Contribution from the Department of Chemistry,
North Texas State University, Denton, Texas 76203

Octahedral Metal Carbonyls. XXXV. Mechanism of the Reaction of 2,2'-Dipyridyltetracarbonylchromium(0) with Alkyl Phosphites

Billy J. McKerley, Gary C. Faber, and Gerard R. Dobson*

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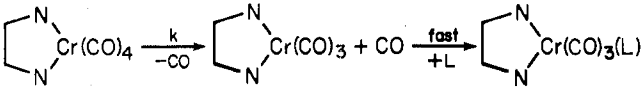
Rate data for reactions of (dipy)Cr(CO)$_4$ (dipy = 2,2'-dipyridyl) with alkyl phosphites (L)

$$\text{(dipy)Cr(CO)}_4 + \text{L} \rightarrow cis\text{-(dipy)Cr(CO)}_3\text{(L)} + \text{CO} \qquad (1)$$

have been reported to obey a rate law

$$-\mathrm{d}[\text{(dipy)Cr(CO)}_4]/\mathrm{d}t = k[\text{(dipy)Cr(CO)}_4] \qquad (2)$$

for which mechanism 3, in which rate-determining fission of



(3)

a Cr–C bond is followed by rapid reaction of L with the resulting five-coordinate activated complex or intermediate, was proposed.[1] It was observed, however, that the first-order rate constants, k, varied with the identity of L, a result inconsistent with the proposed mechanism. Recently, an explanation was offered[2] for a similar variation in k for analogous reactions of (dipy)Mo(CO)$_4$ and (dipy)W(CO)$_4$ with phosphites.[3] However, that explanation was predicated on an interpretation of the nature of a ligand-dependent term which is observed in the rate law for reactions of those complexes; that explanation thus was not applicable to the (dipy)Cr(CO)$_4$ system, for which no ligand-dependent term was reported.[1]

The kinetics and mechanism of the (dipy)Cr(CO)$_4$ system have been reinvestigated in an attempt to resolve the anomalous rate behavior.

Experimental Section

The substrate, (dipy)Cr(CO)$_4$, was prepared and purified through use of the published procedure.[4] Chlorobenzene and 1,2-dichloroethane were fractionally distilled from P$_2$O$_5$. Triethyl phosphite (Aldrich) was fractionally distilled over sodium, was stored under nitrogen, and was again fractionally distilled immediately prior to use. All runs employing this ligand were completed within 5 days of the last distillation. The "constrained phosphite" 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P(OCH$_2$)$_3$CCH$_3$, was prepared by the method of Verkade et al.[5] and was vacuum-sublimed five times (0.05 Torr, 50°).

Kinetic runs were carried out as described previously[1] through observation of the disappearance of the high-energy carbonyl stretching absorption of the substrate (ca. 2015 cm^{-1}) employing a Perkin-Elmer Model 621 grating spectrophotometer under pseudo-first-order reaction conditions (at least a tenfold excess of ligand) except as noted. Values of the pseudo-first-order rate constants k_{obsd} were obtained from plots of ln ($A_t - A_{\text{bl}}$) vs. t, where A_t and A_{bl} are the absorbances of the reaction solution at time t and of a solvent–ligand blank, respectively. For L = P(OCH$_2$)$_3$CCH$_3$ these plots were linear over at least 2 half-lives; for L = P(OC$_2$H$_5$)$_3$, however, such plots for low concentrations of ligand deviated from linearity after about 1 half-life, behavior also noted by Angelici and Graham,[1] and it was thus necessary to employ the initial slopes of the plots in the determination of k_{obsd}.

By infrared examination of reaction solutions at t_∞ it was confirmed, as reported by Angelici and Graham,[1] that (dipy)Cr(CO)$_3$(L) was the sole reaction product.

Data were treated employing a nonlinear least-squares computer program (IBM 360-50). The cited limits of error (in parentheses) are one standard deviation.

Table I. Rate Data for Reaction of (dipy)Cr(CO)$_4$ with Phosphites at 47.9°

[L], M	$10^4 k_{\text{obsd}}$, sec^{-1}	[L], M	$10^4 k_{\text{obsd}}$, sec^{-1}
L = P(OCH$_2$)$_3$CCH$_3$, Chlorobenzene Solvent			
0.0099	0.952 (51)[a]	0.1001	1.916 (24)
0.0150	1.355 (43)[a]	0.1114	1.811 (25)
0.0150	1.283 (23)[a]	0.1500	1.903 (14)
0.0201	1.133 (47)[a]	0.2500	2.011 (25)
0.0250	1.513 (50)[a]	0.3220	2.041 (47)
0.0298	1.639 (13)[a]	0.3502	2.276 (30)
0.0298	1.664 (16)[a]	0.3960	2.293 (37)
0.0599	1.621 (34)	0.4997	2.225 (19)
0.0825	1.654 (22)	0.6840	2.349 (58)
0.0944	1.895 (16)		
L = P(OC$_2$H$_5$)$_3$, 1,2-Dichloroethane solvent			
0.0242	3.869 (85)	0.0697	4.325 (12)
0.0348	4.041 (137)	0.1023	4.299 (55)
0.0398	4.171 (92)	0.1486	4.312 (32)
0.0434	4.222 (46)	0.1486	4.633 (30)
0.0548	4.222 (97)	0.1720	4.528 (40)
0.0658	4.451 (78)	0.2896	4.439 (38)

[a] Data taken for less than a tenfold excess of L (non-pseudo-first-order reaction conditions).

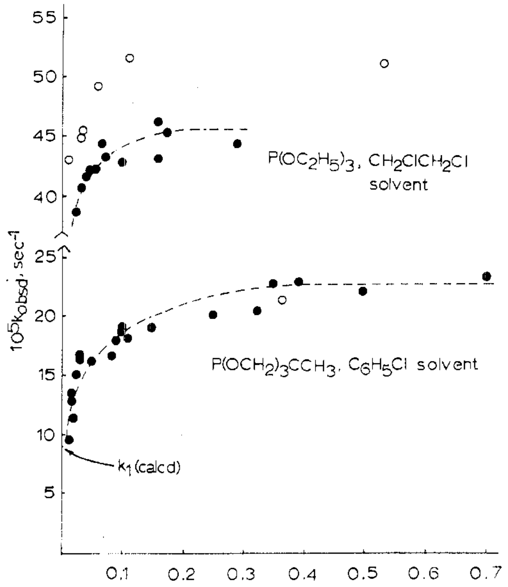
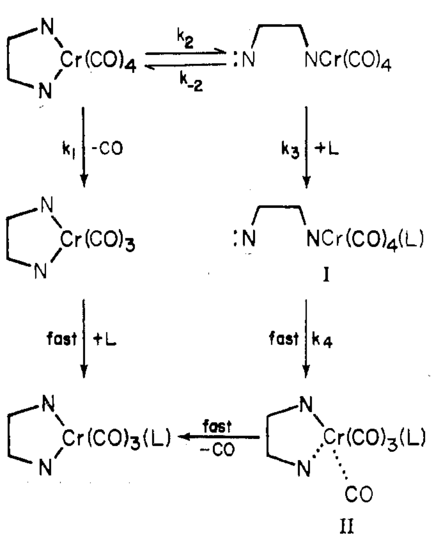


Figure 1. Plots of k_{obsd} vs. [L] for reactions of (dipy)Cr(CO)$_4$ with phosphites in various solvents at 47.9°: ●, this work; ○, data taken from ref 1.

Results and Discussion

Rate data for the reaction at 47.9° of (dipy)Cr(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ in chlorobenzene and of P(OC$_2$H$_5$)$_3$ in 1,2-dichloroethane are presented in Table I. Figure 1 exhibits plot of k_{obsd} vs. [L] for these data; data of Angelici and Graham for these ligands and solvents and that temperature are included for comparison. The results support a mechanism (4) which envisions, in addition to the mechanism favored by Angelici and Graham,[1] a second pathway, one commonly observed in substitution reactions of metal carbonyl complexes containing chelating ligands,[6] in which reversible dissociation of one end of the dipy ligand is followed by attack by L at the five-coordinate intermediate and other, rapid steps. The observation that *cis*-(dipy)Cr(CO)$_3$(L) is the only reaction product at t_∞ indicates this reversible dissociation path to proceed through formation of a seven-coordinate activated complex or intermediate (II) in which attack of the free end of dipy in I results in displacement of a carbonyl. The fact that $k_1 \sim k_2k_3[\text{L}]/(k_{-2} + k_3[\text{L}]) << k_4$ (see eq 4 and 5) in this system is supportive of assistance of the free end of the



(4)

dipy ligand in carbonyl dissociation in that there is no reason to expect carbonyls in I to be appreciably more labile than in the (dipy)$Cr(CO)_4$ substrate, which undergoes CO loss via a dissociative path governed by k_1. Rate data for ligand replacement reactions of (2,2,8,8-tetramethyl-3,7-dithianonane)tetracarbonyltungsten(0) with phosphites are interpretable in terms of an analogous intermediate,[7] and, while examples of seven-coordination about the small Cr atom are not plentiful, a seven-coordinate activated complex or intermediate has been proposed for reactions of $Cr(CO)_6$ with strong nucleophiles such as tri(*n*-butyl)phosphine.[8] Further, the high "local concentration" of the free end of dipy should favor the formation of such a species.[9]

The steady-state rate law corresponding to mechanism 4 is

$$-\mathrm{d}[(\mathrm{dipy})\mathrm{Cr(CO)_4}]/\mathrm{d}t = k_1[(\mathrm{dipy})\mathrm{Cr(CO)_4}] + k_2k_3[(\mathrm{dipy})\mathrm{Cr(CO)_4}][\mathrm{L}]/(k_{-2} + k_3[\mathrm{L}]) \qquad (5)$$

which may be arranged, in terms of the pseudo-first-order rate constant, k_{obsd}, to,

$$1/(k_{\mathrm{obsd}} - k_1) = 1/k_2 + k_{-2}/k_2k_3[\mathrm{L}] \qquad (6)$$

Thus a plot of $1/(k_{\mathrm{obsd}} - k_1)$ vs. $1/[\mathrm{L}]$ is expected to be linear, with slope k_{-2}/k_2k_3 and intercept $1/k_2$. From k_{obsd} data for L = $P(OCH_2)_3CCH_3$ (the system for which k_{obsd} plots were linear over 2 or more half-lives), the value of k_1 was estimated as follows. From values of k_{obsd} were subtracted the arbitrary constant (k_1) which provided the best linear plot of $1/(k_{\mathrm{obsd}} - k_1)$ vs. $1/[\mathrm{L}]$. The value of k_1 thus determined, 9.0×10^{-5} sec^{-1}, is in excellent agreement with values of the first-order rate constants obtained at very low ligand concentrations (see Figure 1), for which the contribution to the rate of the reversible dissociation path is expected to be minimal.

The existence of the reversible dissociation path for reactions of (dipy)$Cr(CO)_4$ raises the possibility that such a path also exists for the analogous reactions with phosphites of (*o*-phen)$Cr(CO)_4$ (*o*-phen = *o*-phenanthroline) and related substrates containing substituted *o*-phen ligands of varying basicities.[10] The greater rigidity of the *o*-phen's presumably would lead to greater $k_{-2}/k_3[\mathrm{L}]$ ratios (eq 5), rendering ligand-dependent rate behavior less likely to be observed. However, greater values for k_{-2}, and thus slower rates of reaction, would be expected for the more basic *o*-phen's should their reactions proceed predominantly through the reversible dissociation mechanism. The opposite behavior is, in fact, observed.[10] The existence of this mechanism in competition with that involving rate-determining dissociation of CO for the (dipy)$Cr(CO)_4$ system does offer an attractive explanation for the deviation of the dipy complexes from an otherwise excellent linear free energy plot of log k (eq 2) vs. the pK_a of the bidentate ligand for dipy and *o*-phen complexes.[10]

In the limit of high [L], $k_3[\mathrm{L}] >> k_{-2}$, and rate law 5 reduces to that reported by Angelici and Graham,[1] i.e.

$$-\mathrm{d}[(\mathrm{dipy})\mathrm{Cr(CO)_4}]/\mathrm{d}t = (k_1 + k_2)[(\mathrm{dipy})\mathrm{Cr(CO)_4}] \qquad (7)$$

Thus the existence of the reversible dissociation path in this system cannot explain the observed[1] variation in the first-order rate constants with the identity of L. Figure 1 indicates, however, that, while the present data are in good agreement with those of Angelici and Graham for $P(OCH_2)_3CCH_3$, there is a significant variation in the data for $P(OC_2H_5)_3$, which was rigorously purified in this study but which was used as obtained from a commercial source by Angelici and Graham.[1] It would thus appear reasonable to presume that differences in the purity of the ligands are the cause of observed variations in k, particularly since it has been observed that impurities in the phosphites which have been employed in other kinetic investigations of metal carbonyl derivatives have had pronounced effects on the rates of those reactions.[7,11]

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Registry No. (dipy)$Cr(CO)_4$, 15668-63-0; $P(OCH_2)_3CCH_3$, 1449-91-8; $P(OC_2H_5)_3$, 122-52-1.

References and Notes

(1) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965).
(2) M. N. Memering and G. R. Dobson, *Inorg. Chem.*, **12**, 2490 (1973).
(3) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965).
(4) M. H. B. Stiddard, *J. Chem. Soc.*, 756 (1963).
(5) J. G. Verkade, T. J. Hutteman, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).
(6) See, for example, W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 627 (1974), and references cited therein.
(7) L. D. Schultz and G. R. Dobson, manuscript in preparation.
(8) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967).
(9) R. J. Angelici, *Organomet. Chem. Rev.*, **3**, 173 (1968).
(10) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).
(11) A. Pidcock, J. D. Smith, and B. W. Taylor, *Inorg. Chem.*, **9**, 638 (1970).

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Acetate Complexes of Dirhodium and Diruthenium. Aquation and Reduction-Oxidation

C. R. Wilson and H. Taube*

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Previous to 1968, the only well-established example of Rh(II) in combination with saturated ligands was $Rh_2(OAc)_4$ and its adducts.[1] At that time, Maspero and Taube succeeded in synthesizing the fully hydrated species $Rh_2^{4+}(aq)$ in the anaerobic reaction[2]

$$Cr^{2+}(aq) + (H_2O)_5RhCl^{2+} \rightarrow (H_2O)_5CrCl^{2+} + {}^{1}/_{2}Rh_2^{4+}(aq)$$

In attempts to find a convenient route to preparing $Rh_2^{4+}(aq)$ at relatively high concentration both Ziolkowski[3] and the present authors studied the hydrolysis of $Rh_2(OAc)_4$ in strong noncomplexing acids but without producing $Rh_2^{4+}(aq)$. In 1969 Legzdins et al.[4] published a communication indicating that new homogenous hydrogenation catalysts could be obtained through the protonation of $Rh_2(OAc)_4$ and its subsequent interaction with triphenylphosphine. They proposed the aquo ion $Rh_2^{4+}(aq)$ as an intermediate even though their