and the results, together with the $\nu(\text{CO})$ frequencies, are included in Table 4; K_1 refers to the equatorial CO's, K_2 to the axial, K_e is the equatorial-axial interaction constant, and K'_e , the equatorial-equatorial. The force constants calculated for *trans*-[Mn(CO)₂(dpm)L₂]ClO₄ are listed in Table 5.

In all cases the number of bands and their relative intensities are consistent with the structures proposed for the compounds. Furthermore, the trends observed for the force constant values clearly reflect the expected changes in the π -acceptor abilities of the ligands from Py to P(OPh)₃ and also the degree of substitution. In most cases, the force constants for the homologous compounds increase in the order dpm > dpe > dpp > dpb. The assignments in each case are briefly discussed below.

TABLE 3

$\nu(\text{CO})$ FREQUENCIES (cm^{-1}) AND CK PARAMETERS (nm^{-1}) FOR *mer*-[Mn(CO)₃(dpm)L]⁺ IN DICHLOROMETHANE

Compound	A'	A'' and A'	K ₁	K ₂	K _i
XXII	2044w	1967s(br)	1576	1618	28
XXIII	2057w	1975s(br)	1590	1634	30
XXIV	2065w	1985s(br)	1606	1649	29

TABLE 4

$\nu(\text{CO})$ FREQUENCIES (cm^{-1}) AND CK PARAMETERS (Nm^{-1}) FOR $[\text{Mn}(\text{CO})_4(\text{diphos})]^+$ IN DICHLOROMETHANE ^a

Compound	A_1	A_1^c	B_1	B_2	K_1	K_2	K_c	K_c'	K_t
VII	2099w	2033(sh)	2020s	2005(sh)	1650 (1662)	1700 (1698)	26 (25)	26 (39)	52 (50)
VIII	2095w	2027(sh)	2016s	2005(sh)	1649 (1657)	1693 (1692)	26 (25)	26 (33)	52 (50) ^b
IX	2090w	2028m	2002s(br)	2002s(br)	1646 (1661)	1674 (1669)	28 (25)	28 (43)	52 (51)

^a In parentheses, are presented the CO force constants calculated by the method of Delbecke, Claeys, Van der Kelen and Kaluwe [23]. ^b 1655, 1690, 25, 37 and 48, from ref. [13]. These frequencies were not used to calculate the CK parameters.

The highest frequency band in the spectra of the *fac*- $\text{Mn}(\text{CO})_3(\text{diphos})\text{X}$ can be unambiguously assigned to one of the A' modes (C_s symmetry), the other two bands are assigned by considering the π -acceptor ability of X relative to that of the diphosphine. We have adopted the assignments (see Table 2) which lead to $K_1 < K_2$ when L is a poorer π -acceptor than the diphosphine, and vice versa. Of course, where only two bands (one of them broader) appear in the spectrum (X = PPh_3 , PEt_3 and, rather surprisingly, THT) the symmetry may be considered C_{3v} , the lowest band corresponding to the double degenerated E mode, and there is only one $K(\text{CO})$ and one K_i . In all cases our assignment are consistent with those found for related compounds [22,24,25], but different from those reported in ref. 3.

For *mer*- $[\text{Mn}(\text{CO})_3(\text{dpm})\text{L}]\text{ClO}_4$ the intensity arguments advanced by Orgel [26] suggest that the weaker band at higher frequency is to be assigned to the A' mode (C_s symmetry), and so because of the accidental degeneracy of the other two, no problems arose in these case.

As shown in Table 4, the assignments for the tetracarbonyls agrees with those reported for the analogous $\text{Wo}(\text{CO})_4(\text{dpe})$ [21], and it is evident that the resulting $\nu(\text{CO})$ constants for the $[\text{Mn}(\text{CO})_4(\text{dpe})]^+$ obtained by the method of Van der Kelen et al. are closer to those obtained by Darensbourg and Froelich following a more rigorous procedure [13], than are those obtained by the Cotton and Kraihanzel method.

Selection rules suffice to determine the assignment for the *trans*- $[\text{Mn}(\text{CO})_2(\text{dpm})\text{L}_2]\text{ClO}_4$. The strong band at the lower frequency corresponds undoubtedly to the A_{2u} mode and the very weak band to the forbidden A_{1g} (assuming rigorous D_{4h} symmetry) (Table 5).

TABLE 5

$\nu(\text{CO})$ FREQUENCIES (cm^{-1}) AND CK PARAMETERS (Nm^{-1}) FOR *trans*- $[\text{Mn}(\text{CO})_2(\text{dpm})\text{L}_2]^+$ IN DICHLOROMETHANE

Compound	A_{1g}	A_{2u}	K	K_t
XXV	2029w	1948vs	1597	65
XXVI	2019w	1931vs	1576	70

Experimental

All reactions were carried out under N_2 . The diphosphines dpm [27], dpe [28] and dpp [29], were prepared as described in the literature, while the other ligands were taken from commercial sources. IR spectra were recorded on a Perkin Elmer 599 spectrophotometer and were calibrated against the polystyrene absorption at 1602 cm^{-1} . Analyses were performed with a Perkin Elmer 240 microanalyzer.

fac-BrMn(CO)₃(diphos)

1 g (3.4 mmol) or $BrMn(CO)_5$ and a stoichiometric amount of the diphosphine are refluxed in 15 ml of toluene for 20 minutes (dpm), 10(dpe), 5(dpp) or 1(dpb). The solution is filtered, hexane is added, and the yellow-orange precipitate is dried. Yield: 80–90%. Recrystallization from dichloromethane-hexane or dichloromethane-ethanol gives the pure compounds as orange crystals.

fac-O₃ClOMn(CO)₃(diphos)

A mixture of 1.5 mmol of *fac-BrMn(CO)₃(diphos)* and 0.34 g (1.65 mmol) of $AgClO_4$ in 25 ml of dichloromethane is stirred at room temperature in the absence of light for 1 or 2 hours (rather less than 1 hour for diphos = dpm). The $AgBr$ and the excess of $AgClO_4$ are filtered off and the yellow filtrate evaporated under reduced pressure. The residue is stirred with ether and dried. Yield: 70–80%. The products may be recrystallized from dichloromethane.

fac-[Mn(CO)₃(diphos)L]ClO₄

To a solution of 0.3 g of *fac-O₃ClOMn(CO)₃(diphos)* in 20 ml of dichloromethane the ligand L is added in 3 to 5 fold excess, and the mixture is stirred at room temperature until the spectrum of the solution no longer shows bands of the starting perchlorate complex. The solvent is removed under reduced pressure and the residue is washed several times with ether until free of ligand. Yields are of the order of 80%. The compounds may be recrystallized from dichloromethane-ethanol and washed with ether. In the case of $L = PPh_3$, a 20 fold excess of the ligand was used, and the product purified from toluene-hexane.

mer-[Mn(CO)₃(dpm)L]ClO₄

0.3 g of the *fac-[Mn(CO)₃(dpm)L]ClO₄* (or *fac-O₃ClOMn(CO)₃(dpm)*) and a five-fold excess of $L = P(OPh)_3$ or $P(OEt)_3$ are refluxed in n-butanol for 3–4 hours. The solution is filtered, concentrated under reduced pressure, and the product precipitated by adding ether. Yields: 50%. The products are recrystallized from dichloromethane-ethanol and washed with ether.

mer-[Mn(CO)₃(dpm)(PPh₃)]ClO₄

A solution of 0.22 g (0.35 mmol) of *fac-O₃ClOMn(CO)₃(dpm)* and 0.14 g (0.53 mmol) of PPh_3 in 15 ml of dichloromethane, is stirred for 16 days in the absence of light. The solvent is then removed in vacuo and the residue washed with ether. Yield: 0.28 g (90%). The product is purified by dissolving it in

toluene-dichloromethane, removing the latter under reduced pressure, and adding hexane.

trans-[Mn(CO)₂(dpm)L₂]ClO₄

A dichloromethane solution of 0.4 g of *mer*-[Mn(CO)₃(dpm)L]ClO₄ (or *fac*-O₃ClOMn(CO)₃(dpm)) and a seven-fold excess of (L = P(OPh)₃ or P(OEt)₃), is irradiated with UV light until the bands of the starting complex have almost disappeared. The yellow solution is filtered, the solvent is removed in vacuo, and the residue washed with ether or hexane. The products are recrystallized from dichloromethane-ethanol and washed with ether. Yields: 62%. When L = P(OEt)₃, the *trans*-[Mn(CO)₂(dpm)₂]ClO₄ is also found among the products but is removed by recrystallization.

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