Journal of Organometallic Chemistry, 152 (1978) C5—C8

Preliminary communication

DIENE EXCHANGE AT FIVE-COORDINATE IRON: A KINETIC STUDY

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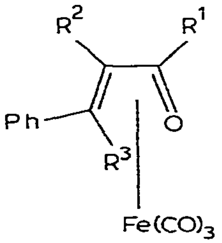
(Received February 20th, 1978)

Summary

A kinetic study of the exchange between various (η^4-enone)Fe(CO)$_3$ complexes and 1,3,5-cycloheptatriene (chpt) to yield (η^4-chpt)Fe(CO)$_3$ shows that the reaction proceeds via competing associative and dissociative pathways.

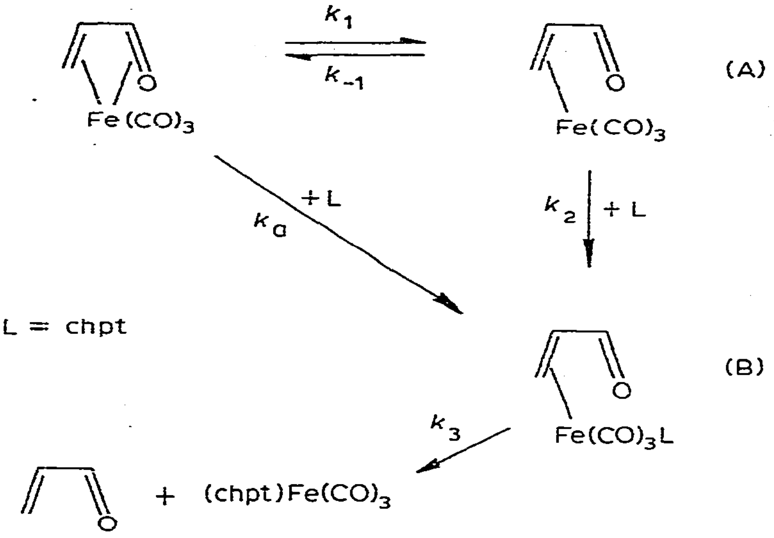
Complexes of structure I have been used in the last few years as a convenient source of the Fe(CO)$_3$ moiety in the preparation of (η^4-polyolefin)-Fe(CO)$_3$ complexes by exchange of the ketone on reaction with the free polyolefin [1a—c]. Although several mechanistic studies have been performed on substitution reactions of I [2] and the related (α,β-unsaturated Schiff base)-Fe(CO)$_3$ complexes [3] with Group V ligands, little is known about the diene exchange reaction. We report here our preliminary results on the mechanism of this substitution involving reaction of Ia—Id with 1,3,5-cycloheptatriene (chpt) to yield (η^4-chpt)Fe(CO)$_3$.



(Ia) $R^1 = CH_3, R^2, R^3 = H$
(Ib) $R^1, R^2, R^3 = H$
(Ic) $R^1 = Ph, R^2, R^3 = H$
(Id) $R^1 = Ph, R^2 = H, R^3 = CH_3$

Reactions were performed in dry, degassed toluene under nitrogen; relative concentrations of chpt of between 10/1 and 200/1 (chpt/complex) ensured pseudo-first-order conditions. Infrared monitoring of the disappearance of complex over at least four half-lives yielded first-order rate constants (k_{obs}). Figure 1 shows a plot of k_{obs} vs. [chpt] for complexes Ia and Ic; similar plots were obtained for Ib and Id.

The results are consistent with the mechanism shown in Scheme 1, containing both an associative pathway and a dissociative pathway involving initial cleavage of the Fe—CO π-bond.



Application of the steady state approximation to (A) yields the rate law $\frac{-d[C]}{dt} = \frac{k_1k_2[L][C]}{k_{-1} + k_2[L]} + k_a[L][C]$ where C is Ia—Id. Thus,

$$k_{obs} = \frac{k_1k_2[L]}{k_{-1} + k_2[L]} + k_a[L] \tag{1}$$

For large [L] where $k_2[L] >> k_{-1}$, eq. 1 reduces to $k_1 + k_a[L]$. From the gradient of the linear portion of Fig. 1, a value of k_a may be calculated, while the intercept of this line gives k_1. These values are tabulated in Table 1. Rearrangement of eq. 1 yields eq. 2.

$$\frac{1}{\frac{k_{obs}}{[L]} - k_a} = \frac{k_{-1}}{k_1k_2} + \frac{[L]}{k_1} \tag{2}$$

Figure 2 illustrates a plot of the left hand side of eq. 2 as a function of [chpt] for Ia and Ic. From these and the similar linear plots obtained for the other complexes, values of k_{-1}/k_2 were obtained, and are tabulated in Table 1;

TABLE 1

KINETIC DATA AT 90°C FOR REACTION SCHEME

	$10^4 k_1$ (s^{-1})	$10^4 k_a$ (M^{-1} s^{-1})	$10^2 k_{-1}/k_2$
Ia	8.10	21.26	8.4
Ib	3.97	18.91	3.1
Ic	1.92	6.34	12.6
Id	1.87	9.58	27.2

values of k_1 obtained from Fig. 2 were consistent with those obtained from Fig. 1. The intermediacy of (B) is indicated by (a) direct infrared observation in the case of Id, and (b) the non-linear nature of the rate of appearance of (chpt)Fe(CO)$_3$.

An increase in the electron donor ability of R^1 results in an increase in k_1 (Ph < H < Me), consistent with previous results [3], although substitution of an electron donor at position R^3 (Id) remote from the dissociation site has little effect. K_a values also increase in the same order, implying a greater bond-breaking than bond-making character in the S_N2 transition state [4], although steric effects may also have some influence.

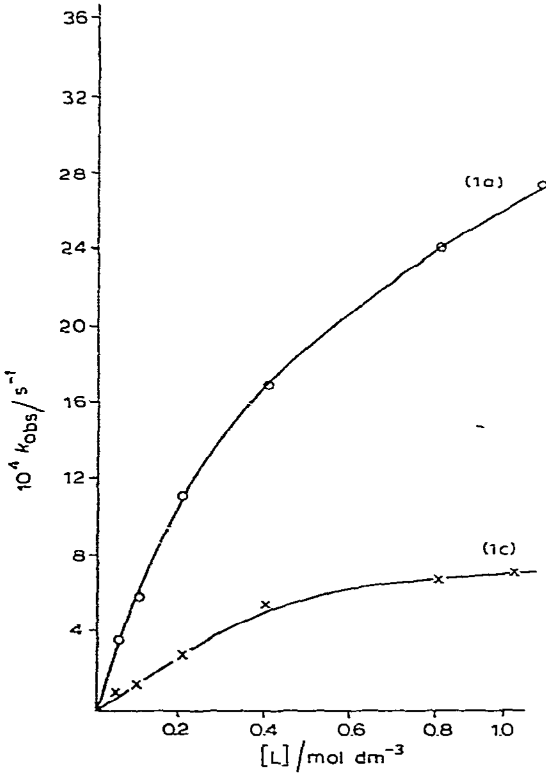


Fig. 1.

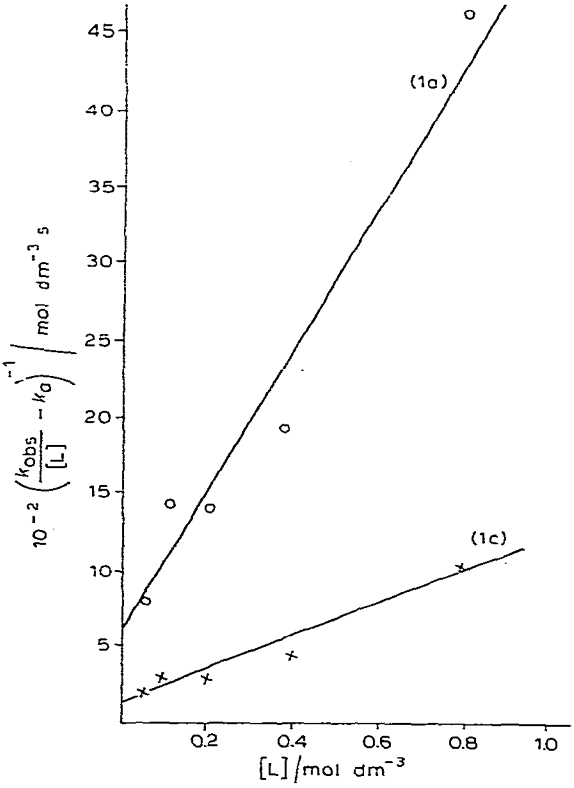


Fig. 2.

The remarkable selectivity exhibited by these reagents towards tautomeric polyolefin mixtures [1b] is perhaps the most interesting aspect of these reactions, and we are currently investigating kinetically reactions of Ia with a wide range of polyolefins.

References

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