Tetraethyl Diphosphite-bridged Binuclear Carbonyl Derivatives of Decacarbonyldimanganese and Pentacarbonylmanganese Halides

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Reactions of $(EtO)_2POP(OEt)_2$ (tedip) with $[Mn_2(CO)_{10}]$ led to complex mixtures from which $[Mn_2(CO)_8(\mu\text{-tedip})]$ (**1**) and $[Mn_2(CO)_6(\mu\text{-tedip})_2]$ (**2**) were identified as major products. However, the reactions of tedip with $[MnX(CO)_5]$ (X = Br or I) were more dependent on experimental conditions and could lead to either $[Mn_2X_2(CO)_8(\mu\text{-tedip})]$ (**3**), $[Mn_2(\mu\text{-}X)_2(CO)_6(\mu\text{-tedip})]$ (**4**), $[Mn_2X_2(CO)_6(\mu\text{-tedip})_2]$ (**5**), or $[Mn_2(\mu\text{-}X)_2(CO)_4(\mu\text{-tedip})_2]$ (**6**), in all of which the tedip ligand is bridging. Other minor products not completely characterized were also observed. Rhenium analogues of compounds (**4**) and (**6**) were also obtained from $[ReBr(CO)_5]$ and tedip. An extension of this study to the reactions of $Ph_2PCH_2PPh_2$ (dppm) with $[MnX(CO)_5]$ (X = Cl, Br, or I) revealed that binuclear dppm-bridged complexes analogous to compounds (**4**) can be obtained under appropriate conditions.

Transition-metal carbonyl derivatives of tetraethyl diphosphite (tedip), $(EtO)_2POP(OEt)_2$, are known for Mo,[1] Re,[2] Fe,[1,3] Pd and Pt.[4] In all the cases the ligand is acting in a bridging mode, although some examples are known where related ligands containing the POP unit form chelate complexes.[5–7] The reluctance of tedip to form chelated species has been ascribed[1,4] to the relatively large P–O–P angle and, in fact, chelate complexes are much more common with ligands containing less open chains such as P–N(R)–P (R = Me, Et, or Ph)[8] or P–CH_2–P.[9]

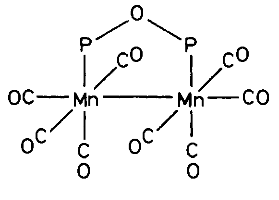
In this paper we describe the results of the reactions of tedip with $[Mn_2(CO)_{10}]$ and $[MnX(CO)_5]$ (X = Br or I) which confirm the predominance of the bridging mode for this ligand. This preference was also observed in some reactions of tedip with $[ReBr(CO)_5]$ and an extension of these studies to reactions of the dppm ligand ($Ph_2PCH_2PPh_2$) with $[MnX(CO)_5]$ (X = Cl, Br, or I) showed that, under appropriate conditions, binuclear dppm-bridged complexes analogous to the tedip derivatives can be obtained. A preliminary account of part of this work has appeared.[10]

Results and Discussion

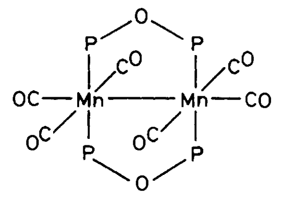
(*a*) *Reactions of tedip with* $[Mn_2(CO)_{10}]$.—The reaction of tedip with $[Mn_2(CO)_{10}]$, either under heating or u.v. irradiation, showed little selectivity irrespective of the conditions (time, temperature, or molar ratio) and led to complex mixtures containing $[Mn_2(CO)_8(\mu\text{-tedip})]$ (**1**) and $[Mn_2(CO)_6(\mu\text{-tedip})_2]$ (**2**) as major products.

Compound (**1**) is best obtained when an equimolar mixture of tedip and $[Mn_2(CO)_{10}]$ is exposed to u.v. light for 2 h at −5 °C. The spectroscopic data (Table) are in accord with the proposed structure. The i.r. spectrum displays eight bands, one more than required for ideal C_{2v} symmetry ($3A_1 + B_1 + 3B_2$); this may be indicative of a slight staggering distortion, which implies a decrease in symmetry to C_s, making the eighth mode i.r. active. Such distortion has been found in the crystal structures of the related compounds $[Mn_2(CO)_8(\mu\text{-}Ph_2AsCH_2AsPh_2)]$[11] and $[Mn_2(CO)_8(\mu\text{-}Me_2AsC{=}CAsMe_2CF_2CF_2)]$.[12] Although for such a distorted structure the Me groups of the ligand in complex (**1**) should be in two different environments, the ^1H n.m.r. spectrum measured at room temperature (r.t.) shows only one resonance for these protons, probably indicating that the structure is not rigid at that temperature.

Compound (**2**) can be obtained selectively by reaction of $[Mn_2(CO)_{10}]$ and 3 equivalents of tedip in refluxing mesitylene, although the yield is not very good. Its structure is proposed on the basis of spectroscopic data (Table). As for compound (**1**), the i.r. spectrum of (**2**) shows more bands than those expected for ideal D_{2h} symmetry, so a slight distortion must be present. Unfortunately we are not aware of any structure determination for a related complex.



(**1**)



(**2**)

Compounds (**1**) and (**2**) are very similar to those obtained in the reactions of $[Mn_2(CO)_{10}]$ with dppm;[13] however, in our case, all attempts further to decarbonylate compound (**2**) to afford $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-tedip})_2]$ resulted only in decomposition. This fact can be rationalized, following Wolff and Klemann,[14] on the basis of the low steric requirements of the tedip ligand as compared with dppm.

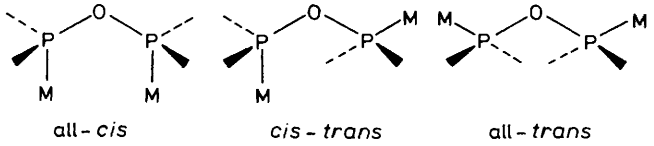
(*b*) *Reactions of tedip with* $[MnX(CO)_5]$ (X = Br *or* I).—In contrast with the absence of selectivity in the reactions of tedip with $[Mn_2(CO)_{10}]$, those with $[MnX(CO)_5]$ proved to be strongly dependent on the experimental conditions and could be selectively directed to give different products. The general results are summarized in the Scheme.

Reaction of $[MnX(CO)_5]$ with 0.5 equivalent of tedip in toluene under mild conditions (X = Br, 40 °C; X = I, 60 °C) afforded $[Mn_2X_2(CO)_8(\mu\text{-tedip})]$ [X = Br (**3a**) or I (**3b**)] as major products [(*i*) in Scheme]. The i.r. spectra of these compounds (Table) are indicative of a *cis*-tetracarbonyl geometry at each manganese centre and consist of five bands, suggesting the existence of some interaction between the CO oscillators at each metal centre. Three possible limiting structures for this type of complex (the nomenclature employed is that suggested by Lorenz and co-workers[15]) are shown below. An interaction between the CO oscillators of both metal fragments is expected only for an all-*cis* disposition and the i.r. spectra of $[Mn_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}Me_2POPMe_2)]$[16] and $[Cr_2(CO)_{10}(\mu\text{-}Ph_2POPPh_2)]$,[15] whose crystal structures are of type *cis–trans* and all-*trans* respectively, contain the number of

Table. Spectroscopic data for the complexes

			N.m.r., δ/p.p.m	
	Compound	$\tilde{\nu}$(CO)/cm^{-1}	^{1}H^{a,b}	^{31}P^{c}
(**1**)	[$Mn_2(CO)_8$(μ-tedip)]	2 081m, 2 018s, 1 996vs, 1 990s, 1 972s, 1 960m, 1 950m, 1 942s^{d}	4.08 (m, 2 H, OCH_2), 1.36 (t, 7, 3 H, Me)	174.8 (br)^{e}
(**2**)	[$Mn_2(CO)_6$(μ-tedip)$_2$]	2 035vw, 1 972s, 1 948vs, 1 912m (sh), 1 902m ^{d}	4.0 (m, 2 H, OCH_2), 1.32 (t, 7, 3 H, Me)	181.5^{c}
(**3a**)	[$Mn_2Br_2(CO)_8$(μ-tedip)]	2 105s, 2 044s, 2 024vs, 1 988s, 1 970s^{d}	4.37 (m, 2 H, OCH_2), 1.48 (t, 7, 3 H, Me)	145.5 (br)^{e}
(**3b**)	[$Mn_2I_2(CO)_8$(μ-tedip)]	2 098s, 2 038s, 2 016vs, 1 989s, 1 970s^{d}	4.37 (m, 2 H, OCH_2), 1.38 (t, 7, 3 H, Me)	146.0 (br)^{e}
(**4a**)	[Mn_2(μ-Br)$_2$(CO)$_6$(μ-tedip)]	2 070s, 2 052s, 1 987vs, 1981vs, 1 944vs^{d}	4.44 (m, 2 H, OCH_2), 1.50 (t, 7, 3 H, Me)	145.9
(**4b**)	[Mn_2(μ-I)$_2$(CO)$_6$(μ-tedip)]	2 061s, 2 046vs, 1 984vs, 1 979vs, 1 943vs^{d}	4.44 (m, 2 H, OCH_2), 1.46 (t, 7, 3 H, Me)	141.4^{e}
(**5a**)	[$Mn_2Br_2(CO)_6$(μ-tedip)$_2$]	2 045vs, 1 981vs, 1 946s^{f}	4.3 (m, 2 H, OCH_2), 1.34 (m, 3 H, Me)	139.3^{e}
(**5b**)	[$Mn_2I_2(CO)_6$(μ-tedip)$_2$]	2 042vs, 1 980s, 1 946s^{f}	4.3 (m, 2 H, OCH_2), 1.37 and 1.35 (2t, 7, 3 H, Me)	
(**6a**)	[Mn_2(μ-Br)$_2$(CO)$_4$(μ-tedip)$_2$]	1 957s, 1 888s^{f}	4.36 (m, 2 H, OCH_2), 1.42 (t, 7, 3 H, Me)	162.2
(**6b**)	[Mn_2(μ-I)$_2$(CO)$_4$(μ-tedip)$_2$]	1 953s, 1 887s^{f}	4.36 (m, 2 H, OCH_2), 1.41 (t, 7, 3 H, Me)	161.1^{e}
(**7**)	[Re_2(μ-Br)$_2$(CO)$_6$(μ-tedip)]	2 066s, 2 052s, 1 970 (sh), 1 967vs, 1 927vs^{f}	4.29 (m, 2 H, OCH_2), 1.44 (t, 7, 3 H, Me)	107.0
(**8**)	[Re_2(μ-Br)$_2$(CO)$_4$(μ-tedip)$_2$]	1 955s, 1 877s^{f}	4.32 (m, 2 H, OCH_2), 1.43 (t, 7, 3 H, Me)	113.8
(**9a**)	[Mn_2(μ-Cl)$_2$(CO)$_6$(μ-dppm)]	2 054vs, 2 039s, 1 966vs, 1 957vs, 1 925vs^{f}	7.5—7.3 (m, 20 H, Ph), 4.01 (t, 12, 2 H, CH_2)	33.7

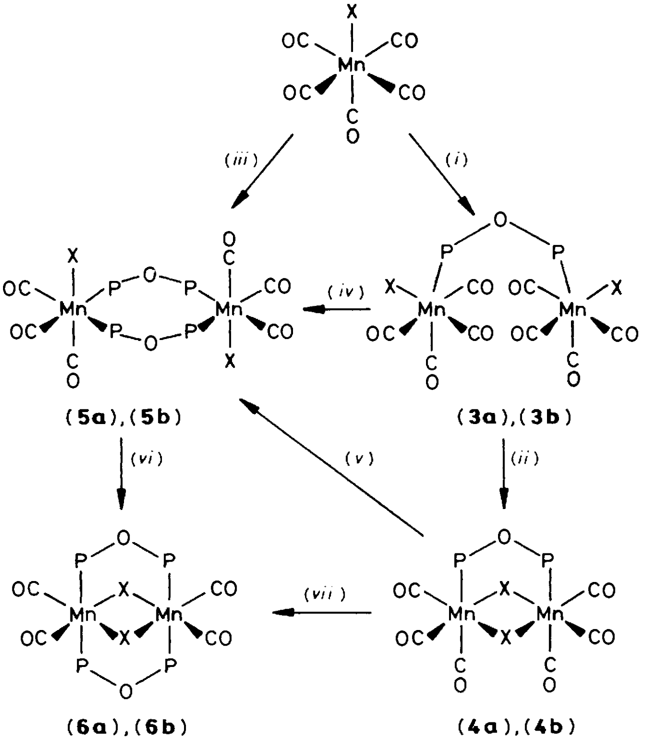
[a] In $CDCl_3$ solution, relative to $SiMe_4$. [b] Coupling constants in Hz. [c] Relative to external 85% H_3PO_4. [d] Light petroleum solution. [e] In CD_2Cl_2, at −60 °C. [f] In CH_2Cl_2 solution.



bands expected for each isolated metal fragment; therefore, we propose an all-*cis* type geometry for compounds (**3**). However, the presence of several isomers in solution cannot be completely ruled out; thus the ^{31}P-{^{1}H} n.m.r. spectra of compounds (**3**) consist of one broad peak even at −60 °C, probably due to a strong quadrupolar broadening effect of the manganese nuclei, and so no information could be obtained about the presence of isomers in solution.

When toluene solutions of compounds (**3**) were heated at higher temperatures [(**3a**), 80 °C; (**3b**), 100 °C] a further decarbonylation occurred, leading to the halogen-bridged complexes [Mn_2(μ-X)$_2$(CO)$_6$(μ-tedip)] [X = Br (**4a**) or I (**4b**); see (*ii*) in Scheme]. The spectroscopic data (Table) are in accord with C_{2v} symmetry and the structure shown; in particular, the i.r. spectra exhibit five strong bands and are similar to the well studied group of complexes of general formulae [M_2(μ-X)$_2$(CO)$_6$(μ-L-L)] (L-L = E_2Ph_4 or E'_2Ph_2; E = P, As, or Sb; E′ = S, Se, or Te; M = Mn[17] or Re[18]; L-L = $Ph_2AsCH_2AsPh_2$, M = Mn[19] or Re[20]).

Reaction of [$MnX(CO)_5$] with 1 equivalent of tedip in toluene (X = Br, 50 °C; X = I, 70 °C) led to [$Mn_2X_2(CO)_6$(μ-tedip)$_2$] (**5a**) and (**5b**) as major products [reaction (*iii*) in Scheme]; the octacarbonyls (**3**) were detected as intermediates by i.r. spectroscopy [reaction (*iv*)]. Complexes (**5**) are also formed when the halide-bridged compounds (**4**) are heated (70—90 °C) with tedip in toluene [reaction (*v*)]. The iodo-compound (**5b**) could not be isolated from the reaction mixture



Scheme. (*i*) ½ tedip, toluene (X = Br, 40 °C; X = I, 60 °C); (*ii*) toluene (X = Br, 80 °C; X = I, 100 °C); (*iii*) 1 equivalent tedip, toluene (X = Br, 50 °C; X = I, 70 °C); (*iv*) 1 equivalent tedip, toluene (X = Br, 50 °C; X = I, 70 °C); (*v*) 1 equivalent tedip, toluene (X = Br, 70 °C; X = I, 90 °C); (*vi*) refluxing toluene; (*vii*) refluxing toluene (with decomposition) in appreciable yield because of the easy formation of orange oils; however, the spectroscopic data (Table) clearly indicate that this compound is very similar to the bromo-complex (**5a**). The binuclear nature of (**5a**) was also supported by its mass spectrum which showed peaks of relative intensity 1:2:1 (separated by two atomic mass units as expected for a molecule with two Br atoms) at *m/z* 675.2, 572.4, and 480.6 (the parent ion is not observed). Furthermore, the i.r. spectrum (KBr disc) contains a strong band at 910 cm^{-1} which can be assigned to a POP asymmetric stretching mode[21] of a bridging ligand, while in a chelate complex this band is expected to shift to the 750—790 cm^{-1} region.[5]

It is known[22] that the reaction of phosphines or phosphites (L) with [MnBr(CO)$_5$] affords the *cis*-disubstituted complexes [MnBr(CO)$_3$L$_2$], which at higher temperatures can isomerize to their *trans* isomers, the isomerization being favoured by increasing bulk of the ligands. Thus we tested whether isomerization of complexes (**5**) could be promoted thermally. The results indicated that some isomerization occurred but the process was very complex, depending on many factors and not always reproducible.

Complexes (**5**) lose CO when refluxed in toluene, with formation of halogen bridges to afford [Mn$_2$(μ-X)$_2$(CO)$_4$(μ-tedip)$_2$] (**6a**) and (**6b**) [reaction (*vi*) in Scheme)]; this reaction parallels the formation of the hexacarbonyls (**4**) from the octacarbonyls (**3**) [reaction (*ii*)]. Spectroscopic data for compounds (**6**) (Table) are in accord with D_{2h} symmetry and the structure shown which has been confirmed by an *X*-ray diffraction study on the bromo-complex (**6a**).[10] The crystal structure of (**6a**) is shown in the Figure; to our knowledge, only one manganese complex similar to (**6**) of composition [MnCl(CO)$_2$(dpam)] (dpam = Ph$_2$AsCH$_2$AsPh$_2$) has been reported previously,[19] being formed as a minor product from a decomposition reaction of [Mn$_2$(μ-Cl)$_2$(CO)$_6$(μ-dpam)]. This process is also observed in the thermal decomposition of complexes (**4**) [reaction (*vii*) in Scheme].

Compounds (**6**) were also obtained directly by refluxing an equimolar mixture of [MnX(CO)$_5$] and tedip in toluene; however, when a large excess of ligand (2.5 equivalents) was employed, another intermediate different from compounds (**5**) was observed. This intermediate can be obtained as the major product (for X = Br) if the reaction is carried out in refluxing benzene for 30 min [but after this time slow conversion into compound (**6a**) occurs]; its i.r. spectrum shows two strong bands at 1 982 and 1 917 cm^{-1} in light petroleum, at higher frequency than those of the final product (**6a**). Our attempts to isolate this compound led to the formation of oils or to decomposition giving complex (**6a**). The ^{31}P-{^{1}H} n.m.r. spectrum of the intermediate shows resonances assignable to co-ordinated and unco-ordinated phosphorus atoms; therefore, we suppose it is formed by substitution of two CO by the tedip prior to the formation of the halogen bridges [equation (1)].

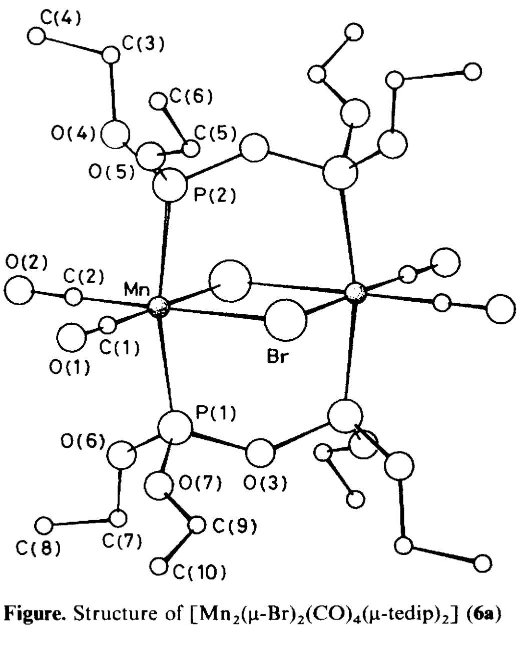


Figure. Structure of [Mn$_2$(μ-Br)$_2$(CO)$_4$(μ-tedip)$_2$] (**6a**)

$$[\mathrm{Mn_2Br_2(CO)_6(\mu\text{-}tedip)_2}] \xrightarrow[(-2\mathrm{CO})]{2\ \mathrm{tedip}} [\mathrm{Mn_2Br_2(CO)_4(\mu\text{-}tedip)_2(tedip\text{-}}P)_2] \longrightarrow [\mathrm{Mn_2(\mu\text{-}Br)_2(CO)_4(\mu\text{-}tedip)_2}] + 2\ \mathrm{tedip} \quad (1)$$

As indicated in Scheme, complexes (**6**) are the final product of the thermal reactions of [MnX(CO)$_5$] and tedip, irrespective of the molar ratio employed.

(*c*) *Reactions of tedip with* [ReBr(CO)$_5$].—The fact that the halogen-bridged manganese compounds (**4**) and (**6**) are suitable starting materials for binuclear anions and hydrides[10] led us to attempt to synthesize analogous rhenium complexes. Although we have not studied the reaction of tedip with [ReBr(CO)$_5$] extensively, our observations indicate that the general features are the same as in the manganese case (Scheme). The compound [Re$_2$(μ-Br)$_2$(CO)$_6$(μ-tedip)] (**7**) is obtained by treating [ReBr(CO)$_5$] and 0.5 equivalent of tedip in toluene at 100 °C; the initial formation of an octacarbonyl intermediate analogous to complexes (**3**) can be observed by i.r. spectroscopy. The spectroscopic data for (**7**) (Table) are similar to those of their manganese analogues (**4**) and no further comments are necessary. The tetracarbonyl complex [Re$_2$(μ-Br)$_2$(CO)$_4$(μ-tedip)$_2$] (**8**) was obtained by refluxing an equimolar mixture of [ReBr(CO)$_5$] and tedip. Yields, however, are low because of the increased difficulty for CO dissociation from rhenium complexes as compared with manganese. Again, i.r. monitoring shows that the reaction proceeds through an hexacarbonyl intermediate analogous to complexes (**5**). Spectroscopic data for complex (**8**) (Table) indicate that it is structurally identical to the manganese complexes (**6**).

(*d*) *Reactions of dppm with* [MnX(CO)$_5$].—Reactions of manganese carbonyl halides with dppm have been studied previously[19,23,24] but only mononuclear products with the ligand acting in a chelate or unidentate mode were reported. However, the compound [Mn$_2$Br$_2$(CO)$_8$(μ-dppm)], analogous to (**3a**), has been reported[23] as the result of bromination of [Mn$_2$(CO)$_8$(μ-dppm)] and it is a stable complex. Thus we decided to reinvestigate the reaction of dppm with the manganese carbonyl halides with the hope that complexes with both halogen and dppm bridges could be synthesized.

Reactions of [MnX(CO)$_5$] and 0.5 equivalent of dppm at several temperatures were carried out. In all the cases the initially formed [Mn$_2$X$_2$(CO)$_8$(μ-dppm)] readily decarbonylated to the halogen-bridged complexes [Mn$_2$(μ-X)$_2$(CO)$_6$(μ-dppm)] [X = Cl (**9a**), Br (**9b**), or I (**9c**)]; however, a competitive process occurred leading to the mononuclear complexes [MnX(CO)$_3$(dppm)],[19] identified by i.r. spectroscopy. Independent experiments showed that the octacarbonyl compounds [Mn$_2$X$_2$(CO)$_8$(μ-dppm)] (X = Br or I) decompose under the above reaction conditions according to equation (2), in addition to the transformation (3). It therefore appears that this competi-

$$[\mathrm{Mn_2X_2(CO)_8(\mu\text{-}dppm)}] \longrightarrow [\mathrm{MnX(CO)_5}] + [\mathrm{MnX(CO)_3(dppm)}] \quad (2)$$

$$[\mathrm{Mn_2X_2(CO)_8(\mu\text{-}dppm)}] \longrightarrow [\mathrm{Mn_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}dppm)}] + 2\mathrm{CO} \quad (3)$$

tive reaction is responsible for the formation of mononuclear products in the aforementioned reactions of $[MnX(CO)_5]$ and dppm; similar observations were made on the thermal treatment of $[Mn_2I_2(CO)_8(\mu\text{-}Me_2As\overline{C{=}CAsMe_2CF_2C}F_2)]$.[12] Furthermore, we have found that higher temperatures favour reaction (2); this fact explains the predominance of this reaction over (3) in the order Cl < Br < I. Thus, yields for compounds (**9b**) and (**9c**) are low and we have only isolated (**9a**), although spectroscopic data indicate that all are isostructural. From the i.r. and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**9a**) (Table) we conclude that it has the same structure as the tedip complexes, the resonance of the methylene protons at 4.0 p.p.m. being in accord with a bridging dppm ligand {*cf.* the ^1H n.m.r. spectra of $[MnCl(CO)_3(dppm)]$ (chelated dppm) and $[MnCl(CO)_4(dppm)]$ (unidentate dppm)[19]}.

Experimental

All reactions were performed under an argon atmosphere. Solvents were purified according to standard procedures[25] and distilled prior to use. I.r. spectra were recorded on a Perkin-Elmer 298 spectrophotometer using polystyrene as reference, ^1H and ^{31}P n.m.r. spectra on a Varian FT-80A spectrophotometer, and mass spectra on an AEI MS 902 instrument. Elemental analysis were performed on a Perkin-Elmer 240 microanalyser.

The compounds $[Mn_2(CO)_{10}]$,[26] $[MnCl(CO)_5]$,[27] $[MnBr(CO)_5]$,[28] $[MnI(CO)_5]$,[29] $[ReBr(CO)_5]$,[30] tedip,[31] and dppm[32] were prepared by literature methods. All other reagents were obtained from commercial sources. Light petroleum refers to that fraction of b.p. 60—65 °C. Chromatographic separations were performed using Alumina BDH (activity II). A 250-W mercury vapour lamp (Philips) was employed for u.v. irradiations.

$[Mn_2(CO)_8(\mu\text{-tedip})]$ (**1**).—The compounds $[Mn_2(CO)_{10}]$ (0.32 g, 0.815 mmol) and tedip (0.21 g, 0.815 mmol) in light petroleum (50 cm^3) were exposed to u.v. light at −5 °C for 2 h. After evaporation of solvent, chromatography on alumina with elution by light petroleum gave unreacted $[Mn_2(CO)_{10}]$ and other minor products. Elution with light petroleum–CH_2Cl_2 (9:1) gave a yellow fraction which was dried to afford yellow microcrystalline (**1**) (0.1 g, 20%); M^+ 591.8 (calc. 591.95) (Found: C, 33.75; H, 3.65. Calc. for (**1**)·1/6 C_6H_{14}: C, 33.65; H, 3.70%). The presence and amount of solvent in the crystallized samples of (**1**) was verified by ^1H n.m.r. spectroscopy. Further elution with mixtures more rich in CH_2Cl_2 gave a number of unidentified minor products and complex (**2**) (0.03 g, 5%).

$[Mn_2(CO)_6(\mu\text{-tedip})_2]$ (**2**).—The compounds $[Mn_2(CO)_{10}]$ (0.481 g, 1.23 mmol) and tedip (0.987 g, 3.826 mmol) in mesitylene (25 cm^3) were refluxed for 90 min. The mixture was dried in vacuum, dissolved in the minimum of CH_2Cl_2, and chromatographed on alumina. Elution with light petroleum–CH_2Cl_2 (10:3) gave a yellow band; removal of solvent in vacuum and washing the residue with cold light petroleum (4 cm^3) gave complex (**2**) as a yellow microcrystalline solid (0.49 g, 41%); M^+ 794.1 (calc. 794.08) (Found: C, 33.1; H, 5.35. Calc.: C, 33.25; H, 5.10%).

$[Mn_2Br_2(CO)_8(\mu\text{-tedip})]$ (**3a**).—The compounds $[MnBr(CO)_5]$ (0.448 g, 1.628 mmol) and tedip (0.2 cm^3, 0.814 mmol) in toluene (20 cm^3) were warmed at 40 °C for 2 h. The resulting red solution was evaporated in vacuum to give an orange oil which was then extracted with light petroleum (3 × 10 cm^3), filtered, concentrated in vacuum, and left to stand at −20 °C overnight. Orange microcrystalline aggregates of compound (**3a**) were deposited, which were washed with cold light petroleum (3 cm^3) and dried in vacuum (0.25 g, 40%). Repeated recrystallizations in iso-octane showed (according to ^1H n.m.r. spectroscopy) that the product retains *ca.* 1/8 C_8H_{18} (Found: C, 26.4; H, 2.85. Calc. for (**3a**)·1/8 C_8H_{18}: C, 26.6; H, 2.9%).

$[Mn_2I_2(CO)_8(\mu\text{-tedip})]$ (**3b**).—The compounds $[MnI(CO)_5]$ (0.76 g, 2.36 mmol) and tedip (0.29 cm^3, 1.18 mmol) in toluene (30 cm^3) were heated at 60 °C for 5 h. After work-up as for (**3a**), compound (**3b**) was obtained as orange microcrystalline aggregates (0.39 g, 40%); $M^+ - 2CO$ 789.8 (calc. 789.76) (Found: C, 23.25; H, 2.40. Calc.: C, 22.7; H, 2.40%).

$[Mn_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-tedip})]$ (**4a**).—The compounds $[MnBr(CO)_5]$ (4 g, 14.55 mmol) and tedip (1.79 cm^3, 7.277 mmol) in toluene (100 cm^3) were heated at 60 °C for 2 h and then at 80 °C for 18 h, while argon was slowly bubbled through the solution. The solvent was removed in a rotatory evaporator and the residue extracted with CH_2Cl_2 (4 × 20 cm^3); the extracts were filtered and evaporated in vacuum to afford a red crystalline solid which was washed with cold light petroleum (4 × 5 cm^3) and dried in vacuum (4.28 g, 84.5%) (Found: C, 24.35; H, 2.65. Calc.: C, 24.15; H, 2.90%).

$[Mn_2(\mu\text{-}I)_2(CO)_6(\mu\text{-tedip})]$ (**4b**).—The compounds $[MnI(CO)_5]$ (1.025 g, 3.183 mmol) and tedip (0.39 cm^3, 1.592 mmol) in toluene (40 cm^3) were heated at 65 °C for 2.5 h and then at 100 °C for 17.5 h while argon was slowly bubbled through the solution. After work-up similar to that for (**4a**), compound (**4b**) was obtained as a red crystalline solid (1.03 g, 82%) (Found: C, 21.6; H, 2.65. Calc.: C, 21.2; H, 2.55%).

$[Mn_2Br_2(CO)_6(\mu\text{-tedip})_2]$ (**5a**).—The compounds $[MnBr(CO)_5]$ (0.112 g, 0.407 mmol) and tedip (0.1 cm^3, 0.407 mmol) in toluene (15 cm^3) were heated at 50 °C for 3 h. The mixture was evaporated in vacuum to give an orange oil which was extracted with light petroleum–CH_2Cl_2 (3:1) (3 × 10 cm^3), filtered, concentrated, and left to stand overnight at −20 °C. The yellow microcrystalline solid deposited was washed with cold light petroleum (4 cm^3) and dried in vacuum (0.1 g, 51%) (Found: C, 27.7; H, 4.65. Calc.: C, 27.7; H, 4.20%).

$[Mn_2(\mu\text{-}Br)_2(CO)_4(\mu\text{-tedip})_2]$ (**6a**).—The compounds $[MnBr(CO)_5]$ (0.82 g, 2.98 mmol) and tedip (0.74 cm^3, 3.02 mmol) were refluxed in toluene (50 cm^3) for 90 min. The mixture was then evaporated to dryness and the residue extracted with CH_2Cl_2 (3 × 15 cm^3) and filtered. Removal of the solvent in vacuum afforded an orange crystalline solid which was washed with cold light petroleum (3 × 8 cm^3) and dried in vacuum (1.02 g, 75.7%); $M^+ - 2CO$ 839.9(1), 841.9(2), and 843.9(1) (relative intensity in parentheses) (calc. 841.93 ± 2) (Found: C, 26.65; H, 4.70. Calc.: C, 26.75; H, 4.50%).

$[Mn_2(\mu\text{-}I)_2(CO)_4(\mu\text{-tedip})_2]$ (**6b**).—The compounds $[MnI(CO)_5]$ (0.966 g, 3 mmol) and tedip (0.74 cm^3, 3.02 mmol) were refluxed in toluene for 12 h. After work-up similar to that for (**6a**), an orange powder of compound (**6b**) was obtained (0.67 g, 45%). Recrystallization from CH_2Cl_2–light petroleum at −20 °C gave red prismatic crystals (Found: C, 24.5; H, 4.10. Calc.: C, 24.2; H, 4.0%).

$[Re_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-tedip})]$ (**7**).—The compounds $[ReBr(CO)_5]$ (0.298 g, 0.732 mmol) and tedip (0.09 cm^3, 0.366 mmol) in toluene (15 cm^3) were heated at 65 °C for 2.5 h and then at 100 °C for 7 h while argon was bubbled through the solution. After this time, the solution was filtered and evaporated to dryness in vacuum to give a colourless solid, which was washed with cold light petroleum (5 cm^3) and dried in vacuum (0.257 g, 73%). Recrystallization from CH_2Cl_2–light petroleum at

-20 °C gave colourless prismatic crystals found (by ^{1}H n.m.r. spectroscopy) to retain *ca.* 1/6 C_6H_{14} [Found: C, 18.35; H, 2.20. Calc. for (**7**)·1/6 C_6H_{14}: C, 18.5; H, 2.30%].

$[Re_2(\mu\text{-}Br)_2(CO)_4(\mu\text{-tedip})_2]$ (**8**).—The compounds $[ReBr(CO)_5]$ (0.218 g, 0.536 mmol) and tedip (0.14 cm^3, 0.59 mmol) were refluxed in toluene (20 cm^3) for 24 h. The resulting yellow solution was evaporated to dryness and the residue extracted with CH_2Cl_2 and filtered. Removal of the solvent in vacuum and washing the residue with cold light petroleum (4 × 3 cm^3) afforded a yellow-cream powder (0.175 g, 56%). Recrystallization from CH_2Cl_2–light petroleum at -20 °C gave prismatic yellow crystals of compound (**8**) (Found: C, 20.7; H, 3.45. Calc.: C, 21.3; H, 3.45%).

$[Mn_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-dppm})]$ (**9a**).—To a solution of $[MnCl(CO)_5]$ (0.3 g, 1.302 mmol) in CH_2Cl_2 (15 cm^3), dppm (0.25 g, 0.65 mmol) in CH_2Cl_2 (40 cm^3) was added dropwise during 6 h with magnetic stirring at r.t. Stirring was maintained for 40 h while argon was slowly bubbled through the solution. The reaction mixture was filtered, concentrated to minimum volume, and chromatographed on alumina; elution with CH_2Cl_2–light petroleum gave a yellow band corresponding to an orange microcrystalline solid (0.24 g, 50.2%) (Found: C,50.35; H, 3.00. Calc.: C, 50.75; H, 3.00%).

Acknowledgements

We thank the Spanish Ministerio de Educacion y Ciencia for a scholarship (to M. A. R.) and Comisión Asesora de Investigación Cientifica y Técnica for support.

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Received 17*th January* 1986; *Paper* 6/131