Intramolecular Methyl Migration in Dinuclear Rhodium Complexes

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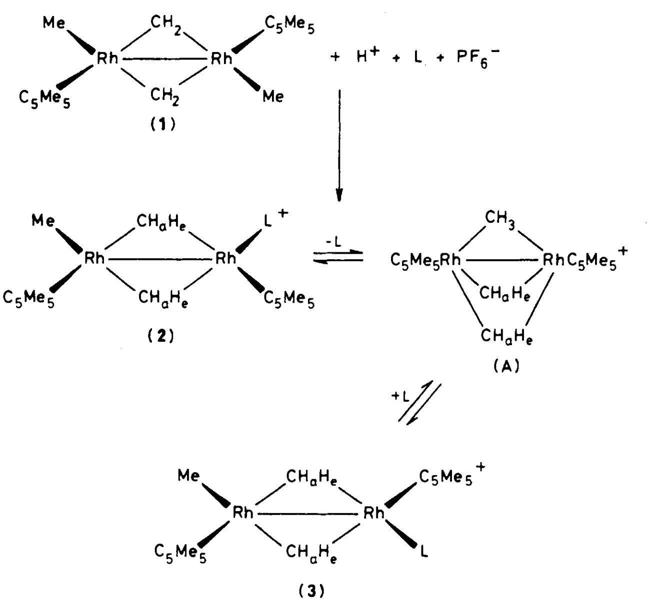
trans-[$(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2Me_2$] reacts with acid and L (MeCN, pyridine, *etc.*) to give *cis*- plus *trans*-[$(C_5Me_5RhL)(\mu\text{-}CH_2)_2(MeRhC_5Me_5)$][$PF_6$] which, at higher temperatures, equilibrate by a process which involves the methyl moving from one metal to the other.

Although a number of molecules containing methyl ligands bridging two d-block transition metals have been reported,[1] and although there are many examples of alkyl ligands migrating intermolecularly from one metal to another, much less is known about the migration of alkyl ligands between two metal atoms within a di- (or poly-)nuclear complex. We describe one such system.

Reaction of *trans*-dimethyl-di-μ-methylenebis(pentamethylcyclopentadienyl)rhodium (**1**)[2] with one equivalent of toluene-*p*-sulphonic acid in the presence of acetonitrile and potassium



a; L = MeCN
b; L = pyridine
c; L = 2-methylpyridine
d; L = CO

hexafluorophosphate yields the cationic monomethyl complex $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2Me(MeCN)]PF_6$.†

At −70 °C the ^{1}H n.m.r. spectrum of this salt shows two pairs of C_5Me_5 resonances and two pairs of CH_2 resonances as well as two Rh-bound methyl resonances, all in the ratio of 1:2.‡ These are assigned to the *cis*- and *trans*-isomers (**2a**) and (**3a**), respectively. Confirmation is provided by the −85 °C ^{13}C n.m.r. spectrum, in particular, the two pairs of doublets in the C_5Me_5 region (Figure 1). The smaller pair of doublets is assigned to the two different rings of the *cis*-isomer (**2a**) while the larger pair of doublets arise from the inequivalent rings of the *trans*-isomer (**3a**).

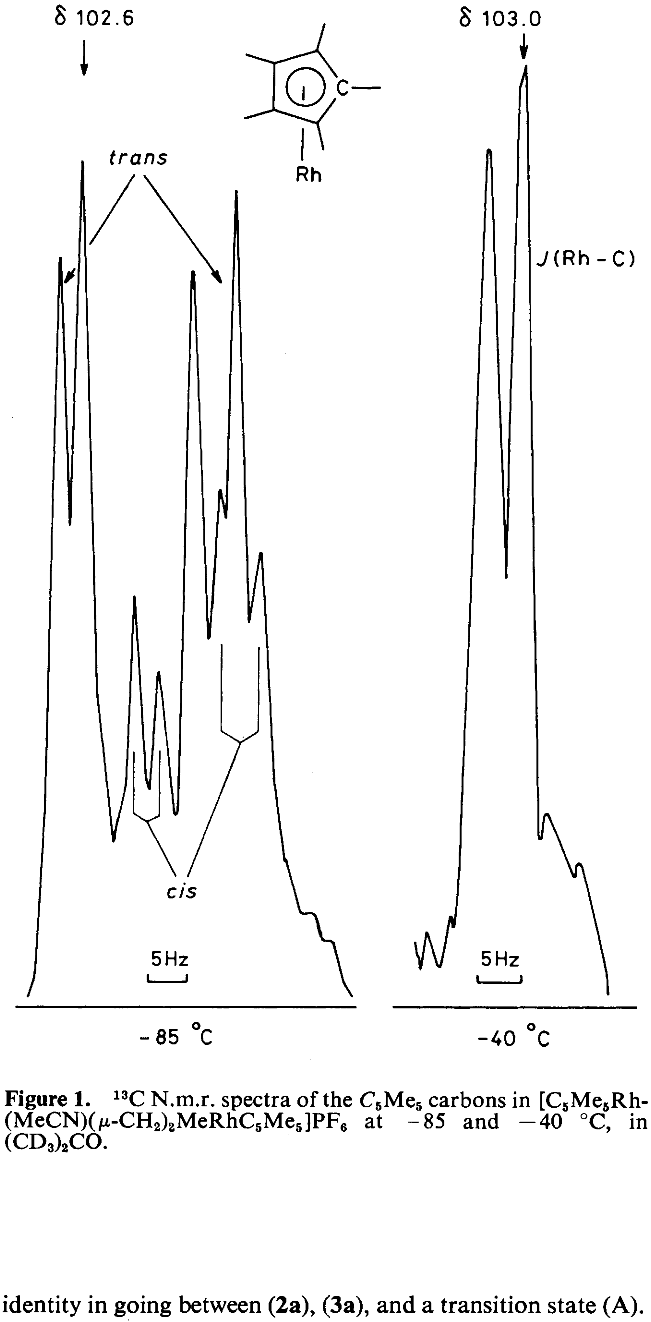


Figure 1. ^{13}C N.m.r. spectra of the C_5Me_5 carbons in $[C_5Me_5Rh(MeCN)(\mu\text{-}CH_2)_2MeRhC_5Me_5]PF_6$ at −85 and −40 °C, in $(CD_3)_2CO$.

At higher temperatures, the signals in the ^{1}H n.m.r. spectrum coalesce to give a greatly simplified spectrum for the resultant dynamic system, composed of rapidly equilibrating (**2a**) and (**3a**).§ The methyl–rhodium signal now appears as one triplet. This indicates that on the n.m.r. time-scale the methyl sees two rhodiums, the coupling to each of which is about half (1.5 Hz) of the value in (**2a**) or (**3a**), in both of which it appears as a doublet [*J*(Rh–H) 2.5 Hz]. The axial and equatorial hydrogens, H$_a$, H$_e$, on the methylene groups {assigned by comparison with those deduced for *cis*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2Me_2]$[2]} do *not* interconvert but retain their identity in going between (**2a**), (**3a**), and a transition state (A). This is again confirmed by the ^{13}C n.m.r. spectrum (Figure 1) which shows the presence of only one type of C_5Me_5 resonance (coupled to ^{103}Rh) at temperatures above −40 °C. The coalescence temperature (^{1}H n.m.r.) is independent of concentration and since the axial and equatorial hydrogens do not interconvert, the methyl transfer must be intramolecular.

A number of related complexes with other ligands (**2**/**3** **b**—**d**) have been prepared. The rate of methyl migration is retarded by better π-acceptor ligands, for example the complexes with L = pyridine or CO are static at ambient temperature. Steric factors are also significant, the bulkier ligands favouring the *cis*-form (**2**); thus the *cis*/*trans* ratios are 1:2 for L = MeCN, 2:3 for L = pyridine, and 1:1 for L = 2-methylpyridine. The *cis*/*trans* interconversion is slowed down by added L indicating that the rate-determining step is loss of co-ordinated L. As might be anticipated, bulkier L ligands (2-methylpyridine) dissociate more readily and hence give faster interconversions.

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† All new complexes gave satisfactory microanalytical and spectroscopic data.

‡ ^{1}H N.m.r. in $(CD_3)_2CO$ at −70 °C *cis*-(**2a**): δ −0.70 [d, *J*(Rh) 2.5 Hz, RhMe], 1.72, 1.73 (2 × s, C_5Me_5), 2.68 (s, MeCN), 8.59, 9.52 (2 × br., CH_2); *trans*-(**3a**): δ −0.22 [d, *J*(Rh) 2.3 Hz, RhMe], 1.78, 1.79 (2 × s, C_5Me_5), 2.58 (s, MeCN), 8.49, 8.94 (2 × br., CH_2). The isomers are assigned on the basis of the chemical shift differences of the μ-methylene protons; these are smaller than *ca.* 0.5 p.p.m. for the *trans*- and larger for the *cis*-isomers.

§ ^{1}H N.m.r. in $(CD_3)_2CO$ at +22 °C, δ −0.35 [t, *J*(Rh) 1.5 Hz, RhMe], 1.74 (s, C_5Me_5), 2.42 (s, MeCN), 8.67 [d, *J*(HH) 2 Hz, CH_2, H$_a$], 9.27 [dt, *J*(HH) = *J*(Rh) = 2 Hz, CH_2, H$_e$].

The monoethylmonoacetonitrile cation $[C_5Me_5Rh(Et)(\mu\text{-}CH_2)_2Rh(MeCN)(C_5Me_5)]PF_6$ has also been made. The ^1H n.m.r. spectra showed that the molecule was still dynamic in $(CD_3)_2CO$ down to −70 °C and in CD_3CN down to −40 °C; rather surprisingly, therefore, ethyl appears to migrate faster than methyl.

These results show that alkyl groups migrate readily between metal atoms, and that the rates are strongly influenced by other ligands present. Presumably related factors influence alkyl migration on metal surfaces.

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