Inorganica Chimica Acta, 8 (1974) 317–321

Mechanism of Ligand Substitution on Five-Coordinate Iron and Cobalt Dithiolene Complexes

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Received June 25, 1973

The kinetics of the substitution reactions of five-coordinate iron and cobalt 1,2-dithiolene complexes $M(S_2C_2(CN)_2)_2X^-$ *(X = a phosphine or phosphite) are reported. The X group is replaced by monodentate and bidentate nucleophiles by a process consisting of both associative and dissociative pathways with the associative pathway predominating. It is shown that a purely dissociative process is definitely excluded. The iron complexes react about ten times faster than the analogous cobalt complexes. The kinetics of the replacement of bidentate groups L–L from* $Fe(S_2C_2(CN)_2)_2(L\text{–}L)^-$ *by* $P(n\text{-}Bu)_3$ *to yield* $Fe(S_2C_2(CN)_2)_2P(n\text{-}Bu)_3^-$ *are also reported. The L–L groups are bipyridine, o-phenanthroline, 1,2-bis(diphenylphosphino)ethane, and cis-1,2-bis(diphenylphosphino)ethylene. These reactions proceed by a dissociative process and are orders of magnitude faster than the corresponding cobalt reactions.*

Introduction

Little is known concerning the mechanism(s) of ligand substitution at five-coordinate centres. The few studies that have been reported are insufficient to permit generalities.

Zumdahl *et al.*[1] suggested a dissociative mechanism for ligand exchange in Co(2,6-lutidine N-oxide)$_5^{2+}$. Likewise Muetterties[2] reported S_N1 ligand exchange in cobalt(I) isonitrile complexes. A dissociative pathway was also found by Tobe *et al.*[3] for substitution of the X group in M(QAS)X$^+$ (M = Pt, Pd; QAS = tris(*o*-dimethylarsinophenyl)-arsine). Studies of five-coordinate organometallic systems[4] suggest mostly S_N1 pathways although Basolo *et al.*[5] report that a S_N2 contribution is important in the CO substitution reactions of $Mn(NO)(CO)_4$.

We[6] recently reported the study of a five-coordinate low spin nickel(II) complex that substitutes strictly *via* a dissociative pathway. However, our belief has been that many substitution reactions proceeding *via* associative pathways will become evident as more studies are made. In particular we expect associative pathways to appear whenever the formation of the required six-coordinate intermediate does not necessitate a spin change. Thus we expect, for example, square pyramidal d^8 complexes to react S_N1 when low spin and both S_N1 and S_N2 when high spin. The S_N2 contribution is expected in spite of the fact that these are 18 electron systems. The $Mn(NO)(CO)_4$ system mentioned above would appear to be an exception to this, but it is usually considered that an electron pair becomes localized on the NO group in the transition state so the metal is effectively d^6.

The curious behavior of transition metal 1,2-dithiolene complexes has generated considerable interest.[7] A few years ago we reported[8] the kinetics of reaction (1) where L–L was one of several bidentate nucleophiles.

$$Co(S_2C_2(CN)_2)_2PPh_3^- + L\text{–}L \rightarrow Co(S_2C_2(CN)_2)_2(L\text{–}L)^{z-} + PPh_3 \quad (1)$$

The 1,2-dithiolene ligand in reaction (1) is maleonitriledithiolate (mnt). At the time we suggested that substitution at this five-coordinate center proceeded *via* both dissociative and associative pathways. We have completed extensive studies of the $M(mnt)_2X^-$ system where M is iron or cobalt and X is either a monodentate or bidentate ligand. This paper reports the results of these studies and will show that a S_N2 pathway is very prominent in these reactions when X is monodentate. Studies of the substitution reactions of other five-coordinate 1,2-dithiolene complexes $M(S_2C_2R_2)_2PR_3^{z-}$ (M = Fe, Co; R = Ph, CF_3) are now in progress in this laboratory. Initial results[9] with the R = Ph, z = 0 system suggest that the replacement of PR_3 with other monodentate ligands is predominently or exclusively associative in character. These studies will be published in the near future.

Experimental

The complexes $Et_4NFe(mnt)_2$ and $Et_4NCo(mnt)_2$ (mnt = maleonitriledithiolate) were prepared by standard methods. All of the nucleophiles were purchased from commerical sources and checked for purity. The five and six-coordinate adducts, $M(mnt)_2X^-$, were prepared *in situ*. The kinetics were followed in purified methanol[10] on a Durrum stopped-flow apparatus at 25° C. The ionic strength was maintained at 0.1 *M* with sodium perchlorate. Spectra of reactants and products agreed with those reported previously.[11] The total metal concentration was generally 10^{-5} to $10^{-4}M$ and the nucleophile concentration was kept at least ten times larger to ensure pseudo-first order conditions.

Results and Discussion

The results of the kinetic studies are given in Tables I and II. We first consider reactions (2) and (3) (Table I) where X is monodentate.

$$M(mnt)_2X^- + L \rightarrow M(mnt)_2L^- + X \qquad (2)$$

$$M(mnt)_2X^- + L\text{–}L \rightarrow M(mnt)_2(L\text{–}L)^- + X \qquad (3)$$

TABLE I. Rate Data for Five-Coordinate $M(mnt)_2X^-$ Substrates, M = Fe, Co.

Substrate	Nucleophile	C_M[a]	Range of [Nucl] *M*[b]	Excess Leaving Group *M*	Observations[c]
$Co(mnt)_2PPh^-$	P(*p*-tolyl)$_3$	5×10^{-5}	$5\text{–}30 \times 10^{-4}$	0	$k_{obsd} = 175 \times 10^3$ [Nucl]
$Co(mnt)_2PPh_3^-$	P(*p*-tolyl)$_3$	5×10^{-5}	$5\text{–}30 \times 10^{-4}$	5×10^{-4}	no change in k_{obsd}
$Co(mnt)_2P(p\text{-tolyl})_3^-$	PPh_3	1×10^{-4}	$10\text{–}30 \times 10^{-4}$	0	$k_{obsd} = 20 + 25 \times 10^3$ [Nucl]
$Co(mnt)_2P(p\text{-tolyl})_3^-$	PPh_3	1×10^{-4}	$10\text{–}30 \times 10^{-4}$	5×10^{-4}	$k_{obsd} = 73 + 25 \times 10^3$ [Nucl]
$Co(mnt)_2P(n\text{-}Bu)_3^-$	diphos[d]	2×10^{-5}	$2\text{–}10 \times 10^{-4}$	0	$k_{obsd} = 1.50 \times 10^3$ [Nucl]
$Co(mnt)_2P(n\text{-}Bu)_3^-$	diphos[d]	2×10^{-5}	$2\text{–}10 \times 10^{-4}$	1.8×10^{-4}	no change in k_{obsd}
$Co(mnt)_2P(n\text{-}Bu)_3^-$	diphos[d]	2×10^{-5}	10×10^{-4}	4.8×10^{-4}	no change in k_{obsd}
$Co(mnt)_2P(n\text{-}Bu)_3^-$	diphos[d]	2×10^{-5}	10×10^{-4}	5.0×10^{-3}	k_{obsd} reduced by factor of 1.7
$Co(mnt)_2P(OBu)_3^-$	diphos	2×10^{-5}	$2\text{–}10 \times 10^{-4}$	0	$k_{obsd} = 48 \times 10^3$ [Nucl]
$Co(mnt)_2P(OBu)_3^-$	diphos	2×10^{-5}	2×10^{-4}	1.8×10^{-4}	no change in k_{obsd}
$Co(mnt)_2P(OBu)_3^-$	diphos	2×10^{-5}	10×10^{-4}	5.3×10^{-3}	no change in k_{obsd}
$Fe(mnt)_2P(OBu)_3^-$	diphos	2×10^{-5}	$2\text{–}5 \times 10^{-4}$	0	$k_{obsd} = 180 + 130 \times 10^4$ [Nucl]
$Fe(mnt)_2P(OBu)_3^-$	diphos	2×10^{-5}	$2\text{–}5 \times 10^{-4}$	1.8×10^{-4}	no change in k_{obsd}
$Fe(mnt)_2P(OBu)_3^-$	dtc[e]	5×10^{-5}	$5\text{–}50 \times 10^{-4}$	0	$k_{obsd} = 190 + 5 \times 10^4$ [Nucl]; reaction does not go to completion
$Fe(mnt)_2P(OBu)_3^-$	VPP[f]	2×10^{-5}	$2\text{–}10 \times 10^{-4}$	0	$k_{obsd} = 225$; dependence on [Nucl] is zero within error
$Fe(mnt)_2P(OBu)_3^-$	VPP[f]	2×10^{-5}	$2\text{–}10 \times 10^{-4}$	9×10^{-5}	k_{obsd} is reduced by factor of ≈1.5
$Fe(mnt)_2P(n\text{-}Bu)_3^-$	diphos	2×10^{-5}	$2\text{–}5 \times 10^{-4}$	0	$k_{obsd} = 10 + 1.33 \times 10^4$ [Nucl]
$Fe(mnt)_2P(n\text{-}Bu)_3^-$	diphos	2×10^{-5}	$2\text{–}5 \times 10^{-4}$	1.8×10^{-4}	k_{obsd} increases because reaction does not go to completion

[a] Total concentration of metal. [b] [Nucl] is concentration of nucleophile. [c] All k_{obsd} values are in sec^{-1} units and at 25° C. [d] diphos = 1,2-bis(diphenylphosphino)ethane. [e] dtc = diethyldithiocarbamate anion. [f] VPP = *cis*-1,2-bis(diphenylphosphino)ethylene.

TABLE II. Rate Data for Six-Coordinate $Fe(mnt)_2X^-$ Substrates.

Substrate	Nucleophile	C_M[a]	Range of [Nucl] *M*[b]	Excess Leaving Group *M*	Observations[c]
$Fe(mnt)_2bipy^-$	$P(n\text{-}Bu)_3$	1×10^{-4}	$1\text{–}25 \times 10^{-3}$	0	$k_{obsd} = 4.95$
$Fe(mnt)_2bipy^-$	$P(n\text{-}Bu)_3$	1×10^{-4}	$3\text{–}25 \times 10^{-3}$	5×10^{-3}	no change in k_{obsd}
$Fe(mnt)_2phen^-$	$P(n\text{-}Bu)_3$	1×10^{-4}	$1\text{–}25 \times 10^{-3}$	0	$k_{obsd} \times 0.055$
$Fe(mnt)_2phen^-$	$P(n\text{-}Bu)_3$	1×10^{-4}	$1\text{–}25 \times 10^{-3}$	5×10^{-3}	no change in k_{obsd}
$Fe(mnt)_2diphos^-$	$P(n\text{-}Bu)_3$	1×10^{-4}	$5\text{–}25 \times 10^{-3}$	0	$k_{obsd} = 34 + 300$ [Nucl]
$Fe(mnt)_2VPP^-$	$P(n\text{-}Bu)_3$	1×10^{-4}	$5\text{–}25 \times 10^{-3}$	0	$k_{obsd} = 0.046 + 1.0$ [Nucl]

[a] Total concentration of metal. [b] [Nucl] is concentration of nucleophile. [c] All k_{obsd} values are in sec^{-1} units and at 25° C.

We previously[8] studied some reactions like (2) and (3) with X = PPh_3. As Table I shows, a variety of behavior is seen. We found that often very important mechanistic information can be obtained by studying a reaction with and without an excess of leaving group X present and for this reason such data are included in the Tables.

It should be mentioned that several reactions not appearing in Table I were studied. They are omitted because the results are difficult to present in a Table yet not sufficiently important to warrant separate figures. These reactions are given in (4) where M = Fe, X = $P(n\text{-}Bu)_3$ and M = Co, X = PPh_3 or $P(OBu)_3$.

$$M(mnt)_2X^- + VPP \rightarrow M(mnt)_2VPP^- + X \qquad (4)$$

VPP is *cis*-1,2-bis(diphenylphosphino)ethylene and was a far less effective nucleophile than its saturated analog (diphos), although its thermodynamic stability as the adduct $M(mnt)_2VPP^-$ seemed greater than for diphos. Reaction (4) with M = Fe, X = $P(n\text{-}Bu)_3$ was much slower than the diphos reaction and showed a kinetic order between zero and one in VPP. Excess $P(n\text{-}Bu)_3$, $2 \cdot 10^{-4}M$, slowed the reaction by a factor of 7. Table I shows that excess $P(n\text{-}Bu)_3$ only served to increase the rate of the analogous diphos reaction.

With M = Co, X = PPh_3 or $P(OBu)_3$ again the VPP reaction is peculiar, but this time the kinetic order in VPP is between one and two. The reactions are roughly 100 times slower than the analogous diphos reactions. Excess leaving group (X) markedly reduces the rate, particularly when X = $P(OBu)_3$. Note (Table I) that excess leaving group does not affect the rate when diphos is the nucleophile. These observations are easily explained by the mechanism given below. The inertness of VPP compared to diphos is most likely due to its stereochemical rigidity and reminds one of the familiar case of *o*-phenanthroline.

It was stated above that most studies reported to date suggest a dissociative mechanism for substitution at a five-coordinate centre. It is easy to show that a limiting S_N1 mechanism does not operate for reactions (2) and (3). Consider the simple dissociative scheme:

$$M(mnt)_2X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(mnt)_2^- + X$$

$$M(mnt)_2^- + L \xrightarrow{k_3} M(mnt)_2L^-$$

Assuming that $M(mnt)_2^-$ is in a steady state we obtain eqn (5):

$$k_{obsd} = \frac{k_1k_3[L]}{k_2[X] + k_3[L]} \qquad (5)$$

When the nucleophile is bidentate the same functional form is obtained even if an additional intermediate is included. A comparison of Table I and eqn (5) immediately shows that the S_N1 scheme is not correct. Eqn (5) demands that $k_{obsd}=k_1$ when excess X has no effect, i.e. when $k_3[L] \gg k_2[X]$. But Table I presents several examples where excess X has no effect yet the reaction is first order in L. Eqn (5) predicts that $k_{obsd} = k_1k_3[L]/k_2[X]$ when the reaction is first order in L. Even for reactions affected by excess X, the effect was not α 1/[X] when first order in L as required by (5). This simple technique of using varying excess concentrations of leaving group can often be useful and seems not to have been exploited as fully as possible in the past.

Table I shows that some reactions, other than ones that do not go to completion, have nonzero intercepts in plots of k_{obsd} vs. [Nucleophile]. This strongly suggests that a dissociative pathway does make some contribution. The fact that excess leaving group affects some of the reactions suggests that competition for an intermediate is occurring. The mechanism that can accomodate all of the observations in Table I as well as the VPP reactions discussed above is that presented previously[8] which was based on less convincing evidence. The mechanism is given in Figure 1. The mechanism for a monodentate nucleophile is the same except that k_4, k_5, and k_7 do not exist. Assuming the steady state approximation for B and C one obtains eqn (6) for bidentates (L–L) and eqn (7) for monodentates (L).

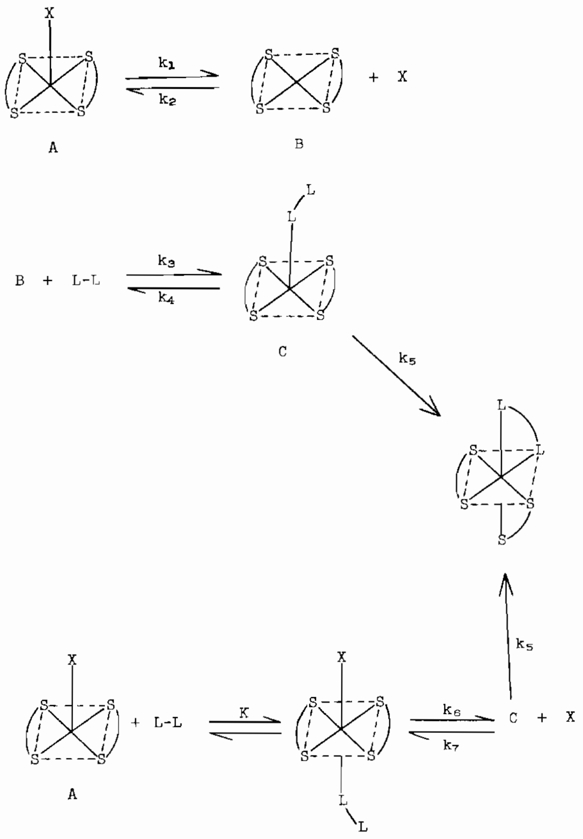

Figure 1. Mechanism of the reaction $M(mnt)_2X^- + L\text{–}L \rightarrow M(mnt)_2(L\text{–}L)^- + X$. Charges are omitted.

$$k_{obsd} = \frac{k_1k_3k_5[L\text{–}L] + k_5k_6K[L\text{–}L](k_2[X] + k_3[L\text{–}L])}{(1 + K[L\text{–}L])(k_2[X](k_4 + k_5 + k_7[X]) + k_3[L\text{–}L](k_5 + k_7[X]))} \qquad (6)$$

$$k_{obsd} = \frac{k_1k_3[L]}{(1 + K[L])(k_2[X] + k_3[L])} + \frac{k_6K[L]}{1 + K[L]} \qquad (7)$$

Equations (6) and (7) show that good first order kinetics may not be obtained when no excess leaving group is present because X is generated during the reaction. We found this to be the case in a few instances, but reasonably good values of k_{obsd} could usually be obtained. Eqn (6) accomodates the fact that two of the VPP reactions show kinetic orders in VPP between one and two.

Equations (6) and (7) are rather complicated so we shall look at some limiting features. When $[X] \approx 0$, the limit of k_{obsd} as [L] or [L–L] → 0 should be k_1, which should be independent of nucleophile. Such a nucleophile independent intercept was observed previously[8] with PPh_3 as the leaving group and cobalt as the metal. Table I also shows this for the reaction of $Fe(mnt)_2P(OBu)_3^-$. The nonzero intercepts strongly suggest that a dissociative pathway exists, but we know from the discussion above that an associative pathway must also exist.

It should be noted that the nonzero intercepts for reactions (8) and (9) exist simply because these reactions did not go to completion under the conditions used.

$$Fe(mnt)_2P(n\text{-}Bu)_3^- + diphos \rightleftharpoons Fe(mnt)_2diphos^- + P(n\text{-}Bu)_3 \qquad (8)$$

$$Co(mnt)_2P(p\text{-}tolyl)_3^- + PPh_3 \rightleftharpoons Co(mnt)_2PPh_3^- + P(p\text{-}tolyl)_3 \qquad (9)$$

When [X] exerts no kinetic effect and when $1 \gg K[L]$ the mechanism requires $k_{obsd} = k_1 + k_6K[L]$. This holds for either monodentate or bidentate nucleophiles. It is possible to reach a limiting rate according to equations (6) and (7) and this behavior has been observed.[8]

The stability series for the $M(mnt)_2X^-$ complexes are:

$M = Co$: $X = P(n\text{-}Bu)_3 > P(OBu)_3 > P(p\text{-}tolyl)_3 > PPh_3$

$M = Fe$: $X = P(n\text{-}Bu)_3 > P(OBu)_3$

The leaving group series simply parallels the stability series, i.e. $PPh_3 > P(OBu)_3 > P(n\text{-}Bu)_3$. The effect of excess leaving group, X, holding the metal and nucleophile constant is $P(n\text{-}Bu)_3 > P(OBu)_3$ and $P(OBu)_3 > PPh_3$. This also parallels the stability series and indicates the relative ability of the X group to compete with the nucleophile for intermediates.

It is interesting to compare the effect of changing the metal in a given reaction. The iron complexes $Fe(mnt)_2X^-$ are all substantially more reactive than the corresponding cobalt complexes. Although this is perhaps the expected order we should keep in mind that the dithiolene complexes possess 'anomalous' electronic structures. It is accordingly unwise to assign formal oxidation states to the metal atoms. For example, $Co(mnt)_2X^-$ formally is cobalt(III) yet the reactions are very rapid.

Table II lists data for reaction (10). Several corresponding reactions for cobalt have been reported.[8] It is immediately clear from Table II that reaction (10) is mainly dissociative. We expect the microscopic reverse of Figure 1 to represent the detailed mechanism, and this is mainly dissociative. Two of the reactions in Table II are strictly independent of nucleophile and the other two show a rather feeble dependence on the $P(n\text{-}Bu)_3$ nucleophile concentration. The leaving group orders are bipy > *o*-phen and diphos > VPP. This ordering is no doubt due to the inflexibility present in *o*-phen and VPP. Compared to the analogous cobalt reactions[8] the six-coordinate iron complexes are more reactive by a factor of ≈ 5000. This factor seems reasonable when comparing 'normal' iron(III) and cobalt(III) complexes.

$$Fe(mnt)_2(L\text{–}L)^- + P(n\text{-}Bu)_3 \rightarrow Fe(mnt)_2P(n\text{-}Bu)_3^- + L\text{–}L \qquad (10)$$

Conclusion

The five-coordinate dithiolene complexes, $M(mnt)_2X^-$ (M = Fe, Co) substitute the X group by both associative and dissociative pathways. The associative pathway is propably dominant in many of the reactions. Heretofore most substitution reactions at five-coordinate centres were reported to be dissociative.

Acknowledgement

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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