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Barrier to Racemization of the Framework of a Chiral Polynuclear Cation

By AGAPIOS AGAPIOU, S. ERIK PEDERSEN, LEONARD A. ZYZYCK, and JACK R. NORTON*
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)

Summary The framework of the chiral polynuclear cation $[Rh\{Fe(PAr_2)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (**2**) racemizes with simultaneous bridge-terminal carbonyl exchange, $\Delta G^\ddagger$ being *ca.* 13 kcal mol^{-1} in CD_2Cl_2 for both processes.

ALTHOUGH an optically active polynuclear complex would be valuable in mechanistic studies, there has been little investigation of chirality in polynuclear metal–metal bonded complexes. Remarkably few known clusters are chiral,[1] and even fewer are amenable to measurement of racemization barriers; the latter generally involve the rearrangement of organic ligands over frameworks not in themselves chiral.[2] We were therefore interested in the recently reported complex (**1**).[3] This molecule [the same basic structure is assumed for the related compounds (**2**) and is drawn in the Figure] has C_2 symmetry and is thus chiral. Furthermore, the low symmetry is inherent in the Fe–P–Rh–P–Fe framework. As racemization of this framework results in the equivalence of all four aryl groups on the phosphide bridges, n.m.r. measurement of the racemization rate is possible.

$$\underset{\textbf{(1)}}{[Rh\{Fe(PPh_2)(CO)_2(\eta\text{-}C_5H_4Me)\}_2]^+X^-}$$

$$\underset{\textbf{(2)}}{[Rh\{Fe(PAr_2)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+X^-}$$

a; Ar = p-MeC_6H_4; X = BF_4^-
b; Ar = Ph; X = PF_6^-; CO groups 60% enriched in ^{13}CO

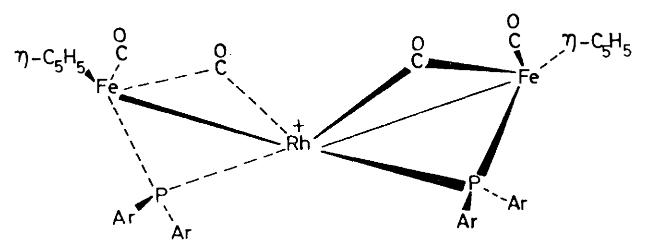


FIGURE. Structure of the chiral cations of $[Rh\{Fe(PAr_2)(CO)_2(\pi\text{-}C_5H_5)\}_2]^+X^-$ (**2a**) and (**2b**).

For ease of analysis, and for solubility, the p-tolyl derivative (**2a**) was synthesized by a modification of the original synthesis[3a,b] [reactions (1)—(4)]. It is essential that reactions (2) and (3) be carried out by adding (**3**) to a solution of 1,8-bis(dimethylamino)naphthalene and $[\{Rh(CO)_2Cl\}_2]$ in acetone; otherwise the very nucleophilic (**4**) reacts with (**3**) to form $[Fp_2PAr_2]^+$ PF_6^-.[4]

$$[FpCl] \xrightarrow{\text{i}} \xrightarrow{\text{ii}} \underset{\textbf{(3)}}{[Fp(PAr_2H)]^+PF_6^-} \tag{1}$$

$$\textbf{(3)} \xrightarrow{\text{iii}} \underset{\textbf{(4)}}{[FpPAr_2]} \tag{2}$$

$$\textbf{(4)} \xrightarrow{\text{iv}} \underset{\textbf{(5)}}{[(FpPAr_2)_2Rh(CO)Cl]} \tag{3}$$

$$\textbf{(5)} \xrightarrow{\text{v}} \textbf{(2)} \tag{4}$$

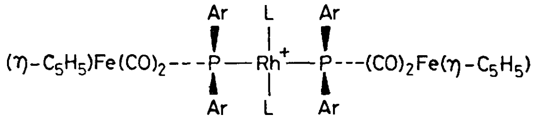
$$Fp = (\eta\text{-}C_5H_5)Fe(CO)_2$$

Reagents: i, PAr_2H in C_6H_6; ii, KPF_6; iii, 1,8-bis(dimethylamino)naphthalene in Me_2CO; iv, $[\{Rh(CO)_2Cl\}_2]$ in Me_2CO; v, $AgBF_4$ or $AgPF_6$ in tetrahydrofuran.

The p-tolyl methyl resonance of (**2a**) which is sharp in CD_2Cl_2 at 37 °C, becomes very broad at −30 °C and below but cannot be resolved into two signals in a 24 kG field.

However, the $\{^{31}P\}$ ^1H spectrum of the aromatic ring changes markedly with temperature. At −50 °C it can be accurately simulated by two partially overlapping AB patterns, one from each of the inequivalent pairs of tolyl groups. At −20 °C this pattern coalesces into a single line, allowing the estimation† of $\Delta G^{\ddagger}$ at this temperature as $12{\cdot}6 \pm 0{\cdot}3$ kcal mol^{-1}. This figure represents the first measured racemization barrier for the chiral metal framework of a polynuclear system and suggests that metal skeletons of clusters may themselves be flexible.

A reasonable racemization mechanism is suggested by the observation[3b] that, in donor solvents L, 'closed' structures such as (**2**) readily become 'open' structures such as (**6**), with framework symmetry increased to C_{2v} and four equivalent aryl groups. In the weak donor solvent CD_2Cl_2 the sequence (**2**)↔(**6**)↔(**2**)* is thus a reasonable path for racemization. As all four carbonyl groups are equivalent in (**6**), such a scheme predicts that the rate of bridge-terminal carbonyl exchange should equal the rate of racemization, and that all four carbonyl groups should exchange. [Transition states related to (**6**), retaining some metal–metal interaction along with less solvent participation, are also possible, but are at present experimentally indistinguishable in view of the limited range of solvents which dissolve (**2a**) in the closed form.]



$$(\eta\text{-}C_5H_5)Fe(CO)_2\cdots\overset{Ar}{\underset{Ar}{P}}—\overset{L}{\underset{L}{Rh^{+}}}—\overset{Ar}{\underset{Ar}{P}}\cdots(CO)_2Fe(\eta\text{-}C_5H_5)$$

The variable temperature $\{^1H\}$ ^{13}C n.m.r. spectra of (**2b**) in CD_2Cl_2 verify that bridge–terminal carbonyl exchange occurs as predicted. The spectrum at −75 °C shows the terminal carbonyl groups as a doublet [^2J(P–C) 8 Hz] at δ 208·5 and the bridging carbonyl groups as a multiplet centred at δ 236·6, with $^2J(P^1\text{–}C)$ 20 Hz, $^2J(P^2\text{–}C)$ 6 Hz, and ^1J(Rh–C) 32 Hz.‡ Although coalescence occurs at +15 ±10 °C in CD_2Cl_2, observation of the high-temperature limit is not possible in that solvent. In $C_2H_4Cl_2$, however, the resonances appear as a broad multiplet centred at δ 222·5 at 86 °C, consistent with the above assignments and demonstrating that the exchange is intramolecular. These results offer an additional example[5] of single bridge–terminal carbonyl exchange and confirm that other mechanisms can operate when pairwise exchange mechanisms[6] are unavailable.

From the coalescence temperature one can estimate $\Delta G^{\ddagger}$ for carbonyl interchange in (**2b**) as $12{\cdot}6 \pm 0{\cdot}5$ kcal mol^{-1}, equal within experimental error to the barrier to racemization measured above for (**2a**). It thus appears that interchange of bridging and terminal carbonyl groups in compounds of general structure (**2**) occurs at about the same rate as interchange of all aryl groups, or racemization, consistent with the (**2**)↔(**6**)↔(**2**)* rearrangement mechanism proposed.

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† Although each tolyl ring is actually a separate AA'BB' spin system, cross-ring couplings are sufficiently small that the observed spectrum at −50 °C is matched by one calculated with $\delta(A_1) = 710$, $\delta(B_1) = 696$, $J(A_1\text{–}B_1) = 9$ Hz; $\delta(A_2) = 694$, $\delta(B_2) = 680$, $J(A_2\text{–}B_2) = 9$ Hz. As the temperature increases, proton A_1 exchanges with proton B_2, and proton B_1 with proton A_2, *i.e.*, the *meta* protons are upfield in one type of tolyl group and the *ortho* protons are upfield in the other type. The average chemical shifts of all protons are thus equal and the spectrum eventually collapses to a broad single peak ($\delta_{av} = 699$ Hz at −5 °C).

‡ $^2J(P^1\text{–}P^2)$ must be very small (< 3Hz) in order to account for the observed simple spectrum, which is the M portion of an AA'MX spin system.

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