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SYNTHESIS OF MANGANESE(I) CARBONYLS WITH σ-BONDED ALKYNYL LIGANDS

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Summary

A number of σ-alkynylcarbonyl complexes of manganese(I), $[Mn(CO)_n(L)_{5-n}(C{\equiv}CR)]$, have been obtained from bromocarbonyl complexes $[Mn(CO)_n(L)_{5-n}Br]$ by treatment with silver(I) or copper(I) actylides, and from perchlorato complexes $[Mn(CO)_n(L)_{5-n}(OClO_3)]$ by treatment with 1-alkyne and base. New σ-alkynyl compounds can also be obtained from other alkynyl complexes by reactions involving replacement of CO ligands.

Introduction

The synthesis of σ-alkynyl complexes of transition metals has been a very active field in the last two decades [1], mainly because such species can be used for the preparation of species containing ligands such as vinylidene [2], carbene [3], or acyl [4]. A large number of square planar, four coordinate σ-alkynyl compounds have been described. Compounds of the type $[(\eta^5\text{-}C_5H_5)M(CO)_n(C{\equiv}CR)]$ are also very common, but σ-alkynyl complexes having an octahedral geometry are scarcer. On the other hand, the σ-alkynyl compounds of the manganese group are much less abundant, and they have been little studied. The first σ-alkynyl complexes of rhenium $[Re(CO)_5(C{\equiv}CR)]$ ($R = C_6H_5$, C_6F_5) were obtained in 1968 by Stone et al. [5] in very low yields, by treating $[Re(CO)_5Br]$ with organolithium derivatives $LiC{\equiv}CR$. Attempts to apply that procedure to the preparation of the analogous $[Mn(CO)_5(C{\equiv}CPh)]$ complexes were unsuccessful [5]. For some years, the only compound of manganese(I) related to the alkynyl complexes was *cis*-$[Mn(CO)_4(C{\equiv}CPPh_3)Br]$ [6] which contains the neutral two electron ylide ligand $:\bar{C}{\equiv}C\overset{+}{P}Ph_3$. The first σ-alkynyl carbonyl compound of manganese(I), $[Mn(CO)_5(C{\equiv}CPh)]$, was prepared in 1982, in 31% yield, by treating pentacarbonyl manganate(−I) anion with a salt of the (triphenyl)(phenylethynyl)phosphonium ion

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[7]. In the same paper, it was reported that the phenylethynylpentacarbonyl complex showed no tendency towards replacement of CO when treated with PPh_3 in refluxing THF or hexane for 12 h.

The poor results from methods based on organolithium reagents [5], the decreasing accessibility of $[Mn(CO)_n(L)_{5-n}]^-$ anions as substitution is increased, and the apparent inertness of $[Mn(CO)_5(C{\equiv}CPh)]$ [7] seemed to indicate that the synthesis of new alkynyl derivatives of manganese(I) with carbonyl and other ligands would be very difficult. This prompted us to explore other possible preparative methods for these compounds, and we have obtained a number of new σ-alkynylcarbonyl complexes of manganese(I) by means of some reactions of three types: (a) reactions of bromocarbonyls with silver(I) and copper(I) acetylides; (b) reactions of perchloratocarbonyl complexes with 1-alkynes and base; and (c) CO replacement in σ-alkynyl complexes. Some of this work has been reported in a preliminary communication [8].

Results and discussion

It has been reported that the reaction of halogeno complexes with silver(I) [9] or copper(I) [10,11] acetylides gives σ-alkynyl compounds via alkynyl/halogen exchange. However, this method has been little employed because the reaction often leads to more complex species, resulting in poor yields of the desired product.

In the case of bromocarbonyl compounds of manganese, the best results are obtained by treating a bromo derivative with the silver(I) acetylide formed in situ from a mixture of $AgBF_4$ and the appropriate 1-alkyne in CH_2Cl_2/H_2O (Method A) shown in eq. 1.

$$[Mn(CO)_n(L)_{5-n}Br] + AgBF_4 + HC{\equiv}CR \xrightarrow{CH_2Cl_2/H_2O} [Mn(CO)_n(L)_{5-n}(C{\equiv}CR)] + AgBr + HBF_4 \quad (1)$$

The application of Method A is fairly general, and complexes of various degrees of substitution and stereochemistry can be obtained. The yields range from 45 to 80% (Compounds I–IX, Table 1). The reaction is very clean and, in most cases, only the desired product is obtained. The only exception is the reaction of *cis*-$[Mn(CO)_2(dppe)(P(OMe)_3)Br]$ with $AgBF_4$ and $HC{\equiv}CPh$, in which variable amounts of the decomposition product *mer*-$[Mn(CO)_3(dppe)(P(OMe)_3)]BF_4$ were produced. This decomposition of the bromodicarbonyl complex upon treatment with silver(I) salts has been previously observed [12].

The required times (see Experimental section) are consistent with the increasing lability of the Mn–Br bond as the number of CO ligands in the complex decreases. It is noteworthy that the complexes *fac*- or *mer*-$[Mn(CO)_3(P(OR)_3)_2Br]$ (R = Me, Ph) appear to be inert under the reaction conditions, whereas both *mer*-$[Mn(CO)_3(PEt_3)_2Br]$ and *cis*-$[Mn(CO)_2(P(OMe)_3)_3Br]$ give the desired products. (The latter product could not be isolated, but was detected by IR spectroscopy.)

Unsatisfactory results were obtained when the method was applied to the monocarbonyl $[Mn(CO)(dppe)_2Br]$; total decomposition was observed, probably because of the oxidation of manganese(I) by Ag^+ cation. On the other hand, the use of $[Mn(CO)_5Br]$ in Method A leads to extensive decomposition and formation of unidentified water-soluble yellow species. A result somewhat similar was obtained when *fac*-[Mn(CO)$_3$(N–N)Br] (N–N = bipy, phen) were used. Since the presence of water in the reaction appears to be unsatisfactory in these cases the direct interaction between bromocarbonyls and solid silver(I) acetylide in dry CH_2Cl_2 was tried. The results were markedly dependent on the nature of the starting bromocarbonyl; thus, treatment of [Mn(CO)$_5$Br] with AgC≡CPh led to almost total decomposition after 30 h stirring. The IR spectra of the products mixtures show some bands attributable to more substituted species, probably tetra- and tri-carbonyl complexes containing one or more phenyl ethynyl ligands. None of these intermediate species could be isolated, and no ν(C–O) bands of [Mn(CO)$_5$(C≡CPh)] were detected. In contrast, stirring of *fac*-[Mn(CO)$_3$(N–N)Br] (N–N = phen) with AgC≡CPh produced the alkynyl (X) in good yield.

We also examined the closely related reactions between bromocarbonyls and copper(I) acetylides as a route to σ-alkynyl compounds of manganese(I). The results were again very dependent on the substrate. Compounds *fac*-[Mn(CO)$_3$(L–L)Br] (L–L = dppe, bipy) were inert even upon prolonged reflux in CH_2Cl_2 or Me_2CO, while *mer-trans*-[Mn(CO)$_3$(PEt$_3$)$_2$Br] reacted with CuC≡CPh in refluxing CH_2Cl_2 to give the alkynyl (II) in 53% yield.

Treatment of a compound containing a labile ligand with 1-alkyne and a base has been commonly used for synthesis of σ-alkynyl compounds, mainly of the platinum group metals. A number of new σ-alkynyl carbonyl complexes of manganese(I) can be obtained in this way from the appropriate perchlorato complex by stirring with the 1-alkyne and KOH in THF (Method B, eq. 2).

$$[\mathrm{Mn(CO)}_n(\mathrm{L})_{5-n}(\mathrm{OClO_3})] + \mathrm{HC{\equiv}CR} + \mathrm{KOH} \xrightarrow{\mathrm{THF}} [\mathrm{Mn(CO)}_n(\mathrm{L})_{5-n}(\mathrm{C{\equiv}CR})] + \mathrm{KClO_4} + \mathrm{H_2O} \qquad (2)$$

In all cases the reaction mixture darkens and decomposition takes place, probably due to the attack of KOH on the carbonyl groups and so the yields are low. In attempts to find better conditions for these reactions we used NEt_3 in CH_2Cl_2 instead of KOH in THF; this gave compound XII in high yield (80%), but in other cases (compounds XIII, XIV) the yields were not improved substantially.

On the other hand, treatment of *fac*-[Mn(CO)$_3$(N–N)Br] (N–N = bipy) with a mixture of HC≡CPh, NEt_3, and $TlPF_6$ gives the alkynyl XI in high yield. This reaction is expected to be not very general, however, since thallium(I) salts only act as halide abstractors when the halide complex is very electron rich (e.g. in manganese monocarbonyls, dicarbonyls, and some tricarbonyls).

Method B is less satisfactory for the preparation of compounds such as *fac*-[Mn(CO)$_3$(L–L)(C≡CPh)], which can be obtained in better yields by other procedures, such as Method A. However, Method B is the only method available for preparing compounds with C≡CH ligand (XII, XIII, XIV), since the instability of the AgC≡CH reagent precludes its use in Method A.

The known pentacarbonyl compound [Mn(CO)$_5$(C≡CPh)] [7] was also prepared by Method B in 9% yield by using diethyl ether as solvent at −70°C.

As mentioned above, it has been reported that [Mn(CO)$_5$(C≡CPh)] does not react with PPh_3 in refluxing THF or hexane [7]. Nonetheless, the pentacarbonyl compound reacts with a small excess of dppm in refluxing toluene for 30 min to give the *fac*-tricarbonyl (IV) (Fig. 1a). This and other substitution reactions which we carried

(Continued on p. 384)

TABLE 1

MELTING POINT, CONDUCTIVITY, ANALYTICAL, AND YIELD DATA FOR ALKYNYL COMPOUNDS

Compound		m.p. (°C)	Λ_{max} [a] (S cm^2 mol^{-1})	Analysis (Found (calcd.)(%))			Yield (%)	Reaction [a]
				C	H	N		
I	*cis*-$\mathrm{[Mn(CO)_4(PCy_3)(C{\equiv}CPh)]}$	162	1.0	65.71	6.91		70	(A)
				(65.79)	(6.98)			
II	*mer-trans*-$\mathrm{[Mn(CO)_3(PEt_3)_2(C{\equiv}CPh)]}$	60	1.8	57.69	7.66		45	(A)
				(57.99)	(7.41)		53	(E)
III	*fac*-$\mathrm{[Mn(CO)_3(dppe)(C{\equiv}CPh)]}$	168	0.8	69.20	4.40		70	(A)
				(69.60)	(4.58)		40	(B)
IV	*fac*-$\mathrm{[Mn(CO)_3(dppm)(C{\equiv}CPh)]}$	185	1.0	68.26	4.24		68	(A)
				(69.24)	(4.36)			
V	*fac*-$\mathrm{[Mn(CO)_3(dppe)(C{\equiv}C^tBu)]}$	172	1.4	67.53	5.35		65	(A)
				(67.97)	(5.38)			
VI	*fac*-$\mathrm{[Mn(CO)_3(dppm)(C{\equiv}C^tBu)]}$	159	0.9	68.13	5.32		56	(A)
				(67.56)	(5.17)			
VII	*cis*-$\mathrm{[Mn(CO)_2(dppe)(P(OMe)_3)(C{\equiv}CPh)]}$	200	5.0	61.44	5.10		45	(A)
				(63.79)	(5.18)			
VIII	*cis*-$\mathrm{[Mn(CO)_2(dppe)(P(OPh)_3)(C{\equiv}CPh)]}$	186	3.0	69.41	4.75		80	(A)
				(70.46)	(4.78)		64	(C)
IX	*cis*-$\mathrm{[Mn(CO)_2(dppm)(P(OPh)_3)(C{\equiv}CPh)]}$	177	2.0	69.05	4.64		73	(A)
				(70.23)	(4.63)			

X	*fac*-[Mn(CO)$_3$(phen)(C≡CPh)]	192	8.0	62.07	2.92	5.76	72	(D)
		dec		(65.72)	(3.12)	(6.66)	25	(B)
XI	*fac*-[Mn(CO)$_3$(bipy)(C≡CPh)]	198	0.8	63.43	3.13	6.48	41	(B)
		dec		(63.45)	(3.31)	(7.07)	82	(F)
XII	*fac*-[Mn(CO)$_3$(dppe)(C≡CH)]	166	1.0	66.21	4.36		48	(B)
				(66.20)	(4.48)		80	(K)
XIII	*fac*-[Mn(CO)$_3$(phen)(C≡CH)]	176	9.3	56.94	3.01	7.24	46	(B)
		dec		(59.32)	(2.64)	(8.13)		
XIV	*fac*-[Mn(CO)$_3$(bipy)(C≡CH)]	179	0.4	56.87	2.88	8.55	61	(B)
		dec		(56.27)	(2.83)	(8.74)		
XV	*mer-trans*-[Mn(CO)$_3$(PCy$_3$)$_2$(C≡CPh)]	175	3.0	69.76	9.13		65	(G)
				(70.46)	(8.93)			
XVI	*fac*-[Mn(CO)$_3$(PCy$_3$)(CN^{t}Bu)(C≡CPh)]	170	5.1	66.70	7.97	3.19	72	(H)
		dec		(67.65)	(7.85)	(2.32)		
XVII	*cis*-[Mn(CO)$_2$(dppe)(P(OEt)$_3$)(C≡CPh)]	114	1.0	65.00	5.77		52	(C)
				(64.95)	(5.71)			
XVIII	[Mn(CO)(dppe)$_2$(C≡CPh)]	145	1.5	74.65	5.76		68	(J)
				(74.69)	(5.45)			

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[a] Reactions: (A) [Mn(CO)$_n$(L)$_{5-n}$Br] + AgBF$_4$ + HC≡CR in CH$_2$Cl$_2$/H$_2$O. (B) *fac*-[Mn(CO)$_3$(L–L)(OClO$_3$)] + HC≡CR + KOH in THF. (C) *fac*-[Mn(CO)$_3$(dppe)(C≡CPh)]+phosphite in refluxing toluene. (D) *fac*-[Mn(CO)$_3$(phen)Br]+AgC≡CPh in CH$_2$Cl$_2$. (E) *mer-trans*-[Mn(CO)$_3$(PEt$_3$)$_2$Br]+CuC≡CPh in refluxing CH$_2$Cl$_2$. (F) *fac*-[Mn(CO)$_3$(bipy)Br]+HC≡CPh+NEt$_3$+TlPF$_6$ in CH$_2$Cl$_2$. (G) *cis*-[Mn(CO)$_4$(PCy$_3$)(C≡CPh)]+PCy$_3$ in refluxing benzene. (H) *cis*-[Mn(CO)$_4$(PCy$_3$)(C≡CPh)] + CN^{t}Bu in refluxing hexane. (J) *fac*-[Mn(CO)$_3$(dppe)(C≡CPh)] + dppe + UV irradiation in CH$_2$Cl$_2$ (−10°C). (K) *fac*-[Mn(CO)$_3$(dppe)(OClO$_3$)]+HC≡CH+NEt$_3$ in CH$_2$Cl$_2$. [b] 5×10^{-4} *M* acetone solution at 25°C.

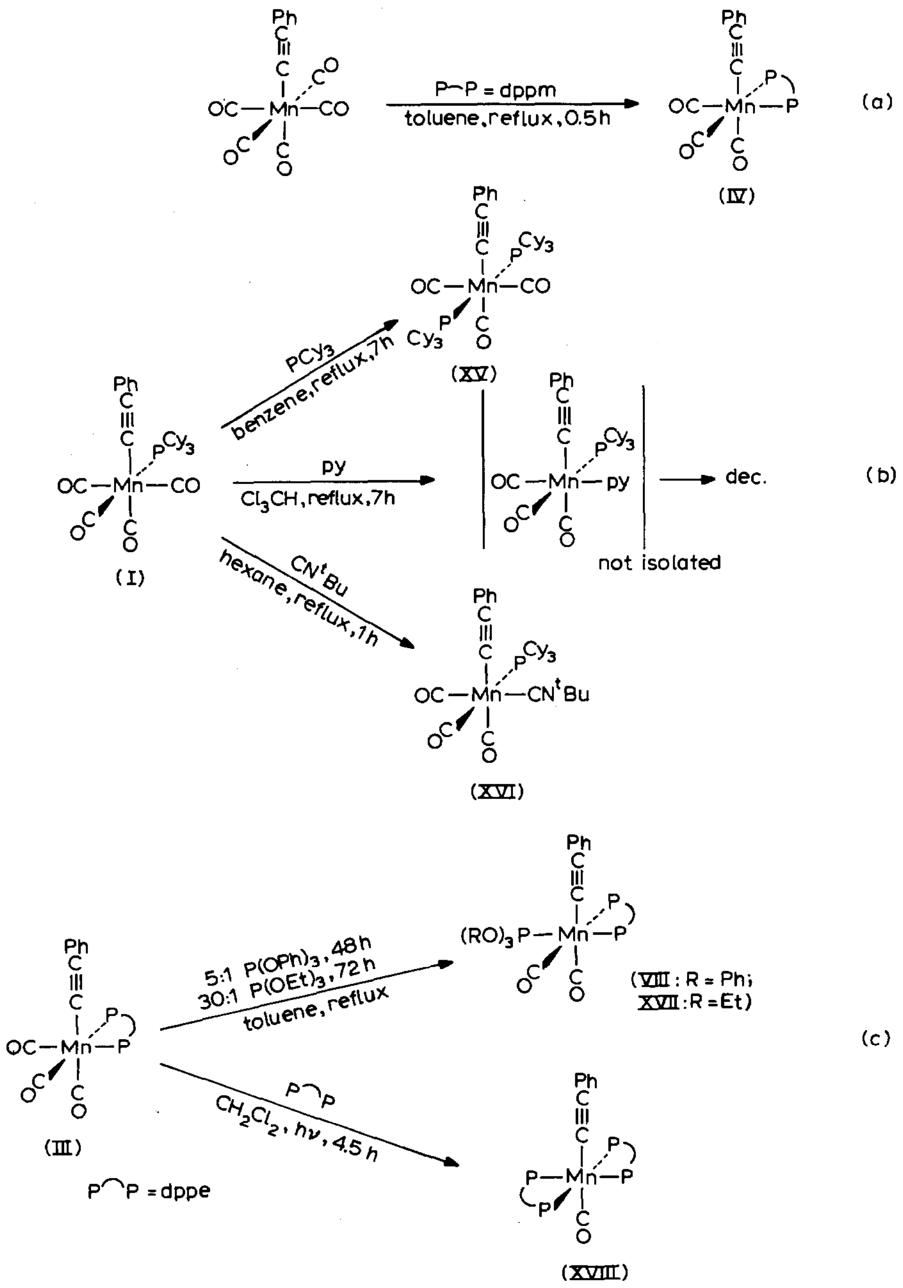

Fig. 1. Reactions of σ-alkynyl compounds involving CO replacement.

out with σ-alkynyl complexes are shown in Fig. 1; the pattern of substitution behaviour is apparently very similar to that for the analogous bromocarbonyl derivatives. This implies that σ-alkynyl compounds can be used as precursors for the synthesis of new more highly substituted σ-alkynyl complexes. Treatment of the tetracarbonyl I with PCy_3 (Fig. 1b) in refluxing benzene gave *mer-trans-*

[Mn(CO)$_3$(PCy$_3$)$_2$(C≡CPh)] (XV) and treatment of I with pyridine (py) in refluxing CHCl$_3$, or with CN^{t}Bu in refluxing hexane produced *fac*-tricarbonyls [Mn(CO)$_3$(PCy$_3$)(L)(C≡CPh)]. The compound with L = py was detected by IR spectroscopy (ν(C–O): 2028s, 1937s, 1905s cm^{-1}), but could not be isolated because of extensive decomposition. Compound XVI (L = CN^{t}Bu) slowly decomposes in solution but was isolated as a crystalline solid, and fully characterized.

The *fac*-tricarbonyl complex III also undergoes CO replacement when treated with phosphorus donor ligands (Fig. 1c). Thus, reaction of III with phosphites produces the *cis*-dicarbonyls [Mn(CO)$_2$(dppe)(P(OR)$_3$)(C≡CPh)] (VIII, R = Ph; XVII, R = Et). From the necessary reaction times, shown in Fig. 1c, it is apparent that these substitutions are slower than those involving bromocarbonyls. (Under the same conditions *fac*-[Mn(CO)$_3$(dppe)Br] reacts with a 5/1 excess of phosphite in 1 h 45 min [12].) (Comparison of the ν(C–O) frequencies of the alkynyl compounds with those of the analogous bromo compounds suggests that the σ-alkynyl ligand must be more electron releasing than bromo, and this could be one of the reasons of the lower lability of the CO groups in the σ-alkynyls.) Nevertheless further substitution can be achieved under more drastic conditions; thus, irradiation of a mixture of III and dppe in CH$_2$Cl$_2$ at −10°C produces the monocarbonyl XVIII. This reaction is the only route to reach compound XVIII since Method A failed when applied to [Mn(CO)(dppe)$_2$Br], as described above, and the perchloratomonocarbonyl complex is not available for use in Method B.

Melting point, conductivity, and analytical data for the σ-alkynyl compounds are presented in Table 1, as well as the yields of the reactions used to obtain them. Compounds with N–N donor ligand are very light-sensitive orange solids. The other

TABLE 2

RELEVANT INFRARED DATA FOR ALKYNYL COMPLEXES [a]

Compound	ν(C≡C) (cm^{-1})	ν(C–O) (cm^{-1})
I [b]	2111w	2074w, 2009w, 1988s, 1952s
II	2092w	2016w, 1925s, 1895m
III	2097w	2019s, 1943s, 1920s
IV	2099w	2019s, 1945s, 1923s
V	2101w	2016s, 1938s, 1916s
VI	2102w	2014s, 1937s, 1917s
VII	2084w	1943s, 1878s
VIII	2093w	1955s, 1893s
IX	2089w	1954s, 1892s
X	2089w	2019s, 1922s, broad
XI	2094w	2018s, 1919s, broad
XII	–	2015s, 1940s, 1916s
XIII	–	2022s, 1922s, broad
XIV	–	2019s, 1920s, broad
XV	2093w	2009w, 1913s, 1885m
XVI [c]	2093w	2014s, 1948s, 1917s
XVII	2084w	1942s, 1875s
XVIII	2056w	1832m

[a] Spectra in CH$_2$Cl$_2$ solution unless otherwise stated. [b] Hexane solution. [c] Stretching C–N of t-butyl isocyanide ligand at 2162m cm^{-1}.

compounds are pale yellow crystalline substances, and are not especially light sensitive. Compound XVI decomposes slowly in solution.

Table 2 presents relevant infrared data for the compounds. Those which contain phenylethynyl or t-butylethynyl ligands exhibit a weak band near 2100 cm^{-1} which, on the basis of literature data [2,7], can be attributed to C≡C stretching. For compounds XII, XIII, and XIV containing an ethynyl ligand, the C≡C stretching frequency, which is expected in the 1968–1923 cm^{-1} range [13] was not detected, probably because it is masked by ν(C–O) absorptions. Nevertheless, the presence of C≡CH ligand in these compounds is clearly established by the ν(≡C–H) band (XII, 3280 cm^{-1}; XIII, 3250 cm^{-1}; XIV, 3260 cm^{-1}, solid state spectra in KBr dispersion).

^{1}H NMR spectra give additional support. Thus, singlets in the spectra of XIII (δ 1.25 ppm) and XIV (δ 1.54 ppm) can be assigned to the acetylenic hydrogen. For compound XII this signal hydrogen appears at δ 1.44 ppm as a triplet because of coupling to the two phosphorus atoms of the dppe ligand (^4J(P–H) 4.4 Hz). The t-butylethynyl ligand gives a sharp signal at δ 0.71 ppm for V and at δ 0.52 ppm for VI.

In the case of *cis*-tetracarbonyl (I) and all *fac*-tricarbonyls (III to VI, X to XIV, and XVI) the structure was unequivocally stablished from IR data, since only one isomer is possible for such compounds.

Compounds II and XV display ν(C–O) bands with a typical pattern for a *mer*-tricarbonyl arrangement. The ^{31}P{^{1}H}NMR spectra of these compounds show

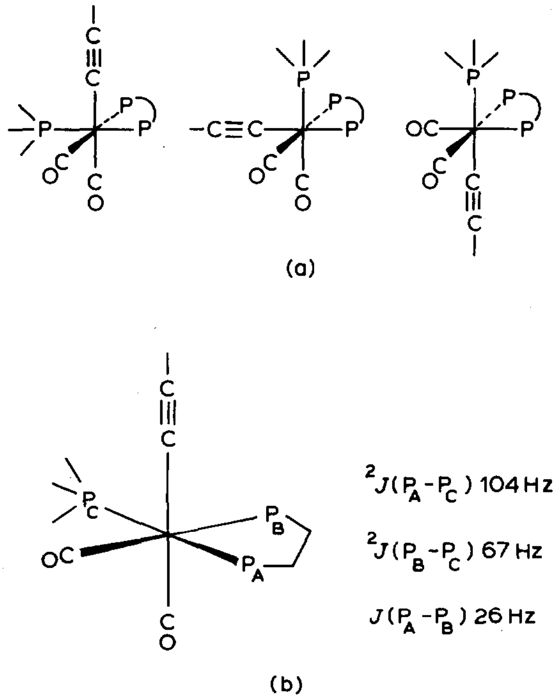

Fig. 2. (a) Possible structures for the dicarbonyls *cis*-[Mn(CO)$_2$(P–P)(P(OR)$_3$)(C≡CPh)] (VII, VIII, and IX); (b) structural assignment and ^{31}P{^{1}H} NMR coupling constants for [Mn(CO)$_2$(dppe)-(P(OR)$_3$)(C≡CPh)] (VIII).

only one signal (at δ 48.2 ppm * for PEt_3 in II, and at δ 62.4 ppm for PCy_3 in XV). All of this, considered together with *cis*-labilization and steric factors, support the formulation of both compounds as having a *mer-trans*-geometry, as depicted for XV in Fig. 1b.

The $^{31}P\{^1H\}$NMR spectrum of the monocarbonyl (XVIII) also exhibits only one broad peak at δ 83.6 ppm for the four phosphorus atoms of the two dppe ligands. This is consistent with a structure with the CO group *trans* to the alkynyl ligands, all the P atoms being equivalent (Fig. 1c).

Dicarbonyls (VII to IX, and XVII) show ν(C–O) bands consistent with a *cis* arrangement of the two CO groups, and three isomers are therefore possible for these compounds (Fig. 2a).

The $^{31}P\{^1H\}$NMR spectrum of VIII shows three groups of signals (δ 172 ppm, broad multiplet, phosphite, P_C; δ 85.1 ppm, doublet of doublets, P_A; δ 71.4 ppm, doublet of doublets, P_B; $^2J(P_A–P_C)$ 104 Hz, $^2J(P_B–P_C)$ 67 Hz, $J(P_A–P_B)$ 26 Hz). This is consistent with a structure in which the phosphite is *trans* to one of the phosphorus atoms of dppe (P_A) and *cis* to the other (P_B). Only one of the three possible isomers has this arrangement of the three phosphorus atoms (Fig. 2b).

Experimental

All reactions were carried out under nitrogen or argon and dry solvents were used. Reactions involving silver(I) salts or *N*-donor ligand compounds were performed with exclusion of light. IR spectra were recorded on a Perkin–Elmer 298 spectrophotometer. ^1H NMR spectra (Cl_3CD solutions, internal Me_4Si reference), and $^{31}P\{^1H\}$ NMR spectra (Cl_2CH_2 solutions, external H_3PO_4 reference) were recorded at room temperature on a Varian FT 80 A. Elemental analyses were carried out on a Perkin–Elmer 240 B Analyzer.

Starting materials $[Mn(CO)_5Br]$ [14], *cis*-$[Mn(CO)_4(PCy_3)Br]$ [15], *mer-trans*-$[Mn(CO)_3(PEt_3)_2Br]$ [16], *fac*-$[Mn(CO)_3(P–P)Br]$ [17], *fac*-$[Mn(CO)_3(P–P)(OClO_3)]$ [18], *fac*-$[Mn(CO)_3(N–N)Br]$ [19], *fac*-$[Mn(CO)_3(N–N)(OClO_3)]$ [20], and *cis*-$[Mn(CO)_2(P–P)(P(OR)_3)Br]$ [12] were prepared by published methods. Technical grade ethyne was purified by bubbling it through concentrated H_2SO_4, then a saturated aqueous solution of sodium bi-sulphite, then concentrated H_2SO_4 again, and finally passed through a column (2 × 20 cm) filled with KOH pellets.

Reactions of bromocarbonyls with 1-alkynes and $AgBF_4$. Compounds I to IX

A mixture of $AgBF_4$ (1.15 mmol), 1-alkyne $RC{\equiv}CH$ (R = Ph, 1.15 mmol; R = ^tBu, 5 mmol), CH_2Cl_2 (45 ml), and water (15 ml), was stirred for 15 min. The solid bromocarbonyl was then added and the stirring continued until completion of the reaction. The mixture was filtered, the aqueous layer removed, and the organic layer stirred with an equal volume of aqueous 1 *M* sodium thiosulphate solution for 30 min. The organic layer was then decanted, dried with anhydrous $MgSO_4$, and filtered. Evaporation of solvent in vacuo afforded a pale yellow residue of the alkynyl compound, which was recrystallized from CH_2Cl_2/EtOH. Yields: 45–80%,

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* In this paper, a positive sign for δ denotes signals downfield from the H_3PO_4 reference. The signs of the coupling constants were not determined.

see Table 1. Reaction times: I, 22 h; II, 20 h; III, 24 h; IV, 20 h; V, 15 h; VI, 11 h; VII, 10 h, VIII, 12 h; IX, 4 h.

In the preparation of compound VII, variable amounts of *mer*-[Mn(CO)$_3$-(dppe)(P(OMe)$_3$)]BF$_4$ were obtained (ν(C–O)(CH$_2$Cl$_2$): 2059w; 1979s cm^{-1}, broad; from ref. 12). A mixture of this compound and VII was dissolved in CH$_2$Cl$_2$ (20 ml), and the ionic compound was precipitated by adding an equal volume of hexane. The solution was then filtered and the solvents were removed in vacuo, to leave a pale yellow residue of VII (45%).

Reaction of fac-[Mn(CO)$_3$(phen)Br] with AgC≡CPh

A mixture of *fac*-[Mn(CO)$_3$(phen)Br] (0.4 g, 1 mmol) and AgC≡CPh (0.24 g, 1.15 mmol), in CH$_2$Cl$_2$ (40 ml) was stirred overnight at room temperature with exclusion of light. The AgBr was filtered off under argon and the solution was concentrated under reduced pressure. Addition of diethyl ether (30 ml) to the resulting oil and stirring (1 h) gave a yellow orange solid. The liquors were decanted off and the solid was washed with diethyl ether (3 × 10 ml) and dried in vacuo. Yield 0.304 g, 72%.

Reaction of mer-trans-[Mn(CO)$_3$(PEt$_3$)$_2$Br] with CuC≡CPh

A mixture of *mer-trans*-[Mn(CO)$_3$(PEt$_3$)$_2$Br] (0.114 g, 0.25 mmol), and CuC≡CPh (0.125 g, 0.75 mmol) in CH$_2$Cl$_2$ (30 ml) was heated at reflux temperature for 4 h under argon. The resulting suspension was filtered, and ethanol (10 ml) was added to the filtrate. The solvents were removed under reduced pressure, and the oily residue was stored in a refrigerator (−10°C) for 24 h. The pale yellow crystals formed were filtered off and washed with cold ethanol (2 × 5 ml). Yield 0.063 g, 53%.

Reactions of perchlorato complexes with 1-alkynes and base

Preparation of [Mn(CO)$_5$(C≡CPh)]. A mixture of [Mn(CO)$_5$Br] (0.825 g, 3 mmol) and AgClO$_4$ (0.776 g, 3.75 mmol) in CH$_2$Cl$_2$ (30 ml) was stirred for 2.5 h with exclusion of light. The AgBr was removed by filtration under argon and the [Mn(CO)$_5$(OClO$_3$)] solution was collected in a Schlenk flask. The solvent was removed in vacuo, and the flask containing the dry yellow residue was cooled in a liquid nitrogen/ethanol bath (−70°C). Diethyl ether (50 ml), HC≡CPh (0.4 ml, 4 mmol) and powdered KOH (0.5 g, 8.9 mmol) were added under a rapid stream of argon and the mixture was stirred, then allowed to warm up slowly, to reach +10°C in 6 h. The solvent was then removed in vacuo and the orange residue was extracted with hexane (5 × 20 ml). The extracts were concentrated and chromatographed on a silica gel (60 mesh) column (2.5 × 12 cm). Elution with hexane (150 ml) afforded, after evaporation, a small amount of Mn$_2$(CO)$_{10}$ (0.049 g, 8%). Further elution with a CH$_2$Cl$_2$/hexane (1/1) mixture (200 ml), and evaporation of solvents yielded pale cream crystals of [Mn(CO)$_5$(C≡CPh)] (0.084 g, 9%) which was identified by its IR spectrum in hexane (ν(C–O): 2144w; 2044s, 2009s cm^{-1}. ν(C≡C): 2119w cm^{-1}; lit. [7], in cyclohexane solution, ν(C–O): 2145, 2045, 2015 cm^{-1}; ν(C≡C): 2120 cm^{-1}).

Preparation of fac-[Mn(CO)$_3$(N–N)(C≡CPh)] (X, XI). Compounds X (N–N = phen), and XI (N–N = bipy) are very light sensitive and all operations must be performed with exclusion of light.

A mixture of *fac*-[Mn(CO)$_3$(N–N)(OClO$_3$)] (1 mmol), HC≡CPh (0.153 g, 1.5 mmol), and powdered KOH (0.2 g, 3.57 mmol) was stirred in THF (30 ml) for 3 h and then filtered. The solvent was removed in vacuo and the dark brown oil was stirred with hexane (30 ml) for 0.5 h. The resulting brown solid was filtered off, washed with hexane (2 × 10 ml) and redissolved in CH_2Cl_2 (50 ml). The orange solution was filtered and hexane (20 ml) was added. The solvents were removed in vacuo to leave an orange solid, which was filtered off and washed with diethyl ether. Yields: X, 25%; XI, 41%. Recrystallisation was from CH_2Cl_2/hexane.

Preparation of fac-[Mn(CO)$_3$(dppe)(C≡CH)] (XII). In a two necked, round bottomed flask, provided with a gas inlet tube and a bubbler was placed a mixture of *fac*-[Mn(CO)$_3$(dppe)(OClO$_3$)] (0.637 g, 1 mmol), powdered KOH (0.2 g, 3.57 mmol), and THF (40 ml). The stirred suspension was purged with a rapid stream of purified ethyne for 15 min and the stirring and a stream of ca. 1 bubble per second were maintained for 2 h. The mixture was then filtered and the filtrate evaporated under reduced pressure. The residue was extracted with diethyl ether (5 × 25 ml) and the filtered extracts were evaporated slowly in vacuo to leave a pale yellow crystalline solid (48%). This product was obtained in better yields by using NEt_3 (1 mmol) instead of KOH, and CH_2Cl_2 (40 ml) instead of THF. The bubbling of ethyne, the reaction time, and the work up were as described for the KOH/THF reaction. The yield was 80%.

Preparation of fac-[Mn(CO)$_3$(N–N)(C≡CH)] (XIII, XIV). Compounds XIII and XIV are very light sensitive, and all operations must be carried out with exclusion of light.

The reactions were carried out under the conditions described for compound XII, starting from a mixture of *fac*-[Mn(CO)$_3$(N–N)(OClO$_3$)] (1 mmol), powdered KOH (0.2 g, 3.57 mmol) and THF (40 ml). After 2 h stirring the solution was filtered, the THF was removed in vacuo, and the oily residue was worked up as described above for compounds X and XI. Yields: XIII, 46%; XIV, 60%.

Reactions involving CO replacement

Reaction of [Mn(CO)$_5$(C≡CPh)] with dppm. A small sample of [Mn(CO)$_5$(C≡CPh)] (0.07 g, 0.24 mmol) was dissolved in toluene (30 ml) and dppm (0.1 g, 0.26 mmol) was added. The mixture was heated under reflux for 30 min, then filtered and concentrated in vacuo. Addition of hexane (20 ml) to the oily residue afforded a pale yellow precipitate *fac*-[Mn(CO)$_3$(dppm)(C≡CPh)] (IV), which was filtered off, and washed with hexane. Yield: 0.092 g, 62%.

Preparation of mer-[Mn(CO)$_3$(PCy$_3$)$_2$(C≡CPh)] (XV). A mixture of *cis*-[Mn(CO)$_4$(PCy$_3$)(C≡CPh)] (I) (0.6 g, 1.09 mmol), PCy$_3$ (0.36 g, 1.09 mmol) and benzene (30 ml), was heated under reflux for 7 h. The solvent was then removed in vacuo, and the residue was dissolved in CH_2Cl_2 (30 ml). The solution was filtered and ethanol (10 ml) was added. Slow evaporation under reduced pressure afforded pale yellow crystals of XV. Recrystallization was from CH_2Cl_2/EtOH. Yield: 0.567 g, 65%.

Preparation of fac-[Mn(CO)$_3$(PCy$_3$)(CN^{t}Bu)(C≡CPh)] (XVI). A mixture of I (0.3 g, 0.545 mmol), CN^{t}Bu (0.1 ml, ca. 1 mmol), and hexane (35 ml), was heated under reflux for 1 h. The mixture was then filtered, and evaporation of solvent at reduced pressure afforded a white solid which was recrystallized from CH_2Cl_2/EtOH. Yield: 0.237 g, 72%.

Preparation of cis-[Mn(CO)$_2$(dppe)(P(OR)$_3$)(C≡CPh)] (VIII, XVII). A mixture of *fac*-[Mn(CO)$_3$(dppe)(C≡CPh)] (III) (0.637 g, 1 mmol) and the phosphite (P(OPh)$_3$, 1.550 g, 5 mmol; P(OEt)$_3$, 5 g, 30 mmol) in toluene (30 ml) was heated under reflux

(48 h for VIII, 72 h for XVII). The solution was filtered and the toluene was removed in vacuo. The resulting oil was stirred with hexane (30 ml) for 2 h to give a pale yellow solid, which was recrystallized from CH_2Cl_2/hexane. Yields: VIII, 64%, XVII, 52%.

Preparation of [Mn(CO)(dppe)$_2$(C≡CPh)] (XVIII). A mixture of III (0.2 g, 0.314 mmol), dppe (0.126 g, 0.314 mmol), and CH_2Cl_2 (20 ml) was placed in a Schlenk flask cooled to −10°C. The solution was irradiated with UV light for 4.5 h, the temperature being kept at −10°C during this time. The mixture was then filtered, and ethanol (20 ml) added to the filtrate. Slow evaporation of the solvents produced yellow crystals, which were filtered off and washed with ethanol (2 × 5 ml). Yield: 0.21 g, 68%.

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References

1 R. Nast, Coord. Chem. Rev., 47 (1982) 89.
2 R.D. Adams, A. Davison, J.P. Selegue, J. Am. Chem. Soc., 101 (1979) 7232.
3 M.H. Chisholm, H.C. Clark, J. Am. Chem. Soc., 94 (1972) 1532.
4 P.W. Jolly, R. Pettit, J. Organomet. Chem., 12 (1968) 491
5 M.I. Bruce, D.A. Harbourne, F. Waugh, F.G.A. Stone, J. Chem. Soc., A, (1968) 353.
6 W.C. Kaska, D.K. Mitchell, R.F. Reichelderfer, W.D. Korte, J. Am. Chem. Soc., 96 (1974) 2847
7 N.A. Ustynyuk, V.N. Vinogradova, P.V. Petrovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 3 (1982) 680.
8 G.A. Carriedo, V. Riera, D. Miguel, A.M. Manotti-Lanfredi, A. Tiripicchio, J. Organomet. Chem., 272 (1984) C17.
9 M.H. Chisholm, H.C. Clark, J. Chem. Soc., Chem. Commun., (1970) 763
10 O.M. Abu Salah, M.I. Bruce, J. Chem. Soc., Dalton Trans., (1975) 2311.
11 K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshime, S. Takahashi, N. Hagihara, J. Organomet. Chem., 145 (1978) 101.
12 F. Bombín, G.A. Carriedo, J.A. Miguel, V. Riera, J. Chem. Soc., Dalton Trans., (1981) 2049
13 D.M. Adams, Metal Ligand and Related Vibrations, Edward Arnold (Publishers) Ltd., London, 1967, p. 188.
14 R.B. King, Organometallic Synthesis, vol. 1, Academic Press, New York, 1965, p. 47.
15 F.A. Hartman, M. Kilner, A. Wojcicki, Inorg. Chem., 6 (1967) 34
16 R.J. Angelici, F. Basolo, A.J. Pöe, J. Am. Chem. Soc., 85 (1963) 2215.
17 R.H. Reimann, E. Singleton, J. Chem. Soc., (1973) 841
18 G.A. Carriedo, V. Riera, J. Organomet. Chem., 205 (1981) 371
19 E.W. Abel, G. Wilkinson, J. Chem. Soc., (1951) 1501.
20 R. Usón, V. Riera, J. Gimeno, M. Laguna, Transition Met. Chem., 2 (1977) 123.