Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

THE REACTION OF METAL CARBONYLS WITH LEWIS ACIDS—CARBON- AND OXYGEN-BONDED CO

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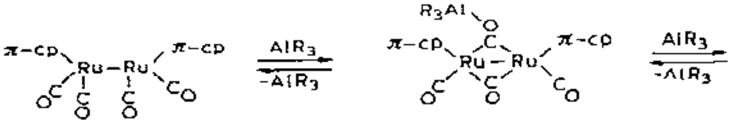
Until recently only carbon—metal bonding was known for metal carbonyls However, within the last few years the interaction of various Lewis acids with the oxygen end of the coordinated CO ligands has been clearly demonstrated

A BASICITY OF BRIDGING CO

The first report[1] of C- and O-bonded carbon monoxide presented the synthesis and structure of $[(\pi\text{-cp})Fe(CO)_2]_2 \cdot 2AlEt_3$ (cp = cyclopentadienyl) This structure involves coordination of $AlEt_3$ to both bridging carbonyl groups (Fig 1), indicating that the bridging carbonyls are more basic than the terminal carbonyls in these compounds It was later shown[2] that this difference in basicity may be used as a driving force to induce a terminal-to-bridge carbonyl shift in $[\pi\text{-cp})Ru(CO)_2]_2$, viz



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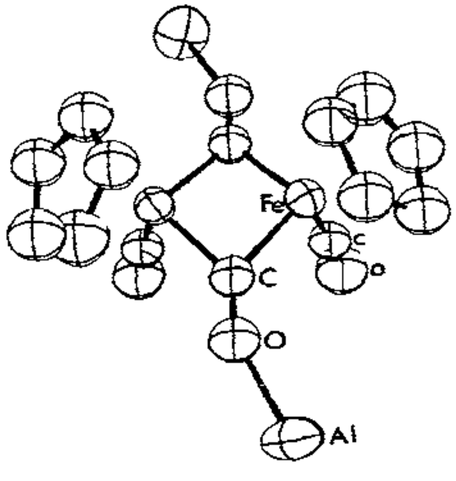


Fig 1 The structure of $[\pi\text{-cp}Fe(CO)(COAlEt_3)]_2$ Ethyl groups and hydrogen atoms have been omitted for clarity. (See ref 1)

TABLE 1

Interaction of polynuclear carbonyls with aluminum alkyls

Compound	Ratio of metal compound to AlR_3 (R = Et, i-Bu)
$[\pi\text{-cpNiCO}]_2$	1 1[a]
$(\pi\text{-cp})_3Ni_3(CO)_2$	1 1[a], 1 2[a]
$[\pi\text{-cpFe(CO)}_2]_2$	1 1[a], 1 2[a, b]
$[\pi\text{-cpFeCO}]_4$	1 4[a,b]
$[\pi\text{-cpRu(CO)}_2]_2$	1 1[a] 1 2[a]
$[\pi\text{-cpMo(CO)}_3]_2$	Adduct
$CH_3CCo_3(PPh_3)(CO)_8$	Decomposed
$Co_2(CO)_8$	Decomposed
$Co_4(CO)_{12}$	Decomposed

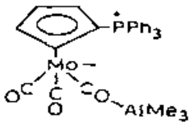
[a] Characterized by solution infrared spectra

[b] Characterized as a solid for which good analytical data were obtained

The Lewis basicity of bridging carbonyls has been demonstrated for about half a dozen polynuclear carbonyl derivatives (Table 1)[3], indicating that the phenomenon of bridging CO basicity is general

B BASICITY OF TERMAL CO

A report by Kotz and Turnipseed[4] marked the first example of Lewis basicity of a terminal carbonyl Reasoning from the observed lowering of a CO stretching frequency and appearance of two higher frequency CO stretches, these authors assigned structure I to their compound.



I

A variant of the above system was soon reported[5] involving the 1 1 interaction of the simple anion $(\pi\text{-cp})Mo(CO)_3^-$ and $AlPh_3$ An interesting new member of the series is the aluminum salt $Al[(\pi\text{-cp})W(CO)_3]_3 \cdot 3THF$ which was shown by an X-ray single crystal structure determination to contain three $(\pi\text{-cp})W(CO)_3^-$ anions, each coordinated through one carbonyl oxygen to the Al^{3+} cation[6] (Fig 2) In a clever approach to CO bridge formation, Brown and Brown found that upon forming a Co^{II} salt the carbonyl of $Fe(CN)_5(CO)^{3-}$ is forced into a bridging environment[7] At the time of its discovery, this represented the

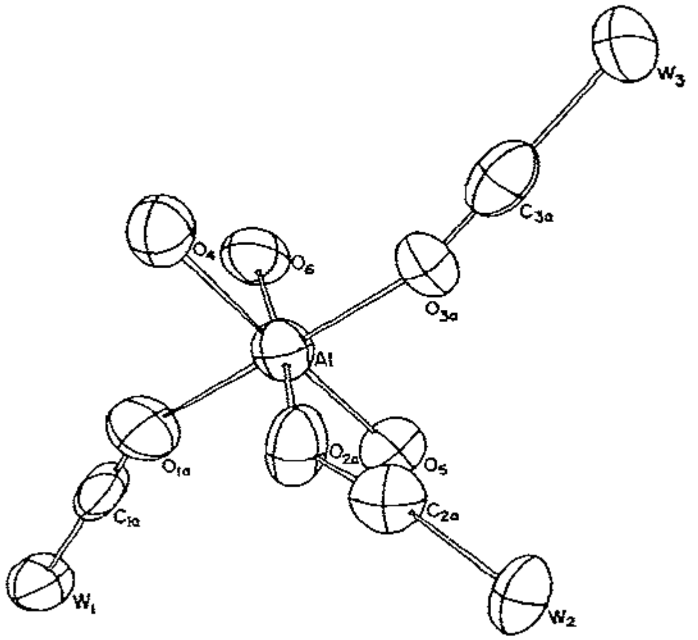
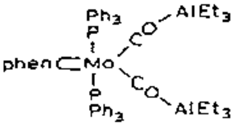


Fig 2 The structure of $Al[\pi\text{-}cpW(CO)_3]_3 \cdot 3THF$ C_5H_5, non-bridging CO groups, and methylene groups have been omitted for clarity O_4-O_6 belong to the three tetrahydrofuran molecules (Reproduced by permission of the copyright owner The American Chemical Society see ref 6)

the only recognized example of the oxygen end of carbon monoxide associated with a metal other than aluminum

It is well known that the substitution of donor ligands for CO leads to a large reduction in the remaining CO frequencies of a metal carbonyl[8]. This decrease in frequency implies an increase in electron density on the carbonyl ligands Furthermore, the range of ν_{CO} for suitably substituted carbonyls falls within that of anionic carbonyl derivatives, suggesting that donor-substituted metal carbonyls may exhibit Lewis basicity. This expectation has been realized for the deep blue $Mo(CO)_6$ derivative, $Mo(phen)(PPh_3)_2(CO)_2$ (ref 9) which reacts with $AlEt_3$ in hydrocarbon solution to form a brick-red 1 2 adduct, the composition of which is established by C, H, N, Al and C_2H_5 (by hydrolysis) analyses With few differences the infrared spectrum resembles that of the parent The two infrared ν_{CO} bands, which are characteristic of *cis* CO groups, are shifted from 1800s and 1729s cm^{-1} in the parent to 1731s and 1633s cm^{-1} in the adduct In addition, two, or possibly three, new frequencies are evident in the spectra taken on Nujol mulls (635s, 683?m, 1183w cm^{-1}) The decrease in ν_{CO} is characteristic of adduct formation on the oxygen of a coordinated carbonyl[1-5], and the new features in the low frequency region are characteristic of coordinated trialkylaluminum[4]. Water, air, or triethylamine bring about a rapid regeneration of the parent, Mo(phen)$(PPh_3)_2(CO)_2$, presumably via reaction with, or simple displacement of, the trialkylaluminum moiety These chemical properties indicate that no drastic changes in the molybdenum complex have occurred upon adduct formation Therefore, both physical and chemical evidence support structure II



II

This represents the first terminal CO adduct in which more than one Lewis acid is bound per molecule and the first example in which the terminal carbonyl in a neutral compound serves as a base ((π-$Ph_3PC_5H_4$)$Mo(CO)_3$, which is formally neutral, is best considered as a zwitterion)

The vivid color change upon adduct formation is associated with a blue shift in the lowest energy electronic transition from 693 nm ($\epsilon = 7,600$) to 499 nm ($\epsilon = 4,320$) Similar shifts have been observed upon the addition of triethylaluminum to Mo(5,6-dimethylphenanthroline) $(PPh_3)_2(CO)_2$ and to $Mo(phen)_2(CO)_2$ We assign this low frequency band to a Mo(*d*) → phen(π^*) transition, based on its high intensity, as well as analogy with assignments[10] for $Mo(phen)(CO)_4$, and the absence of a similar band in compounds lacking a conjugated amine, e g $Mo(NCCH_3)_2(PPh_3)_2(CO)_2$ As illustrated in Fig 3, the shift in this charge transfer band may be explained by a large decrease in *d*-orbital energy, arising from much greater metal–carbonyl back-π-bonding in the adduct than in the parent This explanation is similar to one which has been applied to the charge transfer spectra of some cyanide complexes which undergo a dramatic blue shift on adduct formation[11].

Evidence for a trimethylgallium adduct of Mo(phen)$(PPh_3)_2(CO)_2$ is obtained from visible spectroscopy of solutions of the molybdenum complex to which incremental additions of the acid have been made (Fig.4) The appearance of clear isosbestic points (Fig.4), as well as the position of the low frequency charge transfer absorption maximum, 623 nm (which is close to that of a 1 1 Et_3Al adduct), is consistent with 1 1 adduct formation*

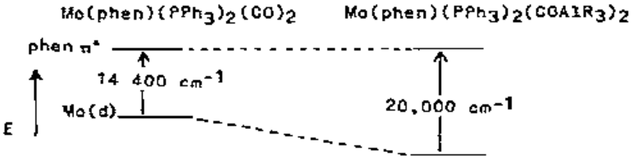


Fig 3. Origin of the shift in charge transfer band The addition of an electron acceptor to the oxygen of CO increases Mo–CO back-π-bonding lowering the highest filled *d* orbital energies relative to the phen π* level

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* For footnote see next page

Interest in this adduct stems from the fact that simple molecular adducts with the metal coordinated carbonyl have been demonstrated in the past only for aluminum acceptors[1–6]

In a recent NMR study of various organometallic and coordination compounds[12] evidence was obtained for the interaction of $[(\pi\text{-cp})\text{-Fe(CO)}_2]_2$ and of $\text{Mo(phen)(PPh}_3)_2(\text{CO})_2$ with the paramagnetic NMR shift reagent, Eu(fod)_3 (ref.13), where fod is a fluorinated β-diketone The principle involved is that a paramagnetic dipolar shift is induced in the proton NMR of any molecule coordinated to the shift reagent[13 14] This phenomenon provides a convenient method for probing the Lewis basicity of metal complexes It is found that $[(\pi\text{-cp})\text{Fe(CO)}_2]_2$ and $\text{Mo(phen)(PPh}_3)_2(\text{CO})_2$ are basic toward Eu(fod)_3, while a carbonyl compound with higher ν_{CO}, $(\pi\text{-cp})\text{Fe(CO)}_2\text{CH}_3$, is not Presumably, carbonyl oxygen is the basic site in the two former compounds

To summarize, bridging carbonyls and terminal carbonyls with low ν_{CO} exhibit signifi-

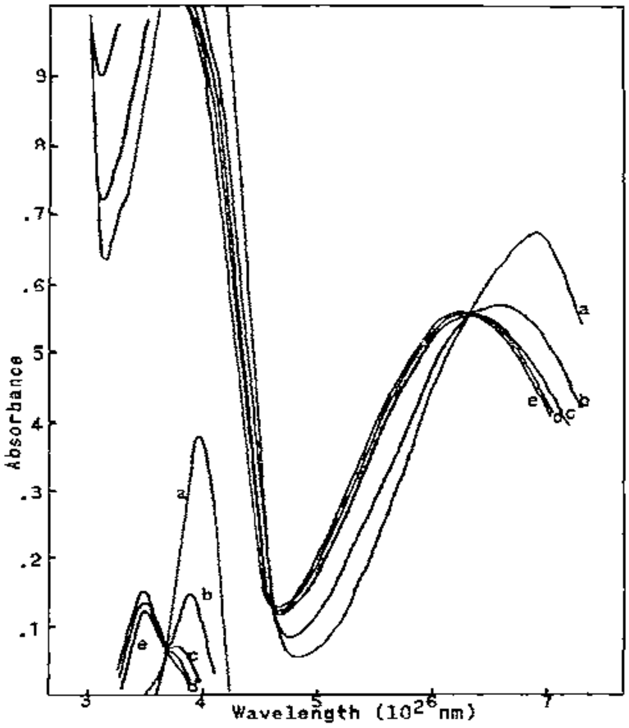

Fig 4 Spectrophotometric titration of 8 15 × 10^{-5} M $\text{Mo(phen)(Ph}_3)_2(\text{CO})_2$ in benzene with GaMe_3 GaMe_3 concentration (a) 0, (b) 2 77 × 10^{-2} M (c) 5 46 × 10^{-2} M, (d) 9 34 × 10^{-2} M (e) 1 45 × 10^{-1} M

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* Footnote from preceding page In all cases studied in detail to date, the usual decrease in successive equilibrium constants appears to be followed It therefore appears unlikely that the isosbestic points can be interpreted in terms of formation of the 1 2 adduct directly Judging from color changes a 1 2 adduct probably forms at low temperatures

cant Lewis basicity toward certain hard Al^{III}, Ga^{III} and Eu^{III} Lewis acids The hard (but weak) Lewis base character of the oxygen end of carbon monoxide contrasts with the soft π-acid character of the carbon end Therefore, in conventional carbonyl chemistry, which involves the soft low oxidation state transition metals, one finds carbon bonding exclusively

ACKNOWLEDGEMENT

Our research on the interaction of metal carbonyls with Lewis acids was supported by grants from the NSF, an Alfred P Sloan Foundation Research Fellowship to D. F. S , and an NSF Science Faculty Fellowship to A A We thank Professor Turco and Dr Peloso for the opportunity to present this work at the Bressanone Conference

REFERENCES

1 N J Nelson, N E Kime and D F Shriver, *J Amer Chem Soc* 91 (1969) 5173
2 Sr A Alich N J Nelson and D F Shriver *Chem Commun* (1971) 254
3 Sr A Alich, N J Nelson and D F Shriver unpublished work
4 J C Kotz and C D Turnipseed, *Chem Commun* (1970) 41
5 J M Burlitch and R B Peterson, *J Organometal Chem* , 24 (1970) C65
6 R.B. Petersen, J J Stezowski C Wan, J M Burlitch and R L Hughes, *J Amer Chem Soc* 93 (1971) 3532
7 L L Brown and D B Brown, *Chem Commun* , (1971) 67
8 F A Cotton and G Wilkinson, *Advanced Inorganic Chemistry* 2nd edn , Wiley-Interscience, New York 1966 p 731
9 H T Dieck and H Friedel, *J Organometal Chem* 14 (1968) 375, *Chem Commun* (1969) 411
10 H Saito, J Fugita and K Saito, *Bull Chem Soc Japan,* 41 (1968) 359, 863
11 N K Hammer and L E Orgel, *Nature*, 190 (1961) 439, D F Shriver and J Posner, *J Amer Chem Soc* , 88 (1966) 1672
12 T J Marks, J S Kristoff Sr A Alich and D F Shriver *J Organometal Chem* , 33 (1971) C35
13 R E Rondeau and R E Sievers, *J Amer Chem Soc* , 93 (1971) 1522
14 C C Hinckley *J Amer Chem Soc* 91 (1969) 5160