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Xenophilic transition metal clusters

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Abstract

A new subset of the class of compounds containing polar metal–metal bonds is described in which two transition metals with open d-shells form a direct, unbridged bond between a metal center attached to π-acceptor ligands and one which is bound only to donor ligands that have no π-acceptor capabilities. The heterogeneous character of the metal–metal bond in these compounds is generated by the nature of the metal–ligand interactions, either with or without additional contributions from the differing identities and formal oxidation states of the metals. The clusters are remarkable in that they often exhibit unusually short metal–metal distances, and a number of them are highly paramagnetic. The term 'xenophilic' metal cluster has been proposed to refer to transition metal compounds that contain this type of metal–metal interaction. The group includes both heteronuclear 'early–late' transition

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metal clusters as well as homonuclear compounds in which the two metal centers are the same element, but differ in the type of ligands attached.

Keywords: Transition metal; Metal cluster; Paramagnetic; Metal–metal bond

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1. Introduction

Transition metal complexes have long been divided into two major groups [1]. 'Type A' complexes contain metals with moderate to highly positive formal oxidation states (generally 2+ or greater), that tend to bond well to hard Lewis base ligands such as water, ammonia, or fluoride ions, which act as strong σ-donors, and typically lack any electron acceptor capabilities. 'Type B' complexes contain electron-rich transition metals in low formal oxidation states (e.g. 1+, 0, or 1−) that bond to soft, polarizable ligands that can accept electron density from the metal via π-interactions.

This bifurcation also extends to the field of transition metal cluster chemistry, where it is generally recognized that "the two general types of metal cluster compound, which may be loosely called the 'lower halide' type and the 'carbonyl' type, differ from each other in many ways, and there is very little in the way of chemical reactions to interrelate them" [2]. The 'lower halide' clusters are generally made up of early transition metals in moderately positive formal oxidation states that are bound to anionic σ-donor ligands such as halides, amides, alkoxides, or carboxylates [3]. The 'carbonyl' type contain later transition metals with zero or negative oxidation states that are attached to π-acid ligands such as carbon monoxide, phosphines, or olefins [4]. The gulf between these two groups has recently been bridged by the preparation of transition metal clusters that have metal–metal bonds between the two different types of metal centers. These compounds are the subject of this review.

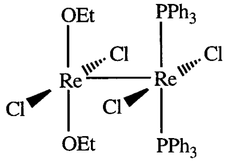
The study of transition metal clusters in which there is a polar or 'heterogeneous' character to the metal–metal interaction has long been an area of interest, primarily for its application to the understanding and development of transition metal catalysts [5,6]. There are two areas of relevance: one is to further the understanding of the 'strong metal–support interaction' (SMSI) that occurs in solid heterogeneous catalysts between an electron-rich transition metal and a transition metal oxide support [7–9], and the other is to develop soluble homogeneous catalysts containing two metal centers with different bonding affinities that are capable of activating and coupling small molecules and olefins. Species such as hydrogen cyanide and sulfur dioxide as well as potential carbon feedstocks such as methanol, carbon monoxide, and carbon dioxide contain polar bonds, which must be activated in order to be used as synthetic building blocks in coupling reactions, particularly with olefins. There is considerable evidence that processes of this type can be controlled and enhanced by the use of an electron-rich transition metal catalyst in conjunction with a Lewis acid co-catalyst [10–13]. Although many combinations of a low-valent, electron-rich transition metal complex with a hard 'oxophilic' Lewis acid metal center are possible, including systems in which the electropositive site is a main group element [14] or a lanthanide metal [15], the most popular approach has been to prepare compounds in which there is a bond between an 'early' and a 'late' transition metal from the left and right-hand groups of the d-block elements, respectively [6]. However, nearly all of these compounds have π-acceptor ligands on both metals, and many are held together by bridging groups that can add stability to the metal–metal linkage but can also obscure the nature of the interaction between the two metals [16].

This review focuses on a new subset of the class of compounds containing polar metal–metal bonds in which two transition metals with open d-shells form a direct, unbridged bond between a metal center attached to π-acceptor ligands and one which is bound only to donor ligands that have no π-acceptor capabilities. In these compounds the heterogeneous character of the metal–metal bond is generated by the nature of the metal–ligand interactions, either with or without additional contributions from the differing identities and formal oxidation states of the metals. The clusters are remarkable in that they often exhibit unusually short metal–metal distances, and a number of them are highly paramagnetic. The term 'xenophilic' metal cluster (from the Greek 'xenos', meaning foreigner or stranger, and 'philos', meaning to have an affinity for) has been proposed to refer to transition metal clusters that have this type of metal–metal interaction [17]. The group includes both heteronuclear 'early–late' transition metal clusters as well as homonuclear compounds in which the two metal centers are the same element but differ in the type of ligands attached. Clusters containing bonds between transition metals and the coinage metals (Cu, Ag, and Au) have not been included on the grounds that the latter are likely to have closed d-orbital subshells and are therefore apt to have more in common with the transition metal clusters containing main group elements such as mercury. However, the field of compounds containing 'heterogeneous' metal–metal bonds is clearly a broad continuum rather than being sharply divided into discrete groups, and therefore some species that have π-acid ligands such as pyridine on the Type A metal center will also be discussed because their chemistry is closely related to that of the xenophilic clusters.

2. Compounds with charged ligands on the Type A metal

2.1. Metal alkyls, alkoxides, and dialkylamides

Homonuclear metal clusters of the 'lower halide' type were among the first examples of this class of compounds to be discovered. The reactions of $Re_2Cl_4(O_2CCH_3)_2(H_2O)_2$ with PPh_3 in methanol, ethanol, or *n*-propanol produced the three complexes $(RO)_2Cl_2ReReCl_2(PPh_3)_2$ ($R = Me$, Et, *n*-Pr) [18]. A crystal structure determination for the ethoxy derivative revealed that the substituents on the two rhenium atoms adopt an eclipsed configuration (Fig. 1), and the compound



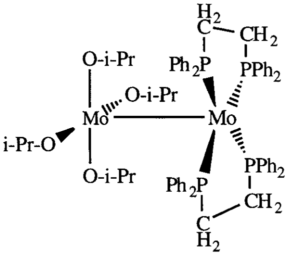
$(EtO)_2Cl_2ReReCl_2(PPh_3)_2$

Fig. 1.

is best described as a quadruply bonded mixed-valence $Re^{IV}Re^{II}$ complex in which one of the components of the quadruple bond is formally dative in character. The electronic absorption spectrum of $(EtO)_2Cl_2ReReCl_2(PPh_3)_2$ is quite different from those of related $Re_2Cl_6(PR_3)_2$ species, in which there is a phosphine ligand on each rhenium [19]. The mixed-valence ethoxy complex can undergo one-electron oxidation to give a stable monocation and it exhibits a chemically irreversible one-electron reduction, as compared to the $Re_2Cl_6(PR_3)_2$ complexes, which undergo two one-electron reductions [20]. This behavior implies that the electronic environments for the metals in the ethoxy complex differ significantly from those found in the centrosymmetric $Re_2Cl_6(PR_3)_2$ species.

The molybdenum complex $(i\text{-PrO})_4MoMo(dmpe)_2$ can be prepared via the reaction of $Mo_2(O\text{-}i\text{-Pr})_4(HO\text{-}i\text{-Pr})_4$ with two equivalents of $Me_2PCH_2CH_2PMe_2$ (dmpe) or by treating $Mo_2(i\text{-Bu})_2(NMe_2)_4$ with isopropanol and dmpe in a hydrocarbon solvent [21]. The compound is made up of a Mo(IV) fragment attached to four isopropoxy groups and a Mo(0) fragment bound to the two bidentate phosphine ligands (Fig. 2). The substituents on the two molybdenum atoms are staggered with respect to each other, and the metal–metal distance is appropriate for a Mo–Mo triple bond.

The great majority of the xenophilic metal clusters that have anionic ligands are of the 'early–late' transition metal type in which a Group 4 metal with alkyl, alkoxide, or dialkylamido groups is attached to a $(\eta^5\text{-}C_5H_5)M(CO)_n$ or a



$(i\text{-PrO})_4MoMo(dmpe)_2$

Fig. 2.

$Co(CO)_3(L)$ fragment to give a compound of the general formula $(R_xE)_3M_A{-}M_B(CO)_nL$. They can be synthesized by two routes, shown in Eqs. (2.1) and (2.2).

$$(R_xE)_3M_AX + [M'][M_B(CO)_nL] \rightarrow (R_xE)_3M_A{-}M_B(CO)_nL + M'X \tag{2.1}$$

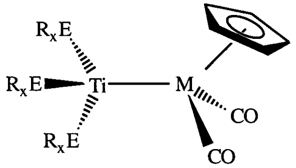
$$(R_xE)_4M_A + HM_B(CO)_nL \rightarrow (R_xE)_3M_A{-}M_B(CO)_nL + HER_x \tag{2.2}$$

$R_xE = R_2N$, RO, or R $\qquad M' =$ Li, Na, K

$X =$ Cl, Br $\qquad L = CO, PR_3, (\eta^5\text{-}C_5H_5)$

The first well-characterized examples were prepared by Sartain and Selegue, and they have the general formula $(Me_2N)_{3-n}(RO)_nTi{-}M(\eta^5\text{-}C_5H_5)(CO)_2$ where M = Ru; RO = Me_2HCO; $n = 0, 1, 2, 3$ [22]. Subsequent papers describe the formation of compounds in which M = Ru; RO = 2,6-$Me_2C_6H_3O$; $n = 1, 2$ [16] and M = Fe; RO = Me_2HCO; $n = 0, 2, 3$ [23] (Fig. 3). All were synthesized by the reaction of $(\eta^5\text{-}C_5H_5)M(CO)_2(H)$ with $Ti(NMe_2)_{4-n}(OR)_n$ ($n = 0, 1, 2, 3$) via the elimination of one equivalent of $HNMe_2$.

Unlike their thermally stable ruthenium cogeners, the titanium–iron compounds decompose to give $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$ and intractable titanium products at room temperature (r.t.). All of the compounds are extremely reactive toward atmospheric oxygen and moisture, and the metal–metal bond in $(Me_2N)_3Ti{-}Ru(\eta^5\text{-}C_5H_5)(CO)_2$ can be cleaved by reaction with alcohols such as Me_3COH to give $(\eta^5\text{-}C_5H_5)Ru(CO)_2(H)$ quantitatively, along with $Ti(OCMe_3)_4$ and $NHMe_2$ [22]. Reaction of the same compound with the metal hydride complex $(\eta^5\text{-}C_5H_5)Mo(CO)_3(H)$ produces $(\eta^5\text{-}C_5H_5)Ru(CO)_2(H)$ and an unidentified Mo–Ti compound. The iron



$(Me_2N)_{3-n}(RO)_nTi{-}M(\eta^5\text{-}C_5H_5)(CO)_2$

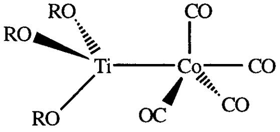
$(R_xE)_3$	M	Reference
$(Me_2N)_{3-n}(2,6\text{-}Me_2C_6H_3O)_n$ $n = 1, 2$	Ru	16
$(Me_2N)_{3-n}(Me_2HCO)_n$ $n = 0, 1, 2, 3$	Ru	22
$(Me_2N)_{3-n}(Me_2HCO)_n$ $n = 0, 2, 3$	Fe	23

Fig. 3.

analog, $(Me_2N)_3Ti–Fe(\eta^5-C_5H_5)(CO)_2$, reacts with *tert*-butyl alcohol and the molybdenum hydride complex to give similar products, but the Ti–Fe bond is not cleaved by tertiary amines or ethers [23]. Comparisons of the carbonyl stretching frequencies in the IR spectra of the series of ruthenium compounds with each other and with $[Na][(\eta^5-C_5H_5)Ru(CO)_2]$ and $(\eta^5-C_5H_5)Ru(CO)_2(GeMe_3)$ led to the conclusion that the Ti–Ru bonds are primarily covalent in character with little $Ti^+–Ru^-$ polarization [16]. Some degree of π-donation of electron density from ruthenium to titanium was postulated to account for the observed shortening of the Ti–Ru distance of 2.663(1) Å in $(Me_2N)_3Ti–Ru(\eta^5-C_5H_5)(CO)_2$ to 2.573(1) Å in $(Me_2N)(2,6-Me_2C_6H_3O)_2Ti–Ru(\eta^5-C_5H_5)(CO)_2$ [16].

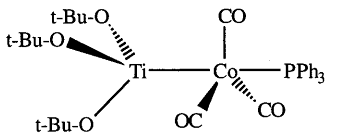
Titanium–cobalt compounds with various alkoxide groups on titanium have been prepared by treating $(RO)_3TiMe$ with $HCo(CO)_4$ [24] or by the reaction of $(RO)_3TiCl$ with $[Na][Co(CO)_4]$ [24,25] to give products of the general formula $(RO)_3Ti–Co(CO)_4$ ($R = Me_3C$, Me_2CH, $(CF_3)_2CH$, Ph) (Fig. 4). The thermal stabilities of the products are highly dependent upon the identity of the alkoxide group, and all except the tertiary butoxide complex decompose in solution at 25°C. The latter complex was sufficiently stable for an X-ray crystal structure determination, which revealed a Ti–Co bond distance of 2.565(2) Å [25]. This value is slightly less than the distance of 2.614 Å that was observed for $[(OC)_9Co_3(CO)]_2(\eta^5-C_5H_5)Ti–Co(CO)_4$ [26], in which there are π-acceptor ligands on both the titanium and the cobalt.

The IR spectra in the C–O stretching region for this series of compounds revealed that the more electron-withdrawing phenoxy and perfluoromethylisopropoxy substituents on the titanium brought about a shift in the cobalt CO stretching frequencies to higher wavenumbers, presumably as a result of increased π-donation from cobalt to titanium and the consequent decreased donation from cobalt to CO [25]. The compounds containing tertiary butyl, isopropyl, and phenyl groups decomposed in solution to form $HCo(CO)_4$, and examination of the decomposition of $(Me_3CO)_3Ti–Co(CO)_4$ in deuterated toluene and cyclohexane revealed the formation of $HCo(CO)_4$ but no $DCo(CO)_4$. The perfluoromethylisopropoxy compound, which has α-hydrogens but lacks hydrogen atoms on the carbons in β-positions relative to oxygen, decomposed to give $Co_2(CO)_8$ [25]. $(Me_3CO)_3Ti–Co(CO)_4$ is sufficiently stable to undergo a carbonyl substitution reaction with triphenylphosphine to give $(Me_3CO)_3Ti–Co(CO)_3(PPh_3)$ [25]. Additional compounds of the type $(Me_3CO)_3Ti–M(CO)_n(L)$ have been prepared where $M(CO)_n(L) = Fe(CO)_2(\eta^5-C_5H_5)$, $Mo(CO)_3(\eta^5-C_5H_5)$, and $Mn(CO)_5$ [27] (Fig. 5). The crystal structure of the latter complex was determined and the Ti–Mn distance was found to be 2.684(1) Å.

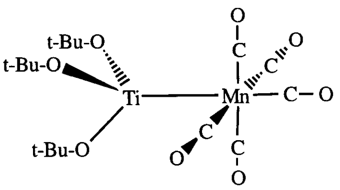


$(RO)_3Ti-Co(CO)_4$ ($R = Me_3C$, Me_2CH, $(CF_3)_2CH$, Ph)

Fig. 4.

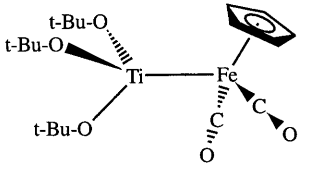


$(Me_3CO)_3Ti\text{-}Co(CO)_3(PPh_3)$

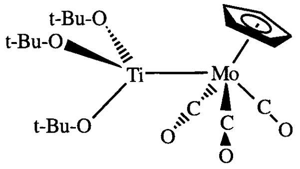


$(Me_3CO)_3Ti\text{-}Mn(CO)_5$

Ti-Mn = 2.684(1) Å



$(Me_3CO)_3Ti\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)$

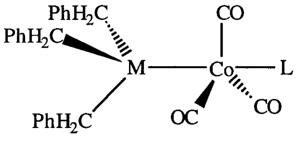


$(Me_3CO)_3Ti\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)$

Fig. 5.

Compounds in which alkyl groups are bound to the Group 4 transition metal have been prepared by reactions of tetrabenzyltitanium and tetrabenzylzirconium with $HCo(CO)_3(L)$ to give $(PhCH_2)_3M\text{–}Co(CO)_3(L)$ (M = Ti, Zr; L = CO, PPh_3) [28] (Fig. 6). Addition of a second equivalent of $HCo(CO)_4$ produces the trinuclear clusters $(PhCH_2)_2M\{Co(CO)_4\}_2$ [28] (Fig. 7). The dinuclear tetracarbonylcobalt products can also be obtained via salt elimination reactions between $(PhCH_2)_3MX$ (M = Ti, Zr; X = Cl, Br) and $[Y][Co(CO)_4]$ (Y = Li, Na, K), while the dinuclear phosphine-substituted compounds can be generated by the reaction of $(PhCH_2)_3M\text{–}Co(CO)_4$ with PPh_3. All of the compounds are thermally unstable, with complete decomposition occurring in solution after 30 min at 25°C, and they were therefore characterized solely by their IR and ^1H-NMR spectra and analysis of the ratio of the two metals.

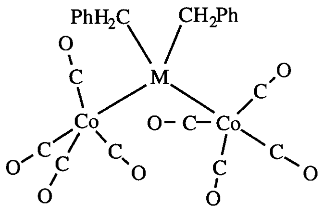
The low thermal stability of many of the compounds containing an unbridged bond between Fe or Co and a Group 4 metal is clearly a hindrance to the



$(PhCH_2)_3M\text{-}Co(CO)_3(L)$

(M = Ti, Zr; L = CO, PPh_3)

Fig. 6.



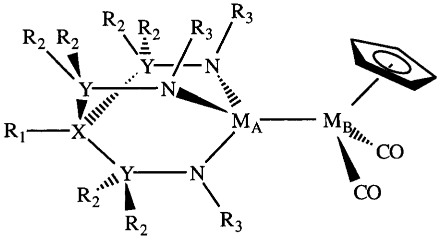
$(PhCH_2)_2M\{Co(CO)_4\}_2$

(M = Ti, Zr)

Fig. 7.

development of their chemistry. Gade and co-workers have overcome this obstacle by preparing an extensive series of compounds in which the three substituents on the Group 4 metal are replaced with a single tripodal (tridentate) triamide ligand. Molecules of the general formula (tripod)M_A–M_B(η^5-C_5H_5)$(CO)_2$ (M_A = Ti, Zr, Hf; M_B = Fe, Ru) (Fig. 8) and (tripod)Ti–$Co(CO)_3(L)$ (L = CO, PPh_3, P(p-tolyl)$_3$) (Fig. 9) were prepared via the reaction of (tripod)M_ABr with the anionic complexes [K][(η^5-C_5H_5)$M_B(CO)_2$] (M_B = Fe, Ru) and [Na][$Co(CO)_3(L)$], respectively. A variety of chelating tridentate ligands were employed, as shown in Figs. 8 and 9.

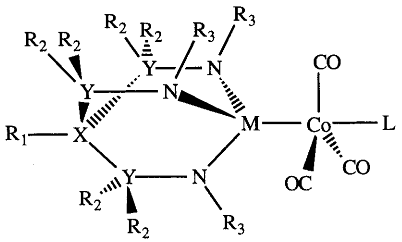
Trinuclear clusters of the type $CH_2(CH_2NSiMe_3)_2Zr\{M(CO)_n(L)\}_2$, in which a zirconium is bound to two metal carbonyl fragments, were prepared by the reaction



(tripod)M_A-M_B(η^5-C_5H_5)$(CO)_2$

M_A	M_B	X	Y	R_1	R_2	R_3	Ref.
Ti	Fe, Ru	C	C	Me	H	$SiMe_3$	29, 30
Ti	Fe, Ru	C	C	Ph	H	$SiMe_3$	30
Ti	Fe, Ru	C	Si	H	Me	4-CH_3-C_6H_4	29, 30
Zr	Fe	C	Si	H	Me	2-C_6H_4F	31
Ti, Zr, Hf	Fe, Ru	Si	Si	Me	Me	4-$C_6H_4CH_3$	32

Fig. 8.

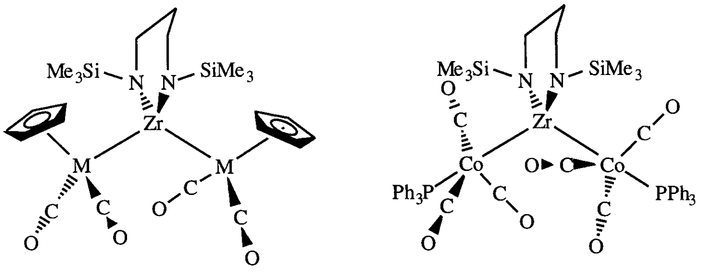


(tripod)Ti-Co(CO)3(L)

M	L	X	Y	R_1	R_2	R_3	Ref.
Ti	PPh_3, $PTol_3$	C	C	Me	H	$SiMe_3$	29, 30
Ti	PPh_3	C	C	Ph	H	$SiMe_3$	30
Ti	PPh_3, $PTol_3$	C	Si	H	Me	4-$C_6H_4CH_3$	29, 30
Ti, Zr	CO, PPh_3, $PTol_3$	Si	Si	Me	Me	4-$C_6H_4CH_3$	33

Fig. 9.

of $CH_2(CH_2NSiMe_3)_2ZrCl_2(L')_2$ (L′ = tetrahydrofuran, pyridine) with two equivalents of $[K][(\eta^5\text{-}C_5H_5)M(CO)_2]$ (M = Fe, Ru) or $[Na][Co(CO)_3(PPh_3)]$ [34] (Fig. 10). The 'half-sandwich' complexes $CH_2(CH_2NSiMe_3)_2(\eta^5\text{-}C_5H_5)Zr\text{–}M(CO)_n(L)$ (where $M(CO)_n(L) = Fe(CO)_2(\eta^5\text{-}C_5H_5)$, $Ru(CO)_2(\eta^5\text{-}C_5H_5)$, and $Co(CO)_3(PR_3)$) have also been synthesized by the same method [35] (Fig. 11). Although the latter compounds have a π-acid cyclopentadienyl ligand on zirconium, they provide a valuable intermediate standard of comparison between compounds containing (tripod)Zr entities and those having $(\eta^5\text{-}C_5H_5)_2Zr$ fragments. All of the compounds listed here,



$CH_2(CH_2NSiMe_3)_2Zr\{M(CO)_2(\eta^5\text{-}Cp)\}_2$ $CH_2(CH_2NSiMe_3)_2Zr\{Co(CO)_3(PPh_3)\}_2$

M = Fe, Ru

Fig. 10.

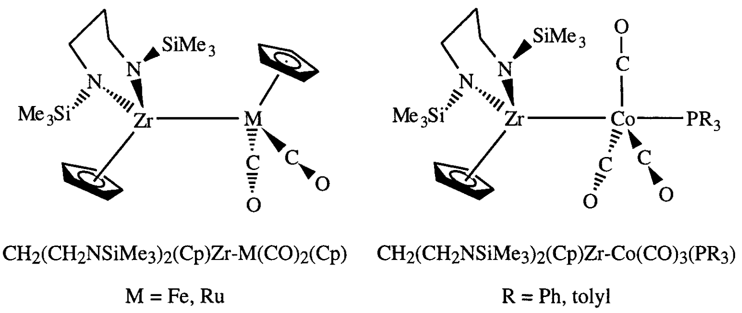
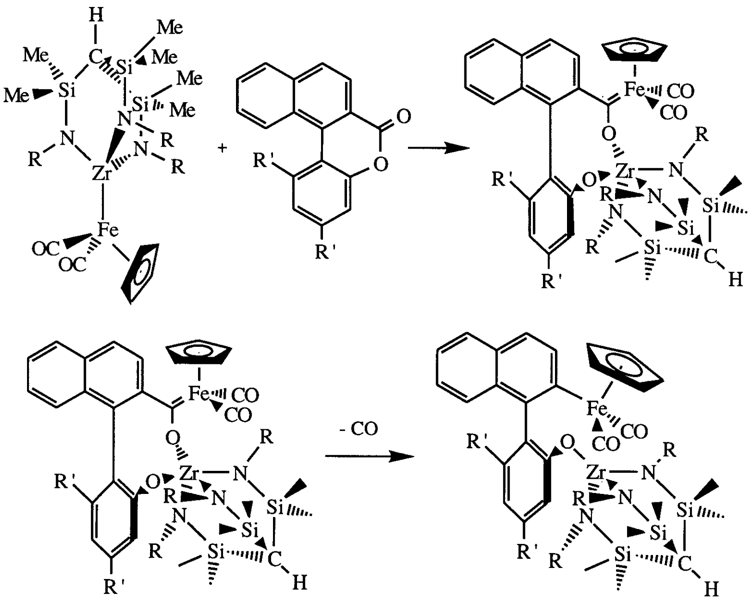


Fig. 11.

exhibit good thermal stabilities that have allowed crystallographic characterization of representative examples in the series as well as the completion of several reactivity studies (vide infra).

The metal–metal bond distances in the (tripod)M–M′(CO)$_n$(L) complexes are generally short and appear to be a diagnostic measurement for the degree of π-donation from the late transition metal to the Group 4 metal, with shortening of the bond and an accompanying shift of C–O stretching modes to higher frequency in the IR spectrum being indicative of increased π-donation. The stability afforded by the use of chelating tripod ligands appears to correlate with the metal–metal distance, as shown in a comparison of the Ti–Fe distance of 2.433 Å in $H_3CC(CH_2NSiMe_3)_3Ti–Fe(\eta^5-C_5H_5)(CO)_2$ [29] and the corresponding distance of 2.568 Å in $(Me_2N)_3Ti–Fe(\eta^5-C_5H_5)(CO)_2$ [23]. This order is also apparent for the ruthenium analogs of these compounds, which have Ti–Ru distances of 2.527 Å [27] and 2.663 Å [22], respectively. A comparison of the Zr–Fe bond distances for the 'half-sandwich' complex $CH_2(CH_2NSiMe_3)_2(\eta^5-C_5H_5)Zr–Fe(\eta^5-C_5H_5)(CO)_2$ (Zr–Fe = 2.745(1) Å) [35] and the tripod complex $MeSi\{SiMe_2N(C_6H_4Me\text{-}4)\}_3Zr–Fe(\eta^5-C_5H_5)(CO)_2$ (Zr–Fe = 2.605(2) Å) [32] as well as the Zr–Ru bond distances for $(\eta^5-C_5H_5)_2Zr\{Ru(\eta^5-C_5H_5)(CO)_2\}_2$ (average Zr–Ru = 2.943(1) Å) [36] and $CH_2(CH_2NSiMe_3)_2Zr\{Ru(\eta^5-C_5H_5)(CO)_2\}_2$ (average Zr–Ru = 2.7412(7) Å) [34] shows that replacement of π-acid cyclopentadienyl ligands on zirconium with amide substituents brings about a shortening of the metal–metal bond, and an increase in the C–O stretching frequencies in the IR spectra of the compounds is observed as well. A decrease of 0.08 Å in the Ti–Co distance results when the carbon monoxide trans to the metal–metal bond in $MeSi\{SiMe_2N(C_6H_4Me\text{-}4)\}_3Ti–Co(CO)_4$ is replaced by the more electron-donating P(p-tolyl)$_3$ ligand [33]. This substitution presumably enhances electron donation from cobalt to titanium, as trialkylphosphines are better σ-donors and worse π-acceptors than CO.

Reactivity studies for the (tripod)M–M′(CO)$_n$(L) complexes have revealed the heterogeneous character of the metal–metal bonds, and they have been characterized as 'masked electrophile–nucleophile pairs' [37]. Reactions of $HC\{SiMe_2N(2\text{-}C_6H_4F\text{-}2)\}_3Zr–Fe(\eta^5-C_5H_5)(CO)_2$ with biaryllactones result in the opening of the lactone ring and subsequent loss of the lactone carbonyl group as free carbon monoxide [38] (Fig. 12). Insertions of X = C = Y heteroallenes (where X = C = Y is

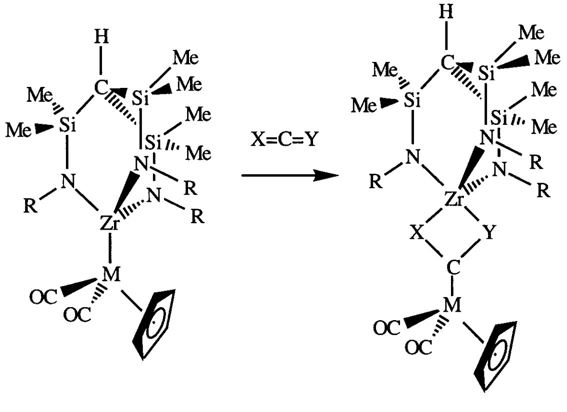


Reactions of HC{$SiMe_2N(2\text{-}C_6H_4F\text{-}2)$}$_3$Zr-Fe($\eta^5$-$C_5H_5$)$(CO)_2$ with biaryllactones

R = 2-C_6H_4F; R' = CH_3, OCH_3

Fig. 12.

CO_2, CS_2, OCNPh, SCNMe, or SCNPh) into the metal–metal bonds of HC{$SiMe_2N(2\text{-}C_6H_4F\text{-}2)$}$_3$Zr–M($\eta^5$-$C_5H_5$)$(CO)_2$ (M = Fe, Ru) give products in which the X and Y substituents are coordinated to zirconium and the carbon atom is attached to the iron or ruthenium [37] (Fig. 13). Methyl isocyanide reacts with



M = Fe, Ru; R = 2-C_6H_4F;

X=C=Y is CO_2, CS_2, OCNPh, SCNMe, or SCNPh

Fig. 13.

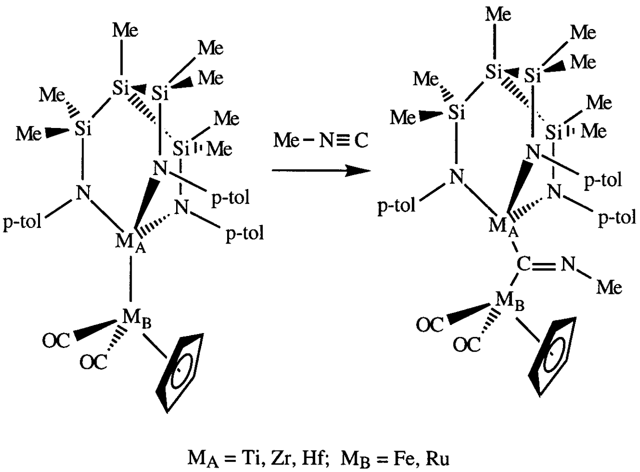
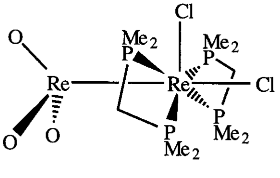


Fig. 14.

the series of compounds $MeSi\{SiMe_2N(C_6H_4Me\text{-}4)\}_3M\text{–}M'(\eta^5\text{-}C_5H_5)(CO)_2$ (M = Ti, Zr, Hf; M′ = Fe, Ru) to give the 1,1-insertion products in which both metal fragments are attached to the isocyanide carbon [32] (Fig. 14). Interestingly, methyl isocyanide will undergo a 1,1-insertion into one but not both of the metal–metal bonds in $CH_2(CH_2NSiMe_3)_2Zr\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2$ (M = Fe, Ru) [34]. For the ruthenium compound this results in an increase in the remaining Zr–Ru distance from an average of 2.7412(7)–2.8639(6) Å.

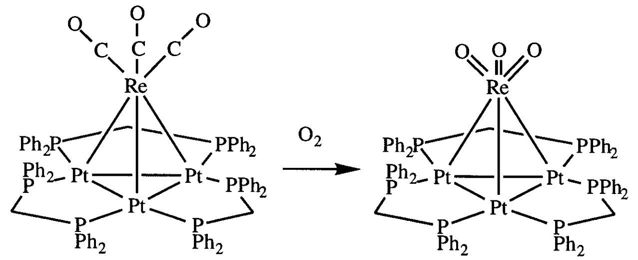
2.2. Metal oxides and imides

Several unusual metal clusters have recently been prepared in which a high-valent rhenium or molybdenum atom is attached to a low-valent transition metal that is bound to π-acceptor ligands. Ara, Fanwick, and Walton have reported that the reaction of *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ with $Me_2PCH_2PMe_2$ (dmpm) produces the dinuclear species $O_3ReReCl_2(dmpm)_2$, among other products, in which there is a four-coordinate tetrahedral ReO_3 fragment connected to a seven-coordinate pentagonal bipyramidal rhenium center that bears the chloride and dmpm ligands [39] (Fig. 15). The Re–Re distance in this compound is 2.4705(5) Å. It is stable to air



$O_3ReReCl_2(dmpm)_2$

Fig. 15.

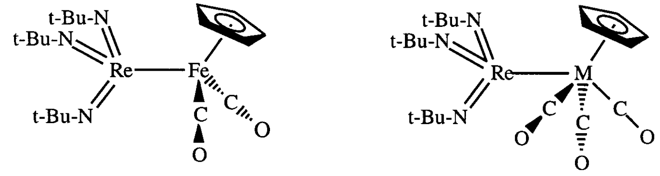


$\mathrm{Pt_3\{Re(CO)_3\}(\mu\text{-}dppm)_3^+ + O_2 \rightarrow Pt_3\{ReO_3\}(\mu\text{-}dppm)_3^+}$

Fig. 16.

and remains unchanged in chloroform solution for several weeks. A larger cluster in which an $\mathrm{ReO_3}$ unit is attached to all three metals of a triangular $\mathrm{Pt_3}$ framework has been synthesized by Puddephatt et al. via the reaction of the cationic cluster $\mathrm{Pt_3\{Re(CO)_3\}(\mu\text{-}dppm)_3^+}$ with $\mathrm{O_2}$ to give $\mathrm{Pt_3\{ReO_3\}(\mu\text{-}dppm)_3^+}$ [40] (Fig. 16). The Re–Pt distances in the parent carbonyl complex average 2.673 Å whereas the average of the Re–Pt distances in the trioxo cluster is 2.726 Å. The Pt–Pt distances remained unchanged.

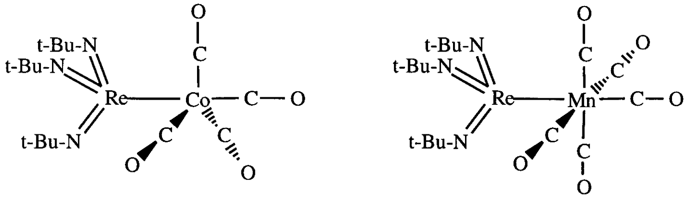
A wide range of compounds in which a metal imido complex is attached to metal carbonyl substituents has been synthesized and characterized by Sundermeyer, Runge, and Field [41]. These include the dinuclear rhenium compounds $\mathrm{(Me_3CN)_3Re\text{–}M(CO)_n(\eta^5\text{-}C_5H_5)}$ (M = Mo, W; $n = 3$ and M = Fe; $n = 2$) and $\mathrm{(Me_3CN)_3Re\text{–}M(CO)_n}$ (M = Co; $n = 4$ and M = Mn; $n = 5$) (Fig. 17) as well as the trinuclear molybdenum compounds $\mathrm{(Me_3CN)_2Mo\{M(CO)_n(\eta^5\text{-}C_5H_5)\}_2}$ (M = Mo,



$\mathrm{(Me_3CN)_3Re\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)}$

$\mathrm{(Me_3CN)_3Re\text{-}M(CO)_3(\eta^5\text{-}C_5H_5)}$

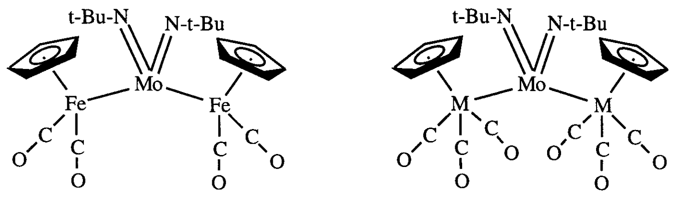
(M = Mo, W)



$\mathrm{(Me_3CN)_3Re\text{-}Co(CO)_4}$

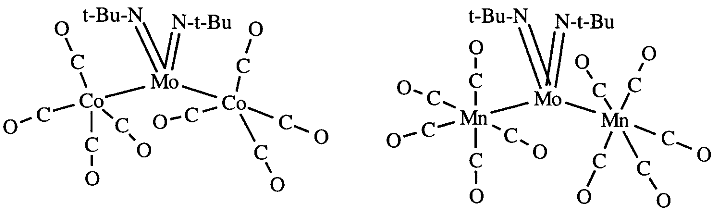
$\mathrm{(Me_3CN)_3Re\text{-}Mn(CO)_5}$

Fig. 17.



$(Me_3CN)_2Mo\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ $(Me_3CN)_2Mo\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2$

(M = Mo, W)



$(Me_3CN)_2Mo\{Co(CO)_4\}_2$ $(Me_3CN)_2Mo\{Mn(CO)_5\}_2$

Fig. 18.

W; $n = 3$ and M = Fe; $n = 2$) and $(Me_3CN)_2Mo\{M(CO)_n\}_2$ (M = Co; $n = 4$ and M = Mn; $n = 5$) (Fig. 18). The Re–Mo distance of 2.844(1) Å in $(Me_3CN)_3Re$–$Mo(CO)_3(\eta^5\text{-}C_5H_5)$ is significantly shorter than the corresponding distance of 3.12 Å in $(OC)_5Re$–$Mo(CO)_3(\eta^5\text{-}C_5H_5)$ [42].

3. Compounds in which the Type A metal has neutral ligands

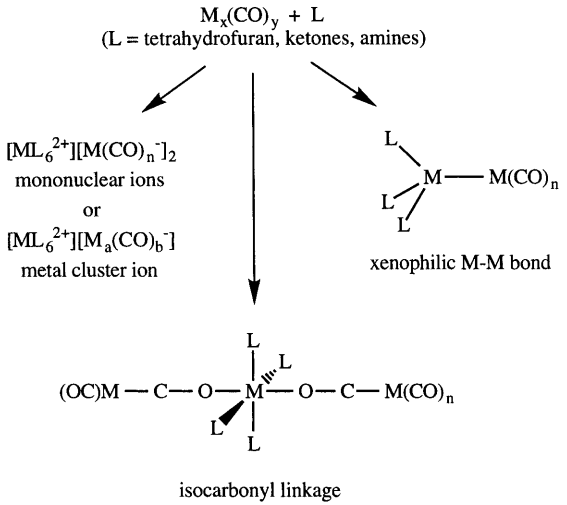
3.1. Disproportionation reactions of transition metal carbonyls

The chemistry of xenophilic transition metal clusters having neutral ligands on the Type A metal has its roots in the disproportionation reactions of neutral first-row transition metal carbonyls. Hieber's pioneering studies in this area [43] revealed that in the presence of strong σ-donor ligands and polar solvents these compounds often form separate ligand-coordinated metal cations and metal carbonylate anions. In some cases the metal cations are coordinated to oxygen atoms of carbonyl groups to form 'isocarbonyl' linkages between the two metals in the solid state. Only recently has it been found that a third possibility exists in which the cationic and anionic metal centers bond directly to each other to form xenophilic metal clusters (Scheme 1).

The neutral homoleptic carbonyl compounds of transition metals with odd atomic number tend to form mononuclear singly charged carbonylmetallate anions according to the general reaction shown below.

(3) $M_x(CO)_y + nL \rightarrow (x)\ [ML_n^{2+}][M(CO)_{y/x}^-]_2$

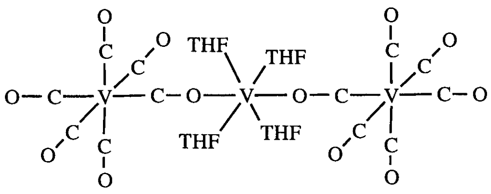
M = V, Mn, Co; L = tetrahydrofuran (THF), ketones, amines



Scheme 1.

For example, the interaction of $V(CO)_6$ with a wide range of ketones, ethers, esters, amines, nitriles, and amides is known to generate compounds of the general formula $[VL_n][V(CO)_6]_2$ in which n designates either four or six coordinating atoms [44]. In the latter case the compound is made up of separate ions. However, a single-crystal X-ray structure determination revealed that $[V(THF)_4][V(CO)_6]_2$ is an isocarbonyl complex. The central vanadium atom is coordinated to four tetrahydrofuran ligands in an equatorial plane and the two axial positions are occupied by the oxygen atoms of two $V(CO)_6$ moieties to form linear isocarbonyl bridges between the metals [45] (Fig. 19). Similarly, $Mn_2(CO)_{10}$ reacts with amines and other donor ligands to give $[MnL_6][Mn(CO)_5]_2$ (L = pyridine, THF, 1/2 ethylene diamine, etc.) [46]. Photolysis of $Mn_2(CO)_{10}$ in THF generates separate $Mn(THF)_6^{2+}$ and $Mn(CO)_5^-$ ions, as does the reaction between elemental manganese and $Mn_2(CO)_{10}$ [47]. $Co_2(CO)_8$ slowly disproportionates in polar coordinating solvents such as THF, pyridine, or methanol to give separate solvent-coordinated Co^{2+} cations and $Co(CO)_4^-$ anions [48].

Neutral homoleptic carbonyl compounds of transition metals with even atomic numbers react with hard Lewis base ligands to form the base-coordinated metal



$[V(THF)_4][V(CO)_6]_2$

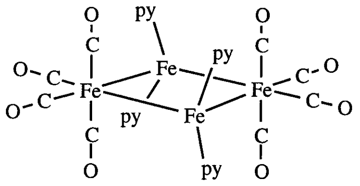
Fig. 19.

cation and an anionic metal carbonyl cluster. $Fe(CO)_5$ in refluxing pyridine forms $[Fe(py)_6][Fe_4(CO)_{13}]$ (py = pyridine) [49], while reactions of nickel tetracarbonyl with various amines generate a series of carbonyl cluster anions, eg. $Ni_2(CO)_6^{2-}$, $Ni_3(CO)_8^{2-}$, $Ni_4(CO)_9^{2-}$, and $Ni_5(CO)_9^{2-}$ [50,51].

The behavior of transition metal carbonyls in the presence of hard Lewis base donors such as ethers, amines, alcohols, ketones, or water is a topic of very broad relevance for the field of organometallic chemistry. Tetrahydrofuran is a ubiquitous solvent for metal carbonyls, and amines are commonly used as promoters in a range of stoichiometric and catalytic transformations. A range of transition metal carbonyls has been used to effect the homogeneous water gas shift reaction in which carbon monoxide and water are converted to carbon dioxide and hydrogen [52]. This process has been used to reduce organic nitro compounds to amines [53]. The reactions are typically carried out in tetrahydrofuran or alcohols and are promoted by bases such as hydroxide ion or trimethylamine. $Co_2(CO)_8$ is a catalyst for a number of important industrial processes that involve the addition of carbon monoxide and a second substrate to an olefin. One example is olefin carboalkoxylation, which involves the addition of carbon monoxide and an alcohol to an olefin to form an ester [54]. This reaction is promoted by the addition of pyridine. Similarly, hydrocarboxylation produces carboxylic acids by the reaction of carbon monoxide and water with olefins in aqueous dioxane [55], and the addition of CO and a secondary amine to an olefin generates amides [56]. The mechanistic features of these reactions have been a subject of great interest for the design of new processes and the optimization of current ones, and though much has been written concerning the role of metal carbonyl anions, the possible participation of transition metal cations formed by disproportionation of the metal carbonyls has only recently been examined.

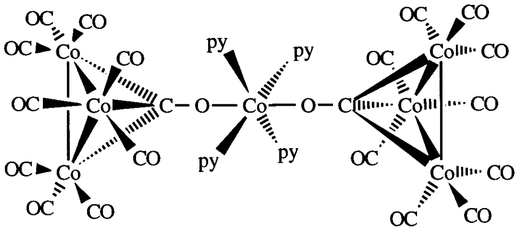
3.2. Metal pyridine complexes

Fachinetti and coworkers have closely examined the behavior of iron and cobalt carbonyls in the presence of pyridine, particularly with regard to the olefin carboalkoxylation reaction. This work led to the isolation of four intriguing species, $[(py)_2FeFe(CO)_4]_2$ [57,58], $[(OC)_4CoCo(py)_3][Co(CO)_4]$ [59], $[(\mu\text{-}OEt)(py)CoCo(CO)_4]_2$, and $(\mu\text{-}OEt)(\mu\text{-}O_2COEt)[(py)CoCo(CO)_4]_2$ (py = pyridine) [60], that have metal–metal bonds between atoms that are attached to carbonyl groups and atoms that are coordinated solely to pyridine or pyridine and ethoxy groups. Although all of the metals in these complexes are bound to ligands that can act as π-acids (CO or pyridine), their chemistry is closely related to that of xenophilic metal clusters. The compounds form cationic metal–pyridine centers and metal carbonyl anions in solution, and for this reason they were termed 'homonuclear ion pair (HNIP)' clusters [61]. $[(py)_2FeFe(CO)_4]_2$ (Fig. 20) was prepared by the reaction of $FeCl_2$ with $Na_2Fe(CO)_4$ in THF with a small excess of pyridine, and it was found to have a magnetic moment of 3.8 μ_B at r.t. [58]. The reaction of $Co_2(CO)_8$ with pyridine in hexane gave the isocarbonyl complex $\{Co_3(CO)_{10}\}_2$Co-



$[(py)_2FeFe(CO)_4]_2$ (py = pyridine)

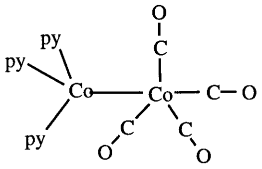
Fig. 20.



$\{Co_3(CO)_{10}\}_2Co(py)_4$ (py = pyridine)

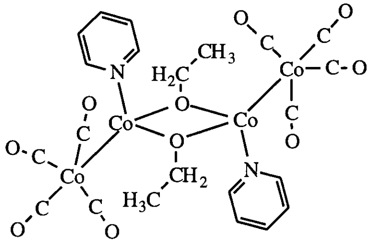
Fig. 21.

$(py)_4$ (Fig. 21), in which the central cobalt is coordinated to four pyridine molecules and two oxygen atoms of the triply bridging carbonyls in the two $Co_3(CO)_{10}$ moieties. Slow diffusion of hexane vapor into a toluene solution of this cluster gave $[(OC)_4CoCo(py)_3][Co(CO)_4]$ [59] (Fig. 22). The Co–Co distance of 2.490(2) Å in the $(OC)_4CoCo(py)_3^+$ cation is slightly shorter than the value of 2.52 Å in $Co_2(CO)_8$. A suspension of $Co(OEt)_2$ in tetrahydrofuran with a stoichiometric amount of $Co_2(CO)_8$ produced a green solution, and subsequent addition of a hexane–ether mixture followed by pyridine allowed the isolation of dark green crystals of $[(\mu\text{-}OEt)(py)CoCo(CO)_4]_2$ [60] (Fig. 23). This product reacted reversibly with one equivalent of carbon dioxide to give $(\mu\text{-}OEt)(\mu\text{-}O_2COEt)[(py)CoCo(CO)_4]_2$, in which the carbon dioxide molecule has inserted into the cobalt–oxygen bonds of one of the bridging ethoxy groups to give a bridging ethylcarbonate ligand (Fig. 24).



$(OC)_4CoCo(py)_3^+$ (py = pyridine)

Fig. 22.



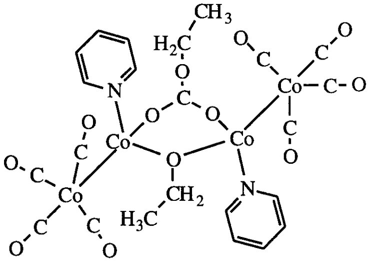
[(μ-OEt)(py)CoCo(CO)$_4$]$_2$

Fig. 23.

3.3. Metal tetrahydrofuran complexes

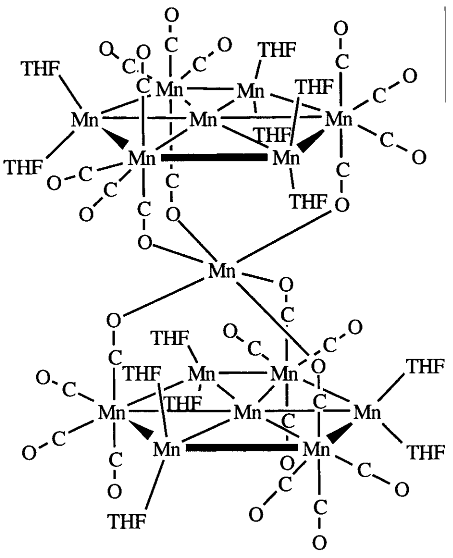
Kong et al. found that dimanganese decacarbonyl reacts with trimethylaluminum in a mixture of hexane and tetrahydrofuran to produce [Mn][Mn$_7$(THF)$_6$(CO)$_{12}$]$_2$, {μ-Mn(THF)$_2$}[Mn(CO)$_5$]$_2$, and [Mn(THF)$_6$][Mn(CO)$_5$]$_2$ [62]. The crystal structure of [Mn][Mn$_7$(THF)$_6$(CO)$_{12}$]$_2$ (Fig. 25) is made up of two Mn$_7$(THF)$_6$(CO)$_{12}^-$ anions, each of which is coordinated to an isolated Mn^{2+} cation via three carbonyl oxygens to give an octahedral coordination geometry about the cation. The framework of each Mn$_7$(THF)$_6$(CO)$_{12}^-$ anion consists of a ring of six manganese atoms, all of which are attached to a seventh manganese in the center of the ring to form a planar Mn$_7$ unit. The six-membered ring is made up of alternating Mn(CO)$_4$ and Mn(THF)$_2$ groups, and if metal–metal bonds to the central manganese are ignored, the former have approximate octahedral coordination while the latter have somewhat distorted tetrahedral geometries. The structure of {μ-Mn(THF)$_2$}[Mn(CO)$_5$]$_2$ consists of two Mn(CO)$_5$ groups connected by metal–metal bonds to a central Mn(THF)$_2$ unit (Fig. 26), and [Mn(THF)$_6$][Mn(CO)$_5$]$_2$ consists of isolated [Mn(THF)$_6$]$^{2+}$ and [Mn(CO)$_5$]$^-$ ions.

The mixed-metal cluster {μ-Mn(THF)$_2$}$_2$[Fe(CO)$_4$]$_2$ can be obtained from the reaction of [Mn][Mn$_7$(THF)$_6$(CO)$_{12}$]$_2$ with Fe(CO)$_5$ in tetrahydrofuran [17] and its structure consists of two Fe(CO)$_4$ fragments connected by two Mn(THF)$_2$ bridges (Fig. 27). An attempt to prepare this compound via the reaction of Na$_2$Fe(CO)$_4$



(μ-OEt)(μ-O$_2$COEt)[(py)CoCo(CO)$_4$]$_2$

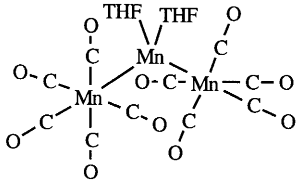
Fig. 24.



$[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (THF = tetrahydrofuran)

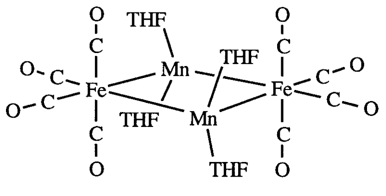
Fig. 25.

with $MnCl_2$ in tetrahydrofuran gave $[Na_2(THF)_5][\{\mu\text{-}Mn(THF)_2\}[Fe(CO)_4]_2]$, in which a single $Mn(THF)_2$ unit bridges two $Fe(CO)_4$ moieties [63] (Fig. 28). The sodium ions in this compound are coordinated to carbonyl oxygen atoms and additional THF molecules.



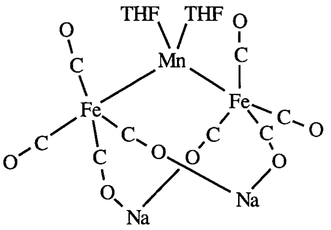
$\{\mu\text{-}Mn(THF)_2\}[Mn(CO)_5]_2$ (THF = tetrahydrofuran)

Fig. 26.



$\{\mu\text{-}Mn(THF)_2\}_2[Fe(CO)_4]_2$

Fig. 27.



$[Na_2(THF)_5][\{\mu\text{-}Mn(THF)_2\}[Fe(CO)_4]_2]$

Fig. 28.

All of these compounds exhibit uncharacteristically short metal–metal distances relative to analogous metal carbonyl clusters. The six $Mn(CO)_4$–$Mn(THF)_2$ metal–metal distances in $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ range between 2.698 and 2.740 Å, with an average length of 2.722(4) Å, and the Mn–Mn contacts in $\{\mu\text{-}Mn(THF)_2\}[Mn(CO)_5]_2$ average 2.732(2) Å [62]. The distances from the hexagonal planar central metal atom of the Mn_7 moiety in $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ to the three $Mn(CO)_4$ metals average 2.651(4) Å, and the average distance to the three $Mn(THF)_2$ metals is 2.785(4) Å. Although these numbers are within the range of distances for normal covalent Mn–Mn bonds [64], they are among the shortest distances yet observed and are considerably less than the more typical Mn–Mn distances of 2.923 Å observed for $Mn_2(CO)_{10}$ [65] and 2.883 Å for $[Ph_4As][Mn_3(CO)_{14}]$ [66]. Likewise, the average Fe–Mn distances of 2.617 Å in $\{\mu\text{-}Mn(THF)_2\}_2[Fe(CO)_4]_2$ [17] and 2.642 Å in $[Na_2(THF)_5][\{\mu\text{-}Mn(THF)_2\}[Fe(CO)_4]_2]$ [63] are substantially shorter than the average values of 2.813 Å found in $FeMn_2(CO)_{14}$ [67] and 2.841 Å in $(\eta^5\text{-}C_5H_5)(OC)_2FeMn(CO)_5$ [68].

The most remarkable feature of these clusters is their paramagnetism. In contrast to the diamagnetic behavior of the great majority of molecules containing metal–metal bonds, $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ has a r.t. molar magnetic susceptibility that in a very simplified spin-only model would be indicative of 13 unpaired electrons per formula unit [69]. The value of 5.0(1) BM for the effective magnetic moment (μ_{eff}) of $\{\mu\text{-}Mn(THF)_2\}_2[Fe(CO)_4]_2$ is in good agreement with the theoretical spin-only value of 4.9 BM for four unpaired electrons per molecule [17]. Ab initio quantum mechanical calculations have been performed in order to examine the metal–metal interactions and magnetic behavior of these species [70]. These studies suggest that the unpaired electrons are almost exclusively localized on the ‘Type A’ manganese atoms attached to THF ligands in both $\{\mu\text{-}Mn(THF)_2\}[Mn(CO)_5]_2$ and $\{\mu\text{-}Mn(THF)_2\}_2[Fe(CO)_4]_2$.

Examination of the carbonyl stretching region of the IR spectrum of $\{\mu\text{-}Mn(THF)_2\}_2Fe_2(CO)_8$ in THF solution indicates that there is substantial polar character to the Mn–Fe interaction. The relatively low frequency absorptions of 1964(s), 1898(s), 1869(s) cm^{-1} are in the region associated with electron-rich anionic species such as $Na_2Fe_2(CO)_8$ (ν_{CO}, *N*,*N*-dimethylformamide solution: 1916(m), 1866(s), 1842(w) cm^{-1}) [71], and they are approximately midway between $Na_2Fe(CO)_4$ (ν_{CO}, *N*,*N*-dimethylformamide solution: 1730 cm^{-1}) [71] and a neutral metal carbonyl such as $FeMn_2(CO)_{14}$ (ν_{CO}, hexane solution: 2067(s), 2019(s), 1987(w) cm^{-1}) [67].

4. Conclusions

Xenophilic transition metal clusters are currently few in number, and therefore any general conclusions concerning the metal–metal interactions should be made with caution. However, a few salient features have emerged. For the series of compounds in which a Group 4 metal with alkyl, amido, or alkoxide groups is attached to a $(\eta^5\text{-}C_5H_5)M(CO)_n$ or a $Co(CO)_3(L)$ fragment, there is general agreement that there is some degree of π-donation from the Type B metal carbonyl fragments to the Type A metal centers [16,30,32,33]. This stands in contrast to the primarily σ-donor/acceptor bonds between transition metals and main group metals [33]. The primary diagnostic tools for examining the degree of π-donation in these compounds have been the values of the carbonyl stretching frequencies in the IR spectra and the metal–metal distances obtained from crystal structure determinations. In comparing similar compounds, a shift to higher frequencies for the C–O stretching modes and a shortening of the metal–metal bond, has been interpreted to mean greater π-donation from the metal carbonyl center to the Type A metal, and hence more covalent character (less ionic character) and less polarity to the metal–metal bond. Increased π-donation to the Type A metal can be achieved by increasing the electron-withdrawing ability of its substituents ($R = (CF_3)_2CH$ and Ph vs. $R = Me_3C$ and Me_2CH in $(RO)_3Ti–Co(CO)_4$, Ref. [25]) or by increasing the electron-donating ability of ligands on the Type B metal–carbonyl fragment ($L = PR_3$ vs. $L = CO$ in $MeSi\{SiMe_2N(C_6H_4Me\text{-}4)\}_3Ti–Co(CO)_3L$, Ref. [33]). For this particular set of compounds, the direction of the electron-donation appears to be governed more by the formal oxidation states of the metals (donation from low-valent metal to high-valent metal) rather than the electron-donating ability of the ligands (donation from the metal with good σ-donor ligands to the metal with π-acid ligands).

Both metal centers are in low formal oxidation states in clusters that have neutral rather than anionic donor ligands on the Type A metal. There are some indications that the direction of electron donation may be reversed in these compounds, and proceeds from the metal with σ-donor ligands to the metal with π-acid ligands. The Fe–Mn bonds in $\{\mu\text{-}Mn(THF)_2\}_2Fe_2(CO)_8$ [17] are shorter but the carbonyl stretching frequencies are lower than the corresponding values for $FeMn_2(CO)_{14}$ [67], in which all of the metals are bound to carbonyl groups. Similar differences are observed in comparisons of other neutral xenophilic clusters of this type with related carbonyl clusters [57,58,60,62], and most of the neutral xenophilic clusters have CO absorptions in the region typically associated with metal carbonyl anions [17]. Unfortunately, a closely related series of compounds in which ligands on both metals are systematically varied is not yet available to provide a clearer indication of the nature of the metal–metal interaction in this set of clusters.

The kinetic stability of the metal–metal bond in the Group IV–Group VIII metal compounds can be enhanced by the use of sterically demanding substituents on the Group IV metal. For the series of compounds $(RO)_3Ti–Co(CO)_4$ ($R = Me_3C–$, $Me_2CH–$, $(CF_3)_2CH–$, Ph) [25], the tertiary-butoxide complex is the only one that does not decompose in solution at 25°C. Compounds in which titanium is bound to a tripod triamide ligand bearing bulky trimethylsilyl or phenyl groups on the nitrogen atoms [29–33] are substantially more stable than analogous compounds that have dimethylamido substituents in place of the tripod [23]. The tripod ligand also lends thermodynamic stability to the Ti–Co bond in $MeSi\{SiMe_2N(C_6H_4Me\text{-}4)\}_3Ti–Co(CO)_4$ [33]. Electronic effects appear to play a role in the greater stability of $(Me_2N)_3Ti–Ru(\eta^5\text{-}C_5H_5)(CO)_2$ [22] relative to $(Me_2N)_3Ti–Fe(\eta^5\text{-}C_5H_5)(CO)_2$ [23], although with only a few representative compounds known it is difficult to say whether this represents a trend towards greater thermodynamic stability for compounds with second or third row transition metals relative to first row metals. Indeed, Gade and co-workers found that Ti acted as the best π-acceptor for the series $MeSi\{SiMe_2N(C_6H_4Me)\}_3M_A–M_B(\eta^5\text{-}C_5H_5)(CO)_2$ where $M_A = Ti$, Zr, Hf and $M_B = Fe$, Ru [32].

The study of xenophilic transition metal clusters is still in its infancy. A great many possible combinations of metals and ligands have yet to be examined, and though there are some early indications as to the nature of the metal–metal interactions in these compounds, many unanswered questions remain.

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