Kinetics and Mechanism of Diene Exchange at Six-co-ordinate Chromium

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The results of kinetic studies on the ligand-exchange and substitution reactions of (buta-1,3-diene)tetracarbonylchromium and tetracarbonyl(*trans,trans*-hexa-2,4-diene)chromium with cyclo-octa-1,5-diene (cod), norbornadiene (nbd), and $P(OR')_3$ (R' = Me or Ph) to yield [Cr(cod)$(CO)_4$], [Cr(nbd)$(CO)_4$], and [Cr$(CO)_4${$P(OR')_3$}$_2$] are consistent with a mechanism involving a stepwise displacement of the diene ligand, which is S_N1 in nature for the diene exchange but contains a ligand-dependent S_N2 component in the case of substitution by phosphite.

ALTHOUGH a great deal of information exists on the kinetics and mechanism of carbonyl- and olefin-substitution reactions involving Group 5 ligands, relatively little work has been carried out on reactions in which olefins or polyolefins function as nucleophiles in substitution reactions, particularly for metals with co-ordination numbers greater than four.[1] In a previous article [2] we have discussed the mechanism of both mono- and poly-olefin exchange at five-co-ordinate iron. Here we report our studies on diene exchange of the type [Cr(diene)$(CO)_4$] + diene' ⟶ [Cr(diene')$(CO)_4$] + diene (diene = buta-1,3-diene or *trans,trans*-hexa-2,4-diene; diene' = cyclo-octa-1,5-diene or norbornadiene) together with a comparison of the analogous substitution by $P(OR')_3$ ligands to yield [Cr$(CO)_4${$P(OR')_3$}$_2$].

RESULTS AND DISCUSSION

The syntheses of (buta-1,3-diene)tetracarbonylchromium, (1a), and tetracarbonyl(*trans,trans*-hexa-2,4-diene)chromium, (1b), have recently been reported by von Gustorf and co-workers.[3] The description of their properties indicated that the diene might in fact be labile, and indeed diene exchange is observed with cyclo-octa-1,5-diene (cod) and norbornadiene (nbd), while substitution of the diene is observed on reaction with $P(OR')_3$, both under very mild conditions. The preference in molecular-orbital terms of a $Cr(CO)_4$ fragment for a non-conjugated rather than a conjugated diene has been discussed by Elian and Hoffmann,[4] and may provide the driving force for this diene exchange.

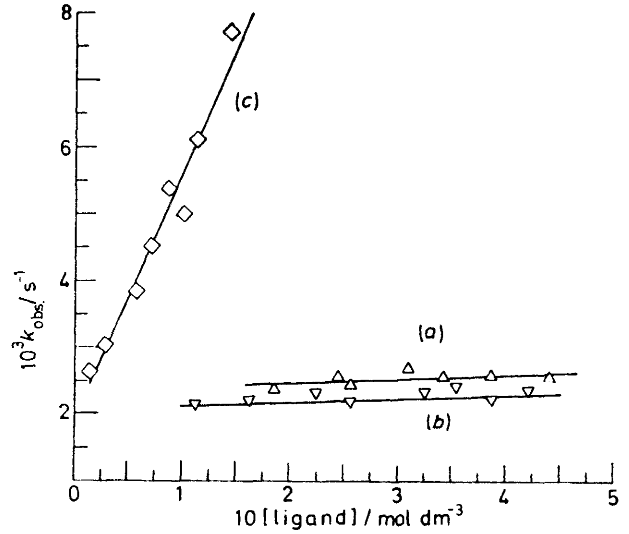


FIGURE 1 Plot of $k_{obs.}$ *vs.* [ligand] for reactions of complex (1a) with (*a*) cod, (*b*) nbd, and (*c*) $P(OMe)_3$ at 26.5 °C in heptane

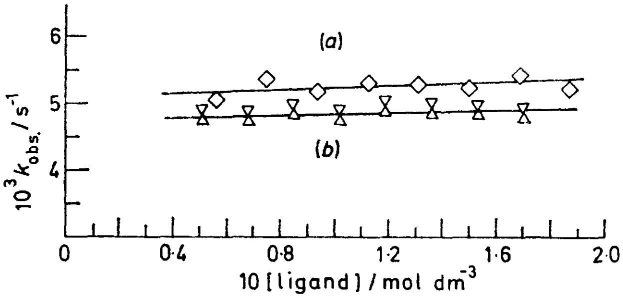
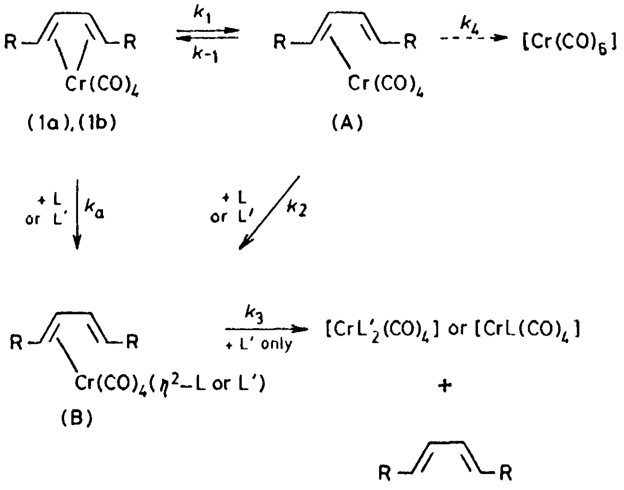


FIGURE 2 Plot as in Figure 1 for reactions of complex (1b) with (*a*) nbd and (*b*) cod

(*a*) *Diene Exchange.*—Reactions were carried out in n-heptane at 26.5 °C using at least a ten-fold excess of cod or nbd to ensure pseudo-first-order conditions. Identity of the product [Cr(cod)$(CO)_4$] and [Cr(nbd)$(CO)_4$] was confirmed by comparison of the i.r. spectra with those of materials prepared by literature methods.[5,6] Despite some overlap in the spectra, pseudo-first-order rate constants ($k_{obs.}$) may be obtained by monitoring the disappearance of both of the two strongest carbonyl-stretching bands of the substrate [1 943 and 1 932 cm^{-1} for (1a) and 1 937 and 1 920 cm^{-1} for (1b); see Experimental section]. Within experimental error, the two $k_{obs.}$ values obtained from the two bands are identical, and were averaged to give the $k_{obs.}$ values used in the plots of $k_{obs.}$ *vs.* concentration of cod and nbd displayed in Figures 1 and 2.

At low concentrations of cod and nbd, diene exchange involving (1a) is complicated by an independent thermal decomposition of (1a) to give [$Cr(CO)_6$]. This is designated by the step associated with k_4 in Scheme 1, and decomposition of the intermediate (A) in this way is only significant at the lowest concentrations of diene used. A similar decomposition has been noted in the case of olefin exchange in [Fe(olefin)$(CO)_4$] complexes.[2] In the absence of cod or nbd, the decomposition has a reproducible stoicheiometry of 1 mol of [$Cr(CO)_6$] produced for every 3 mol of (1a) consumed, but no attempt has been made to characterize the other products of the reaction. The $k_{obs.}$ values used in Figure 1 refer to only those reactions in which quantitative exchange of (1a) to [Cr(cod)(CO)$_4$] or [Cr(nbd)(CO)$_4$] was observed. In the reaction of (1a) with P(OR')$_3$ ligands this decomposition was not competitive. Although (1b) undergoes a similar thermal decomposition, it was not competitive with diene exchange, even at the lowest concentrations of diene used.



SCHEME 1 R = H (1a) or Me (1b); L' = P(OR')$_3$ (R = Me or Ph); L = cod or nbd

The proposed mechanism is shown in Scheme 1. Application of the steady-state hypothesis to intermediates (A) and (B) yields the rate equation (i).

$$\frac{-\mathrm{d}[(1)]}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{L}][(1)]}{k_{-1} + k_2[\mathrm{L}]} + k_a[\mathrm{L}][(1)] \qquad \text{(i)}$$

Thus, $k_{obs.} = \{k_1k_2[\mathrm{L}]/(k_{-1} + k_2[\mathrm{L}])\} + k_a[\mathrm{L}]$ which for cases where $k_2[\mathrm{L}] \gg k_{-1}$ reduces to $k_{obs.} = k_1 + k_a[\mathrm{L}]$. Thus, a plot of $k_{obs.}$ *vs.* [L] should yield eventually a straight line whose intercept is k_1 and whose slope is k_a. It can be seen from the Figures that the present data are consistent with this mechanism, assuming that the approximation $k_2[\mathrm{L}] \gg k_{-1}$ holds true even for the lowest concentrations of cod and nbd used. Calculated values of k_1 and k_a are given in the Table. It can be seen that, for a given substrate, the value of k_1 is independent of the incoming diene, as required by the mechanism. Within the precision of the calculation, the contribution of the step associated with k_a for the diene exchange may be taken as not significant. It can be seen from the k_1 values that the leaving diene in (1b) is considerably more labile than that of (1a). This is expected in view of the electron-donating character of the methyl substituents. Results on substitution of a wider range of [Fe(η^2-CH$_2$CHX)(CO)$_4$] complexes in which the rate-determining step is cleavage of the iron–olefin bond also show the same type of variation in rate with the electron-donating character of the substituent X.[7]

Derived rate constants for reaction of (1a) and (1b) with cod, nbd, or P(OMe)$_3$ *

Complex	Ligand	10^4k_1/s^{-1}	10^4k_a/dm^3 mol^{-1} s^{-1}
(1a)	cod	22.4 (1.2)	10.5 (3.8)
	nbd	20.6 (0.7)	6.3 (2.3)
	P(OMe)$_3$	19.0 (2.6)	376 (30)
(1b)	cod	47.6 (0.5)	8.2 (4.3)
	nbd	51.3 (1.2)	10.6 (8.9)

* Reactions carried out in n-heptane at 26.5 °C; initial concentration of complex was 7.5×10^{-4} mol dm^{-3}. Standard deviations are given in parentheses.

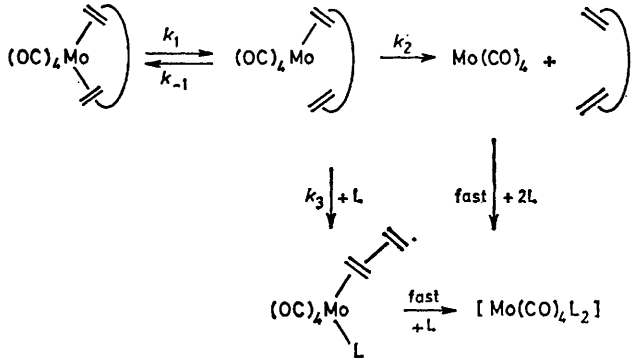
(*b*) *Reaction with* P(OR')$_3$ (R' = Me *or* Ph).—It has been reported that reaction of [Cr(cod)(CO)$_4$] or [Cr(nbd)(CO)$_4$] under controlled conditions leads to a mixture of *cis*- and *trans*-[Cr(CO)$_4${P(OMe)$_3$}$_2$].[8,9] Although a separation of the isomers does not appear to have been achieved, the *cis* and *trans* isomers of the cage phosphite complex tetracarbonylbis(2,8,9-trioxa-1-phospha-adamantane)chromium have been separated and shown to undergo ready *cis*-to-*trans* isomerization.[10] The i.r. spectrum of the solution obtained after reaction of (1a) with P(OMe)$_3$ exhibits bands at 2 026 (38), 1 942 (29), 1 937 (31), and 1 917 (100) cm^{-1} (relative intensities in parentheses), consistent with a *cis–trans* mixture of [Cr(CO)$_4${P(OMe)$_3$}$_2$] [lit.:[8,9] *cis* isomer, ν(CO) at 2 026, 1 947, 1 939, and 1 913 cm^{-1}; *trans* isomer, ν(CO) at 1 914 cm^{-1} (in hexadecane)]. On the basis of Scheme 1, the derived rate law is the same as in equation (i) (substituting L' for L), and again, making the assumption that $k_2[\mathrm{L'}] \gg k_{-1}$, the equation $k_{obs.} = k_1 + k_a[\mathrm{L'}]$ is obtained. Kinetically, the reaction may be followed in the same way as the diene exchange, but using only the band of (1a) at 1 932 cm^{-1} for monitoring, due to overlap of spectra of reactants and products. A plot of $k_{obs.}$ *vs.* concentration of P(OMe)$_3$ is shown in Figure 1, while k_1 and k_a values are given in the Table. It can be seen that while the k_1 value is the same as that obtained from the diene-exchange reaction, the k_a value is much greater, consistent with the greater nucleophilicity of phosphite as compared to olefin.

Reaction of (1a) with P(OPh)$_3$ yields a solution exhibiting carbonyl vibrations at 2 036 (59), 1 957 (81), 1 941 (sh), and 1 930 (100) cm^{-1} (relative intensities in parentheses). Only the *trans*-[Cr(CO)$_4${P(OPh)$_3$}$_2$] isomer has previously been isolated from reaction of [Cr(CO)$_6$] under more vigorous conditions [ν(CO) at 1 930 cm^{-1} in CCl$_4$].[11] In the present case, the additional bands at 2 036, 1 957, and 1 941 cm^{-1} may be assigned to the *cis* isomer; the intensities indicate that more of this isomer is produced than in the reaction using P(OMe)$_3$. In neither case is it possible to determine whether the *trans* isomer arises from isomerization of the initially formed *cis* isomer or whether isomerization of reaction intermediates yields the *trans* isomer directly. Because of overlap between the spectra of products and reactants an accurate determination of $k_{obs.}$ values is not possible in the reaction using P(OPh)$_3$. Qualitatively, however, it is obvious that the k_a value is greater than that for diene exchange but less than that observed for reaction with P(OMe)$_3$. The order of nucleophilicity P(OMe)$_3$ > P(OPh)$_3$ > olefin is the same as that found for substitution reactions at five-co-ordinate iron(0).[12]

In recent years, a considerable number of kinetic studies of substitution of $[M(CO)_5L]$ and $[M(CO)_4L_2]$ complexes (M = Cr, Mo, or W) by mono- and bi-dentate Group 5 and Group 6 ligands have been reported.[13,14] In general, the rate laws observed have the form (ii)

$$-\mathrm{d}[\text{substrate}]/\mathrm{d}t = (k_1 + k_a[L])[\text{substrate}] \qquad \text{(ii)}$$

and have been interpreted in terms of mechanisms analogous to that in Scheme 1. For displacement of a bidentate ligand in the reaction of $[Mo(cod)(CO)_4]$ with various phosphine ligands L to yield *cis*-$[Mo(CO)_4L_2]$ complexes,[14b,i] the mechanism outlined in Scheme 2 has been proposed, for which analysis of the rate law shows that $k_{obs.} = k_1(k_2 + k_3[L])/(k_{-1} + k_2 + k_3[L])$.



SCHEME 2 L = Phosphine

The observed linear dependence of $k_{obs.}$ on the concentration of L can only be explained assuming that k_2 is of the same order as $k_3[L]$ over the total range of phosphine concentrations used [*ca.* 20-fold in ref. 14(*b*) and 10-fold in ref. 14(*i*)] and that $k_{-1} \gg k_3[L]$ at all concentrations of L used. The data can be accommodated quite nicely, however, using Scheme 1, again making the more reasonable assumption that $k_2[L] \gg k_{-1}$ at all ligand concentrations used. Although we have no direct evidence for intermediate (B), analogous intermediates have been isolated from the reaction of Group 5 ligands with tricarbonyl(η^4-heterodiene)iron complexes.[15] For these reasons, and in view of the demonstrated partial S_N2 character of the substitution of $[Mo(CO)_6]$,[14a] we prefer the mechanism outlined in Scheme 1, although on the basis of the assumptions outlined above there is no way kinetically to differentiate between them.

If the results of ref. 14(*b*) and (*i*) are interpreted on the basis of Scheme 1, then values of k_1 and k_a of 0.9×10^{-4} s^{-1} and 25×10^{-4} dm^3 mol^{-1} s^{-1} are obtained for the reaction of $[Mo(cod)(CO)_4]$ with PBu^n_3 at 25 °C in benzene. Values for the similar reaction of $[Cr(cod)(CO)_4]$ are likely to be lower in view of the known greater lability of molybdenum(0) complexes as compared to Cr^0. In particular, the *ca.* 15-fold difference in k_a between (1a) and $[Mo(cod)(CO)_4]$ for reaction with phosphorus-donor ligands would seem to be consistent with an I_d nature for the step associated with k_a in which bond breaking is most important.[13]

EXPERIMENTAL

(Buta-1,3-diene)tetracarbonylchromium [ν(CO) at 2 035, 1 979, 1 943, and 1 932 cm^{-1}], tetracarbonyl(*trans,trans*-hexa-2,4-diene)chromium [ν(CO) at 2 034, 1 959, 1 937, and 1 920 cm^{-1}], $[Cr(cod)(CO)_4]$ [ν(CO) at 2 032, 1 952, 1 938, and 1 910 cm^{-1}), and $[Cr(nbd)(CO)_4]$ [ν(CO) at 2 029, 1 957, 1 945, and 1 915 cm^{-1}; in heptane] were prepared by literature methods.[3,5,6] Norbornadiene, cycloocta-1,5-diene, and the phosphites used in the kinetic experiments were distilled immediately before use under reduced pressure and stored under N_2 at 0 °C. Heptane (AnalaR grade) was dried and degassed on a vacuum line before use. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 1-mm NaCl cells.

In kinetic experiments, a solvent–ligand blank was employed as reference. Reactions were carried out with the exclusion of light in n-heptane in sealed vessels under an atmosphere of nitrogen in a constant-temperature bath thermostatted to 26.5 ± 0.1 °C. Substrate solutions of (1a) or (1b) of concentration 7.5×10^{-4} mol dm^{-3} were prepared and stored at −20 °C under N_2 and aliquots transferred under N_2 to the reaction vessel kept at 0 °C. Ligands were then added by syringe and the solution was mixed and placed in the constant-temperature bath. Sampling was accomplished by direct flushing of an aliquot under N_2 pressure *via* a small-bore plastic tube from the reaction vessel into the i.r. cell. Absorbances and times were then recorded immediately. Reactions were followed to completion, yielding an average of about ten (absorbance, time) data pairs (allowing for initial temperature equilibration). The $k_{obs.}$ values were obtained from a linear least-squares analysis of plots of −lnA *vs.* time; k_1 and k_a values were calculated from an unweighted linear least-squares analysis of the data presented in Figures 1 and 2. All linear plots had correlation coefficients of greater than 0.998. The compounds $[Cr(CO)_6]$, $[Cr(cod)(CO)_4]$, and $[Cr(nbd)(CO)_4]$ obey the Beer–Lambert law.

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