Octahedral Metal Carbonyls. XXXII.[1a] Kinetics and Mechanism of Reactions of Methyllithium with Group VIb Metal Carbonyls and Derivatives in Diethyl Ether

Gerard R. Dobson* and John R. Paxson[1b]

Contribution from the Department of Chemistry, North Texas State University, Denton, Texas 76203. *Received April 4, 1973*

Abstract: The kinetics and mechanism of reactions of methyllithium with group VIb metal carbonyls and derivatives in diethyl ether have been studied employing stopped flow kinetic techniques. The reactions were found to obey a rate law, $-\mathrm{d[substrate]}/\mathrm{d}t = k\mathrm{[substrate][CH_3Li]}^{1/4}$. The reactions of substitution products of Lewis bases (L), $LW(CO)_5$, were observed to afford the products *cis*-$Li[(OC)_4W(L)\{C(O)CH_3\}]$, and the rates of reaction were found roughly to be invariant to the differing electronic and steric properties of L. The observed stereochemistry of the reaction products of the $LW(CO)_5$ substrates, together with the rate data, are consistent with an overall mechanism involving (a) formation of an equilibrium concentration of reactive methyllithium monomer from methyllithium tetramer, (b) production of an equilibrium concentration of a methyllithium–metal carbonyl "adduct," *e.g.*, *trans*-$(OC)_4W(L)[CO\cdot LiCH_3]$, and (c) rate-determining rearrangement of this species to yield, ultimately, the observed products. For the hexacarbonyls, for which $Li[(OC)_5M\{C(O)CH_3\}]$ products were obtained, the rates were found to vary W > Mo $\gtrless$ Cr and to be some 2 orders of magnitude faster than are those observed for the monosubstituted substrates; their reaction may involve direct attack by methyllithium at a carbonyl carbon.

Reactions of strong nucleophiles such as organolithium reagents, alkoxides, azides, and Grignard reagents[2] afford carbonylation products, *e.g.*

$$M(CO)_6 + RLi \longrightarrow Li[M(CO)_5(COR)] \qquad (1)$$

The nature of the reaction products, together with theoretical calculations which have shown, for $Cr(CO)_6$, that a positive charge resides on the carbonyl carbon,[2] have suggested that atom to be the site of reactivity. The limited kinetic data thus far reported for such systems, for reactions of the azide ion[3] and benzylmagnesium chloride,[4] have shown reaction rates to exhibit a first-order dependence upon the concentration of the nucleophile. Arguments have been presented which predict that reactivity of organolithium reagents with metal carbonyls and derivatives should increase with an increase in the Cotton–Kraihanzel[5] carbonyl stretching force constant of the carbonyl attacked.[6]

The present study was undertaken in order to study the reactivity of strong nucleophiles as a function of the varying steric and electronic properties of the metal carbonyl substrates. Because it was anticipated that appreciable variations in rate might be observed, the nucleophile chosen was one which was found to give very fast rates for reactions of the hexacarbonyls, so that as wide a range of reactivities as possible could be studied. Thus reactions of organolithium reagents were selected for investigation.

Experimental Section

General Procedure. All manipulations, except as noted, were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer.

Materials. Tri(*n*-butyl)phosphine and triethyl phosphite were obtained from Aldrich Chemical Co. The hexacarbonyls of Cr and W were purchased from Pressure Chemical, while molybdenum hexacarbonyl was obtained from Climax Molybdenum. Triphenylphosphine was purchased from Cincinnati Milachron, Reading, Ohio, and triphenylarsine from Alfa Inorganics. Tri(cyclohexyl)phosphine, obtained from Columbia Organic Chemicals, Inc., was further purified through recrystallization from acetone. The purified product melted at 76–78° (lit. 78°).[7] The substituted metal carbonyls, $LW(CO)_5$, were prepared through use of the method of Strohmeier for all L except triphenylphosphine and triphenylarsine.[8] The latter complexes were obtained through use of the procedure of Brown and Dobson.[9] Reagent grade anhydrous diethyl ether (Matheson Coleman and Bell) was distilled twice from calcium hydride, was stored under nitrogen in a glove box, and was used within 1 day of distillation.

All dilutions, filtrations, and analytical samplings were carried out in a helium atmosphere glove box, and all glassware was flame- or oven-dried before use. Methyllithium in diethyl ether (Foote) was diluted with the purified ether and was then filtered through a medium porosity glass frit to remove any lithium methoxide which may have precipitated during dilution. Methyllithium solutions were then transferred to cappable glass pressure bottles[10] which were sealed with extruded neoprene liners, and crown tops which were perforated with three $^1/_{16}$ in. holes. After the bottles were removed from the glove box they were pressurized with nitrogen to 30 psi through use of a hypodermic needle.

Analyses in triplicate for methyllithium were effected employing the Gilman double titration technique.[11] Methyllithium concentrations in the range 0.02–0.48 *F* were employed in the kinetic runs.

Metal carbonyl solutions were also prepared in "pop" bottles under a helium atmosphere in a glove box. Their concentrations ranged from 6.2×10^{-5} to 6.2×10^{-4} *M*. These low concentrations were necessary to avoid product precipitation during the kinetic runs.

Kinetic Runs. The reactions of metal carbonyls and methyllithium in diethyl ether were studied employing an Aminco-Morrow stopped flow system coupled to a Bausch and Lomb high-intensity monochromator or the monochromator from a Hitachi Perkin-Elmer Model 137 uv-visible spectrophotometer. The cell tem-

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[1] (a) Part XXXI: F. R. Young, III, R. A. Levenson, M. N. Memering, and G. R. Dobson, *Inorg. Chim. Acta*, in press. (b) Robert A. Welch Foundation Postdoctoral Fellow, 1971–1972.

[2] For a brief review, see K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, 7, 1273 (1968).

[3] (a) W. Beck, H. Werner, H. Engelmann, and H. S. Smedal, *Chem. Ber.*, 101, 2143 (1968); (b) H. Werner, W. Beck, and H. Engelmann, *Inorg. Chim. Acta*, 3, 331 (1969).

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

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

[6] D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).

[7] K. Issleib and A. Brack, *Z. Anorg. Allg. Chem.*, 277, 258 (1954).

[8] W. Strohmeier and F. J. Müller, *Chem. Ber.*, 102, 3608 (1969).

[9] R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, 6, 65 (1972).

[10] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, pp 154–158.

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

Table I. Rate (k_{obsd}) Data for Reactions of Methyllithium with Group VIb Metal Carbonyls and Derivatives in Diethyl Ether at 25.0 ± 0.1°

Substrate	[CH_3Li], F	k_{obsd}, sec^{-1}	Substrate	[CH_3Li], F	k_{obsd}, sec^{-1}
$W(CO)_6$	0.0010	2.75	$(C_6H_5O)_3PW(CO)_5$	0.0054	0.0162
	0.0089	4.47		0.0185	0.0249
	0.0116	4.88		0.0478	0.0302
	0.0353	6.26		0.0896	0.0371
	0.0687	7.88		0.1403	0.0412
	0.1172	9.09		0.1720	0.0432
	0.1393	8.63	$(C_6H_5)_3AsW(CO)_5$	0.0010	0.0091
	0.1755	9.36		0.0089	0.0188
	0.2419	10.83		0.0353	0.0251
$Mo(CO)_6$	0.0071	2.69		0.0687	0.0270
	0.0353	3.65		0.1393	0.0310
	0.0458	3.97		0.1393	0.0328
	0.1172	5.03		0.2419	0.0373
	0.1383	5.18	$(C_6H_5)_3PW(CO)_5$	0.0089	0.0129
	0.2419	6.07		0.0089	0.0132
$Cr(CO)_6$	0.0079	1.91		0.0353	0.0160
	0.0096	2.23		0.0353	0.0163
	0.0159	2.53		0.0687	0.0189
	0.0441	3.47		0.0687	0.0192
	0.1045	4.20		0.1383	0.0257
	0.1514	4.86		0.2419	0.0279
$(n\text{-}C_4H_9)_3PW(CO)_5$	0.0611	0.0239		0.2419	0.0283
	0.1191	0.0271	$(c\text{-}C_6H_{11})_3PW(CO)_5$	0.0302	0.0089
	0.1191	0.0282		0.0561	0.0111
				0.0968	0.0134

perature was maintained through use of an external circulating bath and was monitored employing an iron–constantan thermocouple attached directly to the cell window. Transfer of solutions to the stopped flow system was effected employing gas-tight syringes supplied with cut-off valves (Hamilton). Polysulfide "o" rings (Porter Seal) for compatibility with the methyllithium solutions were used to seal the driving syringes. Their frequent changing was necessitated by their rapid deterioration, particularly at higher methyllithium concentrations. The instrument was standardized immediately prior to each kinetic run. Storage vessels were thermostated at 25°, and the observation cell was maintained at 25.0 ± 0.1°.

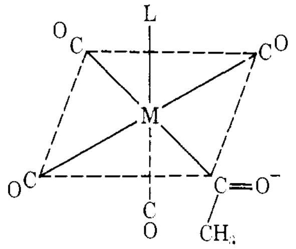
Reactions were monitored under pseudo-first-order reaction conditions (at least a 30-fold excess of methyllithium) at 370 nm for the hexacarbonyls and 410 or 420 nm for the $LW(CO)_5$ complexes. For a given concentration of methyllithium, kinetic runs were repeated until three superimposable oscilloscope traces were obtained; the fourth trace was photographed and employed in the determination of the reaction rate. Plots of ln ($A_\infty - A_t$) *vs.* time were typically linear to two or more half-lives, and rate constants were reproducible to within ±3%. Typical plots are exhibited in Figure 1.

The possible reaction of the metal carbonyls with possible contaminants present in the methyllithium was investigated by scanning the visible spectra of the substrates after addition of lithium halide or lithium alkoxide. No changes in the spectra were observed, and this was taken as evidence that such reactions did not interfere with the determination of the rates being investigated. Pseudo-first-order rate constants were calculated through use of a linear least-squares computer program employing an IBM 360 Model 50 computer.

Identification of Reaction Products. The products of the reactions of the three group VIb metal hexacarbonyls with methyllithium have been well-characterized.[12] Products of reactions of $LW(CO)_5$ with strong nucleophiles, with the exception of the complex of the very bulky (*o*-tolyl)$_3$P[13] (not studied here), have been shown to be the cis isomers.[4,6,13,14] This stereochemistry was confirmed for representative $LW(CO)_5$ substrates (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$) through isolation of the reaction products as tetraethylammonium salts and analysis of their carbonyl stretching spectra.[14] The ultraviolet-visible spectra for the reaction solutions at t_∞ were virtually identical for all Li[$(OC)_4W(L)\{C(O)CH_3\}$], confirming the common (cis) stereochemistry of these products.

Results

Reactions of methyllithium with group VIb metal carbonyls and derivatives in diethyl ether have been found to yield carbonylation products (eq 1); for $LW(CO)_5$ complexes, the products have been found to be the cis isomers



both through this investigation and through the observations of other workers for these and for analogous systems.[4,6,13,14]

Rate (k_{obsd}) data for reactions of methyllithium with the three hexacarbonyls and five $LW(CO)_5$ substrates are presented in Table I. The reaction order with respect to methyllithium was determined from plots of log k_{obsd} *vs.* log [CH_3Li] for data for the hexacarbonyls (Figure 2). From the slopes of these plots the order of reaction with respect to methyllithium was found to be 0.258 ± 0.034, within experimental error, one-fourth order.

Plots of k_{obsd} *vs.* [CH_3Li]$^{1/4}$ for the three hexacarbonyls and for several $LW(CO)_5$ complexes[15] are presented, respectively, in Figures 3 and 4. For the three hexacarbonyls, the intercepts of these plots were found

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[12] E. O. Fischer and A. Maasböl, *Chem. Ber.*, 100, 2445 (1967).

[13] M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *J. Amer. Chem. Soc.*, 95, 5919 (1973).

[14] E. O. Fischer and R. Aumann, *Chem. Ber.*, 102, 1495 (1969).

[15] All data for $LW(CO)_5$ complexes are not shown in order to preserve the clarity of the graphical presentation.

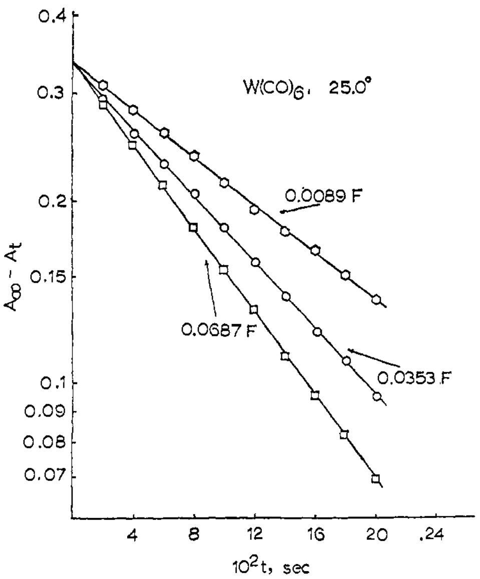

Figure 1. Plots of ln ($A_\infty - A_t$) *vs*. t for the reaction of W(CO)$_6$ with methyllithium in diethyl ether at 25.0 ± 0.1 °.

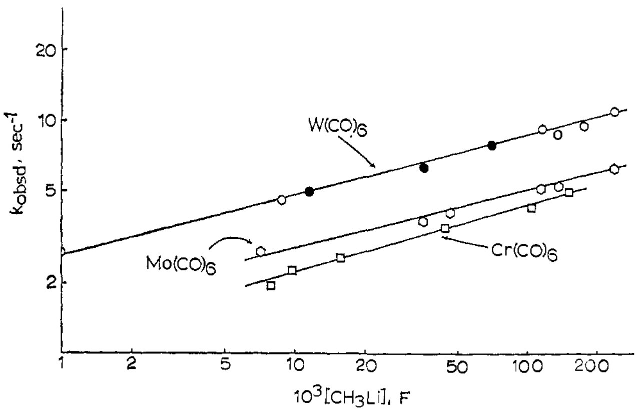

Figure 2. Plots of log k_{obsd} *vs*. log [CH$_3$Li] for reactions of M(CO)$_6$ (M = Cr, Mo, W) with methyllithium in diethyl ether at 25.0 ± 0.1 °. Solid circles refer to the values of k_{obsd} determined from the plots shown in Figure 1.

to be zero, within one standard deviation. The data are thus consistent with a rate law

$$-\mathrm{d[substrate]/d}t = k\mathrm{[substrate][CH_3Li]}^{1/4} \qquad (2)$$

The rate constants, k, are exhibited in Table II.

Discussion

The most plausible general mechanism consistent with the observed rate law is

$$\mathrm{(CH_3Li)_4} \overset{k_{eq}}{\rightleftharpoons} \mathrm{4CH_3Li}$$

$$\mathrm{CH_3Li + (OC)_5M(CO)} \xrightarrow{k_a} \mathrm{Li[(CO)_5MC(CH_3)O]} \qquad (3)$$

under this mechanism, $k = 0.7071k_aK_{eq}$.[16] The kinetic evidence that methyllithium exists predominantly as a tetramer in diethyl ether is fully consistent with other evidence with respect to the state of aggregation of methyllithium in basic solvents. The colligative properties of methyllithium in diethyl ether and tetrahydrofuran[17] and kinetic studies of its reaction in these solvents with other substrates[18,19] both support a predominantly tetrameric state of aggregation. The relative rates of reaction with respect to the slowest rate (1) are also given in Table II.

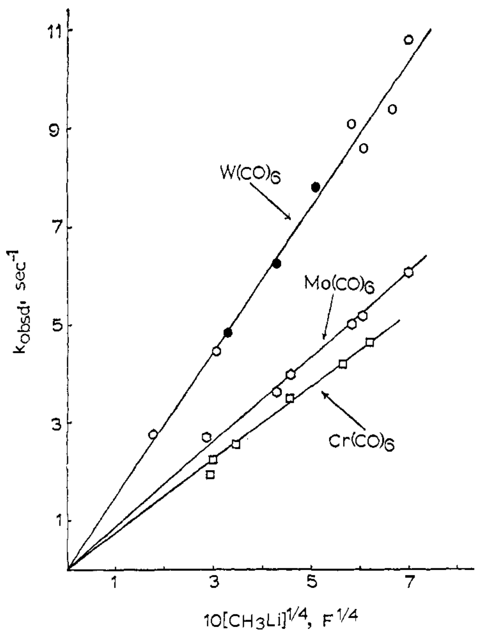

Figure 3. Plots of k_{obsd} *vs*. [CH$_3$Li]$^{1/4}$ for reactions of M(CO)$_6$ (M = Cr, Mo, W) with methyllithium in diethyl ether at 25.0 ± 0.1 °. Solid circles refer to the values of k_{obsd} determined from the plots shown in Figure 1.

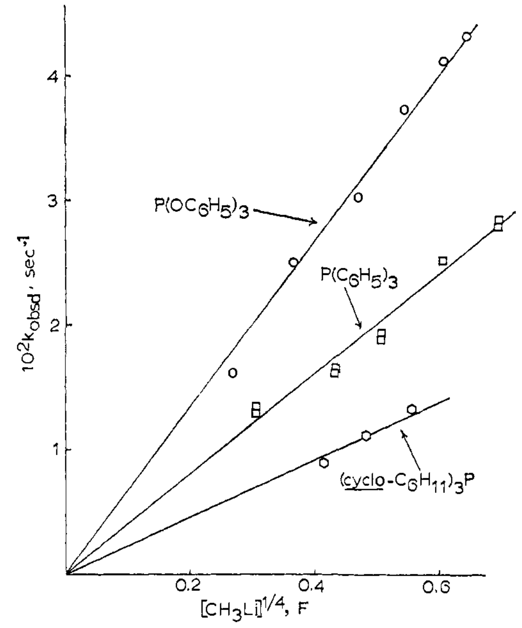

Figure 4. Plots of k_{obsd} *vs*. [CH$_3$Li]$^{1/4}$ for reactions of various LW(CO)$_5$ substrates with methyllithium in diethyl ether at 25.0 ± 0.1 °.

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[16] R. Waack and P. E. Stevenson, *J. Amer. Chem. Soc.*, **87**, 1183 (1965).

[17] P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

[18] (a) R. Waack and P. West, *J. Amer. Chem. Soc.*, **86**, 4494 (1964); (b) R. Waack and M. A. Doran, *ibid.*, **91**, 2456 (1969); P. West, R. Waack, and J. I. Purmort, *ibid.*, **92**, 840 (1970).

[19] S. G. Smith, L. F. Charbonneau, D. P. Novak, and T. L. Brown, *J. Amer. Chem. Soc.*, **94**, 7059 (1972).

Table II. Rate Constants and Relevant Data for Reactions of Metal Carbonyls and Methyllithium in Diethyl Ether

Complex	k,[a] $M^{-1/4}$ sec^{-1}	Rel rate	F_{co}(cis),[b] mdyn/A	pK_a[c]	Cone angle,[d] deg
$W(CO)_6$	14.91 ± 0.53	657	16.41[e]		
$Mo(CO)_6$	8.67 ± 0.31	382	16.52[e]		
$Cr(CO)_6$	7.29 ± 0.47	321	16.49[e]		
$(C_6H_5O)_3PW(CO)_5$	0.0656 ± 0.0032	2.89	16.08[f]	−1.8[h]	121 ± 10
$(C_6H_5)_3AsW(CO)_5$	0.0544 ± 0.0039	2.40	15.90[f]		142 ± 5[i]
$(n\text{-}C_4H_9)_3PW(CO)_5$	0.0474 ± 0.0011	2.09	15.75[f]	8.43	130 ± 4
$(C_6H_5)_3PW(CO)_5$	0.0396 ± 0.0024	1.74	15.88[f]	2.73	145 ± 2
$(c\text{-}C_6H_{11})_3PW(CO)_5$	0.0227 ± 0.0019	1.00	15.79[g]	9.70	179 ± 10

[a] k defined in eq 2 of text; limits of error, one standard deviation. [b] Calculated from equations given in ref 5. [c] Unless otherwise noted, given in ref 22. [d] Unless otherwise noted, given in ref 25. [e] Reference 5. [f] R. A. Brown, Ph.D. Dissertation, North Texas State University, 1971. [g] Calculated from carbonyl stretching frequencies: 2071.5 (A_1, w); 1943.0 (A_1, sh); 1939.0, 1934.5 (E, vs, doublet) in n-hexane solution. [h] Reference 23. [i] Calculated from cone angle for triphenylphosphine, the covalent radius of As, and geometrical considerations (ref 25).

The anticipated variation of rates of reaction of metal carbonyls with strong nucleophiles such as organolithiums with the inferred electronic properties of the substrates has been discussed by Darensbourg and Darensbourg.[6] They have proposed a relationship between reactivity and the Cotton–Kraihanzel carbonyl stretching force constant, F_{co}(cis)[5] for the carbonyl attacked. This relationship is based upon an assumption of attack by the nucleophile at the carbonyl carbon, and the expected variations in the force constant F_{co}(cis) as the electron density at the carbonyl carbon changes. A Lewis base which functions as a net charge donor relative to CO is expected to produce a decrease in the strengths of CO-to-metal σ bonds, and an increase in the strengths of metal-to-CO π bonds. Both effects would be expected to reduce the carbon–oxygen bond strengths, and thus, presumably,[20] the carbonyl stretching force constant, while decreasing the partial positive charge at the carbonyl carbon. Neglecting steric influences, rates therefore would be expected to decrease with decreasing values of F_{co}(cis).[21] Thus it is also to be expected that where reactions of metal carbonyls and derivatives with strong nucleophiles can yield stereochemically different products, the one obtained will be that in which the $-C(O)R^-$ group is derived from the carbonyl possessing the highest carbonyl stretching force constant. This generally has been found to be the case for products thus far prepared.[4,6,13,14]

However, variation of the reaction rates with the carbonyl stretching force constants, F_{co}(cis) (Table II) are not consistent with the proposal of Darensbourg and Darensbourg.[6] The minor variations in rate which are noted are also inconsistent with trends expected on the basis of ligand pK_a's,[22,23] which often have been employed as measures of ligand basicity while assessing the bonding and reactivity of metal carbonyls and derivatives.[24] In particular, ligand pK_a values have been related to the extent of CO-to-metal σ bonding in such complexes. A better, but still by no means satisfactory, correlation with reactivity for this series of complexes is with their steric properties. Rates are observed (Table II) very roughly to decrease with the increasing cone angle[25] appropriate to the substituent L.

However, it is especially significant to note that the observed minor variations in rate among the $LW(CO)_5$ substrates represent the *sum* of both steric and electronic effects. This may be seen through a consideration of the data for $[(c\text{-}C_6H_{11})_3P]W(CO)_5$ and $[(C_6H_5O)_3P]W(CO)_5$, which exhibit only about a threefold variation in rate. The former complex contains the L possessing the largest cone angle, and its carbonyl stretching force constant (F_{co}(cis)) is considerably smaller (0.33 mdyn/Å) than is that for the latter complex. Thus it fairly may be concluded that only minor differences in rate are observed for complexes in which L differs to the widest possible degree in steric and electronic properties.

The detailed mechanism of the reaction of methyllithium with the $LW(CO)_5$ substrates must account for the observed lack of effect upon reactivity of the varying steric and electronic properties of the substrates, as well as the observed stereochemistry of the products of reaction. A mechanism involving initial rate-determining nucleophilic attack by methyllithium monomer at a carbonyl cis to L[6] would involve transfer of electron density from the C–Li σ bond to the π^* orbitals of CO. The rate of such a process therefore should critically depend upon the occupancy of the π^* orbitals and thus upon the value of the carbonyl stretching force constant, F_{co}(cis).[6] That such a dependence is not observed *strongly argues against a mechanism involving initial attack at the carbonyl carbon.* Further, it is not unreasonable to expect the steric nature of L to strongly influence reactivity at the cis carbonyl; evidence for such an effect is marginal at best. The mechanism which appears best to satisfy the stereochemical and kinetic evidence is one which involves initial formation of an equilibrium concentration of an oxygen-bonded intermediate (through the carbonyl

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(20) There need be no necessary relationship between bond strengths and force constants. See, *e.g.*, K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, pp 8–10.

(21) While there has been considerable controversy as to the relative importance of σ, π, or other bonding influences on carbonyl stretching frequencies or force constants for a series of complexes containing the same metal atom, it is generally agreed that changes in metal-to-carbonyl π-bonding exert a dominant influence. For further discussion, see ref 9 and S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).

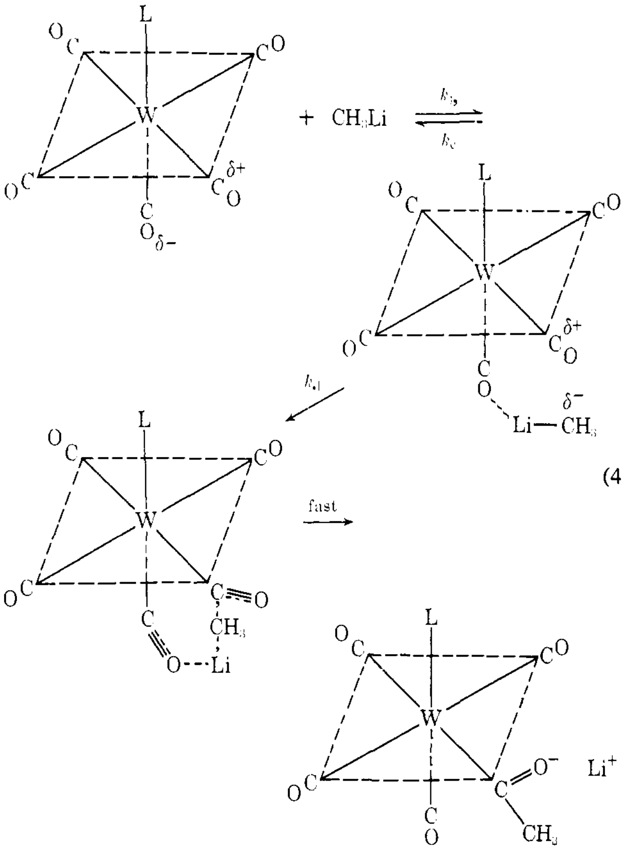
(22) C. A. Streuli, *Anal. Chem.*, 32, 985 (1960).

(23) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967).

(24) See, *e.g.*, (a) R. J. Angelici, *Organometal. Chem. Rev.*, 3, 273 (1968); (b) R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, 11, 72 (1972).

(25) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

oxygen trans to L) followed by rate-determining attack of the methyl carbon at a radial carbonyl carbon



(4)

Employing the steady-state approximation, such a mechanism affords the rate law

$$-\mathrm{d}[\text{substrate}]/\mathrm{d}t = k_bk_d[\text{substrate}][\mathrm{CH_3Li}]/(k_c + k_d) \quad (5)$$

where k_a (eq 3) $= k_bk_d/k_c + k_d$.

There is significant evidence that other, closely related reactions involving electron-deficient metal atoms can proceed *via* initial attack at a carbonyl oxygen. Substantial evidence exists that reactions of ketones with Grignard reagents proceed by way of the initial reversible formation of an oxygen-bonded intermediate, as was originally proposed by Swain.[26] Quite recently, the proton nmr spectrum of such an intermediate to the reaction of benzophenone and methylmagnesium bromide, $H_3CMg\cdot OC(C_6H_5)_2(CCH_3)$, has been obtained.[27] Further, in a recent kinetic study, Holm has suggested a four-center phenyllithium cyanide transition state for reactions of a series of substituted phenyllithiums with benzonitrile.[28] And finally, a number of complexes have been prepared from substituted group VIb metal carbonyls and electron-deficient metal-containing species, *e.g.*, trialkylaluminums.[29] An X-ray structural determination has verified such a linkage in one instance,[29c] and it is interesting to note that the C–O–Al bond angle was found to be significantly less than 180°. For an analogous interaction between methyllithium and a metal carbonyl, such a stereochemistry would facilitate subsequent attack by the methyl at a radial carbonyl carbon, as envisioned in eq 4.

Under the very reasonable assumption of an initial interaction between the Li atom of the methyllithium monomer and a carbonyl oxygen, also the most probable interaction on a steric basis, such attack would likely occur at the carbonyl trans to L since, as dictated by the directional nature of π bonding in these complexes (*cf.* the arguments given in ref 6), that oxygen would be expected to bear the greater negative charge.

The most probable rearrangement of the oxygen-bonded intermediate would be through "migration" of the methyl group to a radial carbonyl carbon through ring closure, followed by fast steps to yield the observed product. An inspection of molecular models indicates that such a "methyl migration" is to be favored over a four-center interaction involving methyl attack at the adjacent carbon. It is also to be noted that attack at a radial carbon rather at the carbon adjacent to the site of CO·Li interaction is also favored on electronic grounds in that these carbons are predicted to bear the greater positive charge both on the basis of the arguments advanced by Darensbourg and Darensbourg,[6] and of the electronic effects accompanying the $-\mathrm{CO}\cdots\mathrm{Li{-}CH_3}$ interaction. Available spectroscopic and structural evidence indicates that carbonyl π^* orbitals are lowered in energy upon coordination of that carbonyl oxygen, which in this case should lead to a flow of metallic d_π electron density from the radial carbonyls to the axial carbonyl.[29e] Thus coordination of the axial carbonyl oxygen should effectively increase the partial positive charge at the radial carbonyls, making them more susceptible to nucleophilic attack. Conversely, such attack is electronically less probable at the carbon adjacent to the coordinated oxygen; adjacent attack would also lead to products of trans, rather than the observed cis stereochemistry.

The proposed mechanism also satisfactorily accounts for the observed lack of steric and electronic effects upon reactivity. The rate constant, k_a $(=k_bk_d/k_c + k_d)$, is composed of two opposing effects upon rate when k_c is not negligible relative to k_d, the equilibrium constant for formation of the $-\mathrm{CO}\cdots\mathrm{Li{-}CH_3}$ intermediate k_b/k_c, and the rate constant for intramolecular rearrangement k_d. A substituent L which has a net charge-releasing effect relative to a second L is expected to increase the electron density both at the carbonyl carbon and the carbonyl oxygen,[30] thus producing a greater equilibrium concentration of the intermediate and a reduced rate of intramolecular rearrangement. It also is evident that steric effects upon rate are expected to be minimal under this mechanism, since the rate-determining steps occur at the side of the molecule opposite the substituent.

It must be emphasized that mechanism 4 is the intermediate case to two limiting mechanisms of interaction of metal carbonyl substrates with strongly nucleophilic reagents. Limiting behavior is likely to be ob-

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(26) C. G. Swain and H. B. Boyles, *J. Amer. Chem. Soc.*, **73**, 870 (1951).

(27) E. C. Ashby, F. W. Walker, and H. M. Neumann, *Chem. Commun.*, 330 (1970).

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served for metal carbonyls and derivatives which possess very low or very high carbonyl stretching frequencies or force constants. In the limit of low carbonyl stretching force constants, which imply a high electron density at the carbonyl ligands, only the $-M-CO\cdots LiCH_3$ interaction should occur since high electron density at the carbonyl carbon should effectively inhibit nucleophilic attack at that site. Such complexes, for the strong nucleophile AlR_3, are nicely represented by $(o\text{-phen})[P(C_6H_5)_3]_2Mo(CO \cdot AlR_3)_2$ ($R = C_2H_5$, $i\text{-}C_4H_9$), recently reported by Shriver and Alich;[29f] the carbonyl stretching force constant for the $(o\text{-phen})[P(C_6H_5)_3]_2Mo(CO)_2$ substrate has been calculated to be 12.74 mdyn/Å.[31] Conversely, for substrates having very high carbonyl stretching frequencies or force constants implying diminished electron density at the carbonyl, direct attack by the strong nucleophile at the carbonyl carbon bearing the higher carbonyl stretching force constant without the intermediacy of an oxygen-bonded species, the mechanism envisioned by Darensbourg and Darensbourg,[6] is probable. Indeed, the observed sensitivity of rates of reaction of axially substituted $LFe(CO)_4$ complexes with benzylmagnesium chloride in THF to carbonyl stretching frequencies[13] may be contrasted to the present results and indicates direct nucleophilic attack at carbon in those complexes; the carbonyl stretching frequencies and force constants in the $LFe(CO)_4$ substrates are appreciably higher than for $LW(CO)_5$ complexes.

Rates of reaction for the hexacarbonyls are observed to vary in the order $W > Mo \gtrsim Cr$ (relative rates, 2.0: 1.2: 1.0) and to be some 2 orders of magnitude faster than are reactions of the $LW(CO)_5$ complexes. The relative rates as a function of the identity of the metal atom may be compared to those observed for reactions of tetraethylammonium azide with $M(CO)_6$ in acetone[3] which also vary $W > Mo > Cr$ (relative rates 8.5: 4.1: 1.0). It is clear that reactions of the azide ion cannot proceed *via* mechanism 4, and it is probable that they proceed by way of direct attack at the carbonyl carbon, as was originally proposed by Werner and coworkers.[3] The relative rates of reaction of methyllithium and the azide ion with the three hexacarbonyls would appear to be sufficiently different so that it is not possible to ascertain whether mechanism 4 or direct attack occurs in the former; direct attack might be possible in view of the higher carbonyl stretching force constants for $M(CO)_6$ than for $LW(CO)_5$.

The observed rates of reaction for the three hexacarbonyls with both methyllithium and the azide ion are inconsistent with those expected on the basis of their carbonyl stretching frequencies or force constants[6] (Table II), nor do they follow the expected trend based on the atomic sizes of the transition metals ($W \sim Mo > Cr$). However, the trends in the observed rates are explicable on the basis of carbonyl stretching and metal–carbon force constants calculated through use of a general quadratic force field by Jones and coworkers.[32] This normal coordinate analysis suggests the W–C σ bond to be stronger than the Mo–C or Cr–C σ bonds; the greater strength of the W–C σ bond should result in a decrease of charge at the carbonyl carbon, thus facilitating nucleophilic attack at this site. Thermochemical and electron impact estimates of M–C bond strengths[33] also indicate W–C bonds to be stronger than Mo–C or Cr–C bonds, although the relative strengths of these differ from those inferred from the study of Jones, *et al.*[32]

The relatively large differences in rate observed between $M(CO)_6$ complexes and the $LW(CO)_5$ substrates might seem surprising in view of the minor variations in rate observed within the $LW(CO)_5$ series, but it should be pointed out that on a statistical basis the proposed mechanism (4) for $LW(CO)_5$ complexes would predict a greater variation in such rates than would a mechanism involving direct attack at the carbonyl carbon. Attack at the trans carbonyl oxygen in the $LW(CO)_5$ complexes is statistically one-sixth as probable as it is in the hexacarbonyls, while the statistical factor is only two-thirds for direct attack, although the steric influence would undoubtedly further decrease the prospects for radial attack. Taking into account the statistical factor, the much faster rates for the hexacarbonyls are not unreasonable in view of the possibility of direct attack at the carbonyl carbon in the hexacarbonyls or, if the reaction proceeds *via* mechanism 4, when it is understood that the rates of reaction are proportional to $k_bk_d/k_c + k_d$, and that all the k are expected to vary with the changing electronic distribution in the axial and radial carbonyl bonds.

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