$(CO)(MeNC)_2CS$ (bis-terminal isomer), 76157-20-5; $[Cp_2Fe_2(CO)_3CSMe]FSO_3$, 76157-22-7; $[Cp_2Fe_2(CO)_3CSEt]BF_4$, 66540-79-2; $[Cp_2Fe_2(CO)_3CSMe]PF_6$, 76189-80-5; $[Cp_2Fe_2(CO)_3CSEt]PF_6$, 76157-24-9; $[Cp_2Fe_2(CO)_3CSPr]PF_6$, 76157-26-1; $[Cp_2Fe_2(CO)_3CSBu]PF_6$, 76157-28-3; $[Cp_2Fe_2(CO)_3CSBz]PF_6$, 76157-30-7; $[Cp_2Fe_2(CO)_3CSAll]PF_6$, 76157-32-9; $[Cp_2Fe_2(CO)_2(PEt_3)CSMe]PF_6$, 76157-34-1; $[Cp_2Fe_2(CO)_2(PMe_2Ph)CSMe]PF_6$, 76157-36-3; $[Cp_2Fe_2(CO)_2(PMePh_2)CSMe]PF_6$, 76157-38-5; $[Cp_2Fe_2(CO)_2(P(OMe)_3)CSMe]PF_6$, 76157-40-9; $[Cp_2Fe_2(CO)_2(MeNC)CSMe]PF_6$, 76157-42-1; $[Cp_2Fe_2(CO)_2(PEt_3)CSBz]PF_6$, 76157-44-3; $Cp_2Fe_2(CO)_2(I)(CSMe)$, 76157-45-4; $Cp_2Fe_2(CO)_2(I)(CSEt)$, 76157-46-5; $[Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe](PF_6)_2$, 76172-96-8; $[Cp_2Fe_2(CO)(MeNC)_2CSMe]PF_6$, 76157-48-7; $MeOSO_2F$, 421-20-5; $[Et_3O]BF_4$, 368-39-8; MeI, 74-88-4; EtI, 75-03-6; *n*-PrI, 107-08-4; *n*-BuI, 542-69-8; BzBr, 100-39-0; AllBr, 106-95-6; $Cp_2Fe_2(CO)_2(MeNC)CS$ (bridge isomer), 76172-97-9.

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# Mechanisms of Iron–Cobalt Bond Breaking in Tetracarbonyliron-μ-(dimethylarsenido)-tricarbonylcobalt(*Fe–Co*)[1]

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The kinetics have been examined of heterolytic fission of the Fe→Co bond in $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ in cyclohexane or decalin. Fission is induced by a series of P-, As-, and Sb-donor ligands that become coordinated to the Co atom, and the rates are all closely first order in the concentration of entering ligand. The variation of the second-order rate constant with the nature of the entering P-donor ligands suggests that a concerted but largely $I_d$ process is occurring with the less nucleophilic ligands but that the reactions become more $I_a$ in character as the ligand nucleophilicity increases.

Complexes of the type $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)M}$ (M = $Mn(CO)_4$, $Fe(CO)_2(NO)$, $Co(CO)_3$, $Mo(CO)_2(\eta^5\text{-}C_5H_5)$, etc.)[2-4] have been shown to react with phosphorus-donor ligands according to eq 1. This involves simple heterolytic fission of

$$(OC)_4\overline{Fe(\mu\text{-}AsMe_2)M} + L \rightarrow (OC)_4Fe(\mu\text{-}AsMe_2)ML \quad (1)$$

the Fe→M bond and the addition of the ligand L to the metal atom in the group M. When M = $Co(CO)_3$[5] and $Mn(CO)_4$[6] a series of Fe→Co and Fe→Mn bond-breaking and bond-making reactions can be carried out, leading to a very extensive array of more highly substituted derivatives. The compounds with M = $Co(CO)_3$ and $Fe(CO)_2(NO)$ have been shown to act as catalysts for the dimerization of norbornadiene.[7] Quantitative kinetic studies of such reactions would be of interest in helping to define their detailed mechanisms and energetics and, possibly, in characterizing reactive intermediates. We report here the results of a kinetic study of the reactions of $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ with some P-, As-, and Sb-donor ligands.

## Experimental Section

The complex $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ was prepared by Dr. H.-J. Langenbach and kindly provided for this work by Professor H. Vahrenkamp. The solvents and phosphorus-donor ligands were obtained and treated before use as described elsewhere.[8,9] Triphenylarsine and -stibine (Eastman Organic Chemicals and J. T. Baker Chemical Co., respectively) were recrystallized from methanol.

Table I. Infrared Spectra[a] of the Products of Reaction of $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ with L in Decalin

| L | ν(Fe–CO), cm⁻¹ | | | ν(Co–CO), cm⁻¹ | | |
|---|---|---|---|---|---|---|
| $P(C_6H_{11})_3$ | 2028 s | 1958 vs | 1926 vs | 2046 w | 1974 vs | 1965 s |
| P-*n*-$Bu_3$ | 2030 m | 1958 s | 1927 vs | 2051 w | 1980 s | 1969 s |
| $PPhEt_2$ | 2031 s | 1959 s | 1928 vs | 2051 w | 1984 s | 1971 s |
| $PPh_2Et$ | 2032 s | 1959 s | 1928 vs | 2055 w | 1986 s | 1974 s |
| $P(OMe)_3$ | 2036 s | 1961 m | 1929 vs | 2063 vw | 1997 s | 1987 s |
| $P(OMe)_3$[b] | 2029 s | 1965 m | 1931 vs | 2054 vw | 1996 s | 1990 s |
| $PPh_3$ | 2032 s | 1960 m | 1929 vs | 2054 w | 1988 s | 1976 s |
| $PPh_3$[b] | 2027 s | 1962 s | 1931 vs | 2048 w | 1992 s | 1978 s |
| etpb[c] | 2037 s | 1962 m | 1930 vs | 2059 vw | 2013 s | 1998 s |
| $P(OPh)_3$ | 2035 s | 1961 m | 1928 m | 2060 vw | 2000 vw | 1988 s |
| $AsPh_3$[d] | 2031 m | 1962 m | 1931 s | 2056 vw | 1987 s | 1975 s |
| $SbPh_3$[d] | 2036 m | 1962 m | 1932 s | 2060 vw | 1988 s | 1976 vs |

[a] Assignments made as in ref 4. [b] Spectra in cyclohexane of $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L$ isolated and characterized as in ref 4. [c] $P(OCH_2)_3CEt$. [d] In cyclohexane.

Solutions of air-sensitive liquid phosphines were prepared by transferring the pure liquid under argon in a syringe to a serum-capped volumetric flask which was flushed with argon. The flask was filled to the mark with degassed solvent driven through a stainless steel needle from a Schlenk tube by a positive pressure of argon. Solid $P(C_6H_{11})_3$ was weighed into a similar flask, which was then flushed with argon and filled to the mark with degassed solvent. Solutions of the less air-sensitive ligands were made up under air and degassed in Schlenk tubes by several freeze–pump–thaw cycles. For most kinetic runs 2.5 mL of ligand solution was transferred by syringe to a serum-capped 10-mm silica cell, which was flushed with argon. The cells were then placed in the thermostated multicell cell holder of a Cary 16K spectrophotometer and left for 20 min for temperature equilibration. Reactions were initiated by rapidly injecting 0.05 mL of a concentrated, degassed solution of complex by means of a syringe and vigorously shaking the cell for a few seconds. Temperature control (±0.1 °C) was maintained by using a circulating Brinkman-Lauda Model K temperature bath, and temperatures were monitored constantly using a Minco Inc. platinum or nickel resistance thermometer. This was immersed in a water-filled cell in the cell holder and was connected to a Data Precision Model 3500 digital multimeter. When the re-

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(1) Part 26 in the series "Reaction Mechanisms of Metal–Metal-Bonded Carbonyls". Part 25: Kramer, G.; Poë, A. J. *Inorg. Chem.*, in press.
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**Table II.** Kinetic Parameters for the Reaction of $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ with L at 20 °C in Decalin

| L | $10^5 a$, $s^{-1}$ | $10^3 k_2$, L $mol^{-1}$ $s^{-1}$ | $\sigma(k_{obsd})$, % | log $k_2$ | Δ(hnp), mV |
|---|---|---|---|---|---|
| $P(C_6H_{11})_3$ | 0.004 ± 0.100 | 16.6 ± 2.0 | 4.0 | −1.78 | 33 |
| $P\text{-}n\text{-}Bu_3$ | 5.3 ± 4.8 | 26.5 ± 0.2 | 1.8 | −1.58 | 131 |
| $PPhEt_2$ | −5.0 ± 6.7 | 19.0 ± 0.6 | 5.9 | −1.72 | 300 |
| $PPh_2Et$ | 10 ± 3 | 10.8 ± 0.1 | 2.5 | −1.97 | 400 |
| $P(OMe)_3$ | 9.3 ± 7.9 | 1.59 ± 0.14 | 10.9 | −2.80 | 520 |
| $PPh_3$ | 1.8 ± 1.0 | 4.09 ± 0.06 | 5.1 | −2.39 | 573 |
| etpb | 8.2 ± 1.5 | 3.31 ± 0.09 | 4.7 | −2.48 | 665 |
| $P(OPh)_3$ | 2.0 ± 4.0 | 0.359 ± 0.010 | 3.4 | −3.44 | 875 |
| $AsPh_3$ | 2.6 ± 0.8[a] | 5.52 ± 0.19[a] | 4.2 | | |
| | | 1.5[b] | | −2.82 | |
| $SbPh_3$ | −0.06 ± 3.2[a] | 13.1 ± 0.7[a] | 6.1 | | |
| | | 3.5[b] | | −2.46 | |

[a] At 34.6 °C in cyclohexane ([L] dependence not studied at 20 °C). [b] At 20 °C, assuming $a = 0$ in cyclohexane.

actions were sufficiently slow ($t_{1/2} >$ ca. 10 min), up to four reactions were followed simultaneously. Faster reactions required the use of the "continuous-drive" mode of the spectrophotometer and only one reaction could be followed at a time. The fastest reactions (with $P\text{-}n\text{-}Bu_3$ at ≥30 °C) were followed by using a Nortech SF-3A ("Canterbury") stopped-flow spectrophotometer.[10] The reservoirs were made so that they could be continuously flushed with $N_2$ while being filled with degassed solutions. The output from the spectrophotometer was stored in a Biomation Model 805 recorder and displayed on a strip-chart recorder when required.

The reactions were followed by measuring the decreasing absorbance of the band at 439 nm ($\epsilon$ 2.5 × $10^3$ L $mol^{-1}$ $cm^{-1}$) due to the complex, the decrease amounting to 20–60% depending on the nucleophilic ligand. The absorption band of the complex is replaced by ones below 350 nm which have broad shoulders extending to ca. 700 nm. When the nucleophiles were $AsPh_3$ and $SbPh_3$, there were sharp isosbestic points at 413 and 499 nm and at 420 and 482 nm, respectively. The infrared spectra of the final products are shown in Table I.

Excellent pseudo-first-order rate plots, linear for up to 3 half-lives, were obtained for all reactions. The rate constants, $k_{obsd}$, were analyzed according to eq 2 by a weighted least-squares program in which each

$$k_{obsd} = a + k_2[L] \quad (2)$$

value of $k_{obsd}$ was assumed to have a constant percentage uncertainty given by the standard deviation $\sigma(k_{obsd})$. Estimates of the uncertainties that were obtained from the program were adjusted for the number of degrees of freedom involved so that doubling the adjusted values provides good estimates of the 95% confidence limits. Values of $a$ and $k_2$ are shown in Table II. In almost all cases the value of $a$ is small or negligible so that the reaction is controlled almost exclusively by the second-order rate constant, $k_2$. In those cases where reactions were followed at several temperature values of $\Delta H_2^*$ and $\Delta S_2^*$ (Table III) were obtained by a least-squares analysis of the dependence of log ($k_{obsd}/[L]T$) on $1/T$, in which the percentage uncertainty of the rate constants was assumed to be independent of temperature as well as of [L].

## Discussion

The agreement shown in Table I between the final spectra obtained by us in the reactions with $P(OMe)_3$ and $PPh_3$ and the published spectra for fully characterized $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L$ (L = $P(OMe)_3$ or $PPh_3$)[3] is excellent. This confirms that we were following reactions as described in eq 1, with M = $Co(CO)_3$, and that L is axial and trans to the As atom in the trigonal-pyramidal disposition of ligands around the Co atom in the product. The final spectra shown by reactions where the product has not been otherwise characterized are all closely similar. The stretching frequencies assigned to those CO ligands attached to the Fe atom are, as would be expected, essentially unaffected by the nature of L, and those assigned to CO ligands attached to the Co atom are sensitive to the nature of L in the way generally observed.[11]

**Table III.** Activation Parameters for the Reaction $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3 + L \rightarrow (CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L$

| L | $T$ range, °C | no.[a] | $\Delta H^{\ddagger}_2$, kJ $mol^{-1}$ | $\Delta S^{\ddagger}_2$, J $K^{-1}$ $mol^{-1}$ | $\sigma$-($k_{obsd}$), % |
|---|---|---|---|---|---|
| $P(C_6H_{11})_3$ | 20.0–50.0 | 24 | 58.7 ± 0.5 | −78.7 ± 1.7 | 3.6 |
| $P\text{-}n\text{-}Bu_3$ | 20.0–70.2 | 27 | 59.7 ± 0.2 | −71.5 ± 0.7 | 2.5 |
| $PPh_3$ | 20.0–38.8 | 41 | 64.7 ± 0.7 | −69.5 ± 2.3 | 3.4 |
| $P(OPh)_3$ | 20.0–50.0 | 17 | 70.1 ± 1.0 | −70.5 ± 3.3 | 6.2 |
| $AsPh_3$ | 20.4–48.9 | 22 | 67.1 ± 1.4 | −69.2 ± 4.3 | 6.6 |
| $SbPh_3$ | 20.4–43.7 | 23 | 72.1 ± 2.5 | −45.6 ± 8.1 | 11.6 |

[a] Number of rate constants determined.

There can be no doubt, therefore, that all these reactions are following the same course stoichiometrically and sterically.

The reactions involve the withdrawal by the Fe atom of the pair of electrons in the Fe→Co bond and its replacement on the Co atom by a pair of electrons from L. They can therefore be regarded as nucleophilic displacements, at a 5-coordinate Co atom, of an Fe-donor atom by a P-, As-, or Sb-donor ligand. The absence of any significant term independent of [L] in the rate equation shows that no rate-limiting unimolecular path is available and that the [L]-dependent path is dominating. Second-order reactions involving 5-coordinate metal atoms in mononuclear complexes have been observed before and are believed to involve nucleophilic attack at the metal atom.[12] However, $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ may be regarded as a cobalt complex containing three CO ligands and a bidentate chelating Fe–As ligand. The reactions can then be described as the displacement of one end of the chelate ligand. Such reactions are known very frequently to occur in a stepwise manner, the first being very readily reversible opening of one end of the chelate ring and the second nucleophilic attack at the vacant site created by the first step.[13] This mechanism is described in eq 3 and 4 and the corresponding rate equation is shown in eq 5. If $k_{-3}$ is always much

$$(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3 \quad (3)$$

$$(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3 + L \xrightarrow{k_4} (OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L \quad (4)$$

$$k_{obsd} = \{k_3(k_4/k_{-3})[L]\}/\{1 + (k_4/k_{-3})[L]\} \quad (5)$$

greater than $k_4[L]$, then $k_{obsd} = k_3k_4[L]/k_{-3}$ and the values

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of $k_2$ obtained from the kinetics could be equated with $k_3k_4/k_{-3}$ instead of with the simple bimolecular rate constant, $k_6$, governing the concerted process shown in eq 6. Since it is

$$\overline{(OC)_4Fe(\mu\text{-}AsMe_2)Co}(CO)_3 + L \xrightarrow{k_6} (OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L \quad (6)$$

indeed quite possible that $k_{-3}$ would be much greater than $k_4[L]$, the linearity of the plots of $k_{obsd}$ against [L] does not rule out the two-step mechanism and the rate equation cannot itself distinguish the two mechanisms. Nevertheless, they can, in principle, be distinguished by an examination of the dependence of $k_2$ on the nature of L.

Reactions that proceed by nucleophilic attack at a metal show a pronounced dependence of the rates on the basicity of the nucleophiles.[14,15] This can be quantified by linear free energy plots of log $k_2$ against Δ(hnp), the half-neutralization potentials for titration of the ligand against perchloric acid in nitromethane. Such plots are generally quite linear, and their gradients are a measure of the selectivity of the complex and, therefore, of the extent of bond making in the transition state.[8,9] In some cases the values of log $k_2$ for larger ligands deviate from what would be expected from their basicity[14,15] by amounts which can be correlated with steric effects, and these, in turn, can be used as an indication of the amount of bond making.[8,9] Thus, gradients between 5.80 ± 0.48 $V^{-1}$ for $Fe(CO)_2(NO)_2$[16] and ca. 0.7 $V^{-1}$ for $Cr(CO)_6$[9,17] are found for mononuclear carbonyls while a steric deviation of 1.8 log units is observed for reaction of $P(C_6H_{11})_3$ with $Fe(CO)_2(NO)_2$ and as much as ca. 3 log units for reaction of this phosphine with the quasi-octahedral $Ru_3(CO)_{12}$.[9]

If, on the other hand, the second-order nature of the kinetics is determined by highly reversible formation of a reactive intermediate and subsequent addition of the nucleophile to a vacant coordination site, then the values of $k_2$ would not be expected to depend greatly on the nature of L, the vacant coordination site causing high reactivity and low discrimination. Steric effects would also be smaller. Several studies have confirmed that the rate of attack of a limited number of ligands on vacant coordination sites is not greatly dependent on the nature of the ligands.[18] The most systematic study of the dependence on L of the ease of nucleophilic attack on a vacant coordination site as compared with attack at a fully coordinated metal center concerned reactions of L with the reactive intermediate $\overline{(OC)_3Co(\mu\text{-}C_2Ph_2)Co}(CO)_2$ and with the fully coordinated complex $\overline{(OC)_3Co(\mu\text{-}C_2Ph_2)Co}(CO)_3$.[8] Attack at the vacant coordination site showed a gradient of the LFER of <1 $V^{-1}$ (and probably much closer to zero) while the plot for attack at the fully coordinated Co atom showed a gradient of 2.92 ± 0.26 $V^{-1}$ and a steric deviation for $PPh_3$ of 0.7 log unit.

A plot of the values of log $k_2$ for the P-donor nucleophiles against the corresponding values of Δ(hnp) is shown in Figure 1. Apart from $L = P(C_6H_{11})_3$ the data lie reasonably close to the straight line drawn. The gradient is 2.48 ± 0.43 $V^{-1}$, the correlation coefficient is −0.931, and the mean deviation of the values of log $k_2$ from the ideal behavior is ±0.20. The value of log $k_2$ for $L = P(C_6H_{11})_3$ lies 0.58 log unit below the line, but the value for $L = PPh_3$ does not deviate significantly. These features show that the substrate is quite discriminating toward the various nucleophiles and that reaction of $P(C_6H_{11})_3$ is significantly inhibited by its large size. The gradient is close to that found from a study of the reactions of $Co_2(CO)_6(C_2Ph_2)$.[8] The steric effects in the latter reactions appear to be somewhat larger (in that log $k_2$ for $L = PPh_3$ deviates from the ideal behavior[8]), and this is not unreasonable since, in a steric sense at least, the Co atoms in $Co_2(CO)_6(C_2Ph_2)$ can be regarded as hexacoordinated. The gradient is also quite close to that observed for $(\eta^5\text{-}C_5H_5)Rh(CO)_2$.[9,12b] The observed characteristics of the reactions of the P-donor ligands are therefore in good agreement with straightforward nucleophilic attack at the Co atom with concerted displacement of the Fe donor atom. They would seem to be quite incompatible with the two-step mechanism described in eq 3 and 4 for which very little discrimination would be expected.

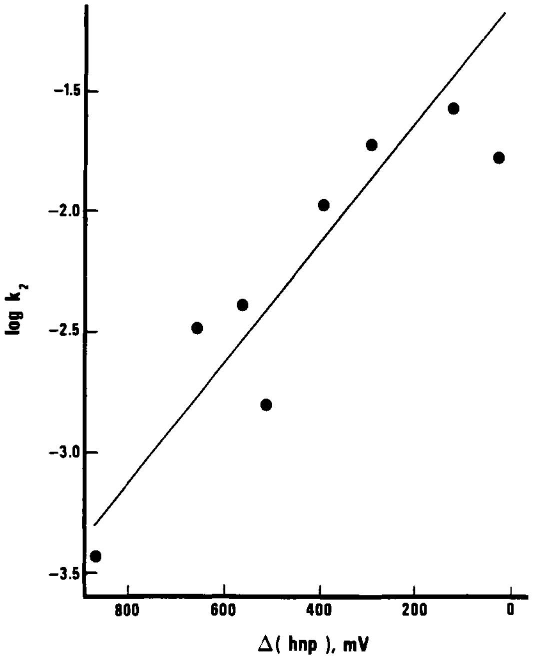

**Figure 1.** Dependence of log $k_2$ on the basicity of L as measured by their half-neutralization potentials (see text). The basicity increases as Δ(hnp) decreases. The nucleophiles are, from left to right, $P(OPh)_3$, etpb, $PPh_3$, $P(OMe)_3$, $PPh_2Et$, $PPhEt_2$, P-*n*-$Bu_3$, $P(C_6H_{11})_3$. The line is the "least-squares" line.

The highly negative values of $\Delta S_2^{\ddagger}$ listed in Table III also support a concerted mechanism. The two-step mechanism would involve a transition state with a monodentate Fe–As ligand, the Fe-donor being completely free and uncoordinated. Analogues of this transition state with more conventional chelating ligands have been shown to be characterized by much less negative values of $\Delta S_2^{\ddagger}$.[19,20]

The behavior of the nucleophiles $AsPh_3$ and $SbPh_3$ is somewhat unexpected. Although values of Δ(hnp) have not been reported, values of $k_2$ for these ligands are generally much smaller than those for $P(OPh)_3$ when nucleophilic attack at a metal atom is clearly indicated.[9,12,14,15,21] However, the values of $k_2$ for $AsPh_3$ and $SbPh_3$ in Table II are considerably larger than that for $P(OPh)_3$ and quite close to those for $PPh_3$, $P(OMe)_3$, and etpb. The values of $\Delta S_2^{\ddagger}$ for $AsPh_3$ and $SbPh_3$ are nevertheless quite negative and indicative of a concerted process. A rather similar pattern was observed for the bimolecular attack by these five ligands on $Mo(CO)_5$(piperidine).[22] A two-step mechanism such as eq 3 and 4 is obviously

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not possible for reactions of this complex, and an $I_d$ mechanism was assigned.[22]

Although it is not clear why reaction of $P(OPh)_3$ should be so slow (or why that of $SbPh_3$ should be so fast), a consistent interpretation of the data would be to conclude that these same five ligands react with $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ by a concerted but largely dissociative $I_d$ mechanism. The values of $k_2$ increase systematically along the series of increasingly basic ligands $PPh_2Et$, $PPhEt_2$, and $P\text{-}n\text{-}Bu_3$ to an extent compatible with increasing amounts of Co–P bond making and increasing $I_a$ character.

The activation parameters in Table III show that $\Delta H_2^*$ decreases along the series $P(OPh)_3 > PPh_3 > P\text{-}n\text{-}Bu_3 > P(C_6H_{11})_3$ in accordance with increasing Co–P bond making. The low value of $k_2$ for $P(C_6H_{11})_3$ compared with $P\text{-}n\text{-}Bu_3$ is due to a more unfavorable value of $\Delta S_2^*$, $\Delta H_2^*$ being slightly more favorable. This suggests that the steric effect may be due to a more limited path of approach for the nucleophile rather than a diminished degree of bond making. The values of $\Delta H_2^*$ for $AsPh_3$ and $SbPh_3$ are both fairly close to that for $P(OPh)_3$ and are higher than that for $PPh_3$. The unexpectedly high value of $k_2$ for $SbPh_3$ is due to an exceptional value of $\Delta S_2^*$, though whether this will turn out to be generally true remains to be seen.

We can conclude that the heterolytic Fe→Co bond-breaking reactions studied here are induced by a concerted but largely $I_d$ bimolecular process for the less nucleophilic ligands. As the nucleophilic character of the ligands increases, there is an increasing degree of bond making in the transition state and the $I_a$ character of the reaction with $P\text{-}n\text{-}Bu_3$ is probably quite large. No kinetic evidence is obtained for the formation of any coordinatively unsaturated intermediates during the reactions, and no estimates can be made from the kinetic parameters of the strengths of the Fe→Co bonds.

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**Registry No.** $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$, 50388-37-9; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P(C_6H_{11})_3)$, 76402-85-2; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P\text{-}n\text{-}Bu_3)$, 76402-86-3; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(PPhEt_2)$, 76402-87-4; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(PPh_2Et)$, 76402-88-5; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P(OMe)_3)$, 54766-35-7; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(PPh_3)$, 54790-06-6; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(etpb)$, 76402-89-6; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P(OPh)_3)$, 76402-90-9; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(AsPh_3)$, 76402-91-0; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(SbPh_3)$, 76402-92-1; $P(C_6H_{11})_3$, 2622-14-2; $P\text{-}n\text{-}Bu_3$, 998-40-3; $PPhEt_2$, 1605-53-4; $PPh_2Et$, 607-01-2; $P(OMe)_3$, 121-45-9; $PPh_3$, 603-35-0; etpb, 824-11-3; $P(OPh)_3$, 101-02-0; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1.

**Supplementary Material Available:** Table IV, a listing of observed pseudo-first-order rate constants (4 pages). Ordering information is given on any current masthead page.

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# Photochemistry of Tetracarbonylbis(cyclopentadienyl)dichromium(I) and Related Compounds: Labilization of Carbon Monoxide

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Photochemistry of three related compounds, $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$, $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$, and $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2CO)_4$, having a chromium–chromium triple bond has been examined, and the principal result is that the CO ligands are labilized by photoexcitation. Spectroscopically, the complexes are similar and exhibit a visible absorption at ~600 nm ($\epsilon \approx 300$ $M^{-1}$ $cm^{-1}$) and a near-ultraviolet absorption at ~400 nm ($\epsilon \approx 10^4$ $M^{-1}$ $cm^{-1}$) in alkane solution. Homolytic scission of the metal–metal triple bond is ruled out as a primary photoprocess by the facts that (i) irradiation of $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ in alkane solution does not yield $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ and $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ and (ii) irradiation of both $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ and $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ as a 1/1 mixture in alkane solution does not yield $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$. Labilization of CO upon photoexcitation is established by irradiation of $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ or $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ in alkane solution under a $^{13}CO$ (90% $^{13}C$, 10% $^{12}C$) atmosphere. Quantum yields for CO exchange are generally low and dependent on the excitation wavelength. The quantum yields for CO exchange for $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ are $<2 \times 10^{-4}$ at 633 nm, $(1.2 \pm 0.3) \times 10^{-3}$ at 458 nm, and $(4.0 \pm 1.0) \times 10^{-2}$ at 366 nm. The wavelength dependence is consistent with dissociative loss of CO from an upper excited state. When the complexes are irradiated in degassed alkane solution (in the absence of CO), decomposition occurs with an initial quantum yield similar to that for CO exchange. The presence of CO generally suppresses decomposition but not completely. The $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ is the least susceptible to decomposition in the presence of CO.

## Introduction

Numerous studies of transition-metal compounds containing single metal–metal bonds have demonstrated that such bonds are subject to photochemical, homolytic scission in nonpolar solvents.[1] However, comparatively few investigations have addressed the question of the photochemical cleavage of metal–metal bonds whose order exceeds 1.[2] Geoffroy, Gray, and Hammond found that photolysis of $Re_2Cl_8^{2-}$, a complex with a quadruple $Re\overset{4}{-}Re$ bond,[3] in acetonitrile leads to mononuclear *trans*-$[ReCl_4(NCCH_3)_2]^-$.[4a] However, subsequent flash-photolysis studies established that the $Re\overset{4}{-}Re$ bond

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