

But thus far,<sup>53</sup> only our redefinition is sufficient; Zink's model is not successful.

We turn to consider the rationalization for Adamson's second rule in which it is maintained that the "strong" ligand will be photoaquated, but strong is redefined in terms of the Coulomb integral of the ligand,<sup>17</sup> perhaps weighted by overlap considerations or in terms of the  $\pi$ -bonding ability of the ligand. In the former statement, it is clear that  $F^-$  is "stronger" than  $Cl^-$ <sup>54</sup> and hence should be the leaving group. It would seem unlikely that overlap effects could change this, since it is necessary to have the Cr-Cl overlap nearly 50% greater than the Cr-F overlap. The second criterion is that the weakest ligand will usually have "the greatest  $\pi$ -bonding character."<sup>17</sup> The available data on the strength of the  $\pi$ -bonding interaction of  $F^-$  and  $Cl^-$  with Cr(III) allows one to choose either of these ligands as the stronger  $\pi$ -bonding group. For instance, Rowley<sup>25</sup> lists  $\delta\pi$  values (the difference between the  $\pi$  interaction of F compared with ethylenediamine) for  $F^-$ ,  $Cl^-$ , and  $Br^-$  in  $trans-Cr(en)_2X_2^+$  as 2017, 473-917, and 705  $cm^{-1}$ , respectively; whereas his values for  $F^-$ ,  $Cl^-$ , and  $Br^-$  in  $Cr(NH_3)_5X^{2+}$  are -195, 414, and 505  $cm^{-1}$ , respectively. The values are exactly reversed in the two systems. (Some of these values are obtained from room temperature polarization measurements; König<sup>55</sup> has commented on how deceptions can arise in such values. Other values

(53) See, however, M. Wrighton, H. B. Gray, and G. S. Hammond, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, No. INOR 47; *Mol. Photochem.*, in press.

(54) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964, p 122.

(55) E. König, *Inorg. Chem.*, **10**, 2632 (1971).

were determined from Gaussian analysis of solution spectra;<sup>56</sup> Yamada<sup>57</sup> has criticized treatments of this type.) On the other hand, Glerup and Schäffer<sup>26</sup> believe that the  $\delta\pi$  series goes  $F^- > Cl^- > Br^-$ . We are uncertain as to which set of data to apply and hence cannot make use of Zink's second measure of "strong" ligand. Any result, however, that predicts that  $Cl^-$  is "stronger" than  $F^-$  violates the first version of the "strong" ligand.

Our own experience with the chemistry of Cr(III) complexes containing  $F^-$  is that the Cr(III)- $F^-$  bond is extraordinarily inert, both thermally and photochemically,<sup>14,51</sup> as long as  $[H^+]$  is not too large. The failure of  $F^-$  to fit Adamson's second rule may reside in this extraordinary stability which changes excited state wave functions so drastically that MO interpretations based on the energies at the ground-state internuclear distances may not be valid in the vibrationally deactivated (distorted) excited state.

**Summary.** Our results have indicated that  $trans-Cr(en)_2FCl^+$  photoaquates to give both  $z$  and  $xy$  activation with the former dominant. Chloride loss is accompanied by stereoisomerization for 90% of the molecules. This result should be carefully considered in dealing with models of the pathway for photoaquation. The observation of the loss of  $Cl^-$  is a violation of Adamson's second rule; a new empirical order of photoactivated groups has been presented.

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(56) W. A. Baker and M. S. Phillips, *Inorg. Chem.*, **5**, 1042 (1966).

(57) S. Yamada, *Coord. Chem. Rev.*, **2**, 83 (1967).

## Electronic and Steric Control of Reactions of Benzylmagnesium Chloride with Substituted Metal Carbonyls

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**Abstract:** Kinetic studies are reported for nucleophilic addition of benzylmagnesium chloride to a series of LM-(CO)<sub>x</sub> complexes,  $LM(CO)_x + C_6H_5CH_2MgCl \rightarrow LM(CO)_{x-1}C(CH_2C_6H_5)O-MgCl^+$ , where L = CO, phosphine, or phosphite, M = Fe ( $x = 4$ ) or W, Mo, or Cr ( $x = 5$ ). Nucleophilic reaction occurs at the cis carbonyl ligand of LM(CO)<sub>5</sub> complexes except when L is the very bulky ligand tri-*o*-tolylphosphine. For LFe(CO)<sub>4</sub> complexes, however, addition is to the trans carbonyl group. Electronic properties of the CO ligand as indicated by the CO stretching force constant or frequency dominate CO reactive sites within a molecule and also reaction rates for Grignard addition to CO ligands trans to a substituent. Reaction rates of addition to cis carbonyl groups are governed by the steric requirements of L. The limitations inherent in applying a force constant/reactivity correlation are discussed.

We have previously suggested<sup>2</sup> that carbonyl stretching force constants may be used as indices to predict the active positions as well as relative reactivities of the carbonyl ligand in metal carbonyl and substituted metal carbonyl compounds. While high

CO stretching force constants (or, as approximated by,  $\nu_{CO}$ ) correlate with a more positive carbon atom and therefore with nucleophilic attack at carbon,<sup>2-5</sup> low values of the CO stretching force constants (or  $\nu_{CO}$ )

(3) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, **5**, 247 (1971).

(4) G. R. Dobson and J. R. Paxson, *J. Coord. Chem.*, **1**, 321 (1972).

(5) R. J. Angelici and L. J. Black, *Inorg. Chem.*, **11**, 1754 (1972).

(1) Petroleum Research Fund Postdoctoral Fellow, 1972-1973.  
(2) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).

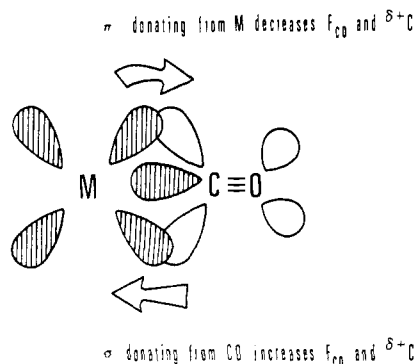
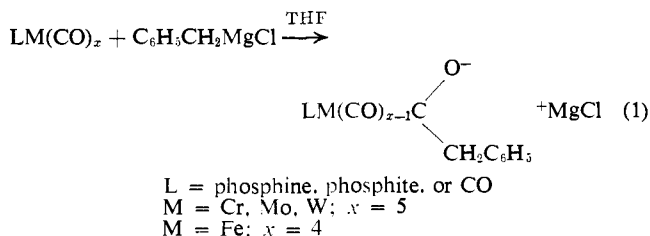


Figure 1. Correlation between the CO stretching force constant and charge at carbon.

correlate with the addition of electrophiles to oxygen.<sup>6</sup> Two modes of increasing  $F_{CO}$  and hence the residual positive charge on the carbonyl carbon (although not necessarily to the same extent) are presented in Figure 1 and this relationship is discussed in ref 2. The proposal relating charge and force constant is formulated so as to predict reactivity based on electronic factors only and neglects steric interactions.

Kinetic studies on addition reactions of benzylmagnesium chloride with metal carbonyls according to reaction 1 are reported in this paper. Substituted



metal carbonyls were chosen according to their geometric, steric, and electronic properties in order to more thoroughly examine the limitations of the force constant/reactivity proposal.

## Experimental Section

**Materials.** Tetrahydrofuran, purified by distillation from lithium aluminum hydride and/or sodium benzophenone dianion and flushed with argon, was used as solvent throughout these studies.  $Mo(CO)_6$  and  $W(CO)_6$  were gifts of the Climax Molybdenum Co.  $Fe(CO)_5$  was purchased from Pressure Chemical Co. and  $Cr(CO)_6$  from Strem Chemical Co. The following ligands were gifts of the sources cited and were generally used as received without further purification: trimethyl and triethyl phosphite (Mobil Chemical Co.), tributylphosphine, triphenylphosphine, and dimethylphenylphosphine (M & T Chemical Co.), methoxydiphenylphosphine and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (the Arapahoe Chemical Co.). Other phosphines were purchased from Strem Chemical Co.

**Preparations.** Benzylmagnesium chloride was prepared using classical techniques from a 25 to 50% excess of triply sublimed magnesium turnings generously donated by the Dow Chemical Co. The Grignard was stored cold under argon in a sealed brown bottle. Active Grignard concentration was determined and monitored by the Gilman technique.<sup>7</sup> Nmr analysis indicated 2–20% production of bibenzyl during the course of these preparations. Since several Grignard preparations were necessary to do the complete kinetic study, each new Grignard was checked for consistency by determining  $k_{obsd}$  at 25 for a reference compound,  $Ph_3PFe(CO)_4$

Table I. Rate Data,<sup>a</sup> Force Constants, and Ligand Cone Angles<sup>b</sup> for Reaction of  $LM(CO)_x$  with  $C_6H_5CH_2MgCl^c$

M	L	$k_2 \times 10^3, \text{sec}^{-1}$	LCA <sup>b</sup>	Force constants, mdyne/Å	
				$F$ (trans)	$F$ (cis)
W	CO	108.00		16.41	16.41
W	$P(OC_2H_5)_3$	25.70	106 ± 2	15.70	15.89
W	$P(CH_3)_3$	19.10	114 ± 2	15.53	15.77
W	$P(CH_3)_2(C_6H_5)$	14.00	~123	15.54	15.79
W	$P(n-C_4H_9)_3$	8.50	126 ± 2	15.42	15.72
W	$P(CH_3)(C_6H_5)_2$	10.40	~132	15.50	15.80
W	$P(C_6H_5)_3$	5.00	142 ± 2	15.57	15.89
W	$P(o-C_6H_{11})_3$	1.42	179 ± 10	15.33	15.68
W	$P(o-C_6H_4CH_3)_2^d$	1.75	>180	15.45	15.79
Cr	$P(OCH_2)_3CC_2H_5$	2.50	99 ± 2	15.85	16.11
Cr	$P(OC_2H_5)_3$	3.17	108 ± 2	15.74	15.88
Mo	$P(CH_3)_3$	14.80	114 ± 2	15.59	15.86
Cr	$P(CH_3)_3$	3.00	116 ± 2	15.54	15.75
Mo	$P(n-C_4H_9)_3$	11.00	126 ± 2	15.56	15.88
Cr	$P(n-C_4H_9)_3$	1.25	128 ± 2	15.43	15.68
Mo	$P(C_6H_5)_3$	4.77	142 ± 2	15.49	15.96
Cr	$P(C_6H_5)_3$	3.25	144 ± 2	15.51	15.85
Mo	CO	91.40		16.52	16.52
Cr	CO	53.00		16.49	16.49

<sup>a</sup>  $[M(CO)_xL] = 4.90 \times 10^{-3} M$ ;  $[C_6H_5CH_2MgCl] = 0.12 M$ ;  $T = 27^\circ$ , solvent = tetrahydrofuran;  $k_2 = k_{obsd}/[C_6H_5CH_2MgCl]$ ; reproducibility within 10%. <sup>b</sup> See C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970). Corrected for metal ligand bond distance assuming Mo–P or W–P = 2.46 Å and Cr–P = 2.36 Å. <sup>c</sup> Addition to cis carbonyl except where noted. <sup>d</sup> Trans addition.

or  $Ph_3PW(CO)_5$ . The deviation of  $k_{obsd}$  was never greater than 7% from Grignard to Grignard.

$M(CO)_5L$  complexes in general were prepared from  $M(CO)_5THF$ , produced photochemically from the hexacarbonyl in THF.<sup>8</sup> Less than stoichiometric amounts of the ligand in THF were added slowly to the bright yellow solution, kept at room temperature or below. After stirring the mixture for about 30 min the solvent was removed by rotovap and the residue was dissolved in a minimum amount of  $CHCl_3$ . Filtration into cold methanol generally lead to crystalline products. Products which were liquids ( $M(CO)_5P(n-C_4H_9)_3$  and  $M(CO)_5P(OC_2H_5)_3$ ) were purified by short path distillation in a sublimator using a Dry Ice–acetone cooled cold finger. Since  $W(CO)_5P(CH_3)_2C_6H_5$  has a melting point of approximately  $-5^\circ$ , it was purified by recrystallization from methylenecyclohexane at  $-10^\circ$  and filtered cold; white crystals of product were collected.

$LFe(CO)_4$  complexes were prepared by combinations of reflux and irradiation of the respective ligand in pure  $Fe(CO)_5$ . Detailed preparative and purification procedures are presented in a separate report. All complexes prepared in this manner were isolated in 60–80% yield.

The reactant complexes were identified by their melting points, infrared spectra, and carbon–hydrogen analyses.

**Kinetic Measurements.**  $LM(CO)_5$  or  $LFe(CO)_4$  weighed samples were placed into dry, argon flushed 50-ml erlenmeyer flasks to which the requisite amount of THF was added. The flask was then sealed with a rubber septum, wired, taped, and further flushed with argon. A slight positive pressure of argon was kept within the flask. Constant temperature was maintained in a thermostated bath ( $\pm 0.1^\circ$ ). The Grignard solution was introduced *via* syringe, and at timed intervals samples were removed by syringe and placed in a 0.1-mm NaCl sealed infrared cell. Rates for the  $LM(CO)_5$  complexes were established by following the decrease of the reactant's most intense CO stretching absorption, the E mode; the less intense but isolated  $A_1^{(2)}$  was used for the  $LFe(CO)_4$  complexes. Molar excesses (25- to 70-fold) of the Grignard reagent were used in order to maintain pseudo-first-order reaction conditions. A minimum of three determinations of  $k_{obsd}$  were made per complex per temperature.

Rate constants were calculated using a linear-least squares program for the first-order rate plots of  $\ln(A_t - A_\infty)$  vs. time, where  $A_t$  is the absorbance at time  $t$  and  $A_\infty$  is the absorbance at time infinity. All reactions went to completion.

(6) For a recent review, see D. F. Shriver, *Chem. Brit.*, 419 (1972).

(7) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

(8) W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964).

**Table II.** Addition of Benzylmagnesium Chloride to  $\text{LFe}(\text{CO})_4$  in Tetrahydrofuran at 25°<sup>a</sup>

L	$k_2 \times 10^3$ , $M^{-1} \text{sec}^{-1}$	$\nu_{\text{CO}}^b$		
		$A_1^{(2)}$	$A_1^{(1)}$	E
CO	229 <sup>c</sup>			
$(\text{C}_6\text{H}_5\text{O})_3\text{P}$	$15.30 \pm 0.70$	2065.5	1996.0	1964.3, 1959.8
$(\text{CH}_3\text{O})_3\text{P}$	$4.90 \pm 0.08$	2063.2	1992.7	1963.3, 1950.6
$(\text{C}_2\text{H}_5\text{O})_3\text{P}$	$2.97 \pm 0.06$	2060.0	1988.4	1959.3, 1945.9
$(\text{CH}_3\text{O})(\text{C}_6\text{H}_5)_2\text{P}$	$3.88 \pm 0.04$	2054.2	1984.0	1948.2, 1945.6
$(\text{C}_6\text{H}_5)_3\text{P}$	$1.84 \pm 0.03$	2051.0	1979.0	1945.3
$(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}$	$0.874 \pm 0.02$	2050.2	1978.1	1944.6, 1937.8
$(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}$	$0.670 \pm 0.01$	2050.5	1978.6	1939.9
$(n\text{-C}_4\text{H}_9)_3\text{P}$	$0.212 \pm 0.003$	2048.0	1974.8	1935.4

<sup>a</sup>  $[\text{LFe}(\text{CO})_4] = 0.010 M$ ;  $k_2 = k_{\text{obsd}}/[\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}]$ ;  $[\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}] = ca. 0.70 M$ . <sup>b</sup> Frequencies observed in hexane solution and are accurate to  $\pm 0.5 \text{ cm}^{-1}$ . <sup>c</sup>  $[\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}] = 0.038 M$ ;  $k_2$  reported is assuming linear dependence of  $k_{\text{obsd}}$  on Grignard down into this concentration range and hence is expected to be a *minimum* value.

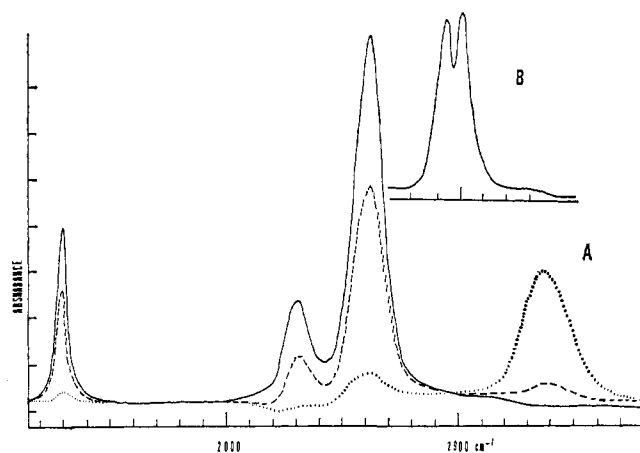


Figure 2. (A) Infrared spectra in the CO stretching region monitoring the reaction of  $\text{Ph}_3\text{PFe}(\text{CO})_4$  with benzylmagnesium chloride in THF at 25°: (—)  $\text{Ph}_3\text{PFe}(\text{CO})_4$  (0.010 M) in THF, (---) 60 sec after addition of Grignard (0.70 M), (....) after extensive formation of product (45 min). At  $t = \infty$  no reactant remains. (B) The ethylated product of A,  $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OC}_2\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_5$  in hexane (split E mode).

Products were identified by their infrared spectra and by preparing the characteristic carbene derivatives<sup>9</sup> of the metal carbonyl acylates by alkylation with triethyloxonium fluoroborate or with methyl fluorosulfonate (Aldrich's Magic Methyl\*). Carbene complexes thus formed *in situ* have ir spectra identical with isolated complexes which were also identified by nmr and elemental analysis.

Force constants were calculated using the familiar Cotton-Kraihanzel approximations.<sup>10</sup>

A Perkin-Elmer 521 grating infrared spectrophotometer, calibrated in the CO stretching region with CO and  $\text{H}_2\text{O}$  vapor, was used to obtain all frequency and rate data.

## Results

**Kinetics.** The rate data for reactions of group VIB metal carbonyls and monosubstituted derivatives with benzylmagnesium chloride according to reaction 1 are presented in Table I. Although infrared bands corresponding to CO stretching vibrations are broad in THF, resolvable spectra characteristic of *cis* disubstituted octahedral complexes were obtained for reactions of  $\text{LM}(\text{CO})_5$  except for the one case where L = tri-*o*-tolylphosphine. No other carbonyl containing species were present; intensities of the product bands compared with those of the reactant in general indicated quantitative reactions. The acylate of  $\text{Ph}_3\text{PMo}(\text{CO})_5$

(9) E. O. Fischer and R. Aumann, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).

(10) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

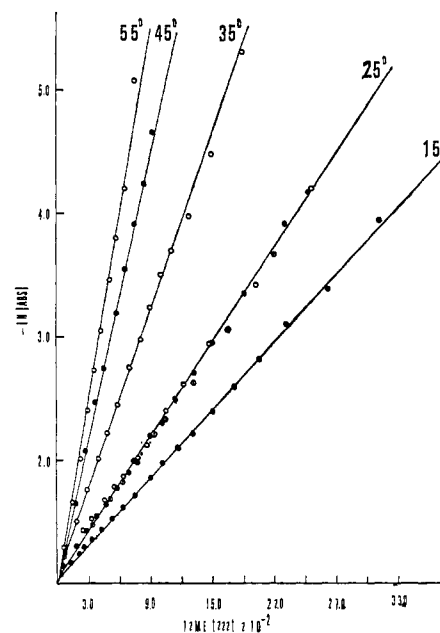


Figure 3. Representative pseudo-first-order rate plots for the reaction of  $\text{Ph}_3\text{PFe}(\text{CO})_4$  (0.010 M) with  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  (0.70 M) in THF at various temperatures. Three independent sets of data are shown at 25°.

is unstable at 27°; however, 0° studies clearly indicated benzyl addition *cis* to the  $\text{Ph}_3\text{P}$  group as expected. Alkylation of the chloromagnesium metal carbonyl acylates led to the hydrocarbon soluble benzylalkoxycarbene derivatives affording more defined spectra. In all cases the ir spectra of the acylates showed a pattern identical with that of the carbene derivatives.

Table II contains rate data for the  $\text{Fe}(\text{CO})_5$  and  $\text{LFe}(\text{CO})_4$  systems. Addition of the benzyl group is to the axial carbonyl carbon, and no by-products were observed. *Trans* ethoxycarbene derivatives were obtained by alkylation with triethyloxonium fluoroborate in THF (See Figures 2A and B).

Linear pseudo-first-order rate plots (examples of which are shown in Figure 3) were obtained over the entire reaction. Values of  $k_{\text{obsd}}$  taken from such plots are reproducible to  $\pm 3\%$ . Within Grignard concentration ranges of 0.4–0.9 M for the  $\text{LFe}(\text{CO})_4$  series and 0.06–0.12 M for the  $\text{LM}(\text{CO})_5$  series,  $k_{\text{obsd}}$  exhibits a linear dependence on Grignard concentration (Figure 4) and hence may be expressed as  $k_2[\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}]$ .

**Activation Parameters.** Rate data measured over a temperature range of 0–55° for compounds offering

Table III. Activation Parameter Studies for the Reaction of Benzylmagnesium Chloride with Metal Carbonyls in Tetrahydrofuran

MCO <sup>a</sup>	Temp, °C	$k_2 \times 10^3, M^{-1} \text{sec}^{-1b}$	Activation parameters
$(n\text{-C}_4\text{H}_9)_3\text{PFe}(\text{CO})_4$	25.0	0.212 ( $\pm 0.003$ )	$\Delta H^\ddagger = 9.4 \pm 0.9 \text{ kcal/mol}$ $\Delta S^\ddagger = -44.0 \pm 3.2 \text{ eu}$
	35.0	0.374 ( $\pm 0.004$ )	
	45.0	0.640 ( $\pm 0.01$ )	
	55.0	0.875 ( $\pm 0.01$ )	
$(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$	15.0	1.20 ( $\pm 0.11$ )	$\Delta H^\ddagger = 8.3 \pm 0.6 \text{ kcal/mol}$ $\Delta S^\ddagger = -43.4 \pm 2.1 \text{ eu}$
	25.0	1.84 ( $\pm 0.03$ )	
	35.0	3.31 ( $\pm 0.03$ )	
	45.0	5.37 ( $\pm 0.06$ )	
	55.0	6.48 ( $\pm 0.12$ )	
$(\text{C}_6\text{H}_5\text{O})_3\text{PFe}(\text{CO})_4$	0.0	4.03 ( $\pm 0.07$ )	$\Delta H^\ddagger = 8.4 \pm 0.8 \text{ kcal/mol}$ $\Delta S^\ddagger = -38.5 \pm 2.7 \text{ eu}$
	15.0	8.93 ( $\pm 0.30$ )	
	25.0	15.30 ( $\pm 0.70$ )	
$\text{W}(\text{CO})_6$	0.0	34.1 ( $\pm 2.6$ )	$\Delta H^\ddagger = 7.4 \pm 0.8 \text{ kcal/mol}$ $\Delta S^\ddagger = -38.1 \pm 2.8 \text{ eu}$
	15.0	74.3 ( $\pm 7.6$ )	
	25.0	108 ( $\pm 12$ )	
$(\text{C}_6\text{H}_5)_3\text{PW}(\text{CO})_5$	0.5	2.58	$\Delta H^\ddagger = 6.17 \pm 1.11 \text{ kcal/mol}$ $\Delta S^\ddagger = -47.9 \pm 4.0 \text{ eu}$
	25.0	4.96	
	35.0	9.50	
	45.0	12.3	

<sup>a</sup>  $[\text{LFe}(\text{CO})_4] = 0.010 \text{ M}$ ;  $[\text{LW}(\text{CO})_5] = 4.90 \times 10^{-3} \text{ M}$ . <sup>b</sup>  $k_2 = k_{\text{obsd}}/[\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}]$ .  $[\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}] = ca. 0.70 \text{ M}$  for  $\text{LFe}(\text{CO})_4$  and  $0.12 \text{ M}$  for  $\text{LW}(\text{CO})_5$  reactions. The errors represent standard deviations—95% confidence level.

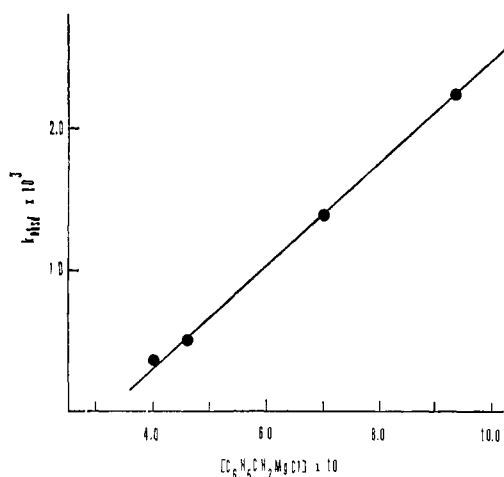


Figure 4. Dependence of  $k_{\text{obsd}}$  on Grignard concentration for the reaction of  $\text{Ph}_3\text{PFe}(\text{CO})_4$  (0.010 M) with  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  in THF at 25°C.

a diversity in ligand steric and electronic requirements are reported in Table III. A representative Arrhenius plot is shown in Figure 5. The activation parameters, also reported in Table III, were determined using a linear least-squares program and the error limits represent standard deviations for a 95% confidence level.

### Discussion

In line with the force constant/reactivity proposal, nucleophilic reaction of benzylmagnesium chloride is at the carbon of the carbonyl group bearing the higher force constant in each set of complexes studied, *i.e.*, addition is to the axial carbonyl group in  $\text{LFe}(\text{CO})_4$  compounds and with one exception to the cis carbonyl group of  $\text{LM}(\text{CO})_5$  compounds. The one exception is for the tungsten compound containing the ligand of greatest steric requirement,  $(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{PW}(\text{CO})_5$ . The bulkiness of this substituent forces the reaction to occur at the carbonyl group of lower force constant. Hence reaction *can* occur at carbonyl groups of force constant of 15.45 mdyne/Å (or even lower as studies

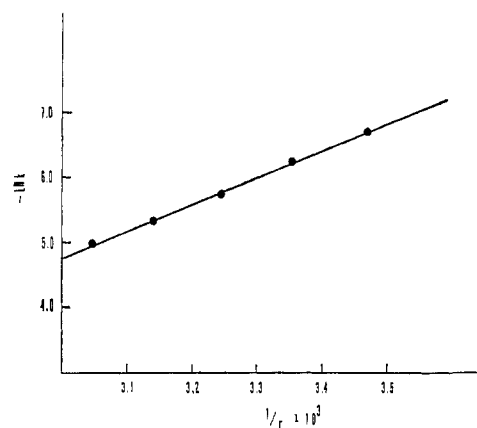


Figure 5. Arrhenius plot of  $-\ln k$  vs.  $1/T$  for reaction of  $\text{Ph}_3\text{PFe}(\text{CO})_4$  (0.010 M) with  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  (0.70 M) in THF.

with  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  and 1,3,5- $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3$ ,  $F_{\text{CO}} = 14.97$ , have shown).<sup>11</sup> It is noteworthy, however, that for cases of less steric hindrance, no trans addition is seen in the  $\text{LM}(\text{CO})_5$  series even for complexes whose trans  $F_{\text{CO}}$  are higher than 15.45, for example,  $\text{W}(\text{CO})_5\text{P}(\text{OC}_2\text{H}_5)_3$  of  $F_{\text{CO}}^{\text{trans}} = 15.70$  and  $\text{W}(\text{CO})_5\text{PPh}_3$  of  $F_{\text{CO}}^{\text{trans}} = 15.57 \text{ mdyne/Å}$ .

Although a strict electronic control governs the site of nucleophilic reaction in the absence of excessively bulky ligands, relative rate constants for the addition of benzyl Grignard to cis carbonyl groups of group VIb  $\text{M}(\text{CO})_5\text{L}$  species (Table I) are found to be dependent on the steric requirements of the phosphorus substituent. Figure 6 shows a plot of  $\log k_2$  (for the  $\text{LW}(\text{CO})_5$  series) vs. Tolman's ligand cone angle<sup>12</sup> of the phosphine and phosphite ligands employed in this study and demonstrates a good correlation between rate constants and steric factors. A similar correlation between rate constants and  $F_{\text{CO}}$  does not exist.

Differences in rate constants for  $\text{LM}(\text{CO})_5$  reactions as L is held constant and M is varied from W to Mo (which have approximately the same covalent radius) to Cr (which is considerably smaller) are also consistent

(11) C. Hasday and D. J. Darensbourg, unpublished results.  
(12) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

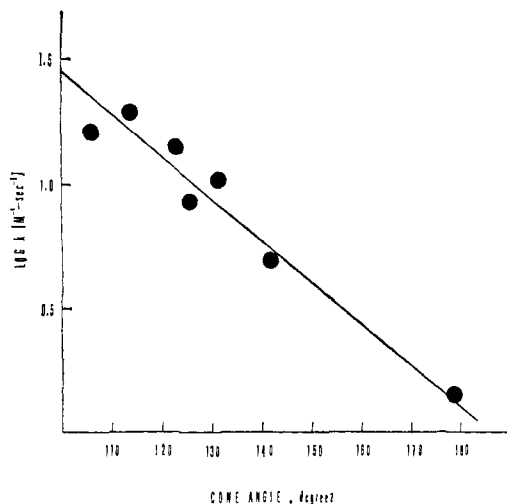


Figure 6. Correlation of  $\log k_2$  vs. Tolman's cone angle<sup>12</sup> for the reaction of  $W(CO)_5L$  with  $C_6H_5CH_2MgCl$ .

with steric arguments. Values of  $k_{obsd}$  or  $k_2$  are approximately the same for analogous W and Mo derivatives but definitely smaller for the Cr derivatives.

Nucleophilic addition to carbonyl groups trans to the substituent ligand in the  $LFe(CO)_4$  series is indeed very sensitive to the electronic character of the carbonyl ligand as dictated by the phosphorus substituent (Table II). Figure 7 shows the correlation of  $\log k_2$  vs.  $\nu_{ax-CO}$ .<sup>13</sup> There is no correlation of cone angle and rate constant for this series.

Mann<sup>14</sup> has indicated that the  $^{13}C$  nmr spectra of  $(Ph_{3-n}Et_nP)Fe(CO)_4$  ( $n = 1-3$ ) contain only one  $^{13}C$  CO resonance and concludes that rapid intramolecular exchange is occurring in these systems. No mechanism for the exchange is proposed and indeed the generally accepted Berry mechanism<sup>15</sup> would necessitate the intermediacy of a high-energy isomer in which the phosphine would occupy an equatorial site. The fluxionality of these iron complexes thus evokes concern about the possibility of fluxional behavior in the acylate products observed in these reactions. Although it is possible that initial nucleophilic reaction occurs at the cis CO group of  $LFe(CO)_4$  with subsequent rapid isomerization to the observed *trans*- $LFe(CO)_3C(O)R^-$  products observed, the relative rates would still correlate with the electronic properties of the phosphorus ligand as indicated assuming steric effects are not dominating (*i.e.*, the cis CO force constants or frequencies vary in a similar, however less dramatic, manner as the *trans*). Since, however, the rates of addition to the  $LFe(CO)_4$  series correlate with electronic factors and not with steric factors (which are clearly very influential for cis addition as indicated for the  $M(CO)_5L$  series), it is most likely that attack is indeed occurring at the axial CO ligand in  $LFe(CO)_4$ .

If it is fairly certain that intramolecular exchange is

(13)  $\nu_{CO}(A_1^{(1)})$ , corresponding primarily to the CO stretching motion of the axial carbonyl group, is employed in this correlation since accurate calculations of force constants in the complete series of  $LFe(CO)_4$  are not available at this time. This is primarily because of the splitting of the E mode vibration in several of these complexes. Currently we are observing  $^{13}CO$  data in order to compute these force constants. Certainly, however, the axial  $F_{CO}$  is greater than the equatorial  $F_{CO}$  in all  $LFe(CO)_4$  complexes.

(14) B. E. Mann, *Chem. Commun.*, 1173 (1971).

(15) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

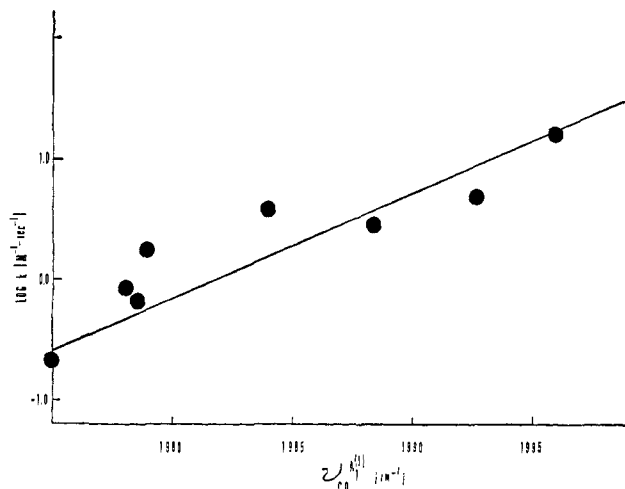


Figure 7. Correlation of  $\log k_2$  vs.  $\nu_{CO}(A_1^{(1)})$  for reaction of  $LFe(CO)_4$  complexes with  $C_6H_5CH_2MgCl$ .

occurring in  $Fe(CO)_5$ .<sup>16-18</sup> Acylate derivatives of these complexes might also be expected to exhibit fluxionality. Again the possibility of equatorial or axial CO reaction with subsequent isomerization of the acylate for the former to yield the observed axial  $Fe(CO)_4C(O)R^-$  does not alter the consistency of the correlation of rate constants with CO frequencies or force constants since both CO force constants are very high for  $Fe(CO)_5$  ( $F_{ax} = 16.95$ ,  $F_{eq} = 16.59$ ).<sup>19</sup>

Comparisons of rate constant per active carbonyl group for electronically controlled reactions suggest that force constant differences are more meaningful within a metal series than between metal series (Table IV). For example, the active CO group in  $Ph_3PFe-$

Table IV. Comparison of Rate Constant per Active Carbonyl Group with the Force Constant of the Active Carbonyl in Electronically Controlled Reactions

	$F_{active\ CO}$ , mdyn/Å	$k_2/active$ CO
$Cr(CO)_6$	16.49	$8.0 \times 10^{-3}$
$Fe(CO)_5$ ax	16.95	$46 \times 10^{-3}$
eq	16.59	
$W(CO)_6$	16.41	$18 \times 10^{-3}$
$(o-CH_3C_6H_4)_3PW(CO)_5$	15.45 (trans)	$1.75 \times 10^{-3}$
$(C_6H_5)_3PFe(CO)_4$	16.22 (trans)	$1.84 \times 10^{-3}$

$(CO)_4$  has a force constant 0.77 mdyn/Å higher than that of the active CO group in  $(o-CH_3C_6H_4)_3PW(CO)_5$ ; however, their rate constants are practically the same. This is perhaps an unfair comparison since steric factors resulting from differences in metal-carbon bond distances obviously are important as is shown for the Cr, Mo, and W series. By extrapolation the  $(o-CH_3C_6H_4)_3PCr(CO)_5$  (Cr being closer in size to Fe) reaction is expected to have a rate constant approximately one-half that of the tungsten analog which still leaves one with similar rate constants for the Fe and Cr de-

(16) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(17) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

(18) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

(19) G. Bor, *Inorg. Chim. Acta*, **3**, 191 (1969).

rivatives. On the other hand a difference in force constant of the active CO in  $\text{Fe}(\text{CO})_5$  and  $\text{Ph}_3\text{PFe}(\text{CO})_4$  is 0.37–0.73 mdyne/Å but the rate constant for  $\text{Fe}(\text{CO})_5$  reaction is at least a factor of 20 times that of the  $\text{Ph}_3\text{PFe}(\text{CO})_4$  reaction.

As was pointed out in the introductory section, the two modes of increasing the carbonyl force constant, increase of carbonyl to metal  $\sigma$  donation or decrease of metal to carbonyl  $\pi$  back-donation, both lead to an increase of positive charge on the carbonyl carbon. One cannot assume, however, that equal electronic charge from either of these modes affects the force constant to the same extent. Furthermore it is reasonable to expect these two modes would be active to different degrees, certainly as the geometry of the complex is changed and probably as the central metal is changed. The gross features of the force constant/reactivity proposal have proven to be correct by our work,<sup>2</sup> by the work of Dobson (rates of reaction of MeLi with  $\text{LM}(\text{CO})_5$  where M = group VIb),<sup>4</sup> and by Angelici's studies of carboxamido formation on reaction of metal carbonyls with primary amines (CO ligands of force constant  $> 17.0$  mdyne/Å readily form carboxamido complexes; equilibrium mixtures are formed with CO's of force constant between 16.0 and 17.0; and no reaction is observed with CO's of  $F_{\text{CO}} < 16.0$ ).<sup>5</sup> It is unreasonable to expect a necessarily linear force constant/reactivity relationship to hold where very small changes of force constant are involved—especially where  $F_{\text{CO}}$  differences are accompanied by a change in geometry of the system.<sup>20</sup>

Activation parameters (Table III) are consistent with eq 1 in that formation of a bi- or termolecular transition state<sup>21</sup> involving some charge separation from starting reagents which do not carry charges should lead to a large negative value for  $\Delta S^\ddagger$  corresponding to the

(20) J. A. Connor and J. P. Lloyd, *J. Chem. Soc., Dalton Trans.*, 1470 (1973).

(21) E. C. Ashby, *Quart. Rev., Chem. Soc.*, 21, 259 (1967).

additional loss of freedom of motion by the solvating molecules.

Our use of benzyl Grignard as a nucleophilic source in these kinetic studies was prompted by its ready availability and by its convenient rate of reaction with the metal carbonyls studied thus far. The well-behaved kinetics of these systems suggests that Grignard reactions with "inorganic" carbonyls might afford a useful mechanistic probe of the Grignard reagent itself.<sup>22,23</sup> In view of the fact that main group organometallics (specifically  $\text{AlR}_3$ ) are known to complex with the oxygen of metal carbonyls,<sup>6</sup> it is noteworthy that the frequencies of the CO stretching modes upon addition of the Grignard are not shifted from their positions in pure THF nor are they broadened (see Figure 2A). Hence the formation of an initial carbonyl oxygen to magnesium complex is not suggested by these studies. Preliminary studies on the effect of the Grignard halo group on such reactions have shown that substitution of bromide for chloride in the benzyl Grignard reagent slows all reactions by a factor of approximately 2. Further investigations along these lines as well as the effect of the Schlenk equilibrium ( $\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$ ) position on these reactions are warranted and currently underway.

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(22) Professor G. R. Dobson has previously intimated the potential usefulness of metal carbonyls as a kinetic handle on main-group organometallics.<sup>4</sup> He found the reaction of group VIb metal carbonyls with methyllithium to follow the rate law, rate =  $k[\text{MCO}][\text{CH}_3\text{Li}]^{1/4}$ , completely analogous to the results of Smith, *et al.*, in their studies of the reaction of methyllithium with 2,4-dimethyl-4'-methylmercaptobenzophenone.<sup>23</sup>

(23) S. G. Smith, L. F. Carbonneau, D. P. Novak, and T. L. Brown, *J. Amer. Chem. Soc.*, 94, 7059 (1972).