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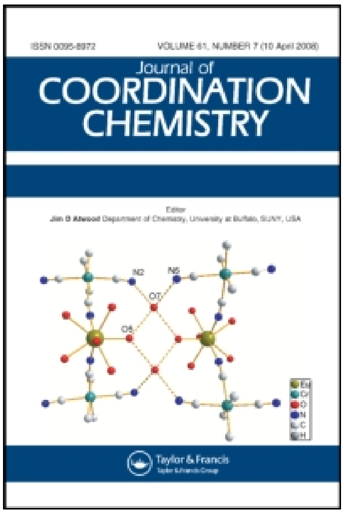

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OCTAHEDRAL METAL CARBONYLS. 55. MECHANISM OF LIGAND-EXCHANGE IN (2, 2'-BIS(PYRIDYL)METHANE)-TETRACARBONYLCHROMIUM(0)

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OCTAHEDRAL METAL CARBONYLS. 55.† MECHANISM OF LIGAND-EXCHANGE IN (2, 2′-BIS(PYRIDYL)METHANE)-TETRACARBONYLCHROMIUM(0)

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(Bpm)Cr(CO)$_4$ (bpm = 2,2′-bis(pyridyl)methane) has been synthesized, and the kinetics and mechanism of the displacement of bpm by tri(isopropyl)phosphite and tri(*n*-butyl)phosphine in 1,2-dichloroethane at various temperatures has been investigated. The data support competitive unimolecular ring-opening and concerted ring-opening *via* interaction of the substrate with the ligand. Unexpectedly small values for the respective rate constants are attributed to residual ring-rigidity in the substrate. Data are compared to other systems containing bidentate chelating ligands coordinating through nitrogen.

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INTRODUCTION

There have been a number of studies of ligand-exchange in (chelate)tetracarbonyl metal complexes in which the chelating ligand coordinates through nitrogen.[2–8] In these investigations, rate and mechanism have been studied as a function of the coordinating properties of the donor atom, ring size and rigidity, the steric properties of the chelating ligand and the identity of the metal atom (M = Cr, Mo or W). These investigations have demonstrated that a wide variety of ligand-exchange mechanisms are accessible (Fig. 1). In systems in which the the chelating ring possesses some degree of rigidity, such as in (*o*-phen)M(CO)$_4$[3] (*o*-phen = *o*-phenanthroline) and (dipy)M(CO)$_4$[2,6,7] (dipy = 2,2′-dipyridyl), the chelating ligand is retained, in most instances. There is some evidence, however, that the chelate ring does open during loss of CO in (dipy)M(CO)$_4$.[6,7] In species in which ring-rigidity is not a factor, however, loss of the chelating ligand is the predominant reaction pathway, as, for example, in (tmen)M(CO)$_4$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) complexes.[4,8]

In non-rigid rings bonding through nitrogen, the effect of chelate ring-size on rate and mechanism of ligand-exchange has also been investigated,[5,8] employing (tmpa)M(CO)$_4$ substrates (tmpa = *N,N,N′,N′*-tetramethyl-1,3-diaminopropane). In comparisons of tmen and tmpa complexes, the rates of chelate ring-displacement are several orders of magnitude faster for the six-membered rings than for their five-membered ring counterparts.

In order to explore further the influences of ring-size and rigidity on rates and mechanisms in such systems, the complex (bpm)Cr(CO)$_4$ has been synthesized, and the kinetics and mechanism of its ligand-exchange reactions with tri(isopropyl)phosphite and tri(*n*-butyl)phosphine (*L*) has been investigated.

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† Part 54 is reference 1.

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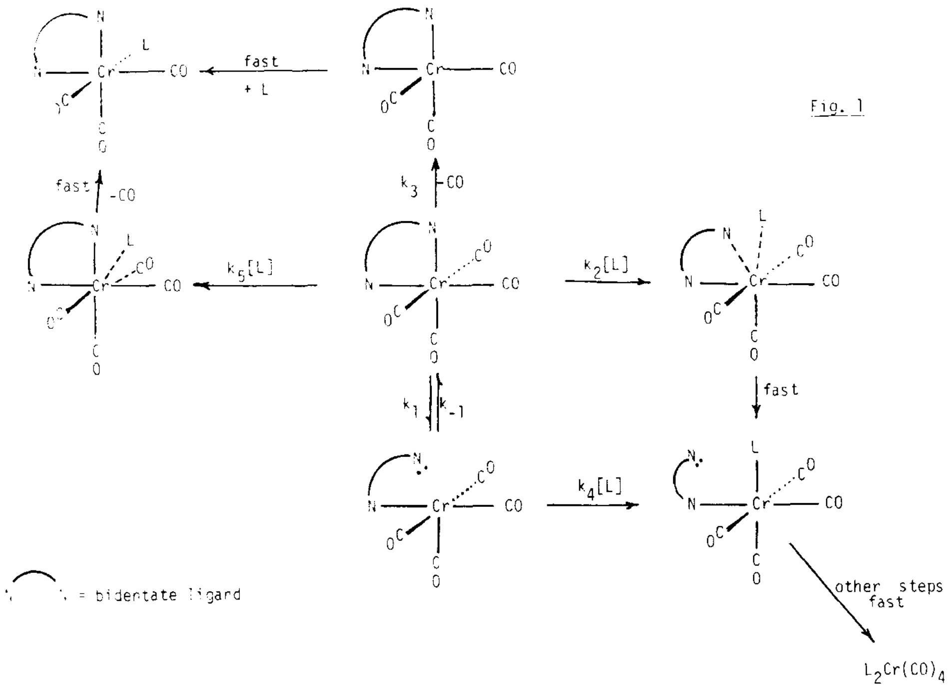

FIGURE 1 Mechanisms for reactions of octahedral metal carbonyl complexes containing chelating ring coordinating through nitrogen.

EXPERIMENTAL

General

Infrared spectra were recorded employing a Perkin Elmer Model 621 grating spectrophotometer. Chemical analyses were performed by Midwest Microlab, Ltd., Indianapolis, IN.

Preparative

2,2′-bis(pyridyl)methane (bpm) was synthesized employing the method of Leete and Marion.[9] It was stored as the bis(pyridinium) salt, from which it was liberated through dissolution in an aqueous solution of K_2CO_3, extraction with $CHCl_3$, and distillation *in vacuo* (0.7 kPa).

(2,2′-(bis(pyridyl)methane)tetracarbonylchromium(0)

1.0 g of bpm (5.9 mmol) and 1.3 g of $Cr(CO)_6$ (Pressure Chemical Co.; 5.9 mmol) were heated at reflux in xylene (20 cm^3) under nitrogen bubbling (through a frit at the bottom of the reaction vessel[10]) for three hr. A green-yellow powder (0.4 g) was separated by suction-filtration and was recrystallized from toluene-hexane to afford bright yellow crystals. *Anal.* Calc'd for $C_{15}H_{10}CrN_2O_4$: C, 53.90; H, 3.12; N, 8.38%. Found: C, 53.68; H, 3.12; N, 8.27%. Carbonyl stretching spectrum (1,2-dichloroethane (DCE)) solution: 2010(m), 1888(vs), 1878(vs), 1833(s) cm^{-1}.

Rate Studies

Kinetics runs were carried out in purified DCE (fractionally distilled from P_2O_5 under nitrogen). Tri(isopropyl)phosphite and tri(*n*-butyl)phosphine were fractionally distilled *in vacuo.* Samples of (bpm)$Cr(CO)_4$ (*ca* 25 mg/50 cm^3) in purified solvent containing a weighed amount of ligand under nitrogen were allowed to come to temperature in a thermostatted bath. Pseudo-first-order reaction conditions were maintained through use of at least a twenty-fold excess of ligand over substrate. Reaction samples were removed *via* a syringe through a rubber septum which sealed the reaction flask and were monitored at 425 nm (an absorbance of the substrate) on a Beckman DU-2 spectrophotometer. At the wavelength monitored, the reaction products did not absorb significantly; plots of $\ln(A_t - A_{bl})$ vs. time (A_t and A_{bl} are the absorbances at time t and of a ligand-solvent blank, respectively) were linear for at least two half-lives. Data were analyzed employing a linear least-squares computer program (Hewlett-Packard Model 2000 Computer). Limits of error for all kinetic data, presented in parentheses, are deviations of the last digit(s) of the given value at the 90 per cent confidence limit. Data for individual kinetic runs are available from the authors on request.

RESULTS AND DISCUSSION

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It is of interest to note that (bpm)$Cr(CO)_4$ is yellow, as is *cis*-(pyridine)-$Cr(CO)_4$[11] and is not solvatochromic or as highly colored as are (phen)$Cr(CO)_4$ and (dipy)$Cr(CO)_4$. Thus it may be concluded that there is no delocalization of charge as a result of the intervening methylene group in bpm, in contrast to the observation for dipy and phen compounds.[12]

An analysis of the carbonyl stretching spectra for reactions of (bpm)$Cr(CO)_4$ with PBu^n_3 and $P(OPr^i)_3$ in DCE indicates that the predominant reaction pathway involves displacement of the bidentate ligand. In the case of $P(OPr^i)_3$, the displacement leads to the formation of the *cis*-$L_2Cr(CO)_4$ product, while for PBu^n_3, *trans*-$L_2Cr(CO)_4$ is the predominant product. While it cannot be determined unequivocally, it appears most likely that there is no CO loss which accompanies formation of the predominant product. Nonetheless, for L = $P(OPr^i)_3$, the *fac*-$L_3Cr(CO)_3$ product is formed over long reaction times; changes in the IR spectra accompanying the reaction indicate the slow conversion of *cis*-$L_2Cr(CO)_4$ to *cis*-$L_3Cr(CO)_3$ over many half-lives of the displacement of bpm. The presence of some *mer*-$L_3Cr(CO)_3$ for L-PBu^n_3 at long reaction times is also noted.

It is reasonable that *trans*-$L_2Cr(CO)_4$ be the ultimate product of displacement of PBu^n_3; for this ligand, the *trans*-$L_2Mo(CO)_4$ product is thermodynamically the more stable,[13] and, given the smaller atomic size of Cr than Mo, an even greater thermodynamic stability of the *trans* than *cis* isomer is reasonable in $L_2Cr(CO)_4$ complexes.

The rate data for both L are consistent with the rate law,

$$-d[(bpm)Cr(CO)_4]/dt = k_1[(bpm)Cr(CO)_4] + k_2[(bpm)Cr(CO)_4][L].$$

Plots of k_{obsd} *vs* $[P(OPr^i)_3]$ are illustrated in Fig. 2. Activation parameters, given together with the first- and second-order rate constants in Table 1, are consistent with competing dissociative and associative pathways. Activation parameters for the first-order processes are, within experimental error, the same for both L, as would be anticipated.

It is most reasonable to attribute the observed rate law to the mechanism exhibited in Fig. 3, in which the two proposed competing processes are those which have been observed in many other metal carbonyl ligand-exchange processes, including, for example, those for the hexacarbonyls themselves.[14]

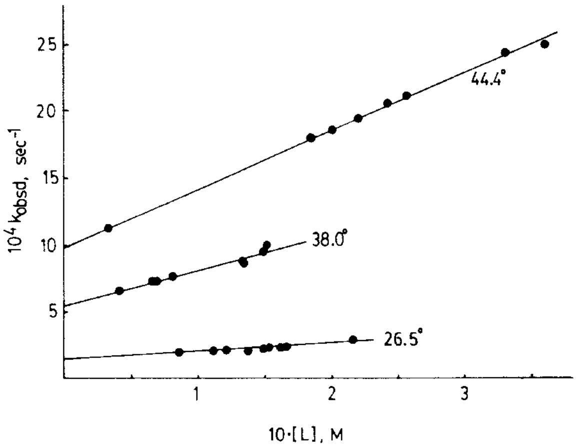

FIGURE 2 Plots of k_{obsd} *vs* [L] for reaction of (bpm)Cr(CO)$_4$ with tri(isopropyl)phosphite in 1,2-dichloroethane at various temperatures.

TABLE I
Rate constants and activation parameters^a for reactions of (Bpm)Cr(CO)$_4$ with P(OPr^i)$_3$ and P(Bu^n)$_3$ in 1,2-dichloroethane

	T°C	$10^4 k_1$ sec^{-1}	$10^4 k_2$ M^{-1}sec^{-1}
L = P(OPr^i)$_3$	26.5	1.19 (14)	7.36 (91)
	38.0	3.38 (20)	28.0 (18)
	44.4	9.56 (28)	44.2 (11)
L = P(Bu^n)$_3$	16.5	0.262 (57)	4.18 (48)
	32.5	1.26 (7)	14.5 (10)
	42.5	8.62 (35)	20.7 (43)

^{a}For P(OPr^i)$_3$, $\Delta H_1^{\ddagger}$ = 93.3 (25) kJ mol^{-1} ; $\Delta S_1^{\ddagger}$ = −15 (15) J K^{-1} mol^{-1} ; $\Delta H_2^{\ddagger}$ = 77.8 (54) kJ mol^{-1} ; $\Delta S^{\ddagger}$ = −59 (18) J K^{-1} mol^{-1}. For P(Bu^n)$_3$, $\Delta H_1^{\ddagger}$ = 96 (15) kJ mol^{-1} ; $\Delta S_1^{\ddagger}$ = 5 (44) J K^{-1} mol^{-1} ; $\Delta H_2^{\ddagger}$ = 48.1 (21) kJ mol^{-1} kcal/mole; $\Delta S^{\ddagger}$ = −151 (17) J K^{-1} mol^{-1}

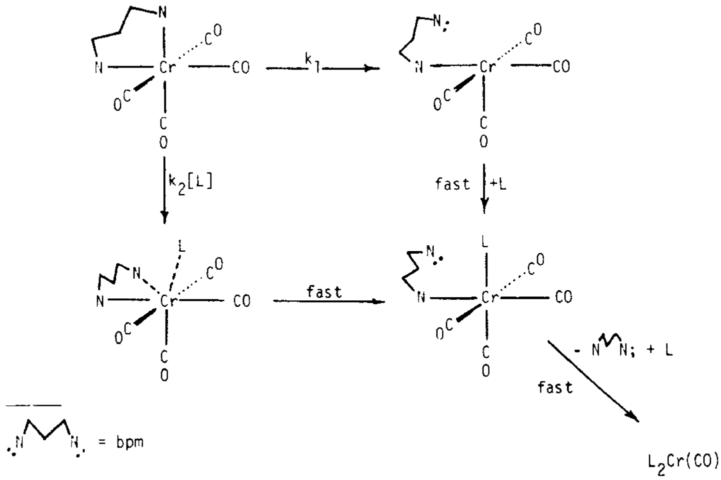

FIGURE 3 Proposed mechanism for reaction of (bpm)Cr(CO)$_4$ with Lewis bases.

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The contrast in mechanism in (bpm)Cr$(CO)_4$ to that for the related (dipy)Cr$(CO)_4$[2] which proceeds largely *via* the path governed by k_3 (Fig. 1), underscores the dramatic effect on mechanism of the presence of a six-membered rather than five-membered chelate ring. In the latter systems, ring displacement is not observed, although evidence for a ring-opening path leading to expulsion of CO in this system has been detailed.[6]

Another significant observation, however, is that the rates of reaction in (bpm)Cr$(CO)_4$ and (dipy)Cr$(CO)_4$ are not greatly different; they may be estimated to be less than one order of magnitude faster in the bpm complex. By contrast, rates of reaction for (tmpa)M$(CO)_4$ with L *vs* those for (tmen)M$(CO)_4$ (M = Cr, W)[4,5,8] are some three or more orders of magnitude faster. These differences cannot, at least for W results,[8] be attributed to a drastic decrease in the k_4/k_{-1} ratio (Fig. 1) in the six-membered ring system, but are attributable instead to a much greater ease of W-N bond-breaking for the six-membered ring system. The lack of such a pronounced effect in the systems under consideration here seems likely to be the result of some residual ring-rigidity in the bpm complex such that there is an inhibition of M-N motion coincident with the bond axis.[15]

The results of this study underscore the sensitive relationships between the unimolecular ring-opening, concerted ring-opening and unimolecular and concerted carbonyl dissociation processes which are noted in these systems. The kinetics of such systems thus offer a fruitful field through which to investigate such subtle effects.

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