tential of ^{113}Cd NMR spectroscopy in biological systems have been recently reviewed.[8]

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Articles

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Mechanism of Heterolytic Iron–Iron Bond Cleavage in (μ-Dimethylarsenido)(tetracarbonyliron)dicarbonylnitrosyliron(*Fe*–*Fe*)

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Reactions of the title complex with a series of P-, As-, or Sb-donor ligands lead to heterolytic cleavage of the Fe→Fe bond and addition of the ligands at the Fe(CO)$_2$(NO) moiety. The rate equations for the reactions in Decalin or cyclohexane are dominated by a term first order in the entering ligand. The dependence of the rate parameters on the nature of the nucleophile suggests that most of the reactions occur by an associative or I$_a$ attack at the Fe atom but that the weak nucleophiles P(OPh)$_3$, AsPh$_3$, and SbPh$_3$ probably react by an I$_d$ mechanism. Spectroscopic and kinetic evidence suggests that equilibrium mixtures of reactant and product complexes are formed in reactions with P(OPh)$_3$ and SbPh$_3$. The data suggest that the Fe→Fe bond strength is probably ≳ca. 100 kJ mol^{-1}. These results are compared with those for similar reactions of (OC)$_4$Fe(μ-AsMe$_2$)Co(CO)$_3$.

Introduction

Synthetic and structural studies of metal carbonyl clusters have proceeded on an increasingly massive scale over the last decade,[1] and this has been in large part due to the hope that useful catalysts may be discovered among them.[2] One of the features necessary for catalysis to be uniquely assignable to a cluster is the absence of fragmentation into active mononuclear species. In this context, the chemistry of polynuclear carbonyls in which the metal atoms are strongly bound together by bridging groups has become of considerable interest.[2,3] Fission of a metal–metal bond to give geminal reactive metal centers is seen as a potentially important modus operandi of catalytically active clusters.[3] Clusters containing more than one type of metal are also believed to be particularly promising.[3] Heteronuclear arsenido- and phosphido-bridged complexes form a class of this type, and (OC)$_4$Fe(μ-AsMe$_2$)M (M = Co(CO)$_3$ and Fe(CO)$_2$(NO)) have been shown to catalyze

the dimerization of norbornadiene.[4]

Kinetic studies of such complexes are important in defining the energetics of their reactions and in suggesting the types of reactive intermediates that might be involved. Thus, an early study concerned the "ring-opening" reaction shown in eq 1.[5] The forward reaction was first order in [L] even when

$$(OC)_3Co(\mu\text{-}CO)(\mu\text{-}GePh_2)Co(CO)_3 + L \rightarrow$$
$$(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3L \quad (1)$$
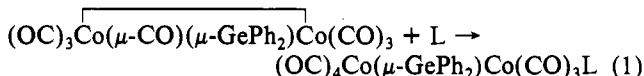
L was the very weak nucleophile CO, and the small dependence of the values of k_2 on the nature of L was taken to indicate reaction via an initial, highly reversible, ring opening to form (OC)$_4$Co(μ-GePh$_2$)Co(CO)$_3$, which was then attacked at the vacant coordination site by the incoming nucleophile. More recently, ring-opening reactions of (η^5-C$_5$H$_5$)MnFe$_2$-(CO)$_7$(μ-PPh)[6] and (OC)$_4$Fe(μ-AsMe$_2$)Co(CO)$_3$[7] have also been shown to be first order in incoming nucleophile.

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Table I. Kinetic Parameters[a] for the Reaction of $(OC)_4Fe(\mu\text{-}AsMe_2)Fe(CO)_2(NO)$ with L at 40 °C in Decalin

L	$10^5 a$, s^{-1}	$10^3 k_2$, L mol^{-1} s^{-1}	$\sigma(k_{obsd})$,[b] %	log k_2	Δ(hnp),[c] mV	cone angle of L,[d] deg
$P(C_6H_{11})$	-0.5 ± 2.1	23.1 ± 1.0	7.2	-1.64	33	179
$P\text{-}n\text{-}Bu_3$	-1.0 ± 0.4	75.3 ± 2.6	4.5	-1.12	131	130
$PPhEt_2$	7.5 ± 2.8	40.7 ± 0.3	1.5	-1.39	300	136
PPh_2Et	2.4 ± 1.1	15.0 ± 0.1	1.5	-1.82	400	141
$P(OMe)_3$	-1.4 ± 0.8	8.87 ± 0.08	2.0	-2.05	520	107
PPh_3	0.4 ± 0.6	4.97 ± 0.12	6.9	-2.30	573	145
$P(OCH_2)_3CEt$	6.7 ± 1.0	18.5 ± 0.1	1.0	-1.73	665	101
$P(OPh)_3$	1.44 ± 0.16	0.31 ± 0.02	8.7	-3.51	875	128
$P(OPh)_3$,[e]	2.57 ± 0.72	0.65 ± 0.03	3.5			
$P(OPh)_3$,[f]	5.96 ± 1.33	1.48 ± 0.06	2.9			
$AsPh_3$,[g]	-1.3 ± 0.1	1.52 ± 0.10	6.7[i]	-2.82	...	~ 127[k]
$AsPh_3$,[e,g]	-5.0 ± 1.4	3.98 ± 0.24	6.7[i]			
$AsPh_3$,[g,h]	6.4 ± 5.0	7.93 ± 0.80	6.7[i]			
$SbPh_3$,[g]	2.4 ± 0.9	2.01 ± 0.09	6.4[i]	-2.70	...	
$SbPh_3$,[e,g]	8.6 ± 2.1	4.25 ± 0.28	6.4[i]			
$SbPh_3$,[g,j]	41.0 ± 3.3	7.82 ± 0.58	6.4[i]			

[a] Obtained by a least-squares fit to eq 3. [b] Standard deviation of an individual measurement of k_{obsd}. [c] Half-neutralization potential of L; ref 10. [d] See ref 9 and footnote 8 in ref 7. [e] At 50.0 °C. [f] At 60.0 °C. [g] In cyclohexane. [h] At 59.6 °C. [i] Method of pooled variances; data at all temperatures pooled. [j] At 55.0 °C. [k] Reference 11.

We report here the kinetics of the reactions[8] shown in eq 2 where L is $AsPh_3$, $SbPh_3$, and a range of P-donor ligands.

$$(OC)_4Fe\text{—}Fe(CO)_2(NO) + L \longrightarrow (OC)_4Fe\quad Fe(CO)_2(NO)L \quad (2)$$

These reactions are also first order in [L], and the dependence of the kinetic parameters on the nature of L allows conclusions to be drawn about the mechanisms of the reactions.

Experimental Section

The complex $(OC)_4Fe(\mu\text{-}AsMe_2)Fe(CO)_2(NO)$ was prepared by Dr. H.-J. Langenbach and kindly provided for this work by Professor H. Vahrenkamp. Deoxygenated reactant solutions of complex and phosphines were prepared in Schlenk tubes exactly as described previously.[7] For reactions that were followed by UV–vis spectroscopy, solutions of the complex were transferred to thermostated silica cells and reactions were initiated and monitored as described previously.[7] Reactions followed by IR spectroscopy were carried out in Schlenk tubes wrapped in foil and immersed in a thermostat bath. Samples were transferred periodically by syringe to small phials and quenched in an ice bath before measurement of the spectra. Reaction was accompanied by the loss of the absorption band at 380 nm due to the complex and its replacement by more intense absorption at lower energy and broad shoulders extending out into the visible region. When the nucleophile was $SbPh_3$, there was a sharp isosbestic point at 401 nm throughout the reaction and the final spectrum remained stable for some time. When the nucleophile was $AsPh_3$, an isobestic point at 395 nm was evident over the first half-life but it then became less clear. This was due to growth of absorbance over the whole spectroscopic region.

The reactions were all accompanied by growth of bands in the IR spectra consistent with the formation of the expected products (Table IV, supplementary material). Thus, when L was PPh_3 and $P(OMe)_3$, the final spectra after reactions in Decalin were virtually identical with those reported[8] for the isolated complexes $(OC)_4Fe(\mu\text{-}AsMe_2)Fe(CO)_2(NO)L$ in cyclohexane, and when L = $P\text{-}n\text{-}Bu_3$, the final spectrum was the same as that for L = PMe_3. The spectra of the initial products of reaction with the other nucleophiles were very closely related to these. The product bands assignable to the $Fe(CO)_4$ moiety were essentially unaffected by L, and the trends in the bands due to the $Fe(CO)_2(NO)L$ moiety varied as expected with the nature of L.[9]

The kinetics of the reaction with phosphorus-donor nucleophiles were monitored by measuring the decrease in absorbance at 424 nm

Table II. Activation Parameters for the Reaction of $(OC)_4Fe(\mu\text{-}AsMe_2)Fe(CO)_2(NO)$ with L in Decalin or Cyclohexane

L	temp range, °C	no. of values of k_{obsd}	$\Delta H^{\ddagger}_2$, kJ mol^{-1}	$\Delta S^{\ddagger}_2$, J K^{-1} mol^{-1}	$\sigma(k_{obsd})$,[a] %
$P(OPh)_3$	40–60	21	66.4 ± 2.1	-101 ± 6	7.3
$AsPh_3$	40–60	12	78.2 ± 3.6	-50.5 ± 11.5	6.7
$SbPh_3$	40–55	27	73.1 ± 2.8	-63.9 ± 8.6	6.4

[a] Obtained by method of pooled variances on the assumption that $\sigma(k_{obsd})$ is independent of [L] and temperature.

($\epsilon = 2.8 \times 10^3$ L mol^{-1} cm^{-1}) when final absorbances, A_∞, varied from ca. 40 to 70% of A_0. Excellent first-order plots were obtained that were linear for ca. 3 half-lives. When L = $P(OPh)_3$, $P\text{-}n\text{-}Bu_3$, and $P(C_6H_{11})_3$, the reactions were also followed by IR spectroscopy. Very good rate plots were obtained, and the rate constants were in excellent agreement with those from UV–vis data. The reaction with $SbPh_3$ involved only a very small change in absorbance at 424 nm, but the reaction was so clean that good kinetic data were obtained. Rate constants were in excellent agreement with those obtained when reactions were followed by IR spectroscopy. The kinetics of the reaction with $AsPh_3$ were monitored only by IR spectroscopy. Rate plots were linear for over 2 half-lives.

The values of the pseudo-first-order rate constants, k_{obsd}, were found to depend on [L] in accord with eq 3 and were analyzed by a weighted least-squares program.[7] Values of a and k_2 are given in Table I, and activation parameters for reactions followed at several temperatures are shown in Table II.

$$k_{obsd} = a + k_2[L] \quad (3)$$

Discussion

The data in Table IV confirm that all the reactions studied follow the same course, stoichiometrically and sterically, the ligand L ending up trans to the bridging As atom in a trigonal-bipyramidal disposition of ligands around the Fe atom.[8] As shown in eq 2, the reactions involve the withdrawal of the electron pair in the Fe–Fe bond onto the Fe atom in the Fe-$(CO)_4$ group and its replacement on the other Fe atom by the donor pair from L.[12] The $(OC)_4Fe\leftarrow AsMe_2^-$ moiety can be regarded as an anionic chelating ligand attached to the Fe(0) in $Fe(CO)_2(NO)^+$ so that the reactions involve nucleophilic displacement of one end of a chelate ligand from a 5-coordinate d^8, Fe(0) center.[7,13]

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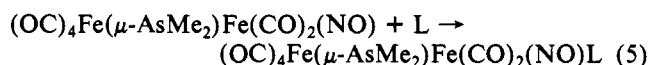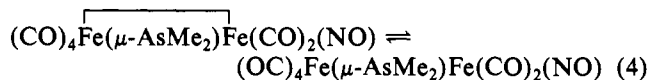(11) Jackson, R. A.; Poë, A. *J. Inorg. Chem.* **1979**, *18*, 3331.

(12) The question of the assignment of the oxidation states of the two metals during such reactions has recently been discussed.[3c,13]

Table III. Some Linear Free Energy Data for Bimolecular Reactions[a] of Some Metal Carbonyls

complex	temp, °C	solvent	$-\mathrm{d}(\log k_2)/$ $\mathrm{d}\Delta(\mathrm{hnp})$,[b] V^{-1}	R[c]	$\Delta[\mathrm{P(C_6H_{11})_3}]$[d]	ref
$\mathrm{Fe(CO)_2(NO)_2}$	25	toluene	5.9 ± 0.5	0.984	-1.8	19
$\mathrm{Co(CO)_3(NO)}$	25	toluene	4.8 ± 0.3	0.989	-1.6	20
$\mathrm{Mn(CO)_4(NO)}$	50	p-xylene	3.65 ± 0.01	1.00		21
$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Rh(CO)_2}$	40	toluene	2.7 ± 0.3	0.967	-2.1	22
$\mathrm{Mo(CO)_6}$	112	Decalin	1.53 ± 0.12	0.994	-0.4[e]	23
$\mathrm{Ru_3(CO)_{12}}$	60	Decalin	3.4 ± 0.7	0.989	-1.1[e]	17, 24
$\mathrm{Co_2(CO)_6(\mu\text{-}C_2Ph_2)}$	55	Decalin	2.9 ± 0.3	0.984	-0.7[e]	14
$\mathrm{Fe_2(CO)_6(\mu\text{-}S_2C_6H_3Me)}$	35	toluene	3.4 ± 0.6	0.964	-2.0	26
$\overline{(\mathrm{OC})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Co(CO)_3}}$	20	Decalin	2.5 ± 0.4	0.931	-0.6	7
$\overline{(\mathrm{OC})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Fe(CO)_2(NO)}}$	40	Decalin	3.3 ± 0.3[f]	0.987[f]	-1.0	this work

[a] All reactions are substitution of CO by P-donor ligands except for the last two, which are nucleophile-induced heterolytic fission of the Fe→Co and Fe→Fe bonds. [b] Values of $\log k_2$ increase linearly with decreasing values of $\Delta(\mathrm{hnp})$, i.e. with increasing basicity.[10,16] These values quantify[17] the dependence of the rates of the bimolecular reactions on basicity[18] and are obtained by linear least-squares analysis of the data given in the references listed. Uncertainties are standard deviations. [c] Correlation coefficients. [d] Deviation from the LFER of log k_2 for reaction with $\mathrm{P(C_6H_{11})_3}$. [e] Deviation of $\log k_2$ for reaction with $\mathrm{PPh_3}$. [f] Omitting the value of $\log k_2$ for reaction with $\mathrm{P(OCH_2)_3CEt}$ and $\mathrm{P(C_6H_{11})_3}$.

The dominant term in the rate equation is $k_2[\mathrm{L}]$, the values of a generally being negligible or small. No deviation from the first-order dependence on [L] is shown even at the highest concentrations used. The term $k_2[\mathrm{L}]$ could arise from a D mechanism involving highly reversible Fe→Fe bond heterolysis, i.e. opening of one end of the chelate ring, followed by weakly competing addition of L to the coordinatively unsaturated Fe atom as in eq 4 and 5. Alternatively, it could arise by direct

$$\overline{(\mathrm{CO})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Fe(CO)_2(NO)}} \rightleftharpoons$$
$$(\mathrm{OC})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Fe(CO)_2(NO)} \quad (4)$$

$$(\mathrm{OC})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Fe(CO)_2(NO)} + \mathrm{L} \rightarrow$$
$$(\mathrm{OC})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Fe(CO)_2(NO)L} \quad (5)$$

attack of L on the complex in an $\mathrm{I_a}$ or $\mathrm{I_d}$ process, the concentration of the intermediate, outer-sphere, encounter complex always being negligible.

The only way to distinguish between these various possibilities is by an examination of the dependence of the kinetic parameters on the nature of L. The ring-opening, D, mechanism would be characterized by a very small dependence of k_2 on the nature of L, the difference between the various values being dependent only on the difference between the rate constants for attack at a vacant coordination site as in eq 5.[7,14] This difference is likely to be very small. Thus, the rate constants for attack by the same group of P-donor ligands (apart from $\mathrm{P(C_6H_{11})_3}$, the effect of which was not studied) at the vacant coordination site in $\mathrm{Co_2(CO)_5(\mu\text{-}C_2Ph_2)}$ are very similar to each other, the mean deviation from the average being only ca. 40%.[14] Another indication of the D mechanism would be a rather small, negative (or even positive) value of ΔS^*_2 caused by the relative freedom of motion in the coordinatively unsaturated $(\mathrm{OC})_4\mathrm{Fe}(\mu\text{-}\mathrm{AsMe_2})\mathrm{Fe(CO)_2(NO)}$ intermediate.[7] Reaction 1 shows a value of ΔS^*_2 of only -11 J $\mathrm{K^{-1}}$ $\mathrm{mol^-}$ when L = CO[5] while reactions of $(\mathrm{che})\mathrm{Cr(CO)_4}$ (che = some bidentate, S-donor ligands) show small positive values of ΔS^*_2.[15] In the reactions studied here the values of k_2 obtained cover a range of a factor of 250. The range is effectively much larger than this because CO fails to react at all, even though the product is quite stable, whereas it reacts relatively quite rapidly when a D mechanism is operative.[5] In
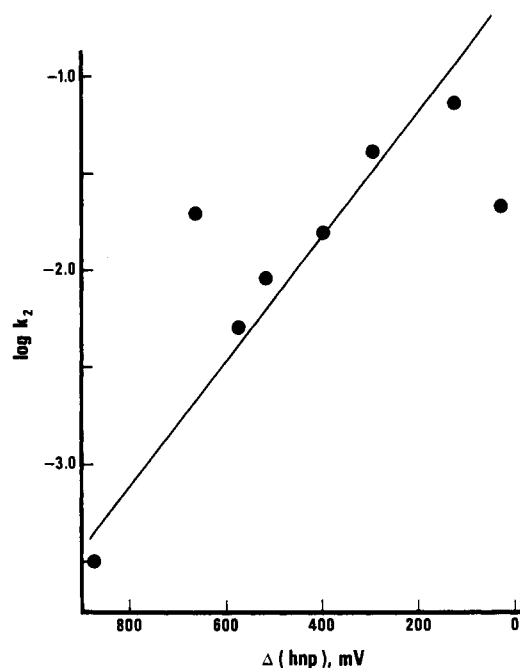

Figure 1. Dependence of $\log k_2$ on the basicity of L as measured by their half-neutralization potentials (see text). The basicity increases as $\Delta(\mathrm{hnp})$ decreases. The nucleophiles are, from left to right, $\mathrm{P(OPh)_3}$, $\mathrm{P(OCH_2)_3CEt}$, $\mathrm{PPh_3}$, $\mathrm{P(OMe)_3}$, $\mathrm{PPh_2Et}$, $\mathrm{PPhEt_2}$, P-n-$\mathrm{Bu_3}$, and $\mathrm{P(C_6H_{11})_3}$. The line is the "least-squares" line estimated with the values of $\log k_2$ for $\mathrm{P(OCH_2)_3CEt}$ and $\mathrm{P(C_6H_{11})_3}$ excluded (see text).

addition, the three values of ΔS^*_2 that were measured are substantially negative (Table II) even though the ligands involved are only weakly nucleophilic and are the most likely to be restricted to a D mechanism. It is, therefore, very improbable that any of the reactions proceed by this mechanism.

On the other hand, an $\mathrm{I_a}$ mechanism would be characterized by a substantial dependence on the nature of L. This can be quantified by the dependence[16] of $\log k_2$ on $\Delta(\mathrm{hnp})$, where $\Delta(\mathrm{hnp})$ is the half-neutralization potential for titration of the ligand against perchloric acid in nitromethane, i.e. a measure of the proton basicity of L.[10] A linear free energy plot of log k_2 against $\Delta(\mathrm{hnp})$ is shown in Figure 1 for the P-donor ligands. With the exception of L = $\mathrm{P(OCH_2)_3CEt}$ and $\mathrm{P(C_6H_{11})_3}$, the points fall close to a straight line of gradient 3.25 ± 0.27 $\mathrm{V^{-1}}$ with a correlation coefficient of 0.987. The mean deviation of the points from the LFER is only 0.112 log unit. We do

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not understand the reason for the deviation of the point for L = P(OCH$_2$)$_3$CEt. However, the point for L = P(C$_6$H$_{11}$)$_3$ lies 1.0 log unit below the value expected for it according to the LFER, and this can be associated with its exceptionally large cone angle[9] and the consequent steric retardation. Similar data obtained from the LFER for other metal carbonyls are shown in Table III. In general, the gradients provide a measure of the discrimination shown by the substrate complex toward the various P-donor nucleophiles and it can be inferred[14,17] that the greater the gradient the greater the degree of associative character in the transition state.[18] The deviation of the value of log k_2 for P(C$_6$H$_{11}$)$_3$ or, in some cases, PPh$_3$ from the LFER can also be taken as a measure of the extent of bond making for complexes of the same coordination number.[17] This is because P(C$_6$H$_{11}$)$_3$ and PPh$_3$ are large ligands (cone angles 179 and 145°),[9] which can approach the electrophilic center less closely (with a consequently high value of $\Delta H^{\ddagger}_2$ because of less bond making) or[7] can approach it along a more restricted path (with a consequently more negative value of $\Delta S^{\ddagger}_2$).

Thus, the gradients of the LFER for (OC)$_4$$\overline{\text{Fe}(\mu\text{-}}$ $\overline{\text{AsMe}_2)\text{Co(CO)}_3}$ and (OC)$_4$$\overline{\text{Fe}(\mu\text{-AsMe}_2)\text{Fe(CO)}_2}$(NO) suggest that the latter generally has a somewhat higher degree of bond making in the transition states, and this is supported by the greater steric retardation for P(C$_6$H$_{11}$)$_3$ as a nucleophile. The higher degree of bond making can be associated with the presence of the NO ligand,[16] which facilitates nucleophilic attack at the metal. The lower rates found for reactions of the Fe(CO)$_2$(NO) complex compared with those for the Co(CO)$_3$ complex may be due to a greater strength of the Fe→Fe bond (see below). The complexes Co(CO)$_3$(NO) and Fe(CO)$_2$(NO)$_2$ show the same sort of effect, the gradient of the LFER being higher for the latter compound and the steric retardation for P(C$_6$H$_{11}$)$_3$ being slightly greater.

As with (OC)$_4$$\overline{\text{Fe}(\mu\text{-AsMe}_2)\text{Co(CO)}_3}$,[7] the data for reactions with AsPh$_3$ and SbPh$_3$ present some problems. Both ligands have higher values of k_2 than that for P(OPh)$_3$, and yet they generally show much lower nucleophilicity toward metal centers in metal carbonyls.[27] In the case of the cobalt complex[7] the values of k_2 for reactions with AsPh$_3$, SbPh$_3$, PPh$_3$, P(OMe)$_3$, and P(OCH$_2$)$_3$CEt were all approximately the same, the average value being 2.8 × 10^{-3} L mol^{-1} s^{-1} at 20 °C with a mean deviation of ca. 30%. From this it was concluded that the mechanism for the less nucleophilic ligands tended to be I$_d$ in character. Any differences in the rates could be ascribed to differences in the formation constants, K_a, of the outer-sphere encounter complexes, and it is conceivable that the low value of k_2 for P(OPh)$_3$ is due to an exceptionally low value of K_a. The quite pronounced increase of the values

of k_2 along the series of nucleophiles PPh$_2$Et, PPhEt$_2$, and P-n-Bu$_3$ was ascribed to an increasingly associative, I$_a$, character in the mechanism. The same approach can be taken toward the data for reaction 2, but now we find that the values of k_2 for L = AsPh$_3$ and SbPh$_3$ are both substantially lower than that for PPh$_3$, which is in turn substantially lower than those for P(OCH$_2$)$_3$CEt and P(OMe)$_3$. The data can therefore be consistently rationalized if we conclude that the tendency to follow an I$_d$ mechanism is most pronounced only for the weakest nucleophiles AsPh$_3$, SbPh$_3$, and P(OPh)$_3$ but that the greater nucleophilicity of PPh$_3$, P(OMe)$_3$, and P(OCH$_2$)$_3$CEt is made use of by the more electrophilic Fe(CO)$_2$(NO) center in a way not shown by the less electrophilic Co(CO)$_3$ center. Thus, the general trend from I$_d$ to I$_a$ is apparent in both complexes, but the I$_a$ mechanism is of relatively greater significance in the Fe(CO)$_2$(NO) complex and appears earlier along the series of ligands of increasing nucleophilicity.

Another difference between the results for the Fe(CO)$_2$-(NO) and Co(CO)$_3$ complexes relates to the significance of the parameter a in eq 3. The values for the Co(CO)$_3$ complex were generally negligible. The values for the Fe(CO)$_2$(NO) complex are also often negligible, but the tendency for significantly finite positive values of a to occur appears to be greater.[28] A significant value of a could, in principle, be ascribed to a limiting rate constant for spontaneous heterolytic cleavage of the Fe→Fe bond, i.e. to the rate constant for dissociation of one end of the chelating Fe–As ligand. However, if this were correct, the values of a would have to be the same irrespective of the nucleophile. This is evidently not true since the value of a for reaction with P(OPh)$_3$ at 60 °C is much less than that for reaction with SbPh$_3$ at 55 °C. Finite values of a can, however, be ascribed to the rate constant for the reverse of reaction 2 so that the values of k_{osbd} are assignable to the pseudo-first-order rate constants for approach to equilibrium.

In the case of reaction with SbPh$_3$ at 55 °C, sufficiently low values of [SbPh$_3$] were used for there to be good evidence for an approach to equilibrium; i.e., the extent of the absorbance change during the reaction increased steadily with increasing [SbPh$_3$]. Thus, at [SbPh$_3$] = 0.0351 M the absorbance, A, decreased by only 7% whereas at [SbPh$_3$] = 0.175 M it decreased by 16%. Although the absorbance changes were small, the reactions were particularly clean as evidenced by the sharp isosbestic point at 401 nm. The extent of the absorbance change could be analyzed so as to give values for the equilibrium constant, K_2. Unfortunately, values of the absorbance corresponding to complete reaction were not obtained because insufficiently large values of [SbPh$_3$] were used and so the precision of the equilibrium constant obtained was rather low. Thus, the best agreement between experimental and calculated values of the absorbances at equilibrium was obtained when K_2 = 7.5 M^{-1} ($\sigma(A)$ = {$\sum(\Delta A)^2/(N-1)$}$^{1/2}$ = 0.008; ΔA = ($A_{calcd} - A_{obsd})/A_{calcd}$; N = number of points), but $\sigma(A)$ was still only 0.017 when K_2 = 20 M^{-1}. These values can be compared with the ratio k_2/a = 19 ± 2 M^{-1} that is obtained from the kinetics and that can be equated to $k_2/k_{-2} = K_2$. The agreement is therefore quite good. These experiments were not designed to obtain equilibrium data, but it is clear that such data would be readily available and that relative strengths of the Fe–L bonds in (OC)$_4$Fe(μ-AsMe$_2$)Fe(CO)$_2$(NO)L could quite easily be obtained.

An inference regarding the strength of the Fe→Fe bond in the title complex can be drawn from the kinetics. If we assume that the D mechanism shown in eq 4 and 5 would be characterized by a value of $\Delta S^{\ddagger}$ close to zero,[15] then $\Delta H^{\ddagger}$ for this path would have to be ≳100 kJ mol^{-1} since the value of $\Delta G^{\ddagger}$

(17) Poë, A. J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860.
(18) For those who object to the use of Δ(hnp) values as a measure of basicity and nucleophilicity, these plots can be replaced[14] by plots of log k_2 for reaction of a particular complex with L against the value of log k_2 for reaction of the same L with Co(CO)$_3$(NO), taken as a standard reference compound. It is a good reference because it has been studied with the largest number of different nucleophiles. This leads to essentially the same results since all the gradients have to be divided by 4.8 and are greater than or less than unity to the extent that the complex is more or less discriminating than Co(CO)$_3$(NO). However, the plots against Δ(hnp) have the advantage of indicating steric deviations and the excellent linearity of the plot for Co(CO)$_3$(NO)[16,20] does suggest that the values of Δ(hnp) are empirically satisfactory.
(19) Morris, D. E.; Basolo, F. *J. Am. Chem. Soc.* **1968**, *90*, 2531.
(20) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.
(21) Wawersik, H.; Basolo, F. *J. Am. Chem. Soc.* **1967**, *89*, 4626.
(22) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.
(23) Graham, G. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.
(24) This includes a value[25] of k_2 = 5.62 × 10^{-2} M^{-1} s^{-1} for L = PPh$_2$Me.
(25) Twigg, M. V. *Inorg. Chim. Acta* **1977**, *21*, L7.
(26) Ellgen, P. C.; Gerlach, J. N. *Inorg. Chem.* **1973**, *12*, 2526.
(27) Reference 7 and references therein.

(28) Some negative values of a appear to be satistically significant, but we attribute these to small systematic errors.

would have to be greater than that observed for the I_d mechanism actually followed by reaction with $P(OPh)_3$ (see data in Table II). The value of $\Delta H^\ddagger$ for the addition of $P(OPh)_3$ as in eq 5 would be small so the value of ΔH° for the reversible ring-opening step shown in eq 4 would also be $\gtrsim 100$ kJ mol^{-1}, and this is therefore a reasonable lower limit for the value of the Fe→Fe bond strength. Similar values can be inferred from the activation parameters for reactions with $AsPh_3$ and $SbPh_3$ (Table II). The same analysis of the data[7] for the I_d reactions of the analogous $Co(CO)_3$ complex suggests that the strength of the Fe→Co bond has a similar, or slightly smaller, lower limit. These heteronuclear metal–metal bonds are therefore at worst only moderately weak and could be quite strong.

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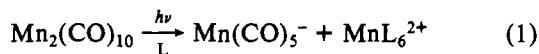
Mechanism of the Photochemical Disproportionation Reaction of Mn$_2$(CO)$_{10}$ with Nitrogen Donor Ligands

ALBERT E. STIEGMAN and DAVID R. TYLER*

The mechanism of the photochemical disproportionation of Mn$_2$(CO)$_{10}$ in the presence of the nitrogen donor ligands pyridine (py), triethylamine (NEt$_3$), trimethylethylenediamine (Me$_3$en), and diethylenetriamine (dien) was investigated. The disproportionation is proposed to follow a radical chain pathway: (1) Mn$_2$(CO)$_{10}$ $\xrightarrow{h\nu}$ 2Mn(CO)$_5$, (2) Mn(CO)$_5$ + N → Mn(CO)$_4$N + CO, (3) Mn(CO)$_4$N + N → Mn(CO)$_3$N$_2$ + CO, (4) Mn(CO)$_3$N$_2$ + N → Mn(CO)$_3$N$_3$, (5) Mn(CO)$_3$N$_3$ + Mn$_2$(CO)$_{10}$ → Mn(CO)$_3$N$_3^+$ + Mn$_2$(CO)$_{10}^-$, (6) Mn$_2$(CO)$_{10}^-$ → Mn(CO)$_5$ + Mn(CO)$_5^-$. The quantum yields for the disproportionation are ϕ(py) = 0.1, ϕ(NEt$_3$) = 0.1, ϕ(Me$_3$en) = 1.2, and ϕ(dien) = 6–19. The key to the mechanism is the formation of the 19-electron intermediate Mn(CO)$_3$N$_3$. Evidence is presented for the formation of this intermediate. The intermediate Mn$_2$(CO)$_{10}^-$ was generated by reacting Mn$_2$(CO)$_{10}$ with Na; in the presence of ligand disproportionation occurred.

We recently showed that 19-electron species are key intermediates in the photochemical disproportionation reactions of Cp$_2$Mo$_2$(CO)$_6$.[1] In order to determine whether 19-electron intermediates were forming in the disproportionation reactions of other metal–metal-bonded carbonyl dimers, we studied the photochemical disproportionation of Mn$_2$(CO)$_{10}$ by amine ligands (eq 1).[2] This paper reports the results of quantum

$$Mn_2(CO)_{10} \xrightarrow[L]{h\nu} Mn(CO)_5^- + MnL_6^{2+} \qquad (1)$$

yield measurements and electrochemical studies that strongly suggest that 19-electron intermediates are important in the photochemical disproportionation of Mn$_2$(CO)$_{10}$ by amines.

Experimental Section

Mn$_2$(CO)$_{10}$ was obtained from Strem Chemical Co. and sublimed before use. [Mn(CO)$_3$(py)$_3$][PF$_6$] (py = pyridine) and [Mn(C-

O)$_3$(CH$_3$CN)$_3$][PF$_6$] were synthesized by literature methods.[3] It was necessary to recrystallize [Mn(CO)$_3$(py)$_3$][PF$_6$] several times from acetone/ether to obtain material free of [Mn(CO)$_3$(py)$_2$-(CH$_3$CN)][PF$_6$]. LiClO$_4$ was obtained from Aldrich, recrystallized from water, and dried in an oven for 3 days at 180 °C. THF (Gold Label) was obtained from Aldrich and used as received. Pyridine and triethylamine were purchased from MCB, stirred over calcium hydride, and distilled under argon.[4] Spectral grade acetonitrile and benzene were purchased from Fisher and used as received. Sodium powder, suspended in mineral oil (40% by weight), trimethylethylenediamine, and diethylenetriamine were purchased from Aldrich and used without further purification.

All photochemical reactions were carried out under anaerobic conditions as previously described.[5] Irradiations were performed with an Oriel 200-W high-pressure mercury lamp or a Tensor high-intensity incandescent lamp. Lamp intensities were determined by using ferrioxalate actinometry.[6] Typical lamp intensities were 5 × 10^{-6} einstein/min for the mercury lamp and 1 × 10^{-9} einstein/min for the incandescent lamp. Radiation of 366-nm wavelength was isolated with a Corning 7-83 narrow band-pass glass filter. The quantum yields were measured for the disappearance of Mn$_2$(CO)$_{10}$. With the monodentate and bidentate ligands at low concentrations, substitution products as well as the ionic disproportionation products form. Thus, in these cases, the reported quantum yields are upper limits for the true quantum yield of disproportionation.

(1) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032.
(2) The photochemical disproportionation reaction of Mn$_2$(CO)$_{10}$ in neat pyridine solvent was recently studied by McCullen and Brown: McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528–3533. They proposed a radical chain mechanism initiated by photochemical homolytic cleavage of the metal–metal bond but not involving 19-electron intermediates. Note that the Mn(I) complex Mn(CO)$_3$N$_3^+$ is the expected product of the disproportionation. Using infrared spectroscopy, McCullen and Brown observed the transitory species Mn(CO)$_3$(py)$_3^+$ during the irradiation. They independently synthesized the Mn-(CO)$_3$(py)$_3^+$ complex and showed that irradiation of this complex in pyridine produced Mn(py)$_6^{2+}$ and small amounts of Mn(CO)$_5^-$:

3Mn(CO)$_3$(py)$_3^+$ + 3py $\xrightarrow{h\nu}$ 2Mn(py)$_6^{2+}$ + Mn(CO)$_5^-$ + 4CO

This reaction is thus the source of the Mn(II) product.

(3) Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579–1584.
(4) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.
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(6) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.