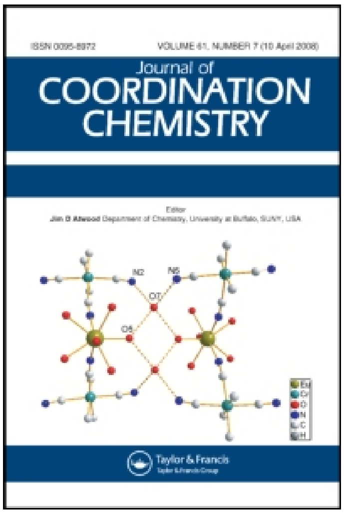

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SHORT COMMUNICATIONS

Octahedral Metal Carbonyls. XXIV[1] Kinetics and Mechanism of Reactions of Methyllithium with Group VI-B Metal Carbonyls and Derivatives

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Sir:

While it is well established that reactions of strongly nucleophilic reagents such as organolithiums with metal carbonyls, *e.g.*,

$$M(CO)_6 + RLi \rightarrow Li[M(CO)_5(COR)] \quad (1)$$
$$(M = Cr, Mo, W)$$

proceed *via* initial attack at a carbonyl carbon[2] (which, in $Cr(CO)_6$, a theoretical treatment has shown bears a positive charge),[3] only for reactions of the azide ion with $M(CO)_6$ (M = Cr, Mo, W)[4] have their kinetics been investigated.* However, such kinetics would be of great interest, especially in light of a recently proposed relationship between the Cotton-Kraihanzel force constant[5] for the carbonyl attacked, and the reactivity *via* such a mechanism.[2] This relationship is predicated on the thesis that expected increases in carbonyl stretching frequencies and force constants resulting from either increased CO-to-metal σ-bonding or decreased metal-to-CO π-bonding will correspond to decreases in electron density at carbon. A test of this proposal would involve a study of reaction rates of a strong nucleophile with a series of metal carbonyls and their substitution products. Herein are reported preliminary results of such an investigation, of the kinetics and mechanism of reactions of the Group VI–B metal carbonyls, $M(CO)_6$ (M=Cr, Mo, W) and substitution products $LW(CO)_5$ ($L=P(C_6H_5)_3$, $A_5(C_6H_5)_3$, $P(OC_6H_5)_3$) with methyllithium in diethyl ether employing stopped flow techniques.

Since methyllithium solutions are extremely air- and moisture-sensitive, glove box and "pop" bottle techniques[6] and air-tight syringes were employed in the preparation of the reagents and their transfer to the stopped flow apparatus.

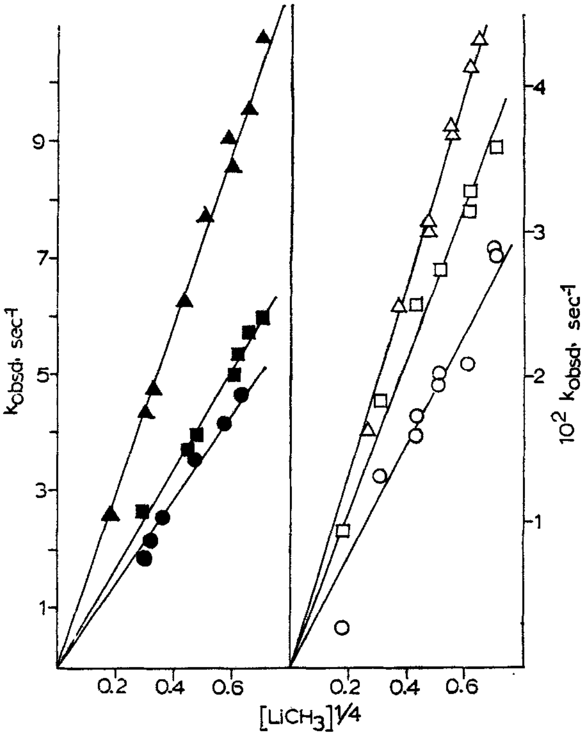

FIGURE 1 Plots of k_{obsd} *vs.* $[LiCH_3]^{1/4}$ for Group VI-B Metal Carbonyls and Derivatives. ● : $Cr(CO)_6$; ■ :$Mo(CO)_6$; ▲ :$W(CO)_6$; △ :$W(CO)_5[P(OC_6H_5)_3]$; □ :$W(CO)_5$–$[As(C_6H_5)_3]$; ○ :$W(CO)_5[P(C_6H_5)_3]$.

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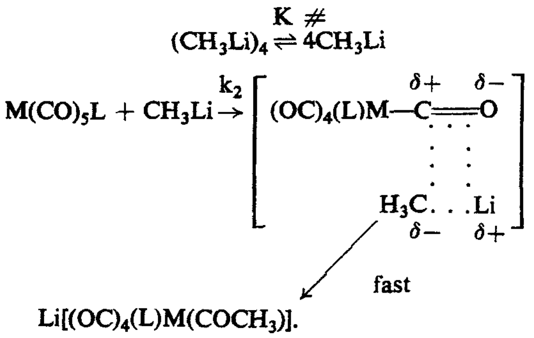
* Note added in proof: Limited kinetic data have recently been reported by Darensbourg and Darensbourg (*Inorg, Chim, Acta*, 5, 247 (1971)) for reaction of benzylmagnesium chloride with $W(CO)_6$ and $W(CO)_5\ [P(C_6H_5)]_3$ in THF.

Methyllithium concentrations were determined immediately prior to kinetic runs through use of the Gilman double titration technique.[7] Polysulfide "o" rings were found to be least susceptible to attack by methyllithium and diethyl ether and were therefore used to seal the driving pistons in the system. Temperature was maintained at 25.0° ±0.1°C as measured through use of a thermocouple attached to the observation cell. Changes in transmittance as a function of time were determined at visible frequencies at which their differences, between substrate and product, were greatest. The reaction products were isolated, where possible, as the tetraethylammonium salts and were identified through their characteristic carbonyl stretching spectra.[8] Pseudo first order reaction conditions were attained through use of at least twenty-fold excesses of methyllithium. Plots of $\ln(A_t - A\infty)$ *vs.* t were typically linear through at least two half lives.

The rate data for each substrate in its reaction with methyllithium in diethyl ether are plotted in Fig. 1, and are consistent with the approximate rate law,

$$\text{rate} = k[\text{substrate}][CH_3Li]^{1/4}, \qquad (2)$$

suggestive of the mechanism,



The actual degree of aggregation of methyllithium in diethyl ether was determined as outlined by Waack and Stevenson[9] and, for $W(CO)_6$, for which the most extensive kinetic data were obtained, corresponds to $(CH_3Li)_{3.71}$. From the slopes of the linear plots of k_{obsd} *vs.* $[CH_3Li]^{1/4}$ were obtained the rate constants, Kk_2, which are given in Table I; also given are rates relative to that of the slowest reaction (= 1).

Rates are observed to vary as a function of the metal atom W > Mo $\gtrsim$ Cr, and as a function of L, for M = W, CO $\gg$ $P(OC_6H_5)_3$ > $As(C_6H_5)3$ > $P(C_6H_5)_3$; the rates for the unsubstituted carbonyls are two orders of magnitude greater than for $LW(CO)_5$ complexes.

TABLE I

Rate and Carbonyl Stretching Data

Complex	Kk_2 (sec^{-1}M$^{11/4}$)	Relative Rate	F_{co}(cis) (mdyn/Å)
$W(CO)_6$	21.2	393	16.41
$Mo(CO)_6$	12.2	227	16.52
$Cr(CO)_6$	10.6	197	16.49
$W(CO)_5[P(OC_6H_5)_3]$	0.0945	1.75	16.08
$W(CO)_5[As(C_6H_5)_3]$	0.0740	1.37	15.90
$W(CO)_5[P(C_6H_5)_3]$	.0540	1	15.88

In the hexacarbonyls, all six carbonyls are equivalent; for the $LW(CO)_5$ species, the *cis*-geometry of the observed products[8] dictates that attack occurs at the carbonyl with the higher carbonyl stretching force constant;[2] these Cotton-Kraihanzel force constants are also given in Table I. Comparison of the reactivities and force constants shows that while rate differences are quite small a qualitative correlation between their magnitude and reactivity within the series of W complexes as predicted by Darensbourg and Darensbourg does exist;[2] no such correlation among reactivities of the three hexacarbonyls is noted. That rates of reaction of the hexacarbonyls and those of the $LW(CO)_5$ complexes differ by two orders of magnitude may be attributable in part to steric inhibition of attack at the *cis* carbonyls in the latter.

However, reactivities within the series of the hexacarbonyls are consistent with those expected on the basis of their bonding properties as inferred from normal coordinate analyses employing a general quadratic force field.[10] The magnitudes of the MC–CO stretch-stretch interaction constants and the MC and CO stretching force constants obtained through these calculations indicate the strength of the C–W σ-bond to be greater than are the strengths of C–Mo or C–Cr σ-bonds.[10] Since increases σ-bonding from carbon to the metal should remove electron density from the carbon atom, greater reactivity for $W(CO)_6$ would be expected. It is interesting to note that a recent study of carbonyl stretching spectra has suggested that

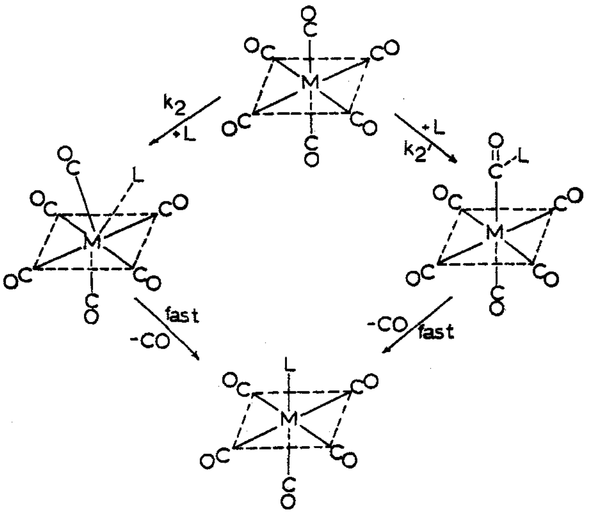


FIGURE 2 Reaction mechanisms for the attack by Lewis bases on metal hexacarbonyls (or derivatives).

changes in CO-to-metal σ-bonding in $LW(CO)_5$ complexes exert a negligible effect on carbonyl stretching frequencies or Cotton-Kraihanzel force constants.[11] Thus it would appear that carbonyl stretching data and the Cotton-Kraihanzel energy-factored force field inadequately predict reactivities in these systems.

It should also be noted that the order of reactivity of the hexacarbonyls differs from that observed for ligand-dependent substitution reactions of Lewis bases,[12] *e.g.*,

$$M(CO)_6 + L \longrightarrow M(CO)_5L + CO \qquad (4)$$

For these reactions, the rate order Mo > W; Cr ~ 0 is observed.[12] While these reactions could proceed *via* either of two mechanisms (Fig. 2), the differences in rate as a function of the identity of the metal atom strongly indicate that reactions (1) and (4) differ with respect to the site of attack. It has been noted previously that relative rates for ligand-dependent reactions of substituted Group VI–B metal carbonyls qualitatively differ for strong nucleophiles and Lewis bases.[13] Rates as a function of the identity of the metal atom as observed in this investigation provide further evidence that reactions of Lewis bases involve attack at the metal atom, while reactions of strong nucleophiles involve attack at a carbonyl carbon.

ACKNOWLEDGMENTS

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REFERENCES

1. Part XXIII: R. A. Brown and G. R. Dobson, *J. Inorg. Nucl. Chem.*, in press.
2. D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.* **9**, 1691 (1970).
3. K. G. Caulton and R. F. Fenske, *Inorg. Chem.* **7**, 1273 (1968).
4. W. Beck, H. Werner, H. Englemann and H. S. Smedal, *Chem. Ber.* **101**, 2143 (1968); H. Werner, W. Beck and H. Englemann, *Inorg. Chim. Acta* **3**, 331 (1969).
5. F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.* **84**, 4432 (1962).
6. D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill Book Co. Inc.: New York, 1969, pp. 154–158.
7. H. Gilman and F. K. Cartledge, *J. Organometal. Chem.* **2**, 447 (1964).
8. E. O. Fischer and R. Aumann, *Chem. Ber.* **102**, 1495 (1969); E. O. Fischer and A. Massböl, *Chem. Ber.* **100**, 2445 (1967).
9. R. Waack and P. E. Stevenson, *J. Amer. Chem. Soc.* **87**, 1183 (1965).
10. L. H. Jones, R. S. McDowell and M. Goldblatt, *Inorg. Chem.* **8**, 2349 (1969).
11. R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, in press.
12. For a compilation of relevant data, see R. J. Angelici, *Organometal. Chem. Rev.* **3**, 273 (1968).
13. G. R. Dobson, *Proc. S. Dak. Acad. Sci.* **50**, 244 (1971).