

## Ligand Substitution at Five-Coordinate Centers. Reactions of Phosphine and Phosphite Adducts of the Bis(trifluoromethyl)-1,2-dithiolene Iron and Cobalt Systems

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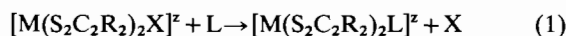
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The kinetics of ligand substitution on the five-coordinate 1,2-dithiolene complexes  $[M(S_2C_2(CF_3)_2)_2X]^z$  ( $M = Fe, Co$ ;  $X =$  a phosphine or phosphite;  $z = 0, -1$ ) are reported. The mechanism is associative for  $z = 0$  and dissociative for  $z = -1$ .

### Introduction

We have reported<sup>1-4</sup> kinetic studies of ligand substitution for a number of five-coordinate square pyramidal iron and cobalt dithiolene systems, reaction (1) ( $M = Fe, Co$ ;  $R = CN, C_6H_5$ ;  $X, L \equiv$  phosphine or phosphite)



With  $R = CN, z = -1$ , the mechanism of reaction (1) consists of both associative and dissociative pathways while with  $R = C_6H_5, z = 0$ , the mechanism is associative with at most a very small dissociative contribution. For our final study of dithiolene systems, which we present herein, we chose  $R = CF_3$  because complexes having both  $z = 0$  and  $-1$  can be conveniently synthesized and studied. We show below that reaction (1) is associative when  $z = 0$  and dissociative when  $z = -1$ , thus demonstrating the role the oxidation state can assume in substitution reactions at five-coordinate centers.

### Experimental

The complexes  $[M(S_2C_2(CF_3)_2)_2]$  and  $[Et_4N][M(S_2C_2(CF_3)_2)_2]$  ( $M = Co, Fe$ ) were synthesized by standard methods<sup>5</sup> and gave excellent C,H,N analyses. Nucleophiles were purchased from commercial sources and checked for purity. The five coordinate complexes,  $[M(S_2C_2(CF_3)_2)_2PR_3]^z$  were prepared *in situ*, the spectra agreeing with published<sup>6</sup> results. The solvents used for rate measurements ( $C_6H_6, CH_2Cl_2$ ) were distilled prior to use. Kinetic results were obtained with a Durrum stopped-flow apparatus operating at  $25 \pm 0.2^\circ C$ . Total metal complex concentration was  $10^{-4}$ – $10^{-5} M$  with the nucleophile in at least a ten-fold excess to provide pseudo-first order conditions.

### Results

Reaction (2) was studied in benzene and gave second order kinetics for all combinations of  $R, R'$  used:

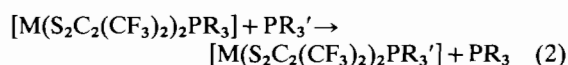


Table I gives the results. The addition of excess leaving group ( $PR_3$ ) was found to have no effect on the kinetics.

TABLE I. Rate Data for Reaction (2) in Benzene at  $25^\circ C$ .

Metal	Leaving Group	Nucleophile	Range of [Nucleophile], $M$	$10^{-4}k/M^{-1}s^{-1}$
Co	$PPh_3$	$P(p\text{-tolyl})_3$	$1-8 \times 10^{-3}$	3.0
Co	$P(p\text{-tolyl})_3$	$P(OBu)_3$	$1-10 \times 10^{-4}$	5.2
Co	$P(OPh)_3$	$PPh_3$	$0.5-6 \times 10^{-3}$	1.7
Co	$P(OPh)_3$	$P(p\text{-tolyl})_3$	$0.5-2 \times 10^{-3}$	15
Fe	$P(p\text{-tolyl})_3$	$P(OBu)_3$	$1-5 \times 10^{-4}$	31
Fe	$P(OPh)_3$	$PPh_3$	$1-6 \times 10^{-3}$	2.5
Fe	$P(OPh)_3$	$P(p\text{-tolyl})_3$	$0.25-2 \times 10^{-3}$	18

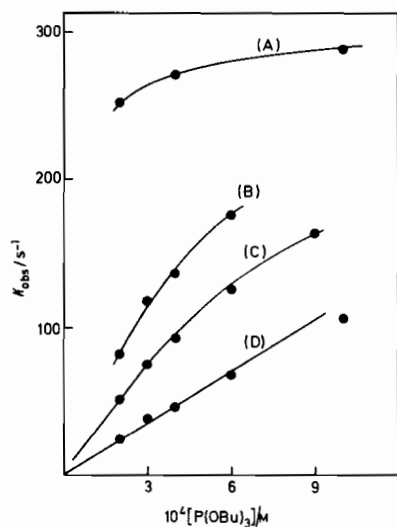
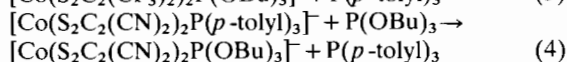
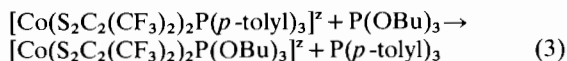


Figure 1. Kinetic results for the reaction of  $P(OBu)_3$  with  $[Co(S_2C_2(CF_3)_2)_2P(p\text{-tolyl})_3]^-$  in dichloromethane at  $25^\circ C$ . Excess  $P(p\text{-tolyl})_3$  concentrations are (A) 0; (B)  $0.54 \times 10^{-3} M$ ; (C)  $1.0 \times 10^{-3} M$ ; (D)  $2.0 \times 10^{-3} M$ .

In addition to these, three reactions were studied in  $CH_2Cl_2$  with tri-*n*-butylphosphite as the nucleophile, reactions (3) and (4).



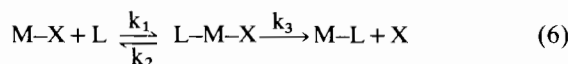
Reaction (3) with  $z = 0$  is second order, having  $k = 1.4 \times 10^4 M^{-1} s^{-1}$ . Excess  $P(p\text{-tolyl})_3$ , up to  $2 \times 10^{-3} M$ , does not affect the rate. The results with  $z = -1$  are very different and are shown in Figure 1. For reaction (4) the observed rate constant is given in equation (5);

$$k_{obs}(s^{-1}) = 2.0 + 1.0 \times 10^4 [P(OBu)_3] \quad (5)$$

excess  $P(p\text{-tolyl})_3$  ( $10^{-3} M$ ) causes a slight lowering of the rate that is clearly discernible only at low nucleophile concentrations.

## Discussion

The kinetic data for reaction (2) are consistent with a simple associative mechanism:



$$k_{obs} = \frac{k_1 k_3 [L]}{k_2 + k_3} \quad (7)$$

That excess leaving group (X) has no effect on the rate shows that competition for an intermediate is not

occurring. These results are completely analogous to those reported by us<sup>3</sup> previously for the  $R = C_6H_5$  series (reaction (1)), except that the  $R = CF_3$  reactions are much more rapid. Some of the  $R = C_6H_5$  reactions with the weaker nucleophiles had small nonzero intercepts in the  $k_{obs}$  vs.  $[L]$  plots and we take this as evidence for the existence of a dissociative pathway that makes a small contribution to the overall rate. Such nonzero intercepts are not observed for any of the reactions of the  $R = CF_3$  complexes with  $z = 0$  (reaction (2)). This is to be expected since the more electron withdrawing  $CF_3$  group should lead to greater adduct stability and hence a slower rate of reaction by a dissociative pathway. On the other hand, the associative pathway should be enhanced since the  $CF_3$  groups render the metal more positive and hence more susceptible to nucleophilic attack, than in the analogous  $C_6H_5$  complexes.

Reaction (3) with  $z = 0$  is consistent with scheme (6), but the reduced complex,  $z = -1$ , clearly follows a different mechanism (Figure 1), and the results are in quantitative agreement with a dissociative scheme:<sup>4</sup>



$$k_{obs} = \frac{k_4 k_6 [L]}{k_5 [X] + k_6 [L]} \quad (10)$$

Thus plots of  $1/k_{obs}$  vs.  $1/[L]$  for fixed  $[X]$ , i.e.  $[P(p\text{-tolyl})_3]$ , are linear with the same intercept within error. The intercept,  $1/k_4$ , yields  $k_4 = 300 \pm 100 s^{-1}$ , in agreement with the directly observed limit (Figure 1). Over the initial linear portion of the plots of  $k_{obs}$  vs.  $[L]$ , we find that  $k_{obs} \propto 1/[X]$  as required by eqn. (10). Thus there seems to be an abrupt change in mechanism of ligand substitution upon a one-electron reduction of the neutral complex. The reduced complex contains sufficient additional electron density on the metal to weaken the  $M-X$  bond and thereby promote the dissociation of  $X$  while inhibiting the direct attack of  $L$  on  $M-X$ . The result is a change to a dissociative mechanism.

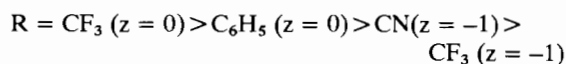
Replacement of the  $CF_3$  in reaction (3) ( $z = -1$ ) by the more electron-withdrawing  $CN$  group should enhance an associative mechanism and hinder a dissociative one. In agreement with this reaction (4) seems to occur by both pathways:

$$k_{obs} = \frac{k_1 k_3 [L]}{k_2 + k_3} + \frac{k_4 k_6 [L]}{k_5 [X] + k_6 [L]} \quad (11)$$

We interpret the intercept (eqn. (5)) as  $k_4$ , since under the experimental conditions used (no excess X) we expect  $k_6 [L] \gg k_5 [X]$ . The first term in eqn. (11) (associative pathway) clearly dominates, for excess leaving group (X) only has a small effect on  $k_{obs}$  and

that at the lowest nucleophile concentration used, while at high values of [L] there is almost no effect. Therefore the change from  $\text{CF}_3$  to CN changes  $k_4$  from  $300 \text{ s}^{-1}$  to  $2.0 \text{ s}^{-1}$  and this reduction is sufficient to allow the associative pathway to dominate in the CN case.

Considering electron withdrawing abilities and published redox potentials<sup>6</sup> we expect the stability of the phosphine or phosphite adducts,  $[\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2\text{X}]^z$ , to follow the order:



This should also be the order of decreasing positive charge on the metal. The mechanisms of reaction (1) for these complexes range from purely associative ( $\text{CF}_3$ ,  $z = 0$ ) to mostly associative ( $\text{C}_6\text{H}_5$ ,  $z = 0$ ) to mixed associative/dissociative (CN,  $z = -1$ ) to purely dissociative ( $\text{CF}_3$ ,  $z = -1$ ). These results nicely agree with the expected decrease in M-X bond strength along the series.

There have not been many kinetic studies of five-coordinate systems. Most studies reported have involves 18 electron diamagnetic systems and dissociative mechanisms have usually been found. We believe<sup>7</sup> that ligand substitution at five-coordinate 18 electron centers will always be dissociative, as implied by empirical

rules presented by Tolman<sup>8</sup>. When less than 18 electrons surround the metal we expect to find associative pathways permitted as well as dissociative ones. The dithiolene systems reported herein are formally 14 to 16 electron complexes and nicely illustrate the suggestions above.

#### Acknowledgment

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