

Correspondence

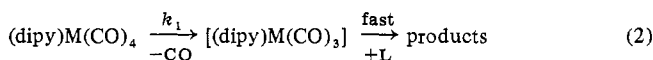
Octahedral Metal Carbonyls. XXX.¹ Mechanism of the Reaction of Tetracarbonyl(2,2'-dipyridyl)tungsten(0) with Lewis Bases

Sir:

The kinetics and mechanism of the reactions of (dipy)M(CO)₄ (dipy = 2,2'-dipyridyl; M = Mo, W) with Lewis bases have been studied by Graham and Angelici.² The rate law proposed for these systems

$$-d[(\text{dipy})\text{M}(\text{CO})_4]/dt = k_1[(\text{dipy})\text{M}(\text{CO})_4] + k_2[(\text{dipy})\text{M}(\text{CO})_4][\text{L}] \quad (1)$$

was attributed to two competing mechanisms. For the ligand-independent path, rate-determining dissociation of CO followed by rapid attack by L at the resulting five-coordinate activated complex or intermediate, (2) was envisioned.

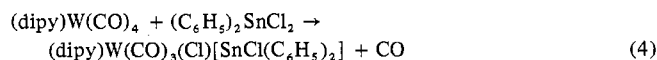


For the ligand-dependent path a mechanism involving nucleophilic attack by L at the metal atom (3) was favored.² How-



ever, the kinetic results for the ligand-independent path were unusual in several respects. For example, the values of k_1 varied significantly with the identity of the phosphite (L), an effect also observed to a lesser extent for M = Cr, for which no ligand-dependent path was observed.³ Further, surprising values and large deviations were observed for the activation parameters, particularly for L = P(O₃C₆H₅). For example, for its reactions with (dipy)Mo(CO)₄ in dichloroethane and with (dipy)W(CO)₄ in chlorobenzene, the entropies of activation were calculated to be -9.1 ± 2.8 and -12.5 ± 15.8 eu, respectively, for a process which presumably involves more bond breaking than bond making in the transition state. Satisfactory explanations for such anomalies were not evident.²

Our attention was drawn to these results in that a recent investigation of the kinetics and mechanism of the oxidative elimination reaction of (dipy)W(CO)₄ with diphenyltin dichloride (=TX)⁴



under the same reaction conditions as were employed by Angelici and Graham for reactions of (dipy)W(CO)₄ with L also exhibited a term in the rate law which was independent of the concentration of (C₆H₅)₂SnCl₂ and which also was attributed to rate-determining unimolecular dissociation of CO (2). However, the rate constants determined through the two studies differed appreciably and, for reactions of (C₆H₅)₂SnCl₂, a positive entropy of activation was calculated, quite reasonable in view of the proposed mechanism.⁴ To attempt to clarify the inconsistencies noted in the data for

(1) Part XXIX: R. A. Brown, J. R. Paxson, and G. R. Dobson, *Org. Mass Spectrom.*, in press.

(2) J. R. Graham and R. J. Angelici, *J. Amer. Chem. Soc.*, **87**, 5590 (1965).

(3) R. J. Angelici and J. R. Graham, *J. Amer. Chem. Soc.*, **87**, 5586 (1965).

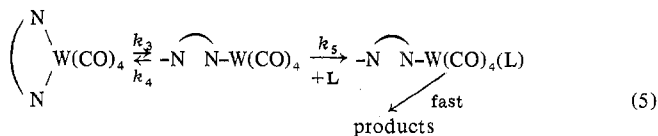
(4) M. N. Memering, A. Moradi-Araghi, and G. R. Dobson, *J. Coord. Chem.*, **2**, 271 (1973).

both reaction systems the kinetics of the reaction of (dipy)W(CO)₄ with the phosphites P(OC₂H₅)₃ and P(O₃C₆H₅) in chlorobenzene have been reinvestigated.

Experimental Part. The ligand P(O₃C₆H₅) was prepared through use of the method of Verkade, *et al.*,⁵ was sublimed twice under vacuum at 70°, was then triturated with small quantities of *n*-hexane, and was resublimed. The trituration-sublimation process was repeated two additional times, after which the ligand was finally sublimed under vacuum three additional times. Triethyl phosphite was twice distilled from sodium under nitrogen, and chlorobenzene was twice distilled from phosphorus pentoxide. The substrate, (dipy)W(CO)₄, was prepared and purified according to the literature method.⁶

Rates were determined as described by Angelici and Graham³ employing a Perkin-Elmer Model 621 infrared spectrophotometer. Plots of $\ln(A_t - A_\infty)$ vs. t exhibited curvature after 1 or more half-lives (depending upon the concentration of the phosphite employed) resulting from the equilibration of reactant and products.² Thus values of k_{obsd} were determined from data taken over the initial portion of the reaction for runs at low [L]. To obtain sufficient data over this period of time for the faster reactions, samples were removed from the reaction vessel at the required time intervals and were stored at 0° in evacuated test tubes sealed with rubber septa for subsequent spectral determination of the relative substrate concentrations. Kinetic data were treated employing a linear least-squares computer program. Limits of error cited are one standard deviation.

Results and Discussion. The overall rate law to be expected for reaction of (dipy)W(CO)₄ with Lewis bases must be examined not only with respect to the two mechanisms favored by Angelici and Graham² (eq 2 and 3) but also with respect to an additional path which involves initial formation of an equilibrium concentration of a five-coordinate intermediate in which dipy functions as a monodentate ligand and subsequent attack by L at this intermediate



Assuming a steady-state concentration of the intermediate, the rate law

$$-d[(\text{dipy})\text{W}(\text{CO})_4]/dt = k_3 k_5 [(\text{dipy})\text{W}(\text{CO})_4][\text{L}] / (k_4 + k_5[\text{L}]) \quad (6)$$

is obtained. In the limit $k_4 \gg k_5[\text{L}]$, this mechanism is kinetically indistinguishable from (3). However, when $k_5[\text{L}]$ becomes significant compared to k_4 , plots of k_{obsd} vs. [L] are expected to deviate from linearity.

Kinetic data have indicated that all three mechanisms are operative for reactions of various (bidentate ligand)M(CO)₄ complexes with Lewis bases. A consideration of the products observed for the present reaction² also suggests all three

(5) K. D. Berlin, C. Hildebrand, J. G. Verkade, and O. C. Dermer, *Chem. Ind. (London)*, 291 (1963); K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, M. Peterson, E. A. Pier, and J. G. Verkade, *Tetrahedron*, **20**, 323 (1964).

(6) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

mechanisms to compete. While *cis*-(dipy)W(CO)₃(L) could arise through mechanisms 2 and 3, the observed *trans*-(L)₂-W(CO)₄ is most reasonably attributed to mechanism 5. Indeed, in all cases where (5) has been the favored mechanism, products in which the bidentate ligand is lost have been the only observed products.⁷ Moreover, for reactions of (phen)M(CO)₄ (phen = *o*-phenanthroline; M = Mo, W), in which the rigidity of the bidentate ligand renders path 5 more improbable, only the (phen)M(CO)₃(L) product is observed.⁸ It is thus probable that mechanism 3 is the ligand-dependent path for reactions of (phen)M(CO)₄ with Lewis bases.^{8b} The similarity in bonding properties of dipy and phen in their metal carbonyl complexes⁹ indicates that mechanism 3 also is operative in the (dipy)M(CO)₄ systems.

That reactions of (dipy)M(CO)₄ might proceed *via* three competing paths is not without precedent. For one other system, for reactions of tetracarbonyl(ethylenediphosphine)molybdenum(0) with Lewis bases, it has been proposed that all three of these mechanisms are competitive.¹⁰

If all three mechanisms are operative, the pseudo-first-order rate constant, k_{obsd} , represents the sum of the contributions of each path to the overall rate

$$k_{\text{obsd}} = k_1 + k_2[\text{L}] + k_3k_5[\text{L}]/(k_4 + k_5[\text{L}]) \quad (7)$$

Rearrangement affords

$$k_{\text{obsd}} = \frac{k_1k_4 + (k_2k_4 + k_1k_5 + k_3k_5)[\text{L}] + k_2k_5[\text{L}]^2}{k_4 + k_5[\text{L}]} \quad (8)$$

Path 5 is most likely to be competitive and complex rate behavior (nonlinear plots of k_{obsd} vs. [L]; eq 8) is most likely to be observed for strong nucleophiles, L, and at high concentrations of nucleophile. Accordingly, for P(O₃C₆H₅), which rate data indicate to be the strongest nucleophile toward (dipy)W(CO)₄,² rates were determined over the widest possible range of concentrations (45-fold variation, 0.03–1.45 M). These and other kinetic data are exhibited in Table I; Figure 1 illustrates the corresponding plots of k_{obsd} vs. [L]. Table II contains the rate constants for reactions of (dipy)W(CO)₄ with both ligands and the calculated activation parameters.

For the reaction of (dipy)W(CO)₄ and P(O₃C₆H₅) at 102.0° in chlorobenzene the plot of k_{obsd} vs. [L] is linear at relatively low [L] (<0.2 M) but exhibits marked deviation from linearity above this concentration, behavior consistent with rate law 8 as $k_5[\text{L}]$ becomes significant with respect to k_4 and $k_2k_5[\text{L}]^2 \approx 0$. Thus kinetic as well as product data indicate that mechanism 5 is operative in this system; the non-linearity of the plots of k_{obsd} vs. [P(O₃C₆H₅)] cannot be rationalized on the basis of either mechanism 2 or 3. Further, previous studies have eliminated aggregation effects as a possible source of the observed deviation.² It is evident, however (eq 8), that it is not possible to extract individual rate constants other than k_1 from the data.

A plot of k_{obsd} vs. [P(OC₂H₅)₃] for data at 102.0° (Figure

Table I. Rates of Reaction of (dipy)W(CO)₄ with Phosphites in Chlorobenzene at Various Temperatures

[L], M	10 ⁴ k _{obsd} , sec ⁻¹	[L], M	10 ⁴ k _{obsd} , sec ⁻¹
Phosphite (L) = P(O ₃ C ₆ H ₅)			
102.0 ± 0.05°			
0.0321	1.06 ± 0.01	0.500	5.63 ± 0.05
0.0562	1.28 ± 0.01	0.599	6.24 ± 0.06
0.0912	1.59 ± 0.03	0.750	7.70 ± 0.03
0.128	2.01 ± 0.02	0.899	8.80 ± 0.05
0.160	2.33 ± 0.02	1.054	10.27 ± 0.04
0.257	3.00 ± 0.04	1.191	11.39 ± 0.12
0.278	3.47 ± 0.03	1.449	13.14 ± 0.07
0.400	4.49 ± 0.02		
112.0 ± 0.05°			
0.0313	2.91 ± 0.05	0.1256	5.19 ± 0.03
0.0624	4.00 ± 0.05	0.1685	6.19 ± 0.03
0.0936	4.37 ± 0.05		
122.0 ± 0.05°			
0.0246	8.94 ± 0.08	0.0755	11.51 ± 0.09
0.0500	9.93 ± 0.08	0.1018	12.44 ± 0.13
0.0752	10.87 ± 0.07	0.1257	13.37 ± 0.11
		0.1511	15.11 ± 0.11
Phosphite (L) = P(OC ₂ H ₅) ₃			
102.0 ± 0.05°			
0.0518	0.94 ± 0.01	0.432	2.55 ± 0.03
0.1090	1.17 ± 0.01	0.648	3.48 ± 0.02
0.218	1.67 ± 0.004		

Table II. Rate Constants and Activation Parameters for Reactions of (dipy)W(CO)₄ with Phosphites in Chlorobenzene

Phosphite	Temp, °C	10 ⁴ k ₁ , sec ⁻¹	10 ⁴ k _a , M ⁻¹ sec ⁻¹
P(O ₃ C ₆ H ₅) ^a	102.0 ± 0.05	0.723 ± 0.028	10.01 ± 0.27
	112.0 ± 0.05	2.32 ± 0.17	22.99 ± 1.58
	122.0 ± 0.05	7.60 ± 0.24	47.93 ± 2.54
P(OC ₂ H ₅) ₃	102.0 ± 0.05	0.717 ± 0.010	4.26 ± 0.03

^a For P(O₃C₆H₅), $\Delta H_1^* = 33.9 \pm 0.6$ kcal/mol, $\Delta S_1^* = 12.5 \pm 1.0$ cal/deg mol, $\Delta H_a^* = 22.3 \pm 0.4$ kcal/mol, and $\Delta S_a^* = -13.3 \pm 0.7$ cal/deg mol.

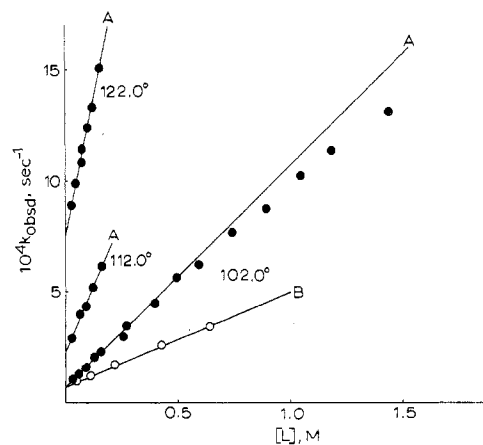


Figure 1. Plots of k_{obsd} vs. [L] for reactions of (dipy)W(CO)₄ with phosphites in chlorobenzene at various temperatures: A, L = P(O₃C₆H₅); B, L = P(OC₂H₅)₃.

1) is linear over the concentration range employed. This is reasonable in that for this weaker nucleophile $k_5[\text{L}]$ will be less important and that a smaller value of k_5 also probably will decrease the contribution of path 5 to the ligand-dependent term (*cf.* eq 8), rendering complex rate behavior less observable. The k_{obsd} vs. [L] plots for the two phosphites at 102.0° yield a common intercept, within experimental error, in contrast to the observations of Angelici and

(7) For a brief review, see, G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **4**, 87 (1970).

(8) (a) A referee has pointed out that it has previously been observed that hydrolysis studies of Fe(II) chelate complexes in acid solution have indicated that the ring-opening mechanism is accessible to dipy but not to phen: F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, pp 218–219. (b) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 992 (1967).

(9) See, e.g., C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); R. T. Jernigan, R. A. Brown, and G. R. Dobson, *J. Coord. Chem.*, **2**, 47 (1972).

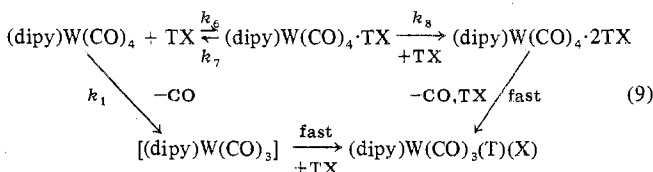
(10) G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, **6**, 507 (1972).

Graham² but fully consistent with the proposed ligand-independent path (eq 2).

From the data at low $[P(O_3C_6H_9)]$ ($<0.2 M$) at three temperatures were extracted activation parameters for the path governed by k_1 (Table II). The observed positive entropy of activation is consistent with the proposed dissociative mechanism (eq 2). Activation parameters for the ligand-dependent path (linear portions of plots of k_{obsd} vs. $[P(O_3C_6H_9)]$) are also presented in Table II.

The data presented here demonstrate that the inconsistencies observed by Angelici and Graham arose from the competitive presence of mechanism 5, manifested for $L = P(O_3C_6H_9)$ by deviations from linearity of the plots of k_{obsd} vs. $[L]$. Indeed, a reexamination of the data of Angelici and Graham confirms the curvature of their plots of k_{obsd} vs. $[P(O_3C_6H_9)]$. It is also to be noted that the values of k_{obsd} differ by *ca.* 25% in the two studies; it is possible that deviations from linearity of these plots as the result of equilibration of the substrate and products at longer reaction times could contribute to the lower values of k_{obsd} as reported by Angelici and Graham.

The favored mechanism for reactions of $(dipy)W(CO)_4$ with $(C_6H_5)_2SnCl_2$ (TX) in chlorobenzene at 95–115° is⁴



Employing the steady-state approximation, the rate law

$$-d[(dipy)W(CO)_4]/dt = k_1[(dipy)W(CO)_4] + \frac{k_6 k_8 [(dipy)W(CO)_4][TX]^2}{k_7 + k_8[TX]} \quad (10)$$

is obtained. The rate law actually observed for these kinetic studies⁴

$$-d[(dipy)W(CO)_4]/dt = k_b[(dipy)W(CO)_4] + k_c[(dipy)W(CO)_4][TX]^2 \quad (11)$$

is consistent with the postulated rate law for $k_7 \gg k_8[TX]$. The values of k_1 were determined through extrapolation of plots of k_{obsd} vs. $[TX]^2$. However, rearrangement of (11) in terms of k_{obsd} affords

$$k_{obsd} = \frac{k_1 k_7 + k_1 k_8 [TX] + k_6 k_8 [TX]^2}{k_7 + k_8 [TX]} \quad (12)$$

and thus, since $k_1 k_8 [TX]$ will become important at very low $[TX]$, the intercept obtained through extrapolation, k_b , will be greater than the true first-order rate constant, k_1 . A comparison of the k_1 values obtained through reactions of L and TX with $(dipy)W(CO)_4$ does indeed show the latter to be somewhat larger than the former for a given temperature.

Thus emerges a consistent picture of the rate behavior observed for the reactions of these systems.

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Registry No. $(dipy)W(CO)_4$, 16743-02-5; $P(O_3C_6H_9)$, 281-33-4; $P(OC_2H_5)_3$, 122-52-1.

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