Journal of Organometallic Chemistry, 168 (1979) C25—C29

Preliminary communication

INTRAMOLECULAR EXCHANGE IN Fe(η^4-diene)[P(OMe)$_3$]$_3$COMPLEXES

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(Received December 22nd, 1978)

Summary

The intramolecular exchange pathway in the complexes Fe(diene)L$_3$ (where L = P(OMe)$_3$ and diene = butadiene, isoprene, and 2,3-dimethylbutadiene) has been delineated by analysis of their temperature dependent ^{31}P{^{1}H} NMR spectra. The basic permutation which is required to produce simulated spectra in agreement with experiment can only be reconciled with a physical mechanism involving cyclical exchange of the three phosphorus ligands. This mechanism is probably best described as a diene rotation.

We wish to report a delineation of the preferred intramolecular exchange pathway in the complexes Fe(diene)L$_3$ where the ligands, L, are identical.

Fluxional behavior in dieneiron complexes was first reported for Fe(butadiene)-(CO)(PF$_3$)$_2$ [1]. Since that time there have been numerous descriptions of nonrigidity in a variety of M(diene)L$_3$ systems [1—14]. The fluxional behavior has also been considered theoretically [15].

TABLE 1

^{31}P NMR DATA [a] AND ACTIVATION PARAMETERS FOR Fe(diene)[P(OCH$_3$)$_3$]$_3$ COMPLEXES

1,3-Diene	δ_A (ppm)	δ_B (ppm)	J (Hz)	$\Delta H^{\ddagger}_{298}$ (kcal/mol)	$\Delta S^{\ddagger}_{298}$ (e.u.)	$\Delta G^{\ddagger}_{298}$ (kcal/mol)
Butadiene (−80° C) [b]	200.1	177.7	31	10.5	−3.1	11.4
Dimethylbutadiene (−90° C) [b]	196.3	174.0	32	10.0	−7.6	12.3
Isoprene (−90° C) [b]	199.3	B: 176.7 C: 173.6	AB: ±34 AC: ±26 BC: ±137	10.8	−4.2	12.1

[a] Positive shifts are downfield from 85% H$_3$PO$_4$. [b] The slow-exchange limit spectral parameters were determined at these respective temperatures.

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*Contribution No. 2605.

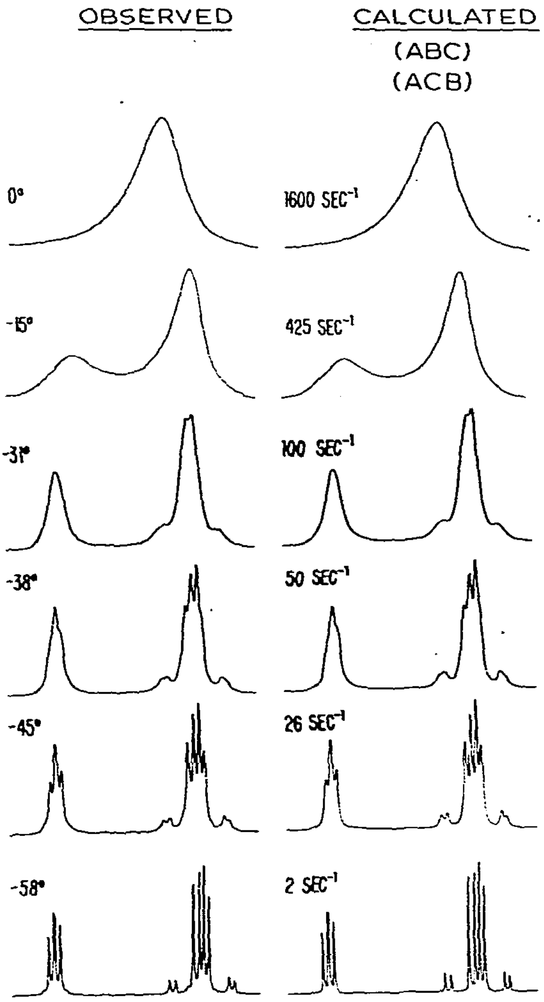
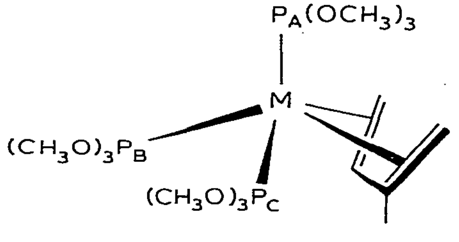


Fig. 1. Observed and calculated 36.43 MHz $^{31}P\{^1H\}$NMR spectrum (36.43 MHz, ABC spin system) of Fe(isoprene)[P(OCH$_3$)$_3$]$_3$ as a function of temperature (rate). The calculated spectra are for permutational mechanism IV.

A series of Fe(diene)[P(OCH$_3$)$_3$]$_3$ complexes were prepared using metal atom evaporation [12,16]. The $^{31}P\{^1H\}$ spectrum for each complex is temperature-dependent, consistent with fluxional character. Spectral and activation parameters for the butadiene, 2,3-dimethylbutadiene, and isoprene complexes are presented in Table 1. The free energies of activation for butadiene and dimethylbutadiene complexes suggest that methyl substitution in the 2 and 3 positions does not materially affect the nature of the exchange process. The relatively minor steric constraints for this substitution pattern have been noted previously [6]. The $^{31}P\{^1H\}$ slow exchange spectra for these two complexes are AB$_2$ patterns, and no mechanistic information can be derived from the data. The isoprene complex, on the other hand, gives a slow exchange ABC spin pattern with $|J_{BC}/\delta_{BC}| = 1.2$ (Fig. 1) allowing possible mechanistic distinctions. Since all $\Delta G^{\ddagger}$ values are about 11.8 ± 0.4 kcal/mol we can reasonably assume that the rearrangement mechanism is the same for all three complexes.

X-ray evidence suggests [17—19] that, in general, M(diene)L_3 complexes have "square pyramidal" geometry as shown for Fe(isoprene)[$P(OCH_3)_3$]$_3$ in configuration 1. (The structure shown is not meant to imply an assignment of resonances B and C.) For our discussion, this geometry will be assumed. The three $P(OMe)_3$ ligands are inequivalent in slow exchange, as shown by the $^{31}P\{^1H\}$ NMR ABC spin—spin splitting pattern (Fig. 1), so that all exchange mechanisms which correspond to particular permutations or linear combinations of permutations of the group S_3 are possible. The basic permutations of the group S_3 are shown in Table 2a. Selected linear combinations, which we have also considered, are shown in Table 2b. Because the $^{31}P\{^1H\}$ spectrum collapses to a single line in the fast exchange limit (Fig. 1), only basic permutation IV and the linear combinations are considered in our mechanistic analysis.



(1)

Figure 2 compares the experimental spectra at three rates (temperatures) with calculated spectra for the five possible cases in Table 2. Only case IV agrees with experiment and the physical mechanism producing the lineshape behavior must result in cyclical exchange of the three phosphorus ligands.

In simulating the effects of the linear combinations of permutations in Table 2b (Fig. 2), it was assumed that the rate constants for the permutations within a linear combination are equal. This is not required by symmetry so these rate constants could be adjusted relative to one another in an attempt to achieve better agreement with experiment for a given combination. Consequently a number of simulations were tried with unequal rate constants. Results confirmed the qualitative conclusion, reached by inspection of Fig. 2, that a fit is not possible for the combinations considered. The generality of the results was confirmed by observation of exactly the same type of line shape behavior in Fe(cycloheptatriene)[$P(OCH_3)_3$]$_3$ [16]. Of course, any linear combination which is mainly set IV with small admixtures of other sets could not be distinguished from IV alone.

TABLE 2

a. BASIC PERMUTATIONS OF THE GROUP S_3

E = (A)(B)(C)	I (AB)	IV (ABC)
	II (AC)	(ACB)
	III (BC)	

b. LINEAR COMBINATIONS OF THE BASIC PERMUTATIONS SIMULATED IN THIS COMMUNICATION

I + II	
I + III	I + II + III
II + III	

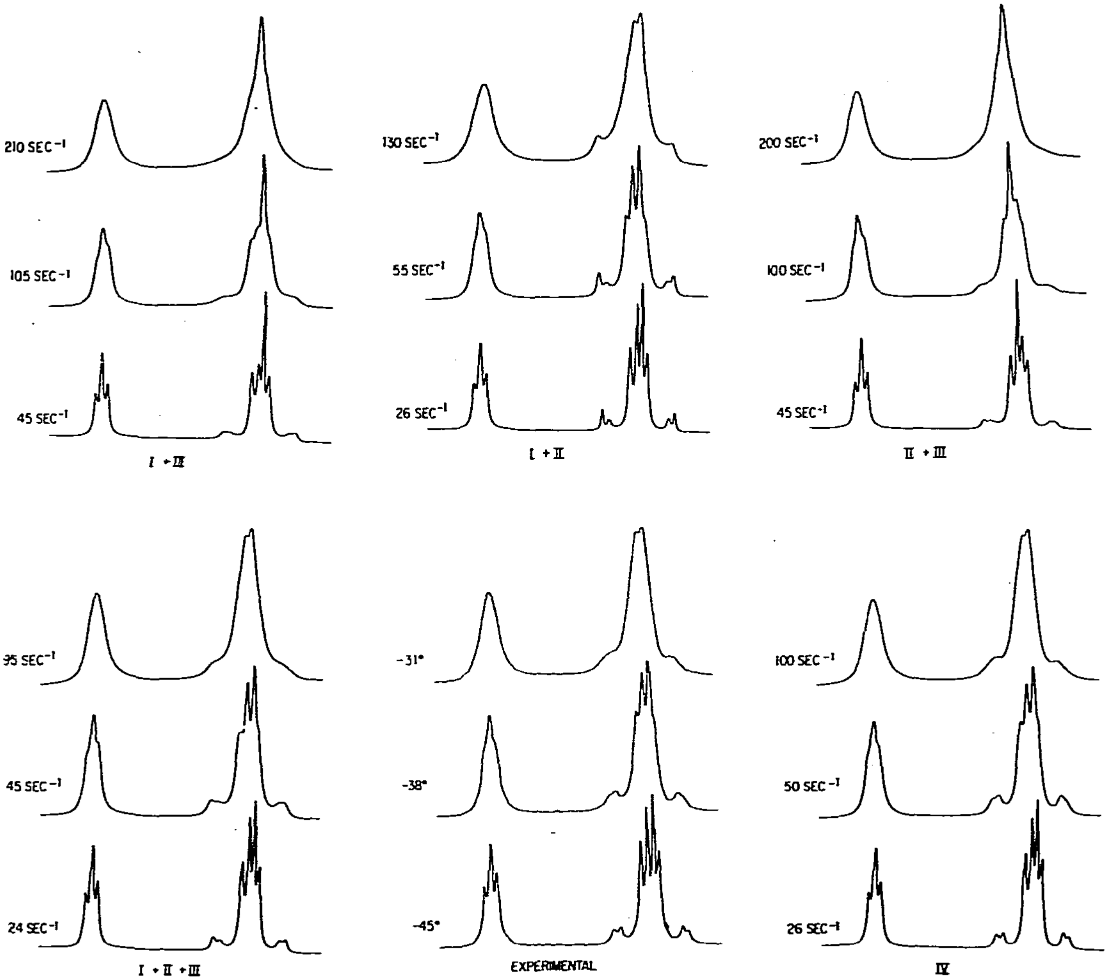
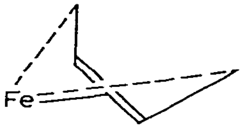


Fig. 2. Comparison of observed $^{31}P\{^{1}H\}$ NMR spectra (36.43 MHz) of Fe(isoprene)[P(OCH$_3$)$_3$]$_3$ at three temperatures with simulations calculated for the permutational mechanisms I+II, I+III, II+III, I+II+III, and IV.

Previous discussions [11] of the mutual exchange mechanism for Fe(diene)L$_3$ complexes (with L$_1$, L$_2$, L$_3$ = CO) have argued that the "symmetrical collapse" of the slow exchange signals constitutes proof of the preferred mutual exchange pathway. Our simulations of such systems as well as a recent report on Fe(dienyl)L$_3^+$ complexes [20] show symmetrical collapse to be a necessary but not sufficient condition for mechanistic delineation. The absence of spin—spin coupling in natural abundance ^{13}C NMR spectroscopy, in fact, precludes conclusive demonstration of the mutual exchange pathway. Studies of Fe(CO)L$_2$ and Fe(CO)$_2$ Ldiene complexes have ruled out pairwise exchange in unsymmetrical systems [6,7].

Having established the permutational mechanism for exchange in Fe(isoprene)[P(OCH$_3$)$_3$]$_3$ we considered the probable physical pathway for the fluxional process. Only two types of physical motion can give type IV behavior: "rotation" of the diene, or cyclical exchange of the three phosphorus ligands. The cyclical exchange mechanism for Fe(diene)L_3 has been described as a Bailar twist [21], a Berry pseudo rotation [22], and a turnstile process [23]. The Bailar twist applies to octahedral coordination and would only be appropriate if the electronic description of the complexes contained a significant contribution from the $(\pi,2\sigma)$ valence bond formulation from the diene (configuration 2). The complexes appear to be adequately described by conventional five coordinate bonding concepts. The Berry process involves interconversion of the various square pyramidal structures via trigonal bipyramidal intermediates. A turnstile type mechanism or diene rotation (pictured in configuration 3) is the simplest physical process corresponding to the permutational behavior defined here. It should be noted, however, that this is indistinguishable on the NMR timescale from rearrangement via two sequential Berry rearrangements [15].



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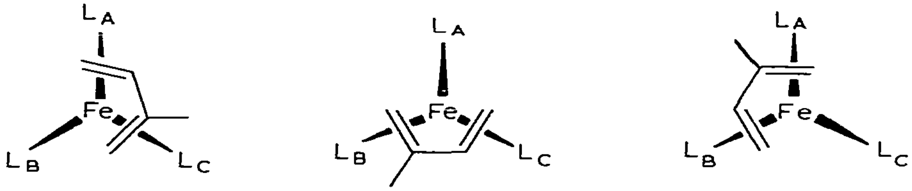

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