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Preliminary communication

A KINETIC INVESTIGATION OF ARENE EXCHANGE AND SUBSTITUTION IN (NAPHTHALENE)$Cr(CO)_3$

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Summary

The rate of (naphthalene)$Cr(CO)_3$ with toluene in n-nonane to give (toluene)$Cr(CO)_3$ is independent of the toluene concentration, whereas the rate of substitution by $P(OMe)_3$ to give *fac*-$Cr(CO)_3[P(OMe)_3]_3$ is first order with respect to the concentration of $P(OMe)_3$. For a series of aromatic and heteroaromatic complexes of tricarbonylchromium, the order of substitutional lability is not necessarily mirrored in lability towards exchange.

The recent interest in the functionalization of arenes using (arene)$Cr(CO)_3$ complexes [1a,b] has focused attention on the phenomenon of arene exchange, since a stoichiometric synthesis may be made cyclical if the functionalized arene can be exchanged for free arene as part of the reaction sequence. Due to the relatively low lability of monocyclic (arene)$Cr(CO)_3$ complexes, most kinetic studies have been conducted in donor solvents which act as catalysts for the exchange process [2a—c]. Recent studies on the uncatalysed exchange of (benzene)$Cr(CO)_3$ with mesitylene [3] reveal a rate law which is first order in both metal complex and mesitylene; these results are in essential agreement with earlier rate studies using radioactively labelled arenes [4a—d]. We report here on the exchange and substitution reactions of the much more labile (naphthalene)$Cr(CO)_3$ which exhibits significantly different kinetic behaviour.

The exchange of (naphthalene)$Cr(CO)_3$ with toluene in n-nonane at ca. 130°C proceeds in essentially quantitative yield (>90%) to give (toluene)-$Cr(CO)_3$, and may be monitored kinetically using the disappearance of naphthalene)$Cr(CO)_3$ [5]. The data of Table 1 at varying concentrations of toluene

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TABLE 1

k_{obs} VALUES FOR REACTIONS OF (naphthalene)$Cr(CO)_3$ WITH TOLUENE AND $P(OMe)_3$

Entering ligand (L)	Solvent	T(°C)	[(naphthalene)$Cr(CO)_3$] (mol dm^{-3})	[L] (mol dm^{-3})	10^4 (k_{obs}/s^{-1})
Toluene	n-Nonane	127.5	0.002	0.04	0.430
				0.08	0.462
				0.12	0.442
				0.14	0.443
				0.16	0.483
				0.20	0.472
Toluene	n-Nonane/toluene (1/1)	133.0	0.0005	4.71	0.599
			0.001		0.572
			0.002		0.563
			0.005		0.583
$P(OMe)_3$	Decalin	37.1	0.0015	0.03	0.643
				0.06	1.31
				0.09	2.08
				0.12	2.85
				0.15	3.58

show clearly that the reaction rate is independent of toluene concentration. The reactions exhibit strict first order kinetic behaviour over at least 2.5 half lives, and the first order dependence of the rate on the concentration of (naphthalene)$Cr(CO)_3$ was confirmed by the independence of k_{obs} as a function of initial concentration of metal substrate in 1/1 n-nonane/toluene (4.71 mol dm^{-3} in toluene). Unlike the exchange of (benzene)$Cr(CO)_3$ with mesitylene, the exchange of (naphthalene)$Cr(CO)_3$ with toluene is not catalysed by (toluene)$Cr(CO)_3$ added in excess at the start of the reaction.

The independence of the rate of reaction on the concentration of toluene contrasts with the first order dependence on mesitylene concentration noted above. The results, however, may be accomodated in terms of a common mechanism under different limiting conditions of rate constants:

$$(\eta^6\text{-naphthalene})Cr(CO)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\eta^x\text{-naphthalene})Cr(CO)_3 \xrightarrow[+\text{ toluene}]{k_2}$$

$$(\text{toluene})Cr(CO)_3 + \text{naphthalene}$$

In the case of (naphthalene)$Cr(CO)_3$, the hapticity (x) of the transition state or intermediate is uncertain, since the ground state structure already reveals some distortion toward η^4-coordination [6], and molecular orbital calculations show similar energies for slippage to both η^2- and η^3-coordination [7]. Steady state treatment of the mechanism above yields the rate law

$$\frac{-d[S]}{dt} = \frac{k_1 k_2 [S][\text{toluene}]}{k_{-1} + k_2[\text{toluene}]}$$

which if $k_2[\text{toluene}] \gg k_{-1}$, reduces to $-d[S]/dt = k_1[S]$ and if $k_{-1} \gg k_2[\text{toluene}]$, reduces to $-d[S]/dt = (k_1 k_2 [S][\text{toluene}])/k_{-1}$.

It seems possible that the two experimentally determined rate laws represent these two limiting conditions. In the case of (naphthalene)$Cr(CO)_3$, the nearzero activation entropy ($\Delta H^{\neq}$ 132 kJ mol^{-1}, $\Delta S^{\neq}$ −1.4 J K^{-1} mol^{-1}) is consistent with a rate determining step involving little or no interaction of the incoming arene in the transition state or intermediate.

In contrast, the data of Table 1 show that substitution of (naphthalene)-$Cr(CO)_3$ by $P(OMe)_3$ in decalin to give *fac*-$Cr(CO)_3[P(OMe)_3]_3$ does proceed by a rate law which is first order in both metal complex and ligand [5]. However, the much faster rates and strongly negative activation entropy ($\Delta H^{\neq}$ 60.5 kJ mol^{-1}, $\Delta S^{\neq}$ −100 J K^{-1} mol^{-1}) [8] argue for a concerted displacement in which there is substantial $Cr—P(OMe)_3$ interaction in the rate determining step:

$$(\eta^6\text{-naphthalene})Cr(CO)_3 \underset{k_{-1},\,-L}{\overset{k_1\,+\,L}{\rightleftharpoons}} (\eta^4\text{-naphthalene})Cr(CO)_3L \xrightarrow[+L]{k_2} \xrightarrow[+L]{k_3}$$

$$Cr(CO)_3L_3 + \text{naphthalene}$$

Provided that $k_2[L] \gg k_{-1}$, the rate equation reduces to $-d[S]/dt = k_1[S][L]$.

In terms of substitution, naphthalene is the most labile of the aromatic and heteroaromatic ligands which we have examined (naphthalene > thiophene > 2,6-dimethylnaphthalene > 2,5-dimethylthiophene ~ pyrene > octamethylnaphthalene > 2,6-dimethylpyridine >> styrene). Indeed, of reported examples, only hexamethylborazine exhibits a greater lability [9]. The reaction rate generally follows the ordering of $\Delta H^{\neq}$, though the strongly negative $\Delta S^{\neq}$ values make an important contribution to the overall rate.

The essential difference in mechanism between exchange and substitution indicates that the lability order established for substitution may not be directly extendable to exchange. Indeed, though (pyrene)$Cr(CO)_3$ undergoes substitution at 70° C approximately 40 times slower than (naphthalene)$Cr(CO)_3$, exchange with toluene at 140°C is about twice as fast for (pyrene)$Cr(CO)_3$ as for its naphthalene analogue. Other complexes, such as (thiophene)$Cr(CO)_3$, maintain their relative order of lability in both substitution and exchange reactions. We are currently exploring this relationship in greater detail.

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5 The k_{obs} values of Table 1 represent the average of duplicate runs (reproducibility ± 5%) obtained from strictly linear plots of $\ln((A_0 - A_\infty)/(A_t - A_\infty))$ against time. Exchange reactions in nonane were monitored over at least 2.5 half lives at 460 nm. For reactions conducted in 1/1 nonane-toluene, k_{obs} values were calculated from initial $t_{1/2}$ values monitored at 470 to 540 nm depending on initial concentration of (naphthalene)Cr(CO)$_3$. Substitution reactions were monitored in decalin at 510 nm over at least 2.5 half lives. Yields were established by infrared calibration with authentic samples.

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