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The stereospecific synthesis of mono- and bi-nuclear (ligand-bridged) carbonyl complexes of manganese: a review *

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Abstract

A review is given of the routes that can be used to give the different isomeric forms of mono- and bi-nuclear manganese carbonyl complexes of the general types $[Mn(CO)_{4-n}(\overline{L\ L})L_n]^+$ and $[L_n(\overline{L\ L})(CO)_{3-n}Mn\text{–}X\text{–}Mn(CO)_{3-m}(\overline{L\ L})'L'_m]^+$, where $\overline{L\ L}$ are chelating bidentate ligands and X is a bridging ligand.

Introduction

The cationic octahedral manganese carbonyl complexes [1] of the general type $[Mn(CO)_{6-n}L_n]^+$, where the *n* monodentate ligands are equal, can be relatively simply prepared from the neutral perchlorate complex $[Mn(OClO_3)(CO)_5]$ and the relevant ligand [2]. Thus, for example, for $L = PHPh_2$ the compounds $[Mn(CO)_5L]ClO_4$, *cis*-$[Mn(CO)_4L_2]ClO_4$, *fac*- or *mer*-$[Mn(CO)_3L_3]ClO_4$ and *cis*- or *trans*-$[Mn(CO)_2L_4]ClO_4$ can be prepared in good yields by simply adjusting the reaction conditions [3]. In general, however, the degree of CO substitution that can be achieved by this method strongly depends on the ligand L. Thus, when L is a nitrile, the formation of the *fac*-tricarbonyls is so favoured that in many cases even the pentacarbonyls are difficult to isolate [4]. For tetramethylthiourea, on the other hand, the *cis*-tetracarbonyl is much more favoured than the tricarbonyl [5]. It is only when L is a phosphorus donor ligand [PR_3 or $P(OR)_3$] that both *fac*- and *mer*-tricarbonyls and *cis*- or *trans*-dicarbonyls can be obtained by this method [2].

The mixed complexes of the types $[Mn(CO)_{4-n}(\overline{L\ L})L_n]^+$, where $\overline{L\ L}$ is a chelating bidentate ligand, are richer in isomeric forms, particularly if the ligands are not identical, and their synthesis is less straightforward. The stereochemistry of the substitution reactions required to introduce each ligand ($\overline{L\ L}$ or L) is dictated by the nature of the ligands already present in the starting complexes and by the

* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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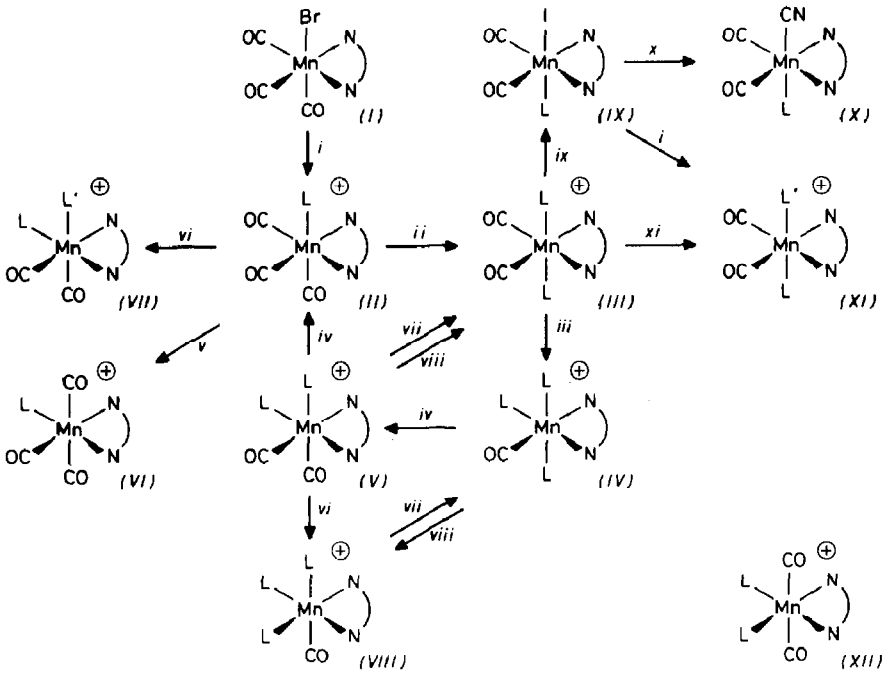
reaction conditions, which may favour thermodynamic rather than kinetic control. Thus, some isomers are difficult to prepare. This is particularly so in the case of binuclear complexes having different metal carbonyl moieties bridged by a symmetric or non-symmetric ligand $[L_{3-n}(\overline{L\ L})(CO)_nMn{-}X{-}Mn(CO)_m(\overline{L\ L})'L'_{3-m}]^+$.

For some time we have been exploring the possibility of finding specific routes for the synthesis of various types of mono- and bi-nuclear manganese carbonyl complexes, the main results obtained are summarized below.

(1) Mononuclear complexes

(a) Complexes having nitrogen-donor chelating ligands. The neutral tricarbonyls *fac*-$[MnBr(CO)_3(\overline{N\ N})]$ (I, where N-N = 2,2′-bipyridine (bipy) or 1,10-orthophenantroline (phen)) are very useful materials for the preparation of other octahedral complexes, both neutral and cationic (see Scheme 1). These compounds can be treated with $AgClO_4$ to give the perchlorate derivatives *fac*-$[Mn(OClO_3)(CO)_3(\overline{N\ N})]$ from which the ClO_4^- salts of many cationic tricarbonyls *fac*-$[Mn(CO)_3(\overline{N\ N})L]^+$ (II) are readily obtained [6,7,3,5,10,17]. The PF_6^- salts of many of these cations can be obtained directly from I and the ligand L in the presence of $TlPF_6$ as halogen abstractor [3,5].

The thermal reaction of II with L (L = PR_3 or $P(OR)_3$) gives the dicarbonyls *cis,trans*-$[Mn(CO)_2(\overline{N\ N})L_2]^+$ (III) (6), which, when L is $P(OR)_3$, react with an excess of L under UV irradiation to give the monocarbonyls *mer*-[Mn(CO)-



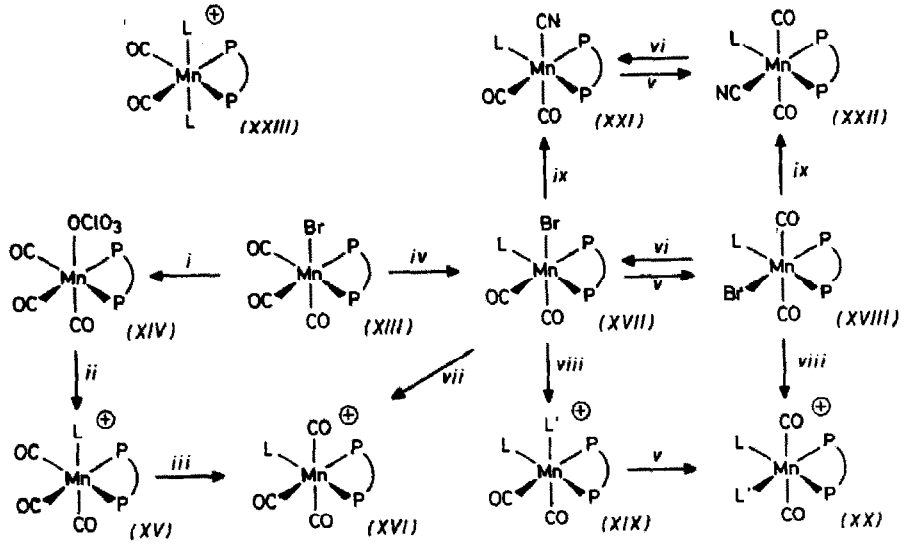
Scheme 1. (i) $AgClO_4$ followed by L, or $TlPF_6$ + L; (ii) L, heat; (iii) L, *hν*. (iv) CO, *hν*; (v) $ONMe_3$ + CO (L = CNR); (vi) $ONMe_3$ + L (L = CNR); (vii) heat; (viii) Na/Hg, followed by air; (ix) KI; (x) AgCN; (xi) L′ reflux.

$(\widehat{N\ N})L_3]^+$ (IV) [8]. Irradiation of IV with UV light in the presence of CO gives the dicarbonyls *cis,cis*-$[Mn(CO)_2(\widehat{N\ N})L_2]^+$ (V) isomeric of III [8], indicating that the photochemical substitution of L by CO in IV occurs preferentially *cis* to both N atoms. However, when V is irradiated with UV light in the presence of CO, the *fac*-tricarbonyls II are formed rather then the expected *mer*-isomers (VI) [8].

The *mer*-tricarbonyls $[Mn(CO)_3(\widehat{N\ N})L]^+$ (VI), which are not expected to be formed in kinetically controlled reactions [9], could, in fact, be obtained only for L = CNR by treating the corresponding *fac*-tricarbonyls II (L = CNR) with $ONMe_3$ and CO [10]. This result is consistent with the formation of the mixed dicarbonyls VII from II (L = CNR) and CNR′ in the presence of $ONMe_3$ that occurs with migration of the CNR ligand [11]. The same effect may be responsible for the formation of the monocarbonyls *fac*-$[Mn(CO)(\widehat{N\ N})(CNR)_3]^+$ (VIII) in the reaction of V (L = CNR) with CNR and $ONMe_3$ [10].

The *cis,cis*-dicarbonyls V with L = PR_3 or $P(OR)_3$ rearrange upon heating to the *cis,trans*-isomers III [8]. This isomerization can be also induced when L = CNR [12] or $P(OR)_3$ [13] by reduction with Na/Hg followed by oxidation of the unstable paramagnetic intermediates. The *fac*-monocarbonyls VIII with L = CNR similarly undergo reductively induced isomerization to give the *mer*-isomer IV, although in this case the rearrangement can be reversed by heating [12]. By contrast, oxidations of the *cis,cis* or *cis,trans* dicarbonyls V and III, and of the *mer*-monocarbonyls IV with L = $P(OR)_3$ occur without stereochemical changes [14].

The *cis,trans*-dicarbonyls III can be treated with I^- to give the useful neutral complexes *cis,trans*-$[MnI(CO)_2(\widehat{N\ N})L]^+$ (IX), or with X^- (X = CN or SCN) to give the cyano (X) or thiocyanate analogues, which can also be obtained from IX and AgX [15]. The reaction of IX with $TlPF_6$ in the presence of a ligand L′ gives the mixed *cis,trans*-dicarbonyls $[Mn(CO)_2(\widehat{N\ N})LL']^+$ (XI), some of which can be also



Scheme 2. (i) $AgClO_4$; (ii) L; (iii) heat; (iv) L, heat; (v) $NOPF_6$ followed by NH_2NH_2; (vi) spontaneously and catalyzed by oxidants; (vii) $TlPF_6$ + CO; (viii) $TlPF_6$ + L′; (ix) AgCN.

prepared (although less specifically) from III and L′ [6], and, in the case of L′ = CNMe, from X and MeI in the presence of KPF_6 [15].

It is noteworthy that attempts to make the *trans*-dicarbonyls $[Mn(CO)_2(\widehat{N\ N})L_2]^+$ (XII) have so far been unsuccessful.

(b) Complexes with chelating phosphorus-donor ligands. A variety of mononuclear manganese carbonyl complexes with diphosphines can be prepared from the neutral tricarbonyls *fac*-$[MnBr(CO)_3(\widehat{P\ P})]$ (XIII) ($\widehat{P\ P} = Ph_2P(CH_2)_nPPh_2$, $n = 1$ (dppm) or 2 (dppe)) (see Scheme 2). In spite of the formal similarity with the bipy or phen derivatives, many important differences are observed, especially in the stereochemistry of the substitution processes.

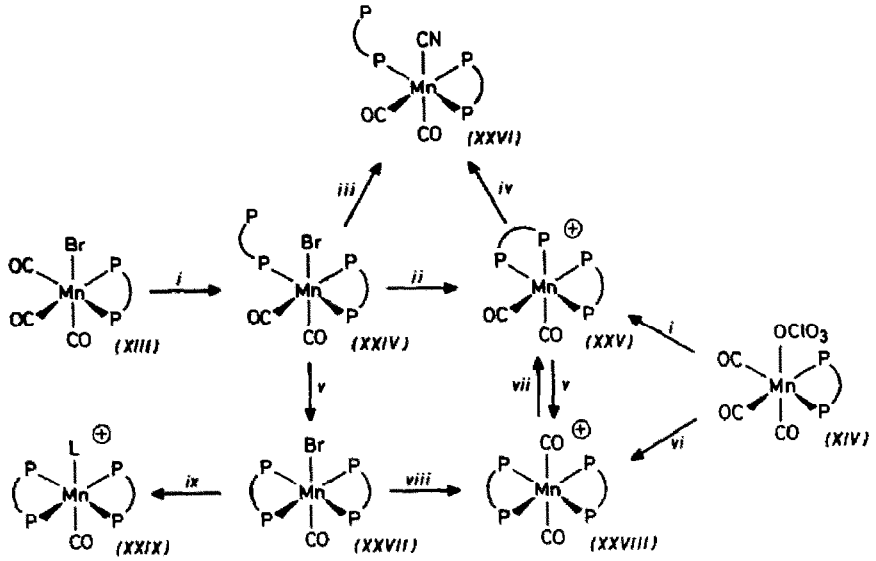
Thus, the reaction of XIII with $AgClO_4$ gives the neutral perchlorate derivatives $[Mn(OClO_3)(CO)_3(\widehat{P\ P})]$ (XIV), which react with various ligands L to give the corresponding cationic complexes *fac*-$[Mn(CO)_3(\widehat{P\ P})L]^+$ (XV) [16,3,5,7,17,18]. In these cases the PF_6^- salts cannot be prepared directly from XIII by use of $TlPF_6$. The complexes XV having $L = PR_3$ or $P(OR)_3$ rearrange to the *mer*-isomers XVI upon heating [16,3,18], or, for $L = PPh_3$ and $\widehat{P\ P}$ = dppm, even at room temperature [16]. On the other hand, only the *mer*-tricarbonyls with $L = P(OR)_3$ react with more L under UV irradiation to give the dicarbonyls *trans*-$[Mn(CO)_2(\widehat{P\ P})L_2]^+$ (XX with L = L′) [16].

By heating the bromotricarbonyls XIII with a ligand L (PR_3 or $P(OR)_3$) the useful dicarbonyls *cis,mer*-$[MnBr(CO)_2(\widehat{P\ P})L]^+$ (XVII) can be obtained [19]. The complexes having $\widehat{P\ P}$ = dppe or $L = P(OR)_3$ with R = Me or Ph, can be also prepared by other routes [20]. In extension of a procedure previously used by Reimann and Singleton [21], compounds XVII can be oxidized, and subsequently reduced to give the isomeric *trans*-$[MnBr(CO)_2(\widehat{P\ P})L]$ (XVIII) [19]. This conversion involves an oxidatively-induced isomerization that has also been well characterized by electrochemical methods [22]. The reverse isomerization XVIII → XVII is spontaneous and, although slow, it can be catalyzed by the cation *trans*-$[MnBr(CO)_2(\widehat{P\ P})L]^+$ [23].

Reactions of XVII with $TlPF_6$ in the presence of CO, or other entering ligand L′, provide a more general route to the cationic *mer*-$[Mn(CO)_3(\widehat{P\ P})L]^+$ (XVI) and allow the synthesis of the dicarbonyls *cis,cis*-$[Mn(CO)_2(\widehat{P\ P})LL']^+$ (XIX) [19]. The complexes XVII also react with AgCN to give the cyano derivatives *cis,mer*-$[Mn(CN)(CO)_2(\widehat{P\ P})L]$ (XXI), and with AgSCN to give the analogous thiocyanate complex [24]. Similarly, the *trans*-dicarbonyls XVIII react with $TlPF_6$ and CO to give XVI, with $TlPF_6$ and L′ to give *trans*-$[Mn(CO)_2(\widehat{P\ P})LL']^+$ (XX) [19], and with AgCN to give *trans*-$[Mn(CN)(CO)_2(\widehat{P\ P})L]$ (XXII) [24]. The latter also revert to the *cis,mer*-isomer (XXI) spontaneously in solution. All the *trans*-dicarbonyls XVIII, XX and XXII can be obtained from the *cis*-isomers by oxidation followed by reduction.

It is noteworthy, that, in contrast to the complexes, containing the $\widehat{N\ N}$ systems, the *trans*-dicarbonyls XX are easy to make whereas the *cis,trans* isomeric forms XXIII have not been prepared.

The two-step preparation of XIX from XIII (Scheme 2) suggested specific synthesis for the cationic dicarbonyl *cis*-$[Mn(CO)_2(dppm)_2]^+$ (XXV) based on the two similar reactions shown in Scheme 3 [25]. First, the tricarbonyl XIII is heated with dppm in toluene to give *cis,mer*-$[MnBr(CO)_2(\widehat{P\ P})(\widehat{P\ P'})]$ (XXIV), in which one dppm is monodentate, and the latter is treated with $TlPF_6$ to remove the Br



Scheme 3. (i) $\widehat{P\ P}$, heat; (ii) $TlPF_6$; (iii) AgCN; (iv) KCN + 18-crown-6; (v) $h\nu$; (vi) $\widehat{P\ P}$, $h\nu$; (vii) heat; (viii) $TlPF_6$ + CO; (ix) MPF_6 (M = K or Tl) + L (or only L).

ligand, leaving a vacant coordination site that is taken up by the phosphorus of the monodentate dppm to give XXV. The complex XXIV also reacts with $TlPF_6$ in the presence of CO to give *mer*-$[Mn(CO)_3(\widehat{P\ P})(\widehat{P\ P'})]^+$, with $TlPF_6$ and NCMe to give *cis,mer*-$[Mn(CO)_2(\widehat{P\ P})(\widehat{P\ P'})(NCMe)]^+$ [26], and with AgCN to give *cis,mer*-$[Mn(CN)(CO)_2(\widehat{P\ P})(\widehat{P\ P'})]$ (XXVI), which can be also prepared by treatment of XXV with KCN in the presence of 18-crown-6 [26].

The *trans*-dicarbonyl *trans*-$[Mn(CO)_2(dppm)_2]^+$ (XXVIII), isomeric with XXV, can be prepared systematically from XXIV in two steps. First, XXIV is irradiated with UV light to give the monocarbonyl *trans*-$[MnBr(CO)(dppm)_2]$ (XXVII) (which can also be made directly from XIII and dppm under UV irradiation [27]), which reacts with $TlPF_6$ and CO to give XXVIII [25].

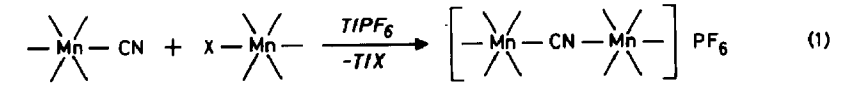
The isomers XXV and XXVIII can be interconverted. Thus, heating the *trans* form XXVIII gives the *cis*-XXV, but the latter reverts to the *trans* isomer under UV light. Likewise, heating the perchlorate complex *fac*-$[Mn(OClO_3)(CO)_3(dppm)]$ (XIV for $\widehat{P\ P}$ = dppm) with dppm gives the ClO_4^- salt of XXV, whereas if the reaction is carried out under UV irradiation the ClO_4^- salt of the *trans*-isomer XXVIII is obtained [25,26]. Like the other dicarbonyls containing diphosphines, XXV can be oxidized to the dication *trans*-$[Mn(CO)_2(dppm)_2]^{2+}$, which gives XXVIII on reduction [22].

The monocarbonyl XXVII (and the dppe analogue) is also useful for the preparation of other carbonyl complexes. Thus, the reaction with ligands in the presence of $TlPF_6$ or KPF_6 (or, sometimes, even in the absence of halogen abstractor) gives the cationic *trans*-$[Mn(CO)(\widehat{P\ P})_2L]^+$ (XXIX) [28]; and the reaction with AgCN gives *trans*-$[Mn(CN)(CO)(\widehat{P\ P})_2]$, which can be treated with MeI and KPF_6 to give *trans*-$[Mn(CO)(\widehat{P\ P})_2(CNMe)]^+$ [24]. Other cationic monocarbonyls of this type can be prepared from XXVII and L in the presence of an oxidant [29].

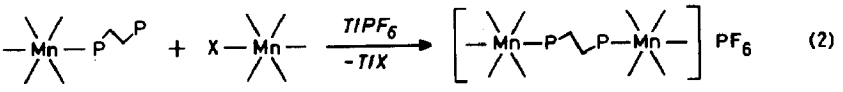
(2) Binuclear ligand-bridged species

When account is taken of the various routes that can be used to prepare cationic carbonyl complexes with a given set of ligands and having a particular stereochemistry, it is possible to design the synthesis of binuclear complexes in which there are two octahedral carbonyl moieties (equal or different) bridged by another (symmetrical or unsymmetrical) ligand.

Thus, the cyano complexes LnMCN may be regarded as N-donor ligands, and so react with a halocarbonyl in the presence of $TlPF_6$ to give bimetallic cationic complexes containing a bridging cyanide (eq. 1). By use of this method the compounds $\{[fac\text{-}Mn(CO)_3(\overline{N\ N})]_2(\mu\text{-}CN)\}PF_6$, $\{[fac\text{-}Mn(CO)_3(\overline{N\ N})][cis,trans\text{-}Mn(CO)_2(\overline{N\ N})L](\mu\text{-}CN)\}PF_6$ (two isomers), and $\{[cis,trans\text{-}Mn(CO)_2(\overline{N\ N})L]_2(\mu\text{-}CN)\}PF_6$, can be obtained from *fac*-$[MnBr(CO)_3(\overline{N\ N})]$, *cis,trans*-$[MnI(CO)_2(\overline{N\ N})L]$, *fac*-$[Mn(CN)(CO)_3(\overline{N\ N})]$ or *cis,trans*-$[Mn(CN)(CO)_2(\overline{N\ N})L]$ ($\overline{N\ N}$ = bipy or phen, L = $P(OPh)_3$) as required [15]. Analogous bridged thiocyanate complexes can be also prepared [15].

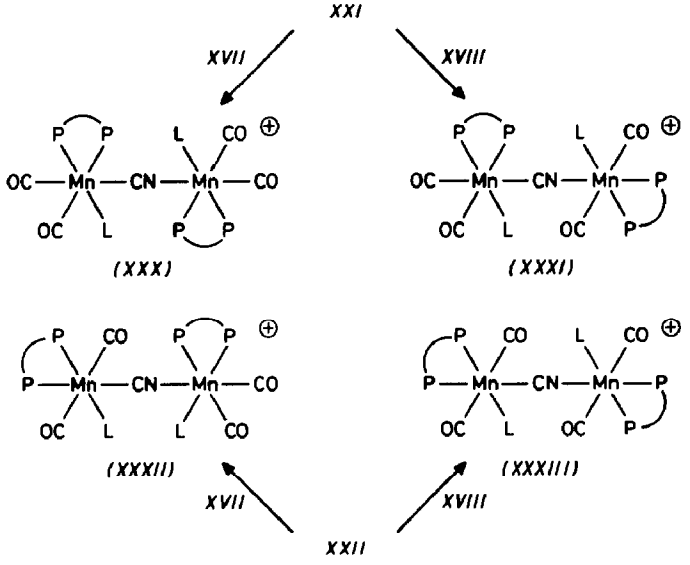


(1)



(2)

By appropriate choice of mononuclear carbonyls, various types of binuclear complexes with different sterochemistries can be obtained. This is illustrated by the systematic preparation of the four isomeric cyano bridged cations, as shown in Scheme 4, starting from the mononuclear cyano complexes XXI and XXII and the bromo derivatives XVII and XVIII [30]. A variety of less symmetrical cations can be



Scheme 4

made using different diphosphines (such as dppm or 1,2-bis(dimethylphosphino)-ethane (dmpe)), and different monodentate ligands L (such as $P(OPh)_3$ or PEt_3) for each side of the CN bridge [30].

These complexes are of interest because of their electrochemical behaviour [31], which allows studies of mixed valence species. For example, all the cations XXX to 'XXXIII (Scheme 4) give the *trans,trans*-isomer XXXIII when oxidized and subsequently reduced, because of the oxidatively induced isomerization of the *cis*-dicarbonyl sites, but, more importantly, this isomerization also takes place in one *cis*-dicarbonyl moiety if the one electron oxidation occurs at the manganese atom in the other side of the CN bridge [31].

Binuclear cationic complexes having dinitriles [28] or diphosphines [7] as bridging ligands can be readily made from a halogen complex (or a neutral perchlorate derivative) and a mononuclear compound with a dinitrile or a diphosphine acting in monodentate mode (eq. 2). Thus, the salts $[\{[fac\text{-}Mn(CO)_3(\overline{N\ N})]_2(\mu\text{-}\overline{P\ P})\}ClO_4]_2$ can be prepared from fac-$[Mn(OClO_3)(CO)_3(\overline{N\ N})]$ and *fac*-$[Mn(CO)_3(\overline{N\ N})(\overline{P\ P'})]ClO_4$ [7]. This approach may allow the preparation of various types of binuclear complexes having two manganese carbonyl moieties (equal or different) bridged by a diphosphine, by using mononuclear complexes such as XXIV or XXVI as phosphorus donor ligands.

Other binuclear compounds with diphosphines (or diphosphites) and halide bridges, without metal–metal bonds, can be made by treating binuclear M–M bonded species with halogens X_2, or treating with $AgClO_4$ other binuclear derivatives having two halocarbonyl moieties bridged by a diphosphine (or diphosphite) [32].

Conclusions

There are many routes to octahedral cationic carbonyl complexes of manganese having different ligands and stereochemistries [1]. A very simple one involves the replacement of a weakly coordinated anionic ligand, such as $OClO_3$, by a neutral ligand, or, alternatively, the replacement of a halide by the ligand L promoted by a halide abstractor. This reactions are usually carried out under very mild conditions, and so, the entering ligand occupies the coordination site left behind by the anionic ligand. Although in some cases salts such as KPF_6 may be effective in, removing a halide, it is frequently necessary to use silver salts such as $AgPF_6$, $AgBF_4$ or $AgClO_4$, because the insolubility of the silver halides provides an important driving force to the reaction. However, the silver salts may also play a direct rôle because of the oxidizing ability of the Ag^+ cation, which sometimes promotes undesired stereochemical changes [19], or because of the possibility that the Ag^+ may coordinate to any donating group, such as a terminal CN group, present in the reacting complexes [26]. For these reasons use of the Tl^+ salts may be advantageous, although it is restricted to those cases in which the halo complex may be easily ionized, such as in electron rich derivatives. Another important reaction is the displacement of CO [33] that can be brought about thermally, photochemically, or by use of $ONMe_3$. The stereochemistry of the process is different in the three cases, and depends on the starting complex as well as on the entering ligand. Normally, the *cis*-labilizing rule, explained in terms of a site preference model [34], is useful as a guide in the case of the thermal reactions, although care is necessary in cases in which the stereochem-

istry of the product is thermodynamically controlled. Experimentally it is observed that the highest degree of CO substitution from a parent carbonyl is achieved by use of ligands which are π-acceptors and sterically undemanding such as $P(OR)_3$, or with diphosphines. In many cases it may be more convenient to replace a weakly coordinated ligand L', such as NCMe, THF, H_2O, Me_2CO, NH_3 etc, by another ligand L, because this can usually be carried out under milder conditions than the CO substitution, permitting better control of the stereochemical course of the reaction. Occasionally, however, the L'/L substitutions may be only weakly selective, and depend on many factors not always understood (see, for example, refs. 6 and 35). Finally, there are several redox-induced stereochemical changes, some of them readily predictable [36], that can be useful in designing the synthesis of isomeric carbonyl complexes.

The information summarized above is relevant for the synthesis of mono- and bi-nuclear compounds with a particular stereochemistry. This, in turn, is of interest because it makes possible systematic studies of the stereochemical effects on the properties of the complexes, such as electrode potentials, electron richness of the coordination sites (Es values), or P_L parameters of the ligands [37,22]. In the case of the bimetallic species, it is possible to make the changes in the ligands and stereochemistries of the fragments connected by a bridging ligand that are necessary for tuning the electron richness at both sides of the bridge in order to study the chemical and electrochemical consequencies.

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