Journal of Organometallic Chemistry, 94 (1975) 259—271
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

BASICITY AND REACTIVITY OF METAL CARBONYLS*

D.F. SHRIVER
Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

Metal carbonyls are for the most part low oxidation state species which are susceptible to attack by electron seeking reagents. Therefore, a significant fraction of the chemistry of metal carbonyls and metal carbonyl derivatives involves their reaction with Lewis acids and nucleophiles, and many important synthetic reactions are of this type. This chemistry gives a unique character to metal carbonyls and similar organometallics, because Werner-type complexes are more resistant to attack by electron seeking reagents owing to the positive oxidation state of the central metal. As shown in equation 1, there are several simple types of reactions which a metal complex, ML_n, may undergo with a Lewis acid. Each of these is discussed here, but the description is brief for metal basicity and for ligand abstraction, because the former is reviewed extensively elsewhere, and the latter area is relatively limited. Greater detail is given for the formation of CO ligand bridged adducts, a recently discovered area which is yielding interesting results.

$$ML_n \left\{ \begin{array}{l} \xrightarrow{A} A{-}ML_n \text{ (metal base—Lewis Acid adduct formation)} \\ \xrightarrow{A} ML_{n-1} + AL \text{ (ligand abstraction)} \\ \longrightarrow L_{n-1}M{-}L{-}A \text{ (ligand bridged adduct formation)} \end{array} \right. \qquad (1)$$

Metal basicity

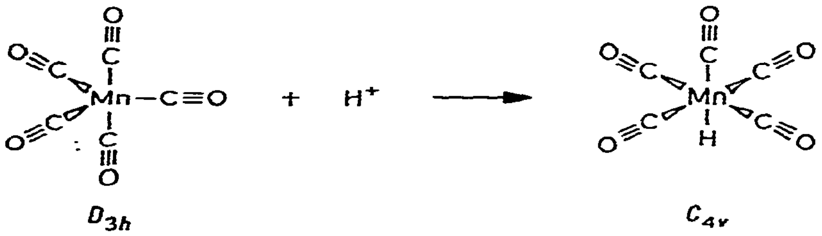
Metal basicity was first clearly demonstrated by Professor Hieber and his students, who showed that metal carbonyls are capable of undergoing reversible protonation [1]. This discovery opened an area in synthetic organometallic chemistry in which the basic and nucleophilic character of carbonyl anions and similar species has been widely exploited [2]. Furthermore, the concept of metal basicity is useful in systematizing many reactions of low oxidation state transition metal complexes [3,4]. For example, the fundamental ideas of acid—base chemistry may be applied, namely an order of basicity can be established with one reference acid which may be used to predict the order of interaction

---

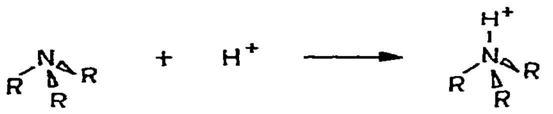
* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

with other acids. There are however some interesting ways in which transition metal and Main Group bases differ, and it is these differences which form the main topic of this section. As will be described in more detail in this section, the unique character of metal bases can be attributed to the difference in symmetry between *d*-orbitals of transition metal bases, and the sp^n hybrid orbitals of Main Group bases.

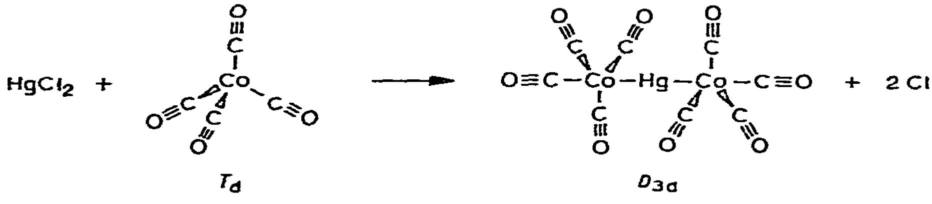
The large structural reorganization which is found when most transition metal bases interact with an acceptor forms a striking contrast with the small structural reorganization found with most Main Group bases. For example, the reaction between manganese pentacarbonyl anion and the proton leads to a rearrangement of $Mn(CO)_5$ from trigonal bipyramidal to square pyramidal (eqn. 2) but in the reaction of a trialkylamine with the proton (eqn. 3), the pyramidal arrangement of the NR_3 group is retained. Extensive structural reorganization also is observed upon the interaction of metal carbonyl anions with heavy metal acceptors (eqn. 4). The apparent difference between many transition metal and Main Group bases is that lone electron pairs on the transition metal center occupy multi-lobed *d*-orbitals which accommodate to highly symmetric geometrics. For example, the standard electron count of 18 electrons for $Co(CO)_4^-$ includes 8 electrons involved in σ bonding between the metal and ligands and the remaining 10 electrons in an π-orbital set which conforms to tetrahedral symmetry. Similarily, for $Fe(CO)_5^{2-}$ and $Mn(CO)_5^-$ there are 10 σ-bonding electrons and the remaining 8 in a "π set" which conforms to D_{3h} symmetry. An adduct of lower symmetry is formed when some of the electrons in the highly symmetric "π set" interact with an acceptor. By contrast, Main Group bases typically do not display the highest symmetry consistent with the



(2)



(3)

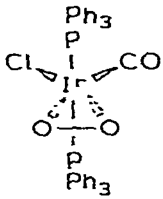


(4)

connectivity of the central atom, thus water is bent, not linear, and ammonia is trigonal pyramidal, not trigonal planar. This observation is incorporated in the highly successful valence shell electron pair repulsion model of chemical bonding by the provision that a non-bonding electron pair appears to occupy a coordination site around a central Main Group atom. Upon donation to an acceptor this stereochemically active lone pair becomes a stereochemically active bonding pair without gross distortion of the base moiety.

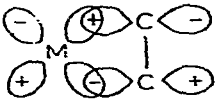
Exceptions to the generalization that transition metal bases undergo large structural reorganization when they interact with an acceptor are found when bulky ligands are present. For example, the structures of $HRh(PPh_3)_4$ [5] and of $HCo(PF_3)_4$ [6] contain a tetrahedral array of phosphorus atoms around the central metal, and the hydrogen does not occupy a full coordination site.

Another contrast with the Main Group bases is the higher propensity which the transition metals have for interaction with π-acids. One example of this type of interaction is the oxygen adduct of $IrCOCl(PPh_3)_2$, where structural and spectroscopic indications are that the predominant mode of bonding involves a transfer of electron density from the metal to O_2 (I).

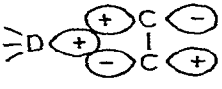


(I)

Other examples of the interaction of metals with π-acids are found with the π-acceptors tetracyanoethylene and tetrafluoroethylene. Main Group bases generally do not form strong adducts with π-acids. One possible reason for this difference is that the multi-lobed d-orbitals overlap more effectively with the π^* orbitals of the π-acids than do the effectively monodirectional orbitals occupied by the lone pairs of the Main Group bases. In the Dewar—Chatt model for the side-on interaction of an olefin with a metal, the metal donor d-orbitals efficiently overlap with ligand π^* orbitals (II). This type of interaction dominates the bonding when a strong π acceptor interacts with a low oxidation state metal atom. A similar π-type bonding is not possible with typical Main Group bases (III).



(II)

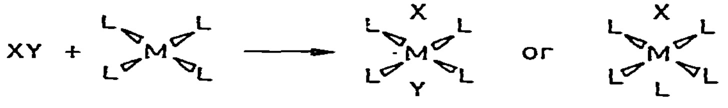


(III)

Yet another difference is found for the trends in basicity within a Group of the Periodic Table. For Main Group bases there is a large decrease in basicity toward hard acceptors from a second period donor atom to a third period donor, and a more gradual decrease upon progressing to heavier members of the group.

With transition metal bases it is more difficult to discern consistent trends, however, there are several instances in which basicity increases from the lighter to the heavier members of a Group. In this connection the increasing "soft" character for heavier Main Group bases does not appear to hold for transition metal bases. Indeed, the whole concept of hard and soft bases, which is so useful in systematizing Main Group bases, does not seem to work for transition metals. A good case in point is the affinity of metal centers for the hard H^+ and the soft O_2 acids.

One important class of reactions, which for the most part lies outside the scope of this review, is oxidative addition. In this type of reaction a molecule XY adds to a metal, M, in the manner illustrated in reaction 5. Frequently X and Y have very different electronegativities and in these cases the product may be viewed as being derived from the addition of an acceptor X^+ and a donor Y^-. If X^+ has a much higher affinity for the metal than does Y^-, the reaction will be dominated by metal—base interaction with the acceptor, X^+. Some good examples of domination of the acceptor interaction involve the reactions of methyl fluorosulfate, CH_3OSO_2F, and methyl trifluoromethylsulfonate, $CH_3OSO_2CF_3$, with low oxidation state metal complexes. In these cases the acceptor, CH_3^+, is firmly held, but the donor SO_3F^- is weakly held, as shown by its dissociation in polar organic solvents (eqn. 6). The facile dissociation of this complex makes it a useful synthetic intermediate (eqn. 7) [10]. For the majority of X groups shown, the direct oxidative addition of CH_3X either does not occur or is unhandy.



(5)

$$CH_3OSO_2F + IrCl(CO)L_2 \rightarrow CH_3IrCl(CO)L_2 + SO_3F^- \qquad (6)$$

$\Lambda = 71$ ohm^{-1} cm^2 mol^{-1} (nitromethane)

$$CH_3IrCl(CO)L_2SO_3F + X^- \rightarrow CH_3IrCl(CO)L_2X + SO_3F^- \qquad (7)$$

($X = F$, Cl, Br, I, NCS, N_3, NO_2, NO_3, CH_3COO, $S_2O_2C_7H_7$, 1/2[$Pt(CN)_4$] and $C(CN)_3$)

Methyl fluorosulfate and related strong carbocation reagents have other properties which make them useful for organometallic syntheses [7-10].

Ligand abstraction

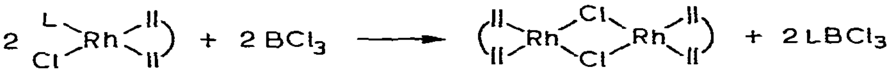
Sufficiently strong Lewis acids may abstract a ligand from a metal complex. This simple type of reaction has synthetic and catalytic applications. Excellent synthetic examples in carbonyl chemistry come from the work of Fischer and Hieber, shown in reactions 8 to 10 [11-13]. In each of these, an acid abstracts a halide from the coordination sphere of a metal carbonyl halide, thus opening a coordination site for the attachment of a carbon monoxide or olefin ligand. The success of these syntheses hinges on the negligible affinity of the Lewis acid for the olefin or the carbon monoxide, coupled with its high affinity for the halide ligand. Reaction 11 illustrates the abstraction of a phosphine, L, rather than a halide, by the acid and it also shows that in the absence of an added ligand the complex may fill its coordination sphere by halide-bridged dimer formation [14].

$$Mn(CO)_5Cl + AlCl_3 + CO \rightarrow [Mn(CO)_6][AlCl_4] \quad (8)$$

$$Re(CO)_5Cl + AlCl_3 + CO \rightarrow [Re(CO)_6][AlCl_4] \quad (9)$$

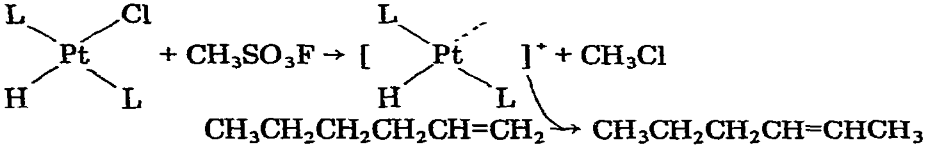
$$(C_5H_5)Fe(CO)_2Br + AlBr_3 + C_2H_4 \rightarrow [(C_5H_5)Fe(CO)_2(C_2H_2)[AlBr_4] \quad (10)$$

The synthetic applications of ligand abstraction in carbonyl chemistry have been primarily confined to the introduction of olefins and carbon monoxide, but the principle should be extendable to other poor σ donor ligands, such as N_2 and phosphorous trihalides.



(11)

One potential application of the ligand abstraction reaction, which has been little explored, is in the promotion of catalytic reactions. The reason for expecting this type of catalytic promotion lies in the observation that the great bulk of homogenous catalyzed reactions of olefins appear to require the presence of a coordinatively unsaturated metal complex species, which is produced by an initial ligand dissociation step. Introduction of a Lewis acid into the system might promote this dissociation by coordination of the free ligand. Clear evidence is lacking for the promotion of catalyzed olefin reactions by this mechanism. However, there are several types of catalytic systems where ligand abstraction may be involved, one of which is the catalysis of olefin methathesis reactions. In olefin metathesis a Main Group Lewis acid frequently is employed in conjunction with a transition metal catalyst [15]. Lewis acid promotion of this type may also be responsible for the increased effectiveness of $RhCl(CO)L_2$ as a hydrogenation catalyst when $AlCl_3$ is present [16]. Finally, Eaborn and coworkers postulated that ligand abstraction is responsible for the increased rate of olefin isomerization when CH_3OSO_2F is added to a olefin—$PtHClL_2$ system [17]. The proposed mechanism involves Cl abstraction by CH_3SO_3F as an initial step, reaction 12.

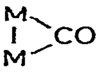


(12)

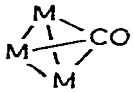
More detailed mechanistic evidence for the role played by the Lewis acid as a catalytic promotor is highly desirable, because Lewis acids may enter into the reaction in a variety of ways. Recent studies have shown that some Lewis acids block the catalytic hydrogenation of olefins owing to coordination of the Lewis acid directly to the metal. In other systems rate enhancement is observed, but ligand abstraction is not involved [18].

Ligand basicity

Ligand bridges between metal atoms play a major role in inorganic chemistry. From the standpoint of mechanisms, ligand bridges are important in both redox and substitution reactions. In addition, many structural features are influenced by ligand bridges. It is not stretching the point too far to classify binary metal halides and oxides having infinite structures as examples of ligand bridged compounds. Carbon monoxide displays great variety in its role as a bridging ligand. The structure of simple two-metal carbonyl bridges (IV) was first elucidated by Powell and Ewens in their classic structure determination of $Fe_2(CO)_9$ [19]. The less common three-metal carbonyl bridge (V) was structurally characterized by Hock and Mills [20], in a compound, $(C_5H_5)_3Ni_3(CO)_2$, which was first synthesized by Fischer and Palm.



(IV)



(V)

As discussed at this conference, transient bridging carbonyl groups of type IV also are implicated in the mechanism for CO scrambling in certain polynuclear carbonyls. In 1969 a new type of CO bridge was reported which involves bonding at both carbon and oxygen. These are formed via the interaction of Lewis acids with the basic carbonyl oxygens in metal carbonyls.

The study of C- and O-bonded carbonyls is greatly aided by the availability of simple diagnostic features in the infrared and Raman spectra. Of particular importance is the observation that the CO stretching frequency is lowered for the carbonyl group involved in C- and O-bonding. A good illustration of this phenomenon is afforded by infrared spectra for the $[(C_5H_5)Fe(CO)_2]_2$—AlR_3 system, Fig. 1 [22]. The parent carbonyl displays two CO stretching frequencies in the 2000 cm^{-1} region which are characteristic of the symmetric and asymmetric stretching frequencies of the two terminal carbonyls*. Only one intense infrared feature is observed in the bridging region, ca. 1800 cm^{-1}, of the uncomplexed parent. This one band is attributed to the asymmetric stretch of the two bridging carbonyls. (The symmetric stretch is very weak owing to the nearly centrosymmetric disposition of the bridging carbonyls.) Addition of a Lewis acid leads to a new infrared band at much lower frequency, ca. 1700 cm^{-1}. For the 1/1 adduct with AlR_3 (Fig. 1) this low frequency stretch, which is attributed to $\geq$CO—AlR_3, is accompanied by another higher-frequency feature, above 1800 cm^{-1}, attributed to the stretch of the bridging $\geq$CO to which the aluminum alkyl is not attached. In other words, the 1/1 adduct no longer possesses a virtual center of symmetry between the bridging carbonyls and therefore displays two carbonyl frequencies, one of which occurs at a greatly reduced frequency owing to the perturbing influence of the attached AlR_3. Upon formation of the 1/2 adduct only a single low-frequency bridging carbonyl stretch is observed, because the virtual center of symmetry is restored with the addition of

---

* A more detailed discussion of the infrared spectrum of $[(C_5H_5)Fe(CO)_2]_2$ is given in ref. 21.

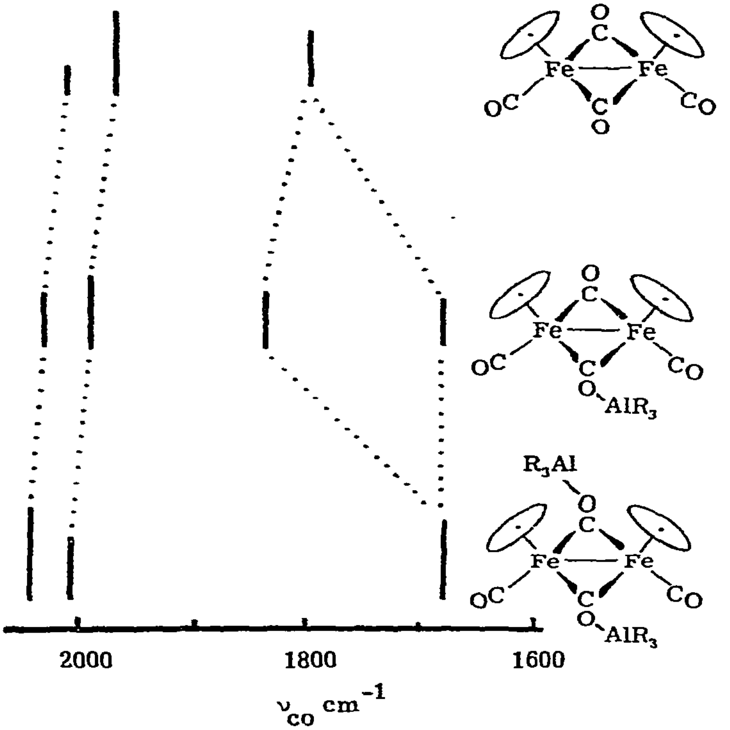


Fig. 1. Infrared CO stretching frequencies for $[(C_5H_5)Fe(CO)_2]_2$, $[(C_5H_5)Fe(CO)_2]_2\cdot AlR_3$ and $[(C_5H_5)Fe(CO)_2]_2\cdot 2\ AlR_3$.

aluminum alkyl to the second bridging carbonyl. In this sequence of solution infrared spectra the first and third can be directly compared with solid state spectra of $[(C_5H_5)Fe(CO)]_2$ and $[(C_5H_5)Fe(COAlR_3)_2]_2$ respectively, which have been characterized by X-ray crystal structure determination. The concentration dependence of the infrared spectra leaves no doubt that the intermediate species is a 1/1 adduct. From these results, plus extensive vibrational data on other adducts, several of which have been characterized by X-ray structure determination, the loweing of ν(CO) upon adduct formation is established as a highly reliable diagnostic feature.

Two other changes are evident in the vibrational spectra of C- and O-bonded carbonyls: (1). ν(CO) is slightly increased for carbonyls not involved in the —CO— bridge. (This feature is evident for both terminal and bridging stretch modes in Fig. 1.) (2). The symmetric metal—metal stretching frequency, which often may be observed in a properly conducted Raman experiment, is only slightly shifted upon adduct formation with a bridging carbonyl. The latter feature is shown in Fig. 2, where a small increase in M—M stretching frequency accompanies adduct formation. This situation contrasts with our observations for M—M protonation, where a frequency reduction is observed.

In a previous example the bridging carbonyl groups are more basic than terminal carbonyls. This turns out to be a general feature of polynuclear carbonyls [22,23]. Other factors being equal, the order of basicity of carbonyl groups is terminal < two-metal bridge < three-metal bridge [22]. This trend and the paral-

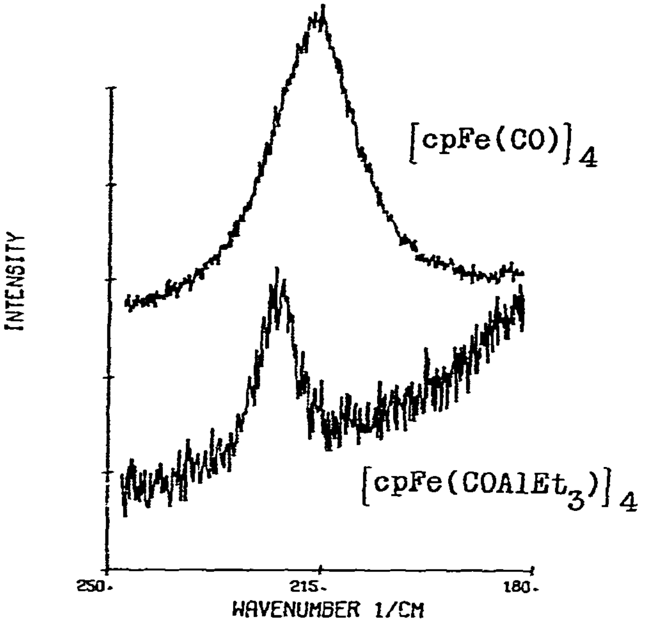
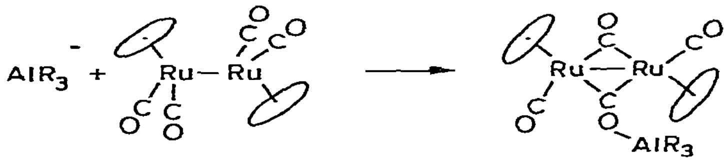


Fig. 2. Raman spectra of $[(C_5H_5)Fe(CO)]_4$, and $[(C_5H_5)Fe(COAlR_3)]_4$ showing the symmetric metal—metal stretching mode.

lel order of decreasing ν(CO), both reflect the greater electron acceptor character of a triple metal bridge toward the metal framework than for a double metal bridge, and the least efficient back acceptor character of a terminal CO toward a metal.

The increased basicity of bridging carbonyls can serve as a driving force for the rearrangement of CO ligands in a polynuclear carbonyl. The first example of this phenomenon was observed for $[(C_5H_5)Ru(CO)_2]_2$ in the presence of aluminum alkyls (eqn. 13) [22]. In the absence of a Lewis acid the ruthenium exists as an approximately 50/50 mixture of CO bridged and non-bridged forms in hydrocarbon solution at room temperature [24].



(13)

Introduction of aluminum alkyl into the solution drives the equilibrium completely to the bridged form, with AlR_3 coordinated to the bridging carbonyls [22]. A more striking example of terminal-to-bridge CO interchange occurs with $Ru_3(CO)_{12}$, which is known from X-ray and solution infrared data to exist exclusively in a non-bridged structure [25]. There is however NMR evidence, discussed elsewhere in this conference, that the carbonyls in this compound are rapidly interchanging on the NMR time scale, and a logical mechanism for this interchange involves CO bridged intermediates or transition states. In line with the NMR evidence that the bridging carbonyl is not too energetically disfavored in $Ru_3(CO)_{12}$, we have found that $AlBr_3$ will form an adduct in which a bridging carbonyl structure has been induced [23]. It should not be concluded that the terminal-to-bridge transformation can invariably be induced by a Lewis acid. For example, we have repeatedly tried to induce bridging in $Mn_2(CO)_{10}$, so far without success.

Given the propensity of Lewis acids to induce the shift of a CO from a terminal to a two-metal bridge position it is natural to ask if a three-metal bridge might be similarly induced. So far such a transformation has not been carried to completion, but a compound has been prepared in which a three-metal semibridge is formed. The chemistry involves the reaction of $HFe_3(CO)_{11}^-$, a compound first isolated and characterized in Professor Hieber's laboratory [26], with CH_3OSO_2F. The resulting volatile red solid was identified by a variety of chemical and spectroscopic methods as $HFe_3(CO)_{10}(COCH_3)$, which has the structure displayed in Fig. 3 [27]. One interesting feature of this structure is the attachment of CH_3^+ to the oxygen of the bridging carbonyl. This result is both surprising and reasonable.

It is surprising because alkylating agents generally have a strong affinity for metal centers, and have never previously been observed to attach to metal carbonyl oxygens in this fashion. However, given the fact that an $Fe—CH_3$ bond was not formed, attachement of CH_3^+ to the bridging carbonyl does have precedent in the known basicity of bridging carbonyls.

There are significant structural differences between $HFe_3(CO)_{10}(COCH_3)$ and its precursor, $HFe(CO)_{11}^-$. Of particular interest is the great decrease in the

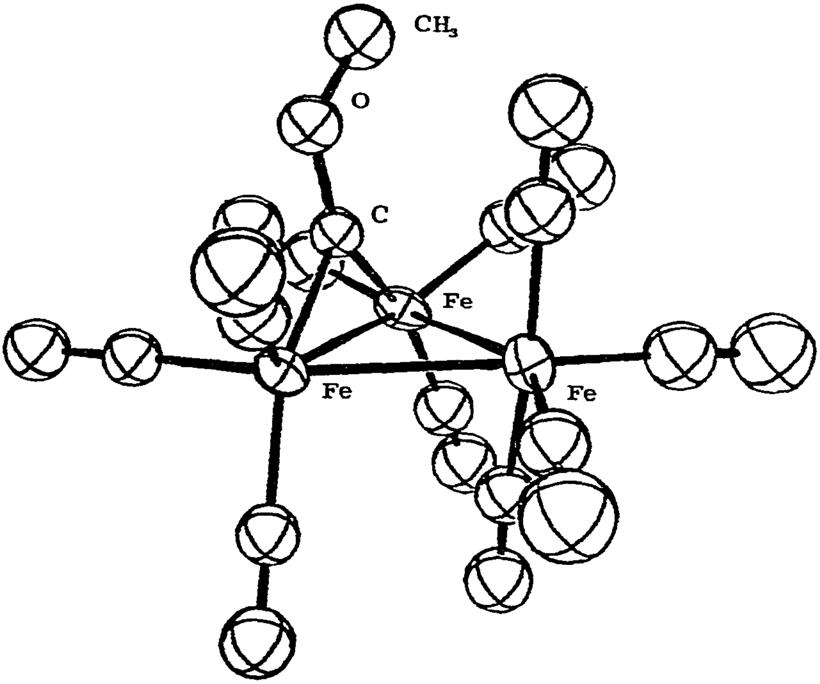
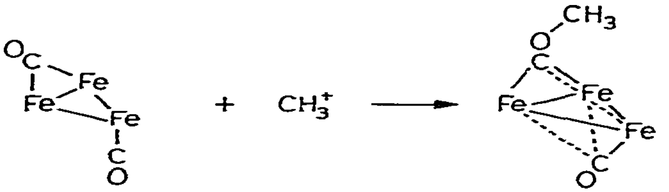


Fig. 3. The structure of $HFe_3(CO)_{10}(COCH_3)$ [23].

distance between the unique iron and the carbon atom of the bridging carbonyl, from 3.00 Å in the parent anion to 2.70 Å in the methyl derivative. This 0.3 Å shortening is accompanied by a large decrease in the dihedral angle between the iron triangle and the triangle formed by the carbon of the bridging carbonyl and its two nearest neighboring iron atoms. These structural changes are interpreted as the shift of CO from a double-metal bridge to a triple-metal semi-bridge*. The shift, which is outlined in reaction 14, presumably occurs because the *O*-alkylation of CO increases its back acceptor character toward the metals, and therefore promotes close approach of the carbonyl carbon to the third iron. Symmetry in the bonding is achieved by concomitant shift of another carbonyl toward the opposite face of the iron triangle.

In the compounds discussed so far, adduct formation occurs on bridging carbonyl ligands and not on terminal carbonyls. However, for certain anionic or donor substituted carbonyls the terminal CO ligand is basic owing to delocalization of electron density from the metal onto the carbonyl ligands. A good clue to this high electron density is the observation of a low CO stretching frequency. Terminal carbonyls having ν(CO) below about 1900 cm^{-1} are appreciably basic. Of course, there is no sharp frequency criterion for basicity since adduct formation is also controlled by the strength of the acid, and steric factors.



(14)

Many examples of basicity for terminal carbonyls have been reported from Burlitch's laboratory [29-32]. As with the CO—acid adducts, the interaction of an acceptor with the oxygen of a terminal carbonyl leads to a large decrease in the CO stretching frequency. Some simple salts of $(C_5H_5)Mo(CO)_3^-$ and related carbonyl anions are found to be C- and O-bonded species. One of these structures (Fig. 4) shows a hard acceptor, Mg^{2+}, bonded to the carbonyl oxygens. The structure also shows that Mg^{2+} is attached to pyridine ligands as well as the carbonyl oxygens. There are still too few data to tell if the added steric constraints imposed by the ancillary ligands is influential in promoting the attachment of the Lewis acid to the carbonyl oxygens rather than the metal. However, a quick scan of Table 1 will show that the general tendency is for hard and bulky acceptors to attach to the oxygen of basic carbonyls, whereas less bulky acceptors attach to the central metal. Apparently the oxygen end of carbon monoxide is a hard base. The hard and soft concept has to be used with some caution here, because as mentioned earlier, metal bases do not appear to fit into the scheme. For example, Table 1 shows that soft heavy metals such as Zn^{2+}, Cd^{2+}, and Hg^{2+}, as well as small hard acceptors such as H^+ and CH_3^+, tend to interact directly with basic metals.

The basicity of donor-substituted metal carbonyls has been much less studied than that of anions. One example of terminal CO basicity in a substitut-

---

* Analogous two-metal semi-bridging carbonyls are discussed elsewhere in this volume. See also ref. 28.

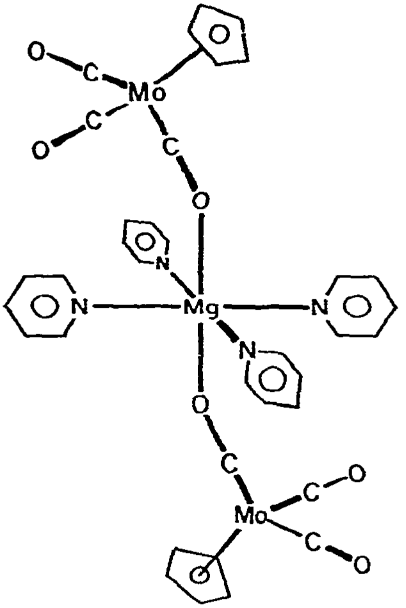


Fig. 4. The structure of $Mg(C_5H_5N)_4[(C_5H_5)Mo(CO)_3]_2$ [31].

ed metal carbonyl is afforded by $Mo(phen)(PPh)_2(CO)_2$, which has an average CO stretching frequency 263 cm^{-1} lower than that of the parent carbonyl, $Mo(CO)_6$. In contrast with the parent carbonyl, the substituted compound is appreciably basic toward aluminum alkyls and trimethylgallium [33]. An interesting aspect of the basicity of this compound is the striking change in color which occurs upon adduct formation, from deep blue-green for $Mo(phen)(PPh)_2(CO)_2$ to deep red for $Mo(phen)(PPh)_2(CO\dot{A}lR_3)_2$. This large shift in transition energy may be discussed in terms of a simple molecular model in which adduct formation on the carbonyl oxygen lowers the energy of a π orbital on the $Mo(CO)_2$ moiety [33]. According to the model this energy decrease is a direct

TABLE 1

COMPARISON OF SOME C- AND O-BONDED AND METAL BONDED LEWIS ACID ADDUCTS[a]

Metal base	Acceptor	
	CO-bonded	M-bonded
$(C_5H_5)M(CO)_3^-$ (M = Cr, Mo or W)	$Al(C_6H_5)_3$, $Al(THF)_3^{3+}$ $Mn(py)_4^{2+}$, $Mg(py)_4^{2+}$, $Yb(C_5H_5)_2^+$	H^+, CH_3^+, $Ga(CH_3)_2^+$, $In(C_6H_5)_3$
$Co(CO)_4^-$	$Mg(py)_4^{2+}$	H^+, CH_3^+, Zn^{2+}, Cd^{2+}, Sn^{2+}, Hg^{2+}
$Mo(phen)(PPh_3)_2(CO)_2$	AlR_3, GaR_3	H^+, CH_3^+
$[(C_5H_5)Fe(CO)_2]_2$	AlR_3, BCl_3, BBr_3	H^+
$Ru_3(CO)_{12}$	$AlBr_3$	H^+

[a] $(C_5H_5)M(CO)_3^-$ [3, 4, 29-32 and 43]; $Co(CO)_4^-$ [1, 2 and 31]; $Mo(phen)(PPh_3)_2(CO)_2$ [8 and 33]; $[(C_5H_5)Fe(CO)_2]_2$ [22, 23 and 44]; $Ru_3(CO)_{12}$ [23 and 45].

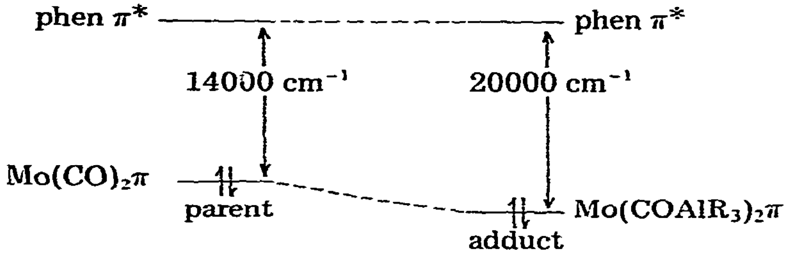


Fig. 5. Simple MO description of the shift in charge transfer band upon addition of AlR_3 to $Mo(phen)(PPh_3)_2(CO)_2$.

consequence of increased Mo-to-CO back-π-bonding, and it results in a greatly increased transition energy from the $Mo(CO)_2$ π orbital to the phen π* orbital, which is relatively unaffected by adduct formation (Fig. 5). Other lines of evidence for the increased back-π-bonding to carbonyls with attached Lewis acids, include the shift of carbonyls to bridging environments upon adduct formation, the increase of ν(CO) for the carbonyl ligands not involved in adduct formation, the decreased ν(CO) for the carbonyl bearing the Lewis acid, and finally the pattern of CO distances in some X-ray structures [30,31].

So far, strong and specific interactions with the carbonyl oxygen have been discussed. In addition, there is some evidence for weaker interactions, such as hydrogen bonding. Over ten years ago it was postulated that hydrogen bonding solvents might interact with bridging carbonyl ligands [34,35]. More recently crystallographic evidence for hydrogen bond formation with basic carbonyls has been obtained. In one case a hydrogen atom of dichloromethane forms the hydrogen bond to a bridging carbonyl [36], and in the other example, the N—H hydrogen of a trialkylammonium ion is hydrogen bonded to the bridging carbonyl of $HFe_3(CO)_{11}^-$ [37].

Weak ion pairing with metal carbonyl anions has also been observed. Examples come from the work of Edgell and his students, who have shown by infrared and Raman spectroscopy that $NaCo(CO)_4$ exists in part as an associated ion pair in solvents such as tetrahydrofuran and pyridine. In contrast with the single T_2 symmetry infrared-active CO stretch for the tetrahedral solvent-separated $Co(CO)_4^-$ ion, the infrared spectrum of the ion pair displays among other features a new low-frequency A_1 mode around 1855 cm^{-1} [38,39]. Very recently, ion pairing has been demonstrated for certain alkali metal and Mg^{2+} salts of $Mn(CO)_5^-$ and of *trans*-$(PhCO)Fe(CO)_3(PPh_3)^-$ in diethyl ether solution [40,41]. For both systems a new low-frequency feature is attributed to a mode primarily involving a C- and O-coordinated carbonyl. This type of ion association appears to be highly influential on some reactions of some metal carbonyl anions [41, 42]. For example, the rates of alkyl-migration (reaction 15) are greatly enhanced by ion pairing [42]. The rate enhancement may arise from cation stabilization of negative charge build-up on the CO group during migration of the alkyl group [42].

$$MRFe(CO)_4 + L \rightarrow M(RCO)Fe(CO)_3L \qquad (15)$$

rate: $M^+ = Li^+ > Na^+ \gg (Ph_3P)_2N^+$

Acknowledgement

Our work at Northwestern University on carbonyl basicity has been made possible by grants from the National Science Foundation. I am grateful to the NSF for this support and to my coworkers who are cited in the references.

References

1 W. Hieber, Advan. Organometal. Chem., 8 (1970) 1.
2 R.B. King, Advan. Organometal. Chem., 2 (1964) 157.
3 J.C. Kotz and D.G. Pedrotty, Organometal. Chem. Rev. A, 4 (1969) 479.
4 D.F. Shriver, Accounts Chem. Res., 3 (1970) 231.
5 R.W. Baker and P. Pauling, Chem. Commun., (1969) 1495.
6 B.A. Frenz and J.A. Ibers, Inorg. Chem., 9 (1970) 2403.
7 C. Eaborn, N. Farrell, J.L. Murphy and A. Pidcock, J. Organometal. Chem., 55 (1973) C68.
8 D. Strope and D.F. Shriver, J. Amer. Chem. Soc., 95 (1973) 8197.
9 J.L. Peterson, T.E. Nappier, Jr. and D. Meek, J. Amer. Chem. Soc., 95 (1973) 8195.
10 D. Strope and D.F. Shriver, Inorg. Chem., 13 (1974) 2652.
11 E.O. Fischer and K. Oefele, Angew. Chem., 73 (1961) 581.
12 W. Hieber and T. Kruck, Angew. Chem., 73 (1961) 580.
13 E.O. Fischer and K. Fichtel, Chem. Ber., 94 (1961) 1200.
14 D.L. Lehman and D.F. Shriver, Inorg. Chem., 9 (1974) 2203.
15 W.B. Hughes, Organometal. Chem. Syn., 1 (1972) 341.
16 W.B. Hughes, U.S. Pat., (1972) 367615.
17 C. Eaborn, N. Farrell and A. Pidcock, Chem. Commun., (1973) 766.
18 R. Porter and D.F. Shriver, J. Organometal. Chem., 90 (1975) 41.
19 H.M. Powell and R.V.G. Ewens, J. Chem. Soc., (1939) 286.
20 A.A. Hock and O.S. Mills, in S. Kirshner (Ed.), The Chemistry of the Coordination Compounds, Macmillan, New York, p. 640.
21 P. McArdle and A.R. Manning, J. Chem. Soc. A, (1970) 2133 and refs. therein.
22 A. Alich, N.J. Nelson, D. Strope and D.F. Shriver, Inorg. Chem., 11 (1972) 2976; N.E. Kim, N.J. Nelson and D.F. Shriver, Inorg. Chim. Acta, 7 (1973) 393.
23 J.S. Kristoff and D.F. Shriver, Inorg. Chem., 13 (1974) 499.
24 F.A. Cotton and G. Yagupsky, Inorg. Chem., 6 (1967) 15; P. McArdle and A.R. Manning, J. Chem. Soc. A, (1970) 2128.
25 E.R. Corey and L.F. Dahl, J. Amer. Chem. Soc., 83 (1961) 2203; R. Mason and A.I.M. Rae, J. Chem. Soc. A, (1968) 776.
26 W. Hieber and G. Brendel, Z. Anorg. Chem., 289 (1957) 324.
27 D.F. Shriver, D. Lehman and D. Strope, J. Amer. Chem. Soc., 97 (1975) 1594.
28 F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 5070.
29 J.M. Burlitch and R.B. Petersen, J. Organometal. Chem., 24 (1970) C65.
30 R.B. Petersen, J.J. Stezowski, C. Wan, J.M. Burlitch and R.E. Hughes, J. Amer. Chem. Soc., 93 (1971) 3532.
31 S.W. Ulmer, P.M. Skarstad, J.M. Burlitch and R.E. Hughes, J. Amer. Chem. Soc., 95 (1973) 4469.
32 T. Blackmore and J.M. Burlitch, Chem. Commun., (1973) 405.
33 D.F. Shriver and A. Alich, Inorg. Chem., 11 (1972) 2984.
34 C.C. Barraclough, J. Lewis and R.S. Nyholm, J. Chem. Soc., (1961) 2582.
35 G. Dobson and R.K. Scheline, Inorg. Chem., 2 (1963) 1313; P. McArdle and A.R. Manning, J. Chem. Soc. A, (1970) 2123.
36 C.B. Dammann, P. Singh and D. Hodgson, Chem. Commun., (1972) 586.
37 L.F. Dahl, private communication.
38 W.F. Edgell, J. Lyford, IV, A. Barbetta and C.I. Jose, J. Amer. Chem. Soc., 93 (1971) 6403.
39 W.F. Edgell and J. Lyford, IV, J. Amer. Chem. Soc., 93 (1971) 6407.
40 C.D. Pribula and T.L. Brown, J. Organometal. Chem., 71 (1974) 415.
41 M.Y. Darensbourg, Inorg. Chem., 13 (1974) 2970.
42 J.P. Collman, J.N. Cawse and J.I. Brauman, J. Amer. Chem. Soc., 94 (1972) 5905.
43 J.P. Oliver, private communication.
44 M.L.H. Green, J.A. McCleverty, L. Pratt and G. Wilkinson, J. Chem. Soc., (1961) 4854.
45 B.F.G. Johnson, R.D. Johnston, J. Lewis, B.H. Robinson and G. Wilkinson, J. Chem. Soc., (1968) 2856.