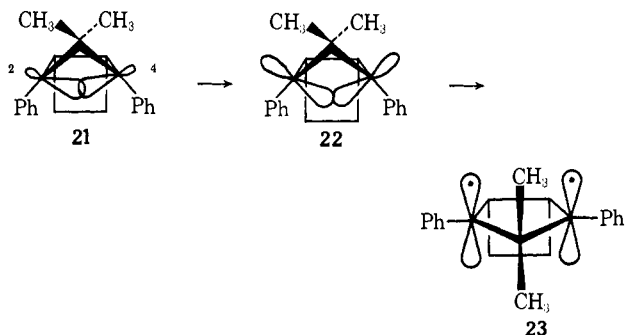As expected,[12] the parent $anti$-tricyclo[3.2.0.0^{2,4}]heptane (19) gave rise only to 1,4-cycloheptadiene (20) when heated at 173° for 15 min.

The subtle role played by the phenyl groups at C_2 and C_4 may be rationalized in stereoelectronic terms. Such aryl substituents are certain to weaken the C_2–C_3 bond of the tricycloheptane nucleus ($cf.$ 21). As frag-

mentation of this bond commences, progressive rehybridization in the sp^2 direction[13] will lead through 22 to 23. Whether the two cyclobutane bonds rupture at intermediate stage 22 where the orbitals of the C_2–C_4 bond have become well canted but not yet completely severed (leading to a concerted reaction) or only after diradical 23 is formed (formally now a stepwise process) is of course not known. The data require only that the two edge bonds in the four-membered ring break essentially simultaneously. The inability of alkyl groups or hydrogen atoms to accomplish a similar end result may be associated with the fact that the C_1–C_5 and C_2–C_4 bonds in these molecules undergo rupture at approximately the same rate because their inherent dissociation energies are quite similar. The phenyl groups can be expected to weaken the C_2–C_4 bond. Surprisingly, however, such substitution provides little acceleration (estimated $\Delta H^{\ddagger} \sim 39$ kcal/mol for 3 → 4 + 5)[14] suggestive perhaps of substantial steric hindrance to proper orientation of the phenyl rings.

(12) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, $Tetrahedron Lett.$, 5345 (1969). These workers have reported the conversion of 19 into a 10:1 mixture of two compounds under these conditions. The minor product in our runs was found to be unreacted 19.

(13) Such hybridization will accord maximum stabilization to the odd electron centers.

(14) We thank Professor John Brauman for his comments on this point.

(15) National Institutes of Health Predoctoral Fellow, 1969–present.

Leo A. Paquette,* Louis M. Leichter[15]

Department of Chemistry, The Ohio State University
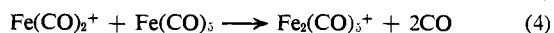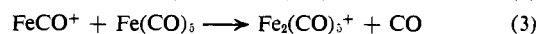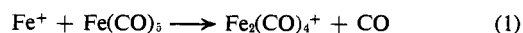*Columbus, Ohio 43210*
Received June 25, 1971

Potential of Ion Cyclotron Resonance Spectroscopy for the Study of the Intrinsic Properties and Reactivity of Transition Metal Complexes in the Gas Phase. Ion–Molecule Reactions of Iron Pentacarbonyl

Sir:

Ion cyclotron resonance spectroscopy (icr) has proven to be a powerful technique for studying ion–molecule
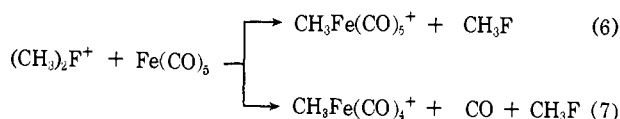
reactions.[1] With the exception of several hydrides,[1-7] however, relatively little research has been concerned with inorganic compounds, and, in particular, transition metal complexes have not been examined. We wish to report the gas-phase ion chemistry of iron pentacarbonyl, both alone and in binary mixtures, indicating the tremendous potential of icr studies for illuminating certain aspects of inorganic and organometallic chemistry.

The volatile iron pentacarbonyl is a logical choice for initial icr studies of metal complexes. The icr spectrum of Fe(CO)$_5$[8] at low pressure is in qualitative agreement with previous electron[9-12] and photon[13] impact results; the ions present at an electron energy of 70 eV include most prominently the species $Fe(CO)_n^+$ ($n = 0$–5). Within the mass range of the present instrument ($\sim$260 amu), ion–molecule reaction products are observed at higher pressures in Fe(CO)$_5$ at m/e 224 and 252, corresponding to $Fe_2(CO)_4^+$ and $Fe_2(CO)_5^+$, respectively. Double-resonance experiments indicate reactions 1–4 to be responsible for the

$$Fe^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_4^+ + CO \qquad (1)$$

$$FeCO^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_4^+ + 2CO \qquad (2)$$

$$FeCO^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_5^+ + CO \qquad (3)$$

$$Fe(CO)_2^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_5^+ + 2CO \qquad (4)$$

formation of these binuclear species.

Binary mixtures of Fe(CO)$_5$ with CH_3F, H_2O, NH_3, and HCl were examined principally to delineate the occurrence of ligand displacement reactions. For example, the ligand substitution reactions of eq 5 are

$$Fe(CO)_n^+ + CH_3F \longrightarrow Fe(CH_3F)(CO)_{n-1}^+ + CO \ (n = 1\text{–}4) \quad (5)$$

observed when CH_3F[14] is added to Fe(CO)$_5$. At the highest CH_3F pressures employed, 2×10^{-4} Torr, only one CO group is replaced in any of the $Fe(CO)_n^+$ ($n = 1$–4) ions, and $Fe(CO)_5^+$ remains inert toward substitution of CO by CH_3F. Additional reaction products observed are $CH_3Fe(CO)_4^+$ and $CH_3Fe(CO)_5^+$, derived primarily from the dimethylfluoronium ion[14] in reactions 6 and 7. Reaction 6 is an example of an

$$(CH_3)_2F^+ + Fe(CO)_5 \begin{cases} \longrightarrow CH_3Fe(CO)_5^+ + CH_3F & (6) \\ \longrightarrow CH_3Fe(CO)_4^+ + CO + CH_3F & (7) \end{cases}$$

(1) For a description of the instrumental techniques employed, see D. Holtz, J. L. Beauchamp, and J. R. Eyler, $J. Amer. Chem. Soc.$, 92, 7045 (1970).

(2) D. Holtz and J. L. Beauchamp, $ibid.$, 91, 5913 (1969).

(3) R. Dunbar, $ibid.$, 90, 5676 (1968).

(4) W. T. Huntress, Jr., M. M. Mosesman, and D. D. Elleman, $J. Chem. Phys.$, 54, 843 (1971).

(5) S. E. Buttrill, Jr., $J. Amer. Chem. Soc.$, 92, 3560 (1970).

(6) J. Brauman and K. Smyth, $ibid.$, 91, 7778 (1969).

(7) J. L. Beauchamp and S. E. Buttrill, Jr., $J. Chem. Phys.$, 48, 1783 (1968).

(8) The only difficulty encountered in handling iron pentacarbonyl in the icr spectrometer was the formation of conducting paths between the filament and the adjacent trapping plate. This was controlled by machining the filament support block such that iron shadowed from the filament did not form a complete conducting pathway.

(9) R. E. Winters and R. W. Kiser, $Inorg. Chem.$, 3, 699 (1964).

(10) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, $Z. Phys. Chem. (Frankfurt am Main)$, 45, 79 (1965).

(11) D. R. Bidinosti and N. S. McIntyre, $Can. J. Chem.$, 45, 641 (1967).

(12) G. A. Junk and H. J. Svec, $Z. Naturforsch. B$, 23, 1 (1968).

(13) Reliable thermochemical data on the ions formed are provided in G. Distefano, $J. Res. Nat. Bur. Stand., Sect. A$, 74, 233 (1970).

(14) For a description of the gas-phase ion chemistry of CH_3F, see A. G. Marshall and S. E. Buttrill, Jr., $J. Chem. Phys.$, 52, 2752 (1970).

Table I. Bond Energies and Relative Rates of Ligand Substitution in $Fe(CO)_n{}^+$

Ligand(M)	PA(M)[a]	Fe(CO)$^+$	Fe(CO)$_2{}^+$	Fe(CO)$_3{}^+$	Fe(CO)$_4{}^+$	Fe(CO)$_5{}^+$
				Relative rates of ligand substitution[b]		
HCl	140			No reaction[c]		
CH$_3$F	151	0.45	0.82	1.00^d	0.16	<0.01
H$_2$O	164	0.86	0.91	1.00^d	0.56	<0.01
NH$_3$	207	0.92	0.98	1.00^d	0.56	0.16
$D[F(CO)_{n-1}{}^+$–CO]^a		63	20	19	24	22

[a] All thermochemical data are given in kilocalories per mole at 298°K. Proton affinity data are from D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970), and J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, unpublished results. CO binding energies are calculated from the data in ref 13. [b] Relative rates were calculated using the analysis described in ref 1. [c] Rates of ligand substitution reaction are all $< 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. [d] Rate constants are in the range 10^{-9}–10^{-10} cm^3 molecule^{-1} sec^{-1}.

oxidative addition reaction of a coordinatively saturated d^8 metal complex,[15,16] in which the formal oxidation state of the metal increases by two.

The more extensive ligand exchange reactions observed when H$_2$O is added to Fe(CO)$_5$ are summarized in Scheme I. The species HFe(CO)$_5{}^+$ and HFe(CO)$_4{}^+$ are also observed,[17] derived from H$_3$O$^+$ by proton transfer.

Scheme I
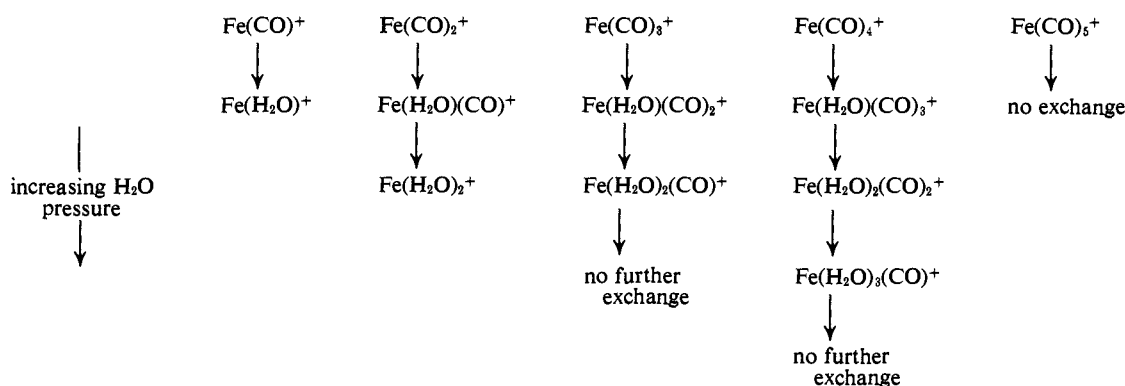
In analogy with H$_2$O (Scheme I), extensive ligand substitution also occurs in a mixture of NH$_3$ and Fe(CO)$_5$, the important difference being that Fe(CO)$_5{}^+$ slowly exchanges two CO groups. Neither HFe(CO)$_5{}^+$ nor HFe(CO)$_4{}^+$ is observed in this case. Since H$_3$O$^+$ protonated Fe(CO)$_5$ while NH$_4{}^+$ does not, we conclude that PA(NH$_3$) $\geq$ PA[Fe(CO)$_5$] $\geq$ PA(H$_2$O).[18]

No ligand substitution reactions were observed in a 40:1 mixture of HCl and Fe(CO)$_5$ at 10^{-4} Torr. The major reaction products are HFe(CO)$_5{}^+$ and HFe(CO)$_4{}^+$, formed by proton transfer from H$_2$Cl$^+$ to Fe(CO)$_5$.

For each of the neutrals CH$_3$F, H$_2$O, and NH$_3$, the relative rates of single substitution in the five Fe(CO)$_n{}^+$ ions are presented in Table I along with the Fe(CO)$_{n-1}{}^+$–CO bond dissociation energies. It is evident that the reactivity of an ion toward substitution depends largely on factors other than metal–CO binding energies. We also conclude that the binding energies of CH$_3$F, H$_2$O, and NH$_3$ in the various substituted fragments are greater than that of the displaced CO group, while the binding energy of HCl is presumably less since it fails to react.

(15) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

(16) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).

(17) HFe(CO)$_5{}^+$ is known in solution as an unstable complex; see, for example, A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(18) The proton affinity (gas-phase basicity) of a species M, PA(M), represents the enthalpy change for the reaction MH$^+$ → M + H$^+$.
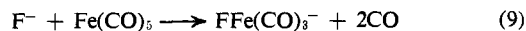
It is of interest to note that the proton affinities of the various ligands (Table I) relative to CO [PA(CO) = 143 kcal/mol] correlate with their ability to effect substitution.

For comparison with the above results, we examined a ligand generally associated with π bonding in organometallic complexes. Among the several products of ligand displacement reactions observed in a mixture of benzene and Fe(CO)$_5$, Fe(C$_6$H$_6$)(CO)$_2{}^+$ formed in reaction 9 by multiple ligand displacement predominates at higher pressures.

$$Fe(CO)_4{}^+ + C_6H_6 \longrightarrow \left[\begin{array}{c} CO \quad CO \\ Fe \end{array} \right]^+ + 2CO \qquad (8)$$
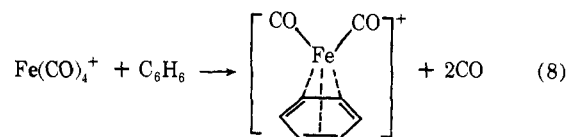
In contrast to the apparent tendency of iron to form relatively stable five-coordinate complexes in processes involving electrophilic attack by positively charged ions, reactions involving nucleophilic attack by negative ions appear to favor four-coordinate products; reactions 9 and 10 illustrate this behavior.[19]

$$F^- + Fe(CO)_5 \longrightarrow FFe(CO)_3{}^- + 2CO \qquad (9)$$

$$C_2H_5O^- + Fe(CO)_5 \longrightarrow C_2H_5OFe(CO)_3{}^- + 2CO \qquad (10)$$

The preliminary results described above comprise only a small fraction of the information available from the study of the ion–molecule reactions of iron pentacarbonyl. In summary, our results indicate the potential of icr studies for examining the following aspects of inorganic and organometallic chemistry in the gas phase: (1) formation of binuclear complexes, (2) ligand displacement reactions, (3) determination of

(19) F$^-$ and C$_2$H$_5$O$^-$ are readily produced by dissociative electron capture from NF$_3$ and C$_2$H$_5$ONO.

Communications to the Editor

relative ligand binding energies, (4) determination of the basicity of transition metal complexes, (5) examination of processes involving both electrophilic and nucleophilic attack on transition metal complexes, and (6) generation and study of unusual σ- and π-bonded organometallic complexes. *Such experiments are of particular interest since they provide information relating to intrinsic properties and reactivity of the species considered, in the absence of complicating solvation phenomena.*

Michael S. Foster, J. L. Beauchamp*
Contribution No. 4238
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91109
Received April 5, 1971

Preparation and Structure of $Co_4(NO)_8(NO_2)_2(N_2O_2)$. A Novel Complex Containing a Quadridentate Hyponitrite Group

Sir:

We wish to report the synthesis and crystal structure determination of a novel complex containing the hitherto unknown linkage of a trans hyponitrite group, $(ONNO)^{2-}$, bridging four different cobalt atoms.

Synthesis. The compound $Co_4(NO)_8(NO_2)_2(N_2O_2)$ was prepared by the reaction of $Co(CO)_3NO$ and gaseous NO in a sealed, inverted J shaped tube. The sample of $Co(CO)_3NO$ was kept in the short arm of the tube, and the long arm was heated at 50–60°. The pressure of NO (which was in excess) in the tube was about 20 atm, and the tube was protected from any exposure to light. After 5–10 days of heating, two black crystalline products were formed. Needles growing at the walls of the heated portion of the tube were shown to be the recently reported polymeric dinitrosyl cobalt nitrite, $[Co(NO)_2(NO_2)]_n$.[1] The second type of crystalline product, isolated from the unheated portion of the tube and representing about 2–5% of the total product, was proved crystallographically to have the molecular formula $Co_4(NO)_8(NO_2)_2$-(N_2O_2). Unlike $Co(NO)_3$, small yields of which are also formed at 60°,[2] both of these products are insoluble in organic liquids and lack air sensitivity.

Because of the small yields of $Co_4(NO)_8(NO_2)_2$-(N_2O_2), and the difficulty of extending the preparative procedure to a larger scale, a detailed elemental analysis of the compound was not possible. However, support for the above chemical formulation was provided by an analysis of the gaseous products from the original reaction mixture, which showed that a quantitative amount of CO was evolved (0.686 mmol of CO from 0.231 mmol of $Co(CO)_3NO$). This indicated a lack of carbon in the crystalline product. The presence of NO_2 in the product was supported by the detection of N_2O in the gaseous mixture. Upon pyrolysis of Co_4-$(NO)_8(NO_2)_2(N_2O_2)$, neither CO nor CO_2 could be detected, again proving the absence of carbon in the

(1) C. E. Strouse and B. I. Swanson, *Chem. Commun.*, 55 (1971).
(2) I. H. Sabherwal and A. B. Burg, *ibid.*, 1001 (1970).

material. Less anticipated was the formation of N_2O (along with NO but not NO_2) during this pyrolysis. This N_2O, however, is believed to be a secondary product (not present as a ligand in the original complex), for no N_2O was produced by heating the compound with iodine at 100°. The absence of NO_2 during pyrolysis is not inconsistent with the behavior of other nitrite compounds, such as $[Co(NO)_2(NO_2)]_n$, which also give N_2O but no NO_2 when heated.

The infrared spectrum of $Co_4(NO)_8(NO_2)(N_2O_2)$ showed two strong NO stretches at 1850 and 1796 cm^{-1}, which are easily assignable to the terminal NO groups. Additional bands were observed at 1377 (s, close doublet), 1327 (s), 1098 (m), and 828 cm^{-1} (m). In the absence of any other reported examples of complexing hyponitrite groups[3] and the rather doubtful assignment[4] of
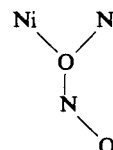

vibrations in $[Ni(\beta\text{-picoline})_2(NO_2)_2]_3 \cdot C_6H_6$,[5] we believe it would be premature to assign any of the four lower frequency peaks specifically to the bridging hyponitrite *vs.* nitrite group found in our complex.

The mode of formation of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ is worthy of discussion. Gaseous NO is known to disproportionate into N_2O and NO_2, through the presumed intermediate N_2O_2.[6] It is therefore likely that, under our conditions, the system $Co(CO)_3NO + NO$, which under other conditions produces $Co(NO)_3$,[2] absorbs NO_2 to form nitrite-containing compounds. The formation of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ evidently depends not only upon the known disproportionation of gaseous NO into N_2O and NO_2[6] but also upon a reductive dimerization of NO. The conditions for the latter may be fairly critical, since the crystals were found only in the cool part of a partially heated tube. For high-yield formation of $Co(NO)_3$,[2] one works at lower temperatures and pressures, so that the alteration of the NO is minimized. It is curious that the polymeric $[Co(NO)_2(NO_2)]_n$ could be formed directly from gaseous reactants.

Structural Determination. Crystals of $Co_4(NO)_8$-$(NO_2)_2(N_2O_2)$ were mounted into thin-walled capillary tubes. Weissenberg and precession photographs indicated that the space group is monoclinic, $P2_1/c$, with $a = 8.26$, $b = 9.34$, $c = 12.29$ Å, and $\beta = 99.48°$. Density determinations were not feasible because the compound is affected by water and halogenated solvents.

(3) Although the vibrational bands of the $N_2O_2{}^{2-}$ ion itself are well characterized, we feel that such assignments are of little help in assigning the vibrational bands of our compound.
(4) We feel that the assignments in ref 5 seem doubtful because of the contradictions in their assignments of the
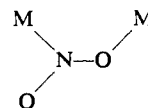
bands with those reported in ref 1.
(5) D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, P. Phavanantha, and D. Rogers, *Chem. Commun.*, 1383 (1969).
(6) T. P. Melia, *J. Inorg. Nucl. Chem.*, 27, 95 (1965).