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Octahedral Metal Carbonyls. 79.[1] Mechanism of the Reaction of Photogenerated (Solvent)$Cr(CO)_5$ Intermediates with Lewis Bases (L) in Binary and Ternary Solvent/L Mixtures (Solvent = Fluorobenzene, Chlorobenzene, *n*-Heptane; L = 1-Hexene, Piperidine)

Shulin Zhang and Gerard R. Dobson*

Department of Chemistry and the Center for Organometallic Research,
University of North Texas, Denton, Texas 76203-5068

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Studies of solvent replacement by Lewis bases (L) from (solvent)$Cr(CO)_5$ intermediates generated by pulsed laser flash photolysis (eq 2) have been carried out in $Cr(CO)_6$/PhX/L and $Cr(CO)_6$/PhX/hep/L solutions (PhX = fluorobenzene (FB) and chlorobenzene (CB), hep = *n*-heptane (the solvents); L = 1-hexene (hex) and piperidine (pip) (the trapping agents). Studies of the $Cr(CO)_6$/PhX/L systems indicate that competitive solvent dissociation and interchange reaction pathways are accessible for CB but that only the dissociative pathway is observed for FB. The differing modes of bonding of PhX to Cr (FB is bonded "side-on" via an isolated ring C=C bond, while CB is coordinated through a lone pair on Cl) thus are reflected in the mechanism of replacement of PhX from their (PhX)$Cr(CO)_5$ complexes by L. Comparisons of rate data for binary (PhX/pip) and ternary (PhX/hep/pip) solutions strongly support the presence of competitive hep dissociation and interchange pathways for (hep)$Cr(CO)_5$ in its reaction with pip. Thus, the evidence presented here indicates that solvent replacement in the $Cr(CO)_6$/CB/hexanes/pip system (G. R. Dobson and S. Zhang, *J. Coord. Chem.*, 1989, *21*, 155) takes place via competitive dissociative and interchange pathways for both CB and hexanes despite the seeming simplicity of the observed rate law, which can be interpreted in terms of a single reaction pathway.

Introduction

It is now widely recognized that in many cases the species produced in predominant concentration after metal–ligand bond fission are not coordinatively-unsaturated but are specifically solvated, with the solvent molecule occupying the vacant coordination site. It has been shown, for example, that upon flash photolysis, vibrationally-excited [$Cr(CO)_5$] produced upon Cr–CO bond fission reacts very rapidly with the solvent, on the picosecond time scale, to afford (solvent)$Cr(CO)_5$ species[2,3] (eq 1). This observation raises the question as to whether a

$$\mathrm{Cr(CO)_6} \xrightarrow{h\nu} [\mathrm{Cr(CO)_5}] \xrightarrow{+\text{solvent}} (\text{solvent})\mathrm{Cr(CO)_5} \tag{1}$$

solvent–$Cr(CO)_5$ molecule or coordinatively-unsaturated [$Cr(CO)_5$] is the species involved in the photocatalytic activity observed in solutions containing $Cr(CO)_6$.[4] This question is intriguing because an interchange mechanism involving nucleophilic attack by Lewis bases, L, at the solvate could confer selectivity among incoming nucleophiles not expected for a dissociative desolvation mechanism. It can be addressed through studies of the mechanism of the much slower (nanosecond to millisecond) replacement of the solvent from (solvent)$Cr(CO)_5$ intermediates[5–12] (eq 2).

$$(\text{solvent})\mathrm{Cr(CO)_5} \xrightarrow{+\mathrm{L}} \mathrm{LCr(CO)_5} + \text{solvent} \tag{2}$$

It has been established that two modes of bonding of haloarenes (PhX) to $Cr(CO)_5$ are accessible.[11] For fluorobenzene, coordination most likely takes place through an isolated arene double bond, a bonding mode also observed in (η^2-benzene)$Cr(CO)_5$,[9] while chlorobenzene is bonded to Cr via a lone pair on the halogen.[11] The studies reported here, of the kinetics and mechanism of the displacement of chlorobenzene (CB) and fluorobenzene (FB) from their (PhX)$Cr(CO)_5$ complexes by 1-hexene (hex) and piperidine (pip; eq 2), were undertaken to probe the influence of the mode of solvent coordination on the mechanism of desolvation.

Flash photolysis of $Cr(CO)_6$ in solutions containing two solvents can afford valuable mechanistic information (at the expense of information about the rate) if the desolvation rates and mechanism for two (solvent)$Cr(CO)_5$ species differ. This method has been employed for FB/hep/pip solutions (hep = *n*-heptane) to study the mechanism of desolvation of (hep)$Cr(CO)_5$, where pip is the trapping agent (eq 2).

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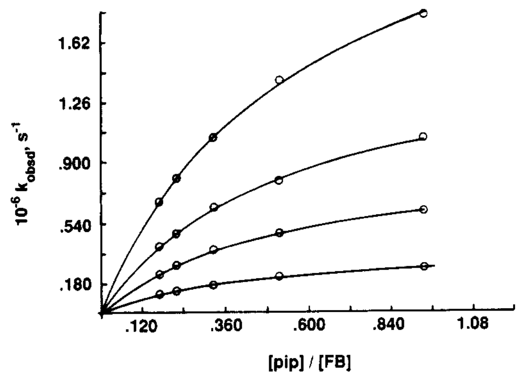

Figure 1. Plots of k_{obsd} vs [pip]/[FB] at various temperatures (bottom to top: 2.3, 15.0, 25.0, 35.0 °C) for the reaction of photogenerated (FB)Cr(CO)$_5$ with pip in FB solution.

Experimental Section

Materials. Cr(CO)$_6$ (Pressure Chemical Co.) was vacuum sublimed before use. Piperidine (pip; Aldrich), fluorobenzene and chlorobenzene (FB, CB; Aldrich), and *n*-heptane (hep; Mallinckrodt) were fractionally distilled under nitrogen from KOH, P_4O_{10}, and Na, respectively.

Laser Flash Photolysis Studies. Flash photolysis studies were carried out at the University of North Texas (UNT) or the Center for Fast Kinetics Research (CFKR), University of Texas at Austin. The flash photolysis system at UNT employed a Lumonics TE-430 excimer laser (Xe/F$_2$; 351 nm; 14-ns fwhi); that at CFKR was based on a Quantel YG 481 Nd:YAG laser (355 nm, 11-ns fwhi). Both systems have been described in detail.[9,13,14] In typical experiments, solutions ca. 3.5×10^{-3} M in Cr(CO)$_6$ also containing large excesses of PhX and L or PhX, hep, and L (to ensure pseudo-first-order reaction conditions) were employed. Both the solvent(s) and L were weighed so that their concentrations would be known with accuracy. No significant differences in the traces of absorbance vs time taken after a single flash or after multiple flashes were observed when employing either photolysis system. The pseudo-first-order rate constants, k_{obsd}, were obtained from averages of from 1 to 10 traces from plots of ln $(A_t - A_\infty)$ vs time (A_t and A_∞ are measured absorbances at time *t* and at infinite time, respectively). The kinetics data were analyzed either at UNT employing ASYST-based computer programs developed in-house or at CFKR. The limits of error, given in parentheses as the uncertainties of the last digit(s) of the cited value, are 1 standard deviation.

Results

Identification of Reaction Intermediates and Products. Previous studies have revealed the positions of the absorption maxima for the intermediates and products generated after flash photolysis: (FB)Cr(CO)$_5$ (477 nm),[10] (CB)Cr(CO)$_5$ (ca. 480 nm),[8] (pip)Cr(CO)$_5$ (417 nm),[9] and (hex)Cr(CO)$_5$ (ca. 344 nm).[9] All reactions were monitored at 490 nm. The time-resolved spectra taken after flash photolysis all exhibit isosbestic points, indicating conversion of the (PhX)Cr(CO)$_5$ transients only to (L)-Cr(CO)$_5$ products (eq 2).

Kinetic Data for PhX/L Solutions. To obtain the maximum mechanistic information, rate studies were carried out so that nonlimiting forms of the rate laws were observed ($0.1 < [L]/[PhX] < 1.7$). Thus, influences of both [PhX] and [L] on the rate could be evaluated. Values of the pseudo-first-order rate constants were obtained from the slopes of plots of ln $(A_t - A_\infty)$ vs time. These plots were linear over three or more half-lives and exhibited *R* values exceeding 0.99. Typical plots of k_{obsd} vs [pip]/[FB] from data taken at four temperatures (2.3–35.0 °C) are curved (Figure 1), and plots of $1/k_{obsd}$ vs [PhX]/[L] are linear (Figures 2 and 3, solid lines). However, the plots for CB do not exhibit a common intercept. The values of k_{obsd} are presented in supplementary Table I.

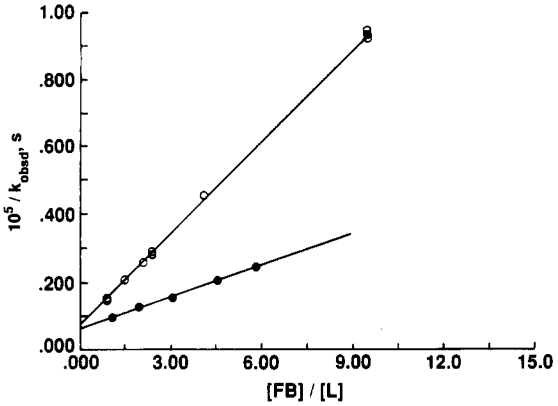

Figure 2. Plots of $1/k_{obsd}$ vs [FB]/[L] for reactions of photogenerated (FB)Cr(CO)$_5$ at 25.0 °C with L for L = hex (top) and pip.

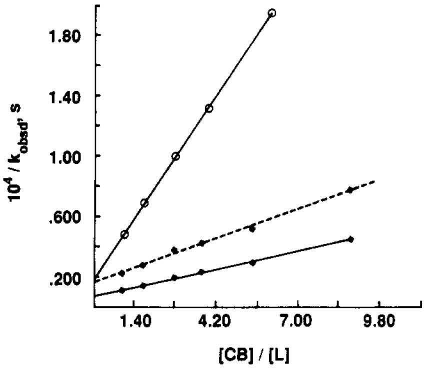

Figure 3. Plots of $1/k_{obsd}$ vs [CB]/[L] (solid lines) for reactions of photogenerated (CB)Cr(CO)$_5$ with L (hex (top) and pip) at 25.0 °C and of $1/(k_{obsd} - k_3[pip])$ vs [CB]/[pip] (dashed line).

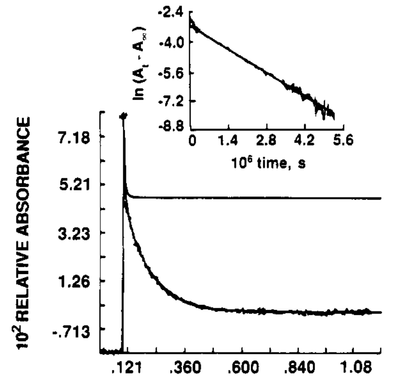

Figure 4. Plot of absorbance vs time monitoring 490 nm for the reaction of photogenerated (FB)Cr(CO)$_5$ with pip in FB/pip/hep solution. Inset: plot of ln $(A_t - A_\infty)$ vs time.

Kinetics Data for PhX/L/hep Solutions. The FB/pip solutions also were diluted with hep so that [hep] = 6.57 M while [FB]/[pip] remained constant and were again subjected to flash photolysis. Plots of ln $(A_t - A_\infty)$ vs time (Figure 4) indicated two decays, for the disappearance of (hep)Cr(CO)$_5$ (fast) and of (FB)Cr(CO)$_5$. Again, plots of k_{obsd} vs [pip]/[FB] (slow decay) were curved (concave downward) with positive slopes and plots of $1/k_{obsd}$ vs [FB]/[pip] were linear. Figure 5 shows plots of $1/k_{obsd}$ vs [FB]/[pip] (25.0 °C) for data taken both before and after dilution. The plots are linear with differing

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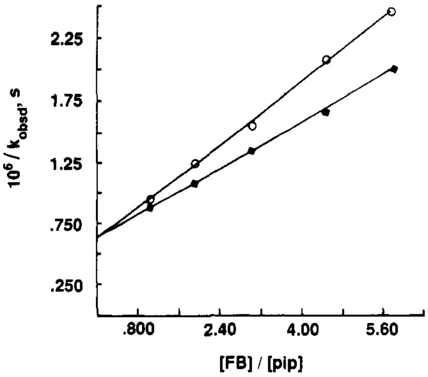
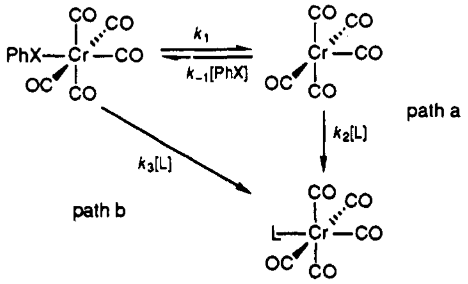


Figure 5. Plots of $1/k_{obsd}$ vs [FB]/[pip] for the reactions of photogenerated (FB)Cr(CO)$_5$ with pip at 25.0 °C in (O) FB/pip solution and (*) in FB/pip/hep solution.

Scheme I



slopes and a common intercept. The values of k_{obsd} are given in supplementary Table II.

Kinetics studies were also carried out in Cr(CO)$_6$/CB/hep/pip solutions where the concentrations of pip and CB were varied but for which [CB]/[pip] was held constant. The hep concentration also was held relatively constant by maintaining [CB] and [pip] each at less than 0.6 M. The values of k_{obsd} taken at 25.0 °C, over the concentration range $0 < [\text{pip}] < 0.21$ M (supplementary Table II), indicate that the rates of CB replacement increase with increasing [pip].

Discussion

Mechanism. Reactions of Photogenerated (PhX)-Cr(CO)$_5$ Species Produced in PhX/L Solutions. The likely predominant mechanism for displacement of PhX from photogenerated (PhX)Cr(CO)$_5$ by L involves reversible dissociation of PhX from (PhX)Cr(CO)$_5$, followed by nucleophilic attack by L at coordinatively-unsaturated [Cr(CO)$_5$], (pathway a, Scheme I). This mechanism has also been implicated in solvent displacement reactions from (η^2-benzene)Cr(CO)$_5$.[9] Assuming a steady-state concentration of [Cr(CO)$_5$], the rate law corresponding to this mechanism is

$$-\text{d}[\text{Cr(CO)}_5]/\text{d}t = k_1k_2[\text{Cr(CO)}_5][\text{L}]/(k_{-1}[\text{PhX}] + k_2[\text{L}]) \quad (3)$$

In terms of the pseudo-first-order rate constant, this expression can be rearranged to

$$1/k_{obsd} = 1/k_1 + k_{-1}[\text{PhX}]/k_1k_2[\text{L}] \quad (4)$$

For the FB data (Figure 2), the plots for L = pip, hex are linear and exhibit a common intercept, within 2 standard deviations, consistent with eq 4. However, for the CB/L data, while the "double-reciprocal" plots appear to be linear (Figure 3), they do not exhibit a common intercept.

These data can be explained if one assumes that replacement of CB in (CB)Cr(CO)$_5$ by pip takes place via competitive dissociative and interchange mechanisms (paths a and b, Scheme I). The steady-state rate law corresponding to both pathways ([Cr(CO)$_5$] is the steady-state intermediate) is

Table I. Rate Data for Cr(CO)$_6$/PhX/L Reactions

PhX	L	T, °C	$10^{-5}k_1$, s^{-1}	k_2/k_{-1}
FB	hex	24.9	13.9 (5)	0.78 (3)
	pip	2.3	4.0 (1)	2.41 (6)
		15.0	9.5 (2)	2.02 (6)
		25.0	16.2 (6)	1.94 (12)
		35.0	29.5 (9)	1.70 (8)
CB	hex	3.8	0.089 (10)	0.80 (12)
		15.2	0.238 (13)	0.73 (5)
		25.0	0.588 (18)	0.58 (2)
	pip[a]	25.0	1.45 (7)	1.60 (9)
	pip[b]	25.0	0.57 (4)	2.4 (3)

[a] As $1/k_{obsd}$ vs [CB]/[pip]. [b] As $1/(k_{obsd} - k_3[\text{pip}])$ vs [CB]/[pip].

$$-\text{d}[\text{Cr(CO)}_5]/\text{d}t = \frac{k_1k_2[\text{Cr(CO)}_5][\text{pip}]}{k_{-1}[\text{CB}] + k_2[\text{pip}]} + k_3[\text{Cr(CO)}_5][\text{pip}] \quad (5)$$

Upon rearrangement and expression in terms of the pseudo-first-order rate constant, eq 5 becomes

$$1/(k_{obsd} - k_3[\text{pip}]) = 1/k_1 + k_{-1}[\text{CB}]/k_1k_2[\text{pip}] \quad (6)$$

Based upon eq 6, plots of $1/(k_{obsd} - k_3[\text{pip}])$ vs [CB]/[pip] are expected to be linear, with intercept $1/k_1$ and slope $k_{-1}/k_1/k_2$. If it is assumed that solvent replacement from (CB)Cr(CO)$_5$ by hex takes place exclusively via a dissociative pathway (Scheme I), the value of k_3 is represented by the difference between the reciprocals of the intercepts of the plots of $1/k_{obsd}$ vs [CB]/[L] for hex and for pip, 1.01 (6) × 10^4 M^{-1} s^{-1}. By employing this value of k_3, a plot of $1/(k_{obsd} - k_3[\text{pip}])$ vs [CB]/[pip] was also found to be linear, with $R = 0.997$ (Figure 3, dashed line). Similar behavior has been observed for the Cr(CO)$_6$/benzene/pyridine system.[9] Further evidence in support of this interpretation will be presented later. Table I presents rate data for these Cr(CO)$_6$/PhX/L systems (PhX = FB, CB; L = pip, hex).

Reactions in FB/hep/pip Solutions: Mechanism of the Desolvation of (hep)Cr(CO)$_5$ by pip. Activation parameters for displacement of hep from (hep)Cr(CO)$_5$ by pyridine and 1-picoline (entropies of activation)[6] and pip and 2-picoline (volumes of activation)[10] (eq 2) have been found to be near zero, consistent with L–Cr bond making in the transition states leading to hep loss. The enthalpies of activation for the first-mentioned reactions were also found to be significantly lower than the hep–Cr bond strengths determined from photoacoustic calorimetric studies.[6,15] Thus, these studies afford evidence, albeit indirect, for the accessibility of a competitive interchange solvent displacement pathway for (hep)Cr(CO)$_5$ since they were carried out under conditions for which [L] ≪ [hep], such that the rate law based on Scheme I, paths a and b, exhibited the limiting form

$$k_{obsd} = (k_1k_2/k_{-1}[\text{hep}] + k_3)[\text{L}] \quad (7)$$

(cf. eq 5). Preliminary "mixed solvent" studies (Cr(CO)$_6$/hep/perfluoromethylcyclohexane (MCH$_f$)/hex) permitted the separation of the two terms in eq 7.[7] However, the scope of that study was severely circumscribed by the limited solubility of hep in MCH$_f$.

Another way to study the mechanism of the replacement of hep from its (hep)Cr(CO)$_5$ complex involves the determination of the rates over a wide-enough range of [L]

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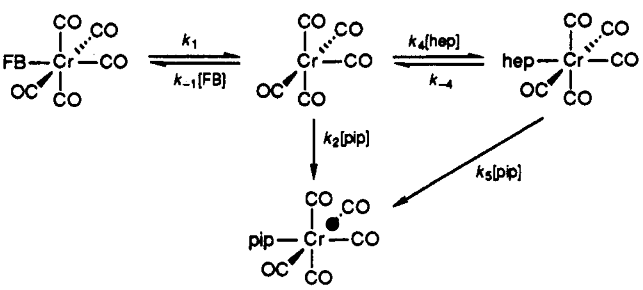
[15] Morse, J.; Parker, G.; Burkey, T. J. *Organometallics* **1989**, *7*, 2471.

Scheme II



so that nonlimiting rate behavior (eq 5) could be observed; such a study has recently been reported for desolvation of (alkane)W(CO)$_5$ complexes (alkane = hep, cyclohexane) employing hex as the trapping nucleophile.[1] However, analogous studies of (hep)Cr(CO)$_5$ employing pip as the trap would require instrumentation unavilable to us, capable of analyzing values of k_{obsd} greater than 10^8 s^{-1}. For the Cr(CO)$_6$/hep/pip system, an alternative method can employ ternary FB/hep/L solutions for which both (hep)Cr(CO)$_5$ and (FB)Cr(CO)$_5$ are produced upon flash photolysis. Since the mechanism for replacement of FB from the (FB)Cr(CO)$_5$ species is known to be dissociative, an accessible interchange pathway for solvent replacement from (hep)Cr(CO)$_5$ will induce changes in k_{obsd}, which can then be evaluated. The applicable mechanism is depicted in Scheme II.

In terms of k_{obsd}, the applicable steady-state rate law ([Cr(CO)$_5$] and (hep)Cr(CO)$_5$ are the steady-state intermediates) is

$$k_{obsd} = \frac{k_1(k_2 + k'_4)[\text{pip}]}{k_{-1}[\text{FB}] + (k_2 + k'_4)[\text{pip}]} \tag{8}$$

where

$$k'_4 = \frac{k_4k_5[\text{hep}]}{k_{-4} + k_5[\text{pip}]} \tag{9}$$

When k_5[pip] $\ll k_{-4}$, likely to be the case at low [pip], eq 9 becomes

$$k'_4 \approx (k_4k_5/k_{-4})[\text{hep}] \tag{10}$$

Where [hep] is held constant, k'_4 also will be constant. Rearrangement of eq 8 thus affords

$$1/k_{obsd} = 1/k_1 + k_{-1}[\text{FB}]/(k_1(k_2 + k'_4)[\text{pip}]) \tag{11}$$

Plots of $1/k_{obsd}$ vs [FB]/[pip] should thus be linear, with intercepts common to those observed in pip/FB solutions but with smaller slopes.

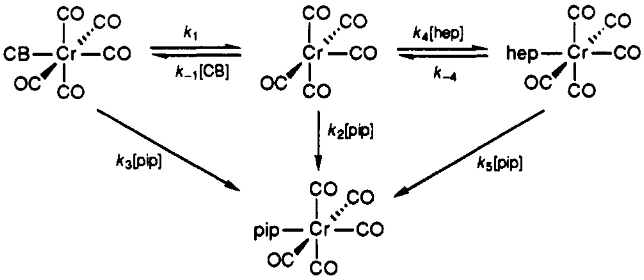
The FB/pip solutions employed in the earlier studies were diluted with hep so that [hep] = 6.57 M, while [FB]/[pip] exhibited their original values; the rates were again determined. Figure 4 shows a plot of relative absorbance vs time for one such solution, which has been analyzed to fit two independent first-order decays. The inset shows a plot of ln $(A_t - A_\infty)$ vs time. The first (short) segment corresponds to the decay of (hep)Cr(CO)$_5$, produced in predominant concentration immediately after the flash. The second (linear) segment monitors the decay of (FB)Cr(CO)$_5$, which takes place after (hep)Cr(CO)$_5$ has largely disappeared (it thus is present in steady-state concentration). Plots of k_{obsd} vs [pip]/[FB] (second decay; eq 8) are curved (concave downward) with positive slopes; plots of $1/k_{obsd}$ vs [FB]/[pip] (eq 11) are linear with positive intercepts. Figure 5 shows plots of $1/k_{obsd}$ vs [FB]/[pip] for data taken at 25.0 °C for both Cr(CO)$_6$/FB/pip and Cr(CO)$_6$/FB/hep/pip solutions; they are linear with differing slopes and a common intercept, as anticipated for the mechanism shown in Scheme II and for eqs 4 and 11. Table II compares the rate data (slopes and intercepts for the reciprocal plots) for Cr(CO)$_6$/FB/pip and Cr(CO)$_6$/FB/hep/pip solutions.

Table II. Slopes and Intercepts of Double-Reciprocal Plots and Values for k'_4/k_2 for Cr(CO)$_6$/FB/pip and Cr(CO)$_6$/FB/hep/pip Reactions[a]

	FB/pip		FB/hep/pip		
T, °C	10^7sl, s	10^7int, s	10^7sl, s	10^7int, s	k'_4/k_2
35.0	1.99 (3)	3.39 (10)	1.38 (4)	3.24 (16)	0.44 (6)
25.0	3.19 (7)	6.19 (25)	2.36 (4)	6.33 (15)	0.35 (5)
15.0	5.19 (6)	10.5 (2)	4.01 (9)	10.9 (3)	0.29 (4)
2.3	10.4 (1)	25.1 (4)	7.49 (14)	26.6 (4)	0.31 (4)

[a] Sl = slope; int = intercept.

Scheme III



Estimates of the ratios of rates via the interchange ($k_i = k_5$) and dissociative ($k_d = k_2k_{-4}/k_4$[hep]) desolvation pathways for the desolvation of (hep)Cr(CO)$_5$ can be obtained (cf. eq 10):

$$k'_4/k_2 = k_4k_5[\text{hep}]/k_2k_{-4} = k_i/k_d \tag{12}$$

The values of k'_4/k_2 (ca. 0.3 near ambient temperature) are also presented in Table II. The data provide strong evidence for the presence of an interchange pathway for the desolvation of (hep)Cr(CO)$_5$ in the presence of pip.

Reactions in CB/hep/pip Solutions: An Alternative Means To Evaluate k_3. The rate constant, k_3, for bimolecular displacement of CB from (CB)Cr(CO)$_5$ by pip was determined under the assumption that the replacement of CB by L takes place exclusively by way of a dissociative mechanism (eq 3). This assumption can be further tested employing an alternative means of evaluation of k_3 (eq 6). The concentrations of pip and CB were varied (up to ca. 0.6 M) so that [hep] was maintained relatively constant (6.5 (2) M), but [CB]/[pip] was maintained at 2.811. Consideration of eqs 5 and 8, modified for the presence of a pathway governed by k_3 (Scheme III), affords

$$k_3 = \frac{k_{obsd} - k'_{obsd} + \alpha}{[\text{pip}] - [\text{pip}']} \tag{13}$$

where k_{obsd} is the pseudo-first-order rate constant for desolvation in pure CB/pip solution (5.08 (12) × 10^4 s^{-1}), k'_{obsd} are the rate constants observed for solutions diluted with hep (supplementary Table II), and

$$\alpha = \{k_1(k_{-1}/k_2)(k_4'/k_2)\}/\{(k_{-1}/k_2 + [\text{pip}]/[\text{CB}]) \times ((k_{-1}/k_2)([\text{CB}]/[\text{pip}]) + k_4'/k_2 + 1)\} \tag{14}$$

In eq 14, k_1 = 5.88 (18) × 10^4 s^{-1} (Table I), k_{-1}/k_2 = 0.42 (6) (Table I),[16] k'_4/k_2 = 0.35 (5) (Table II), and [pip]/[CB] = 0.356. From these values, α is calculated to be 4.4 (17)

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[16] This "competition ratio", k_2/k_{-1}, for CB/pip also can be determined from the values of k_2/k_{-1} for CB/hex (Table I) and for benzene-/pip and benzene/hex (ref 9). This value, 3.2 (8), compares well with that determined experimentally, 2.4 (3), indicative of the internal consistency observed for the mechanistic intrepretation advanced here.

$\times 10^3$ s^{-1}. Substitution of α, k_{obsd}, k'_{obsd}, and [pip]/[CB] into eq 13 afforded a value of 1.09 (4) $\times 10^3$ M^{-1} s^{-1} for k_3. This value is in good agreement with that determined employing eqs 4 and 6 (vide supra), 1.01 (6) $\times 10^4$ M^{-1} s^{-1}.

The internal consistency of all of the data provides strong support for the proposed mechanistic interpretation, which appears to be valid over an extremely wide concentration range (0.05 M < [L] < 5.0 M). This evidently is the case because interactions of PhX and [Cr(CO)$_5$] are strong when compared to "solvation effects", e.g., van der Waals' interactions in the "outer coordination sphere". Thus, the solvents in these homogeneous mixtures are properly viewed as "reactive solvents" rather than as dispersive media.

Energetics and Mechanism. The enthalpies of activation for solvent dissociation from (FB)Cr(CO)$_5$, 9.6 (2) kcal/mol, and (benzene)Cr(CO)$_5$, 9.4 (1) kcal/mol,[9] are very similar, as expected, based on the known mechanistic similarities between the two reactions.[11] Strong evidence has been presented that dissociation of benzene proceeds via a transition state which involves "agostic"[17] interaction between a ring proton and Cr.[9] The near-zero entropies of activation observed for both systems, 2.2 (8) (FB) vs −2.4 (3) (benzene)[9] cal/(deg mol), also support this interpretation for FB dissociation.

In contrast, the enthalpy of activation for CB dissociation from (CB)Cr(CO)$_5$ is significantly larger, 14.0 (4) kcal/mol. The positive entropy of activation for this step, +10.1 (15) cal/(deg mol), is consistent with a dissociative process involving Cl–Cr bond fission with less stabilization of the transition leading to dissociation of CB. These values are similar to the activation parameters observed for the dissociation of tetrachloromethane (TCM) from (TCM)Cr(CO)$_5$: $\Delta H^* = 12.5$ (7) kcal/mol; $\Delta S^* = +7.0$ (24) cal/(deg mol).[12]

The activation parameters for CB dissociation from (CB)Cr(CO)$_5$ in pure CB/hex solutions can be compared to those reported previously for Cr(CO)$_6$ in CB/hexanes/pip solutions,[8] for which ΔH^* is 4.2 (5) kcal/mol less and ΔS^* is 13.0 (19) cal/(deg mol) more negative. From the mechanistic discussion above, it is clear that these differences stem from interchange pathways available for displacement by pip of CB and alkanes from their (solvent)Cr(CO)$_5$ complexes (Scheme III). Comparison of the rate constants, "k_1k_2/k_{-1}", reported as k_{obsd} for Cr(CO)$_6$/CB/pip and Cr(CO)$_6$/CB/hexanes/pip solutions at 24.5 °C, 1.97 (2) $\times 10^5$ and 1.26 (3) $\times 10^5$ s^{-1}, respectively,[8] provides further evidence that pip can displace CB from (CB)Cr(CO)$_5$ via an interchange pathway. The faster rate observed in CB/pip solution is expected since, for a given [CB]/[pip], the contribution to the rate of the interchange pathway will be greater in the absence of hexanes as a result of higher [pip] (eq 5).

It is surprising that linear double-reciprocal plots were observed experimentally in CB/pip/hexanes solutions where two pairs of parallel reaction pathways are accessible.[8] Simple rate behavior evidently can mask great mechanistic complexity, as also was observed for (benzene)Cr(CO)$_5$ in its reaction with pyridine[9] and in this study for reaction of (CB)Cr(CO)$_5$ with piperidine. This mechanistic complexity can account for the significant selectivity observed for solvent displacement in (solvent)Cr(CO)$_5$ complexes. The 25-fold variation in rate observed for hep displacement from (hep)Cr(CO)$_5$[6] may be the result of differing contributions of the dissociative and interchange pathways to the rate as the nucleophilicity and steric bulk of L vary.

Table III. Mechanisms of Solvent Displacement as a Function of the Mode of Bonding in (Solvent)Cr(CO)$_5$ Complexes

		bimolecular displacement obsd for solvent		
solvent	bonding	1-hexene	pip	pyridine
hep	C–H–Cr	yes[a]	yes[b]	yes[c]
CB	Ph–Cl–Cr	no[b]	yes[b]	yes[d]
FB, benzene		no[b,e]	no[b,e]	yes[e]

[a] Reference 7. [b] This work. [c] Reference 6. [d] S. Zhang and G. R. Dobson, preliminary results. [e] Reference 9.

Table IV. Solvent–Cr Bond Strengths Estimated from the Enthalpies of Activation for Solvent Dissociation and from Photoacoustic Calorimetric Data

solvent	act enthalpy, kcal/mol	bond strength, kcal/mol
benzene	9.4 (4)[a]	15.0 (22)[b]
CB	14.0 (4)[c]	19.4 (78)[b]
CCl$_4$	12.5 (7)[d]	19.5 (21)[b]

[a] Reference 9. [b] Reference 19. [c] This work. [d] Reference 12.

Mechanism and the Mode of Coordination of the Solvent to Cr. The contribution of the interchange pathway to the mechanism of desolvation in (solvent)Cr(CO)$_5$ complexes increases FB/benzene < CB < hep (Table III). In these complexes, each solvent is bonded to Cr in a different fashion: hep through a C–H–Cr agostic interaction,[17] Cl by coordination to Cr,[8,11] and FB and benzene side-on through a —C=C— functionality.[9,11] The order observed may reflect the electron-deficient nature of the agostic C–H–Cr bond in (hep)Cr(CO)$_5$ and the steric demands imposed by side-on bonding of benzene and FB in their pentacarbonylchromium solvates.

Kinetics Data and Bond Energies Determined Employing Photoacoustic Calorimetric (PAC) Methods. Studies such as this can afford estimates of Cr–solvent bond strengths. It is observed that combination of a solvent with photogenerated [Cr(CO)$_5$] is extremely rapid,[2,3] suggesting a small activation energy for the process. Consequently, the activation enthalpy for solvent dissociation to form the [Cr(CO)$_5$] intermediate might be expected to approximate the bond dissociation energy for the solvent. Table IV provides comparisons of the enthalpies of activation from kinetic studies with bond strengths obtained from PAC investigations for the solvents benzene, CB, and tetrachloromethane.[18] The data are not in particularly good agreement with the PAC values, which are, on the average, some 5–7 kcal/mol greater. For benzene, agostic bonding inferred in the transition state leading to dissociation might account for the difference. For CB, the mechanistic evidence presented here that reaction of (CB)Cr(CO)$_5$ with 1-hexene is dissociative in nature, together with the positive entropy of activation observed for the process, 10.1 (15) cal/(deg mol), afford some degree of confidence that the enthalpy of activation for CB dissociation, 14.0 (4) kcal/mol, does approach the Cr–CB bond strength; it is within experimental error of the PAC-derived bond strength, considering the large error limits associated with the latter. The dichloromethane data are more equivocal. It is evident, however, that care

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must be taken to ensure that the activation enthalpy attributed to solvent dissociation refers to a true, rather than an apparent, rate constant. Bond strengths determined from time-resolved photoacoustic calorimetry also should be viewed with caution, since they depend upon the experimentally-determined bond strength for CO dissociation from $Cr(CO)_6$ in the gas phase[19] and upon quantum yields for CO dissociation upon photolysis.[15] The latter recently have been found to be sensitive to the identity of weakly-interacting solvents such as perfluoroalkanes.[20]

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Supplementary Material Available: Tables I and II, listing pseudo-first-order rate constants for $Cr(CO)_6$/PhX/L and $Cr(CO)_6$/PhX/hex/pip reactions (5 pages). Ordering information is given on any current masthead page.

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Dimeric and Monomeric Chromium(II) and Monomeric Chromium(III) Aryls. Crystal Structure of Pyramidal $Mz_2Cr(py)$ (Mz = o-$Me_2NCH_2C_6H_4$, py = Pyridine), Dimeric $[(Me_2NC_6H_4)_2Cr]_2$, and Octahedral $(Me_2NC_6H_4)_3Cr$

Jilles J. H. Edema,[†] Sandro Gambarotta,[*,†] Auke Meetsma,[‡] and Anthony L. Spek[§]

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada,
Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands, and Vakgroep Kristal- en Structuurchemie, Rijksuniversiteit Utrecht,
Padualaan 8, 3584 CH Utrecht, The Netherlands

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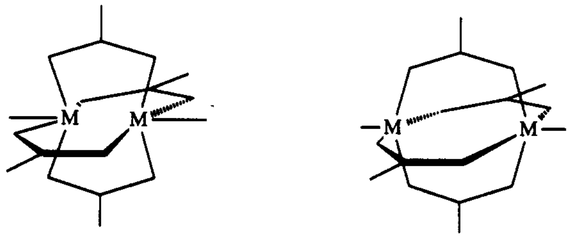
Reaction of $CrCl_2(THF)_2$ with 2 equiv of $[o\text{-}Me_2NCH_2C_6H_4]Li$ and $[o\text{-}Me_2NC_6H_4]Li$ led to formation of the monomeric pyramidal $[o\text{-}Me_2NCH_2C_6H_4]_2Cr$(pyridine) (**2**) and dimeric $[(o\text{-}Me_2NC_6H_4)_2Cr]_2$ (**3**) with a supershort Cr–Cr contact. Both compounds can be thermolyzed in toluene to form the corresponding monomeric Cr(III) $[Me_2NC_6H_4]_3Cr$ (**4**) and $(o\text{-}Me_2NCH_2C_6H_4)_3Cr$ (**5**) derivatives. The structures of **2**–**4** have been clarified by X-ray diffraction analysis. Complex **2**: triclinic, $P1$, $a = 8.766$ (2) Å, $b = 8.825$ (1) Å, $c = 23.582$ (3) Å, $\alpha = 81.41$ (1)°, $\beta = 85.33$ (1)°, $\gamma = 60.31$ (1)°, $V = 1567.0$ (5) Å^3, $Z = 3$, $R = 0.034$ ($R_w = 0.044$), $T = 130$ K for 986 parameters and 6269 significant reflections out of 8191. Complex **3**: monoclinic, $C2/c$, $a = 10.563$ (3) Å, $b = 13.563$ (2) Å, $c = 19.813$ (8) Å, $\beta = 92.92$ (1)°, $V = 2835$ (1) Å^3, $Z = 4$, $R = 0.066$ ($R_w = 0.092$), $T = 130$ K for 261 parameters and 2583 significant reflections out of 3406. Complex **4**: trigonal, $P31c$ $a = b = 12.821$ (1) Å, $c = 7.860$ (1) Å, $V = 1118.9$ (2) Å^3, $Z = 2$, $R = 0.060$ ($R_w = 0.066$), $T = 300$ K for 92 parameters and 573 significant reflections out of 928.

Introduction

The large range of Cr–Cr quadruple bond distances formed by dimeric Cr(II) complexes with three-center chelating ligands (lantern type) and their remarkable response to the coordination of ligands[1] still remains puzzling many years after their discovery.

Chart I



Elegant theoretical work from Hoffmann and Alvarez[2] has recently found a linear correlation between Cr–Cr distances and the α *pyramidality* angle of the $LCrX_4$ fragments which form the dinuclear units of "lantern-type" compounds. In other words, a pyramidal crystal field is expected to expand the lobes of the d_{z^2}, d_{xz}, and d_{yz} orbitals of the chromium atom in the region above the basal plane and therefore to enhance the ability of chromium to form M–M bonds. This sort of *orbital engineering* has recently led to the successful isolation of the first unabridged Cr–Cr multiple bond.[3] What remains unclear is which factors in the "lantern compounds" *pyramidalize* the transition metal and ultimately determine the intermetallic separation by intruding or extruding the metal in the coordination polyhedron (Chart I). Although it is possible that the Cr–Cr multiple bond is responsible for determining the intermetallic distance, it is not likely the primary factor

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[†] University of Ottawa.

[‡] Rijksuniversiteit Groningen.

[§] Rijksuniversiteit Utrecht.

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