Rates of Combination and Selectivity of (*o*-Phenanthroline)tricarbonylchromium(0) with Lewis Bases and their Stereochemical Implications

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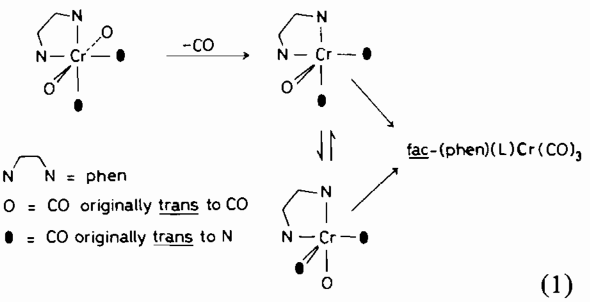
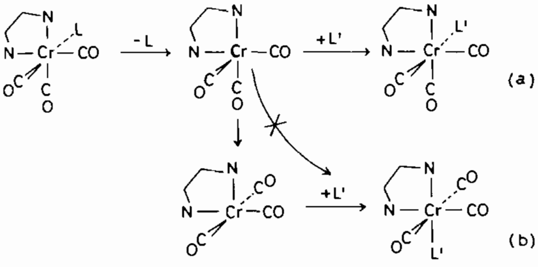
It has been demonstrated that (phen)Cr(CO)$_4$ (phen = *o*-phenanthroline) reacts thermally with 100 per cent stereoselective loss of an axial CO (one *trans* to CO) [2], that the resulting square-pyramidal intermediate, [(phen)Cr(CO)$_3$], is fluxional on the time-scale of ligand substitution [2], and that the products for reactions with Lewis bases (L; phosphines, phosphites, amines, nitriles) are exclusively *fac*-(phen)(L)Cr(CO)$_3$ [3], Scheme 1.



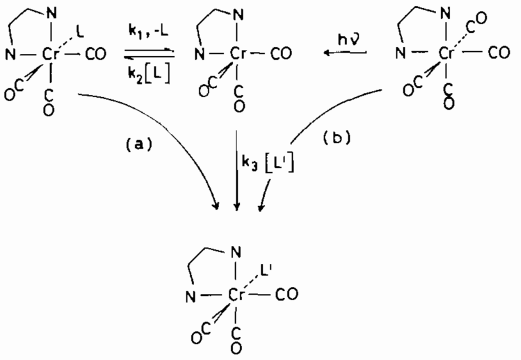
(1)

The origin of this isomeric preference, also observed for ligand exchange in general in these systems (replacement of L by L′; Scheme 2) can be either thermodynamic (greater thermodynamic stability of the *fac* isomer (2a) or kinetic, in which the free energy of activation for the path affording the *fac* isomer is lower than is that affording the *mer* isomer (2b). In this latter context, it has been noted for five-coordinate intermediates which exhibit no selectivity among ligands that exclusive axial CO loss dictates the formation of exclusively the *fac* product, the fluxionality of the five-coordinate intermediate notwithstanding, on the basis of the principle of microscopic reversibility [4] ('quasi-microscopic reversibility') [5].



(2)

Few data which address the selectivity question for octahedral metal carbonyl systems are available [6–8], and, given the exclusive axial CO loss and exclusively *fac* reaction products observed through ligand exchange in (phen)Cr(CO)$_4$, the system is an ideal one through which to investigate it. Herein are reported selectivity data for interaction of [(phen)Cr(CO)$_3$] with various L as determined *via* two independent methods (Scheme 3), which support the kinetic origin of the stereochemical preference exhibited in *fac*-(phen)(L)Cr(CO)$_3$ species.



(3)

Experimental

As indicated in Scheme 3, selectivity of the [(phen)Cr(CO)$_3$] intermediate among various L was determined through ligand competition studies (path 3a) and through investigations of the rates of combination of the intermediate after its production *via* pulsed laser flash photolysis (path 3b).

Rates of formation of *fac*-(phen)(L′)Cr(CO)$_3$ through reaction of *fac*-(phen)(L)Cr(CO)$_3$ prepared through standard procedures [3], with L′ (L = P(OPh)$_3$; L′ = PBu^n_3) were monitored in 1,2-dichloroethane (DCE) at 680 nm. Kinetic control of the reactions was insured since the product is not reactive under the kinetics conditions employed. The [(phen)Cr(CO)$_3$] intermediate was also generated photochemically from (phen)Cr(CO)$_4$ employing a pulsed laser (337 nm, 9 ns FWHI, 3 mJ pulse energy), also in DCE. Rates of combination of the intermediate with L′, (= $P(OPr^i)_3$, P(OEt)$_3$) were monitored at 550 nm.

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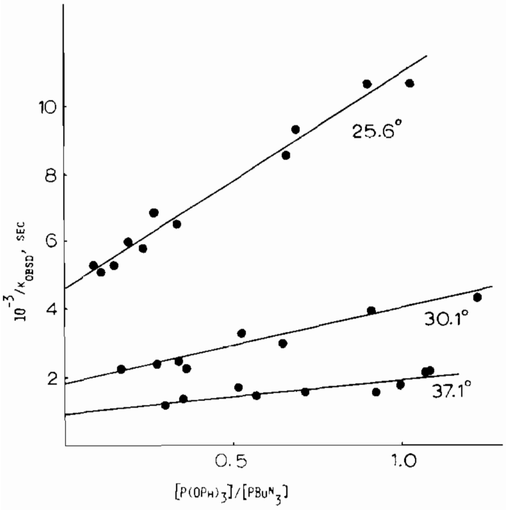

Fig. 1. Plots of $1/k_{obsd}$ *vs.* $[P(OPh)_3]/[PBu^n_3]$ for reaction of *fac*-(phen)$[P(OPh)_3]Cr(CO)_3$ in the presence of both ligands in 1,2-dichloroethane at various temperatures.

Results and Discussion

'Competition ratios', k_2/k_3, Scheme 3, were determined through measurement of the rates of ligand exchange for L = $P(OPh)_3$ and L' = PBu^n_3, assuming a steady-state concentration of $[(phen)Cr(CO)_3]$ and employing large excesses of L and L'. Under these conditions, a pseudo first-order rate law is obtained, for which the pseudo first-order rate constants, k_{obsd}*, obey the relationship,

$$1/k_{obsd} = 1/k_1 + k_2[L]/k_1k_3[L'] \qquad (4)$$

The ratios k_2/k_3 can then be extracted as slope/intercept of plots of $1/k_{obsd}$ *vs.* [L]/[L']. These plots are exhibited in Fig. 1, for data at three temperatures. The competition ratios at each temperature are 1, within experimental error. The entropy of activation for dissociation of $P(OPh)_3$ from the substrate, extracted fron the intercepts of the plots is positive, consistent with an expected dissociative process (governed by k_1).

Figure 2 illustrates a plot of k_3* *vs.* [L'] for combination of L' (= $P(OPr^i)_3$ and $P(OEt)_3$) with $[(phen)Cr(CO)_3]$, generated *via* pulsed laser flash photolysis. These data also provide a competition ratio of 1, the ratio of the rate constants for each L', consistent with the competition data.

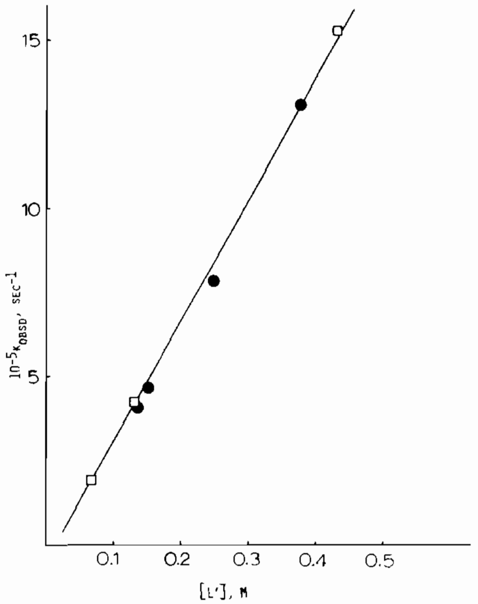

Fig. 2. Plots of k_{obsd} *vs.* [L'] for combination of $[(phen)Cr(CO)_3]$, produced *via* pulsed laser flash photolysis with □ L' = $P(OEt)_3$; ● L' = $P(OPr^i)_3$ in 1,2-dichloroethane at 17 °C.

These ratios for four different L and two methods of determination, aside from indicating that the $[(phen)Cr(CO)_3]$ intermediates produced thermally and photochemically are one and the same, also show the intermediate to be non-selective among incoming nucleophiles, and thus, according to the principle of 'quasi microscopic reversibility' [5], the site of initial Cr–CO or Cr–L bond fission (axial) dictates the ultimate product stereochemistry, the fluxionality of the five-coordinate intermediate notwithstanding.

It has been noted that the *fac*-(phen)(L)$Cr(CO)_3$ complexes such as are produced in this ligand exchange process differ significantly in their ground state energies [9]. In general, it is also noted that values of k_3 (L' = $P(OEt)_3$, k_3 = 3.1(2) × 10^6 M^{-1} sec^{-1}; L' = $P(OPr^i)_3$, k_3 = 3.2(1) × 10^6 M^{-1} sec^{-1}) are significantly smaller than are rates of combination determined in hydrocarbon solvent [8, 10]; thus it is reasonable to presume that a significant portion of the free energy of activation for the combination discussed here (4.5 kcal/mol) results from displacement of DCE from the solvated intermediate by L'; a significant solvent influence on the rates of other such associative processes has been demonstrated [11]. These observations, together with the observed non-selectivity of the intermediate between the L' thus suggest that the intermediate closely resembles the transition state for ligand exchange [12], and thus that the observed energies of activa-

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*Individual values of k_{obsd} and k_3 are available from the author.

tion for the dissociation of L in these complexes [9] very closely approximate the Cr–L bond strengths.

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References

1 Octahedral Metal Carbonyls. Part 53. Part 52: G. R. Dobson and K. J. Asali, *Inorg. Chem., 20,* 3563 (1981).
2 G. R. Dobson and K. J. Asali, *Inorg. Chem., 20,* 3563 (1981).
3 L. W. Houk and G. R. Dobson, *Inorg. Chem., 5,* 2119 (1966).
4 T. L. Brown, *Inorg. Chem., 7,* 2763 (1968).
5 G. R. Dobson, *Inorg. Chem., 19,* 1413 (1980).
6 W. D. Covey and T. L. Brown, *Inorg. Chem., 12,* 2820 (1973).
7 C. L. Hyde and D. J. Darensbourg, *Inorg. Chem., 12,* 1286 (1973).
8 J. M. Kelly, D. V. Bent, H. Hermann, D. Schulte-Frohlinde and E. A. Koerner von Gustorf, *J. Organometal. Chem., 69,* 259 (1974).
9 G. R. Dobson and L. A. H. Smith, *Inorg. Chem., 9,* 1001 (1970).
10 G. R. Dobson and J.-C. Rousche, *J. Organometal. Chem., 179,* C42 (1979).
11 G. R. Dobson and S. Mansour, unpublished results.
12 G. S. Hammond, *J. Am. Chem. Soc., 77,* 334 (1955).