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Preliminary communication

Mechanism of carbon monoxide substitution reactions of the seventeen-electron complex $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$

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Abstract

A kinetic study shows that carbon monoxide substitution reactions of the seventeen-electron complex $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ proceed via an associative process.

There has in recent years been increasing interest in the chemistry of seventeen-electron organometallic compounds, most of which are sufficiently reactive that few have as yet proven amenable to intensive mechanistic studies of their chemistry [1]. Of relevance here, where kinetic studies of substitution reactions of seventeen-electron carbonyl complexes have proven to be feasible, it has been found that the mechanisms differ markedly from those of their eighteen-electron analogues, the reactions proceeding via associative processes involving nineteen-electron intermediates or transition states [1–5]. However, very few systems have as yet been subjected to careful scrutiny, and we now provide preliminary results of a mechanistic study of CO substitution reactions of the seventeen-electron compound $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$, including as yet rarely available activation parameters.

It has been known for some time that the metal–metal bond of the dimer, $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$, is very long (3.281(1) Å) [6] and weak (≈ 53 kJ mol^{-1}) [7], and it has recently been established that low but chemically significant concentrations of the monomeric, metal-centred radical $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ exist in solution in equilibrium with the dimer [8,9].

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\} \qquad (1)$$

Indeed, we have recently demonstrated that the solution chemistry of the dimer reflects the reactivity of the monomer, and a number of ligand substitution, disproportionation and atom abstraction reactions of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ and $\{(\eta^5\text{-}C_5Me_5)Cr(CO)_3\}$, as well as of similar molybdenum species, have been investigated [9–14].

In order to gain a better understanding of the chemistry of this very interesting system, we have initiated a mechanistic study of the substitution reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3]_2$ with tertiary phosphines, as represented by eq. 2.

$$\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3\} + \text{L} \overset{k_2}{\rightarrow} \{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_2\text{L}\} + \text{CO} \qquad (2)$$

Treatment of toluene solutions of the dimer (0.0035 mol dm^{-3}) with cyclohexyldiphenylphosphine (CDPP; 0.01–0.15 mol dm^{-3}) under pseudo-first-order conditions in the temperature range 308–318 K results in the smooth disappearance of the ν(CO) of the dimer [8,12] and the smooth appearance of ν(CO) at 1800 and 1920 cm^{-1}, which may be attributed to the product of substitution, $\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_2\text{(CDPP)}\}$ [12]. The reaction may be monitored by IR spectroscopy using either the dimer peak at 1946 cm^{-1} or the product peak at 1800 cm^{-1}, although treatment of the data is not straightforward in either case. Since the reported equilibrium constant for the pre-equilibrium represented by eq. 1 is $\approx 1.8 \times 10^{-3}$ mol dm^{-3} at 318 K [8] while the same monomer–dimer exchange is rapid on the NMR time scale [9], the proportion of the starting chromium compound present as monomer is significant at all times. The ratio of $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3\}]$ to $[[(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3]_2]$ varies considerably during the course of the reaction, and the intensity of the dimer peak at 1946 cm^{-1} does not vary linearly with the sum of the monomer + dimer concentrations. Furthermore, the substituted product was found generally to decompose to a blue material which exhibited no ν(CO) in the IR spectrum and, in several cases, to the hydride, $(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_2\text{(CDPP)H}$.

The latter processes were relatively slow, however, and by utilizing a simplex optimization program for the determination of A_∞ for the product peak at 1800 cm^{-1}, linear first-order plots for formation of $\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_2\text{(CDPP)}\}$ could generally be obtained over 2–3 half-lives; the values of k_{obs} obtained in this way were, within experimental error, equal to the values of k_{obs} obtained by monitoring the loss of the total tricarbonylchromium reactants. Furthermore, plots of k_{obs} vs. [CDPP] were also linear, indicating that the chemistry of eq. 2 is a second-order process. Values of k_{obs} and k_2 for various concentrations of CDPP at 308 K

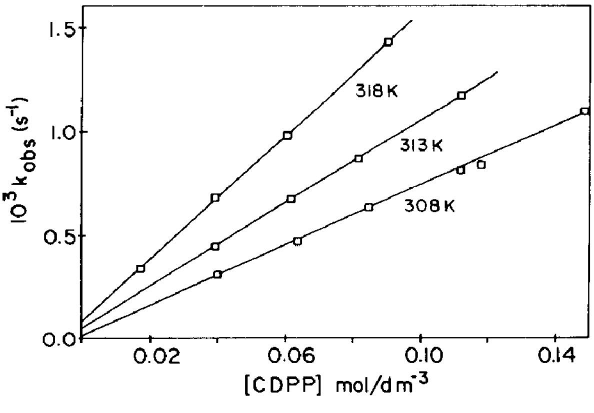

Fig. 1. Plots of observed rate constants vs. [CDPP] at 308, 313 and 318 K for the reaction of $\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3\}$ with CDPP in toluene.

($k_2 = (7.17 \pm 0.05) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}), 313 K ($k_2 = (9.99 \pm 0.42) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}) and 318 K ($k_2 = (14.8 \pm 1.1) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}) were determined, and plots of the data are presented in Fig. 1. For the reaction of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ with CDPP in toluene, $\Delta H^{\ddagger} = 57 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -100 \pm 10$ J mol^{-1} K^{-1}.

The latter datum is similar in sign and magnitude to comparable data for CO substitution reactions of the seventeen-electron species $\{V(CO)_6\}$ [15], $\{(\eta^5\text{-}C_5H_5)_2V(CO)\}$ [16] and $\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(MeCN)^+\}$ [17], and provides further evidence for the associative nature of the process under consideration here. So also does the fact that reactions of the rather sterically demanding CDPP (estimated cone angle 154° [18]) proceed much more slowly than do reactions of much smaller phosphines such as PPh_3 (cone angle 145° [18]) and $PMePh_2$ (cone angle 136° [18]); under comparable conditions, the relative rates of substitution by these three phosphines are $\approx 1/2/65$. Thus the mechanism for substitution reactions of the seventeen-electron species $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ is of the same type of associative process established heretofore only for three other systems [15–17].

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