# Monoalkyl-di-μ-methylene-bis[(η-pentamethylcyclopentadienyl)-rhodium(IV)] Complexes and the Intramolecular Migration of Alkyl Groups between Two Metal Atoms

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Reaction of the *trans* dimethyl complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ (1) with one equivalent of acid in the presence of acetonitrile gave the methyl–acetonitrile complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(MeCN)]PF_6$ (2a); the acetonitrile could be replaced by other ligands to give $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(L)]PF_6$ [L = Bu$^t$CN (2b), PhCN (2c), pyridine (2d), 2-methylpyridine (2e), or CO (2f)]. Reaction of (2a) with halide gave $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)X]$ [X = Cl (3) or I (4)]. The other monoalkyl complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(R)(MeCN)]PF_6$ [R = Et (9), Pr$^n$ (10), or Bu$^n$ (11)] were obtained analogously from reaction of the appropriate dialkyl complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R_2]$ which were in turn synthesised from the *trans* dichloro-complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Cl_2]$. The n.m.r. spectra of (2a) showed the presence of *cis* and *trans* isomers (ratio *ca.* 1 : 2) at −80 °C and of dynamic behaviour at higher temperatures. The dynamic behaviour arises from loss of the MeCN, movement of the methyl into a bridging position in a transition state, followed by readdition of the MeCN. Overall this corresponds to an intramolecular migration of the methyl from one rhodium to the other. The other complexes (2) behave similarly but (2d) and (2f) show the 'frozen-out' spectra even at +22 °C. Under identical conditions the complexes (9)—(11) exhibited similar behaviour to (2a), but the rates of alkyl migration were *ca.* 10 times faster. Complex (2a) also disproportionated to give (1) on reaction with base; this involves an intermolecular methyl migration. The other alkyl complexes did not undergo this reaction. The halide complexes (3) and (4) were rigid and of *cis* configuration in benzene but showed more complex behaviour in dichloromethane.

As part of our study of the chemistry of complexes derived from *trans*-dimethyl-di-μ-methylene-bis[(η-pentamethylcyclopentadienyl)rhodium(IV)] (1)[1] (and its *cis* isomer) we have recently reported on the complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2X_2]^{n+}$ that are obtained when both methyl groups have been cleaved off.[2] We now report on the asymmetric complexes of the type $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)X]^{n+}$ (where X is a neutral or an anionic ligand, and $n = 1$ or 0) that are formed when only one methyl is removed from (1), and on the related complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(R)(L)]^+$ (R = Et, Pr$^n$, or Bu$^n$). A Preliminary Communication on part of this work has been published.[3]

## Results and Discussion

*Syntheses.*—The most convenient entry into the monomethyl complexes was by reaction of the *trans* dimethyl complex (1) with one equivalent of *p*-toluenesulphonic acid in acetonitrile in the presence of $KPF_6$. This gave the methyl–acetonitrile salt (2a) as the hexafluorophosphate in over 90% yield (Scheme 1). The reaction proceeded rapidly and was complete within 15 min at −5 °C (see below). The other salts (2b)—(2e) were prepared, again in high yields (Table 1), by reaction of (2a) with the appropriate nitrile or pyridine. The methyl–carbonyl complex (2f) was obtained by stirring a solution of (2a) under CO [3.5 atm ($3.5 \times 10^5$ Pa) at 0 °C]; the alternative method, of treating (1) with one equivalent of *p*-toluenesulphonic acid under CO gave a much less easily purified product.

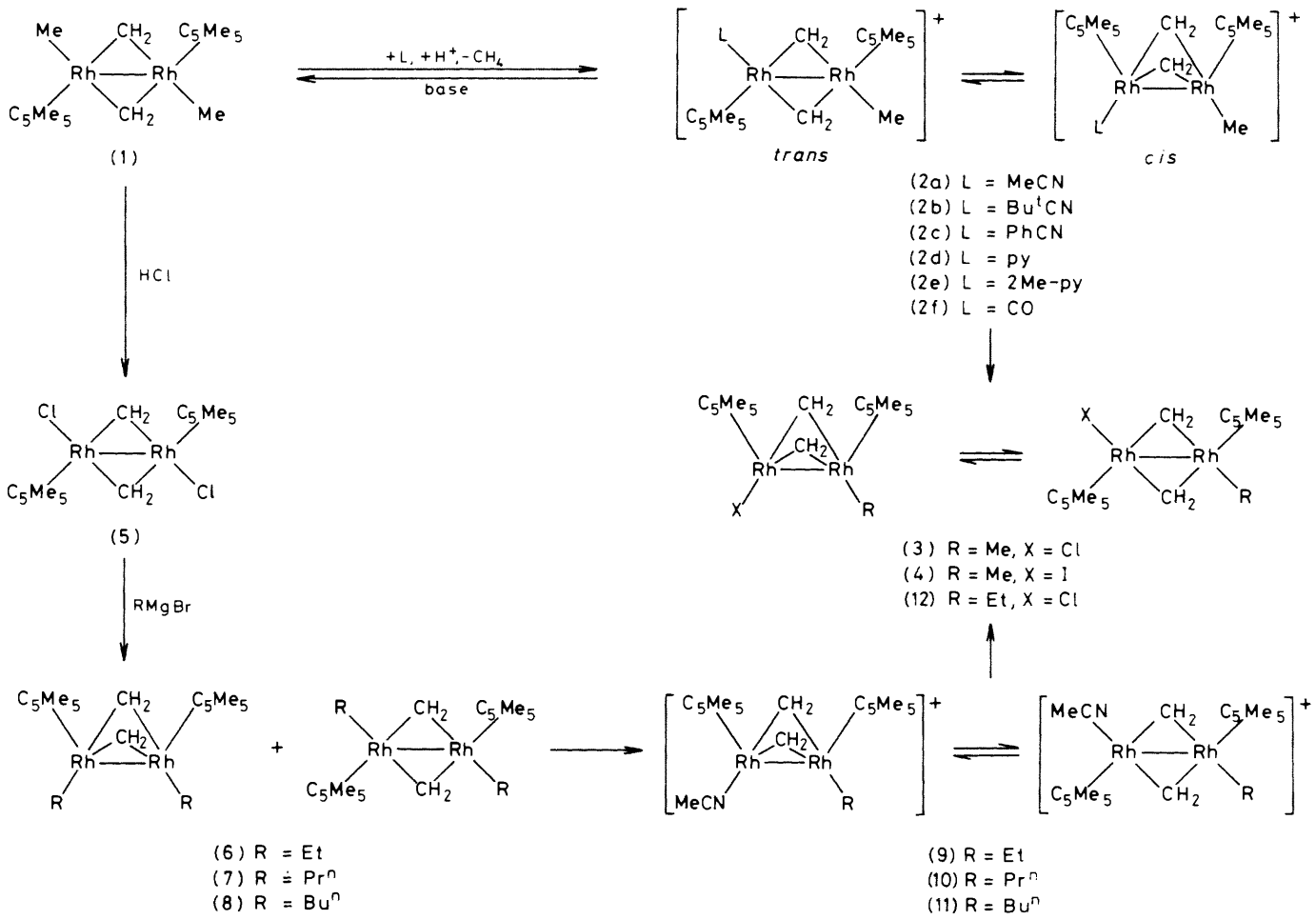
Reaction of (2a) with a suitable soluble halide salt (tetraphenylarsonium chloride or iodide) gave the neutral methyl–chloro- and methyl–iodo-complexes, (3) and (4), in reasonable yield.

The preparation of the diethyl complex (6) from the reaction of (1) with excess triethylaluminium has already been described.[1] It and the di-n-propyl and the di-n-butyl complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R_2]$ [R = Pr$^n$ (7) or Bu$^n$ (8)] were obtained in over 70% yield by the action of the alkylmagnesium bromide on the *trans*-dichloro-complex (5). Their $^1$H n.m.r. spectra, although complicated, were in good agreement with the complexes being a mixture of *cis* and *trans* isomers in a 2 : 1 ratio in each case. These isomers could be separated by high-performance liquid chromatography (h.p.l.c.). The $^{13}$C spectra supported the assignments. Although coupling of rhodium to the hydrogens of the α-$CH_2$ could not be detected, these α-carbon atoms showed a multiplet structure consistent with an AA′X spin system in which they are coupled inequivalently to both rhodium atoms.

By contrast, when the diethyl complex (6) was made by the triethylaluminium route, only the *trans* isomer could be detected. These results suggest that, as in the formation of (1),[1] the *cis* isomer is formed initially and that it then isomerises to the more thermodynamically stable *trans* isomer. This also agrees with our previous observation that powerful Lewis acids such as Al salts readily cause the isomerisation of the *cis* to the *trans* isomers while weaker ones, such as Li and now Mg salts, are much less powerful isomerisation catalysts.

The *trans* diethyl complex (6) gave the monoethyl–acetonitrile salt (9) by the route used to make (2a), and this could in turn be converted into the chloro–ethyl complex (12). [This chloro–ethyl and also the chloro–methyl complex (3) were formed, but in small quantity (detected by $^1$H n.m.r. spectroscopy) when chloroform solutions of the diethyl and dimethyl complexes, (6) and (1) respectively, were left at ambient temperature for extended periods.] It may be noted that the reaction of the diethyl complex (6) with acid to give (9) was quite significantly slower than that of (1) to give (2a). The dipropyl and dibutyl complexes (7) and (8), however, reacted with *p*-toluenesulphonic acid in the presence of acetonitrile to give (10) and (11) at rates more comparable to that of (1).

A rather remarkable and unusual reaction occurred when the methyl–acetonitrile cation (2a) was treated with base. Of those tried, triethylamine (in a variety of solvents) was the




**Scheme 1.**

most effective, and gave the product, the *trans* dimethyl complex, (1), in 45% yield, but diethylamine, 1,8-diazabicyclo-[5.4.0]undec-7-ene, *NNN'N'*-tetramethyl-1,4-diaminonaphthalene, as well as sodium carbonate in methanol were all active for the transformation. Further, when the methyl–acetonitrile complex (2a) was treated with triethylamine in hexadeuterioacetone and $D_2O$, no significant amount of deuterium could be detected in the rhodium methyls (or the methylenes) of the resultant complex (1) by n.m.r. spectroscopy. This result allows us to exclude a reaction mechanism in which the base reversibly removes a proton from the methyl group which is then transferred intermolecularly *via* a μ-methylene intermediate. Since the best reaction gave a 45% yield of (1), bearing two methyls, from (2a), which only has one, this actually corresponds to a 90% utilisation of the available methyls. The reaction did not proceed with the other alkyl–acetonitrile complexes (9)—(11).

The mechanism for this reaction is not clear but it may well occur in a bimolecular fashion *via* a transition state with the methyl bridging two rhodiums on different molecules. The role of a base such as triethylamine may then be to complex a site (in place of the acetonitrile); since this complexation would be very weak, the base could be replaced by the bridging methyl, leading to the transition state (Scheme 2). This intermolecular methyl transfer is then complementary to the intramolecular methyl transfer discussed in the next section.

Pyridine and substituted pyridines did not induce the disproportionation under ambient conditions but formed moderately stable complexes by displacement of the acetonitrile [*e.g.* (2d) or (2e)].

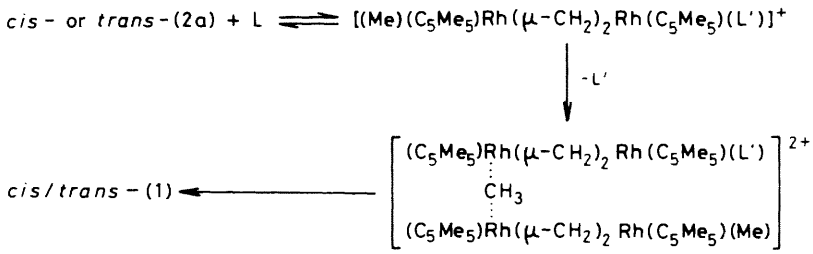
*N.M.R. Spectra of the Monoalkyl Complexes.*—Two geometric isomers, *cis* and *trans*, can exist for all the above complexes. Since neither of these is centrosymmetric for (2), (3), (4), and (9)—(12), four sets of $C_5Me_5$ resonances (two for each isomer) are expected. Further, although the two μ-$CH_2$ ligands will be equivalent to each other by virtue of the plane of symmetry through the two $(C_5Me_5)Rh$ groups and the Me and X (or L) substituents, within each methylene the hydrogens will be inequivalent (diastereotopic) for both the *cis* and the *trans* isomers. In practice this leads to considerable complexity in the $^1H$ n.m.r. spectra; at low temperatures both isomers are usually seen but at higher temperatures exchange processes occur. The $^{13}C$ n.m.r. spectra are significantly simpler and have been used to help define the systems. However, we have relied heavily on the rule-of-thumb that we developed for related systems;[2] namely, that for *trans* isomers the difference of chemical shift between the two methylene resonances in the $^1H$ spectra is less than about 0.5 p.p.m. while for the *cis* isomers it is usually larger than 0.5 p.p.m. This approach also works well for the complexes described here and has allowed us to estimate the relative amounts of *cis* and *trans* isomers for a number of the complexes.

The methyl–acetonitrile complex (2a) was chosen for a more

**Table 1.** Yields (%), microanalytical, and i.r. spectral data

| Complex | Colour (yield) | Microanalysis * (%) C | H | N | Other | I.r. ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|
| (2a) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(MeCN)]PF_6$ | Red | 41.8 | 5.4 | 2.4 | — | ν(CN) | 2 290w, 2 320vw |
| | (91) | (42.6) | (5.7) | (2.0) | | ν($PF_6$) | 845vs, 880s |
| (2b) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(Bu^tCN)]PF_6$ | Red | 45.6 | 6.3 | 2.1 | — | ν(CN) | 2 265vw |
| | (94) | (45.0) | (6.2) | (1.9) | | ν($PF_6$) | 845vs, 877s |
| (2c) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(PhCN)]PF_6$ | Red | 47.6 | 5.9 | 2.0 | — | ν(CN) | 2 260w |
| | (76) | (47.0) | (5.5) | (1.8) | | ν($PF_6$) | 845vs, br, 881m |
| (2d) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(py)]PF_6$ | Red | 45.3 | 5.7 | 2.3 | — | ν(CN,CC) | 1 600w, 1 604w |
| | (85) | (45.2) | (5.7) | (1.9) | | ν($PF_6$) | 845vs, br, 879m |
| (2e) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(2Me\text{-}py)]PF_6\cdot C_6H_6$ | Red | 50.3 | 5.9 | 1.6 | — | ν($PF_6$) | 840vs, 876s |
| | (87) | (50.3) | (6.0) | (1.7) | | | |
| (2f) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(CO)]PF_6$ | Brown | 40.2 | 5.0 | | | ν(CO) | 2 042vs, 2 059vs |
| | (76) | (41.6) | (5.4) | | | ν($PF_6$) | 840vs, br, 876s |
| (3) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)Cl]$ | Violet | 49.3 | 6.7 | | Cl, 7.1 | | |
| | | (49.8) | (6.7) | | (6.4) | | |
| (4) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)I]$ | Deep red | 43.5 | 6.0 | | I, 19.3 | | |
| | | (42.8) | (5.8) | | (19.6) | | |
| (7) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Pr^n_2]$ | Red | 56.4 | 8.1 | | | | |
| | (72) | (57.0) | (8.1) | | | | |
| (8) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Bu^n_2]$ | Red | 57.9 | 7.7 | | | | |
| | (74) | (58.3) | (8.4) | | | | |
| (9) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Et)(MeCN)]PF_6$ | Red | 42.6 | 5.7 | 2.0 | — | ν(CN) | 2 290vw |
| | | (43.4) | (5.9) | (2.0) | | ν($PF_6$) | 844vs, br, 878s |
| (10) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Pr^n)(MeCN)]PF_6$ | Red-brown | 42.8 | 5.9 | 1.6 | | ν(CN) | 2 250w |
| | (52) | (44.2) | (6.0) | (1.9) | | ν($PF_6$) | 835, 850 (sh), 870 (sh) |
| (11) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Bu^n)(MeCN)]PF_6$ | Bright red | 43.5 | 6.1 | 1.9 | | ν(CN) | 2 250w |
| | (58) | (45.0) | (6.1) | (1.9) | | ν($PF_6$) | 835, 850 (sh), 870 (sh) |
| (12) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Et)Cl]$ | Violet | 50.7 | 7.0 | — | Cl, 6.4 | | |
| | | (50.7) | (6.9) | | (6.2) | | |

* Calculated values are in parentheses.




**Scheme 2.**

detailed study. This showed (Table 2) a single $C_5Me_5$ resonance at δ 1.74, two methylene resonances (8.67, d, and 9.27, dt), a rhodium bound methyl resonance at −0.35, as well as a singlet at 2.42 (MeCN), when the spectrum was run at 22 °C in deuterioacetone. The Rh-methyl was observed as a *triplet*, due to an apparent equivalent coupling to two rhodiums, with $J$(Rh–H) = 1.5 Hz (Figure 1).

When the temperature was lowered all the resonances broadened and split; this was especially noticeable for the methylenes where the resonance at δ 9.27 gave rise to two, which appeared (at −80 °C) at 8.94 and 9.52, while that at 8.67 also split into two, at 8.49 and 8.59 (Figure 1). From their intensities, these were grouped into two, δ 8.59 and 9.52 (of intensity 1), assigned to the *cis* isomer and those at 8.49 and 8.94 (of intensity 2), assigned to the *trans* isomer, for the reasons discussed above. The $C_5Me_5$ resonance split, as expected, into four, grouped as two pairs of relative intensities 1 : 1 : 2 : 2 (at δ 1.72, 1.73, 1.78, and 1.79) and the Rh-methyl also split into two resonances that were now *doublets* at δ −0.22 and −0.70 [$J$(Rh–H) = 2.3 and 2.5 Hz], again with relative intensity ratio 2 : 1.

Not all the expected resonances could be observed in the $^{13}C$ n.m.r. spectra of (2a); since the complex was rather unstable in solution, especially above 0 °C, even in the presence of some acetonitrile, long accumulation times were not practicable. However, the resonances that were observed were most informative and reinforced the conclusions drawn from the proton spectra. At −85 °C in hexadeuterioacetone both the methyls and the ring carbons of the $C_5Me_5$ groups showed four resonances, singlets in the approximate ratio 1 : 1 : 2 : 2 for the methyls and doublets in about the same ratios for the ring carbons (Figure 2). The doublets arose from each resonance coupling to one rhodium with $J$ = 3 or 5 Hz for both the *cis* and *trans* isomers. (One may speculate that the larger coupling is associated with the rhodium that also bears the MeCN in each case, since this is probably the better σ donor, leading in turn to stronger metal–ring binding.) In addition resonances due to the Rh-methyl, the μ-methylene carbon, and to the acetonitrile of one isomer (presumably the more prevalent *trans* form) were clearly detectable.

On allowing the temperature to rise to −40 °C, the highest temperature practicable, all the $C_5Me_5$ methyl resonances

**Table 2.** $^1$H N.m.r. spectra (δ/p.p.m.) *

| Complex | $C_5Me_5$ | μ-$CH_2$ | Me | Other | Temp. (°C), solvent |
|---|---|---|---|---|---|
| (2a) | 1.74 | 8.67d (<2), 9.27dt (<2)[2] | −0.35t [1.5] | MeCN, 2.42 | +22, $(CD_3)_2CO$ |
| | 1.72, 1.73 | 8.59br, 9.52br | −0.70d [2.5] | MeCN, 2.68 | −80, $(CD_3)_2CO$ |
| | 1.78, 1.79 | 8.49br, 8.94br | −0.22d [2.3] | MeCN, 2.58 | |
| (2b) | 1.78 | 8.65d (1.5), 9.12dt (1.5) [2] | −0.24t [1.5] | Bu$^t$, 1.41 | +35, $(CD_3)_2CO$ |
| (2c) | 1.81 | 8.85 m, br, 9.37 m, br | −0.18t [1.5] | Ph, 7.75m | +35, $(CD_3)_2CO$ |
| (2d) | 1.60, 1.76 | 8.48br, 9.42br | −0.85br | | +22, $(CD_3)_2CO$ |
| | 1.40, 1.51 | 8.99br, 9.58br | −0.60d [3] | | |
| | 1.39, 1.60 | 8.24br, 9.12br | −0.91d [3] | | +22, $C_5D_5N$ |
| | 1.26, 1.32 | 8.77br, 9.34br | −0.68d [3] | | |
| (2e) | 1.52 | 8.80br, 9.52br | −0.62t [1] | | +35, $CH_2Cl_2$–2Me-py |
| | 1.50, 1.70 | 8.43br, 9.17br | −0.88br | | −50, $CD_2Cl_2$–2Me-py |
| | 1.34, 1.44 | 8.79br, 9.24br | −0.67br | | |
| (2f) | 1.78, 2.02 | 8.42dt (2) [3], 9.65dt (2) [3] | −0.36d [2] | | +22, $(CD_3)_2CO$ |
| | 1.81, 2.04 | 8.68t [2], 8.77m | −0.10d [2] | | |
| (3) | 1.39, 1.70 | 8.76dd (4) [2], 10.04ddd (4) [4,2] | −0.57d [3] | | +20, $C_6D_6$ |
| (4) | 1.55, 1.66 | 8.70m, 10.35m | −0.61d [3] | | +36, $C_6D_6$ |
| *cis*-(7) | 1.68 | 7.39d (1.5), 8.30dt (1.5) [2] | | Rh−$CH_2$−, 0.43br t (8); −$CH_2CH_3$, 1.23q of t, 0.73t (7.5) | +22, $CDCl_3$ |
| *trans*-(7) | 1.67 | 8.09t [1] | | Rh−$CH_2$−, −0.06br t (8.5); −$CH_2CH_3$, 1.08q of t, 0.72t (7.5) | +22, $CDCl_3$ |
| *cis*-(8) | 1.72 | 7.33d (2), 8.33dt (2) [2.5] | | Rh−$CH_2$, 0.51br, t (8.5); −$CH_2CH_2CH_3$, 1.23tt (7) 1.14q of t (7), 0.81t (7) | −22, $CDCl_3$ |
| *trans*-(8) | 1.67 | 8.12 [1] | | Rh−$CH_2$, −0.06br t (8.5); −$CH_2CH_2CH_3$, 0.80t (7), 1.06m | +22, $CDCl_3$ |
| (9) | 1.75 | 8.64br, 9.36br | | $RhCH_2$, 0.41q (7) [<2]; $RhCH_2CH_3$, 0.88t (7) | +35 to −70, $(CD_3)_2CO$ |
| (10) | 1.68 | 8.76d (2), 9.39dt (2) [2] | | $RhCH_2$,0.31m (8) [1.5];−$CH_2$−, 1.20m; −$CH_3$, 0.78t (7) | +22, $CDCl_2$ |
| (11) | 1.75 | 8.81d (2), 9.49dt (2) [1.5] | | $RhCH_2$, 0.37m (8.5); −$CH_2CH_2$−, 1.15m, 1.24m; −$CH_3$, 0.84t (7.5) | +22, $(CD_3)_2CO$ |
| (12) | 1.46, 1.79 | 8.86m, 10.14dt (3) [3,2] | | $RhCH_2$, 0.32dq (7) [3]; $RhCH_2CH_3$, 1.07t (7) | +36, $C_6D_6$ |

* $J$(H−H)/Hz values are in parentheses and $J$(Rh−H)/Hz in square brackets.

collapsed to a singlet and all the $C_5Me_5$-ring carbon resonances collapsed to one doublet [$J$(Rh−C) *ca.* 5 Hz]. This result shows again that on the n.m.r. time-scale a dynamic process occurs which has the effect of equilibrating all the $C_5Me_5$ resonances. It was further shown, by measuring the linewidth of the $^1$H methylene resonance at −49 °C and just below coalescence at −38 °C, that the line-broadening was independent of concentration when the concentration was changed by a factor of ten. This indicates that the dynamic process is an intramolecular one. From the variation with temperature of the proton resonances of the μ-methylene groups we can also say that although the *cis* and *trans* isomers interconvert, the two hydrogens on each $CH_2$ ($H_{ax}$ and $H_{eq}$[1]) do not interconvert but retain their identity. If they were exchanging with each other, only one resonance for the $CH_2$ hydrogens (a triplet, due to coupling to two Rh atoms) would be expected. This means that no Rh−μ-$CH_2$ bonds are broken during the rearrangement; further, since the $C_5Me_5$ resonances retain their coupling to Rh in the $^{13}$C spectrum at −40 °C, the $C_5Me_5$−Rh bonds are also not broken. Since the methyl and methylene hydrogens retain their identity and do not exchange with each other this also implies thatno C−H bonds are broken or formed during the dynamic process.

These data are consistent with a bending or flapping motion of the $\{(C_5Me_5)Rh\}_2(CH_2)_2$ skeleton taking place during the exchange process. The simplest explanation is that the ligand MeCN comes off *trans*-(2a) and the methyl then bridges across to join the two metals in a transition state (A); readdition of MeCN to the same rhodium and the same side from which it departed regenerates the original isomer, *trans*-(2a). Addition of the MeCN to the other side of that rhodium gives the other isomer, *cis*-(2a), and accounts for the equilibration between *cis* and *trans* that is observed (Scheme 3) (clearly, addition of the MeCN to the other rhodium generates the same two species). This scheme also accounts for the rhodium methyl being seen, at −22 °C, as a *triplet* with a coupling to rhodium of *ca.* half that observed for each of the methyl *doublets* at −80 °C, in the $^1$H n.m.r. spectra.

The rates of equilibration (and also the stability of the complex) are very dependent on the amount of extra MeCN added to the solution, the complex being stabilised and the rate decreased when more is added. This indicates that loss of MeCN from *trans*- or *cis*-(2a) is rate limiting. In view of the complications which this introduces, no determinations of rates, other than very qualitative ones, have been attempted.

Even at 400 MHz the $^1$H n.m.r. spectra of the ethyl-, propyl-, and butyl-acetonitrile complexes (9), (10), and (11) were too complex for detailed analysis at low temperature. However it was clear that at −80 °C *cis* and *trans* isomers were again present and that they equilibrated in the same manner as (2a) at higher temperatures. Spectra recorded under identical conditions [0.015 mmol complex (2a), (9), (10), or (11)] in hexadeuterioacetone (0.5 $cm^3$) containing $CD_3CN$ (0.3 mmol) were examined in the bridged methylene region (δ 8—10) at different temperatures (−80 to −50 °C). They showed that the methyl complex (2a) coalesced more slowly

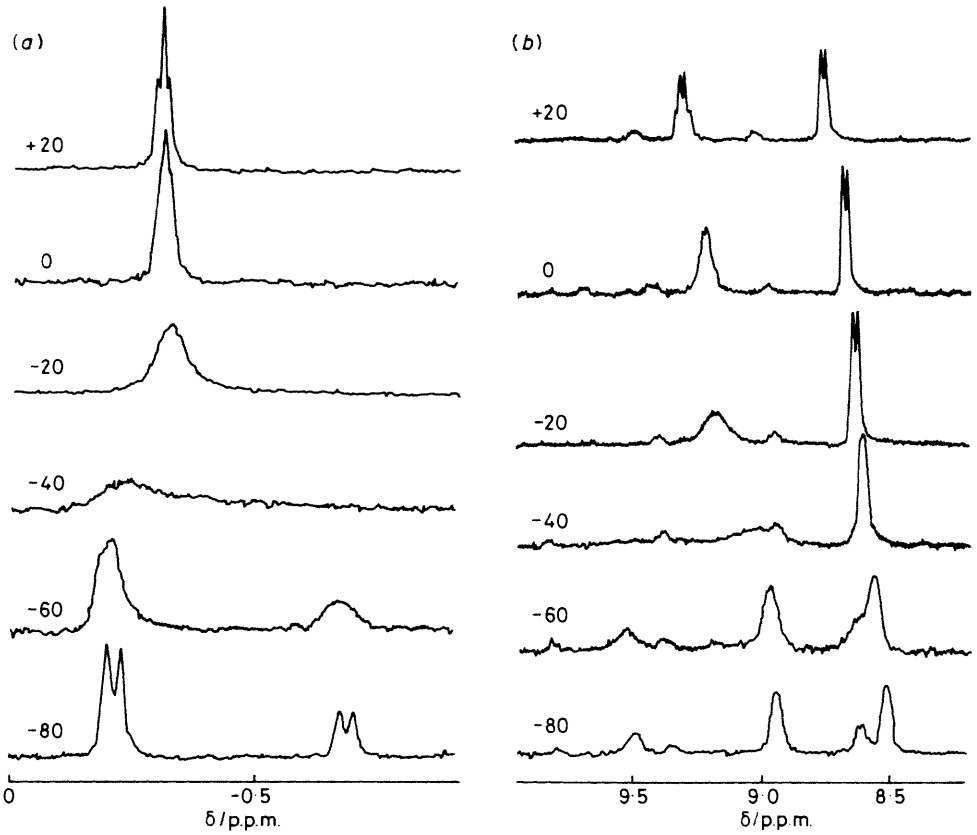



**Figure 1.** Variable-temperature (°C) $^1$H n.m.r. spectra (100 MHz) of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(MeCN)]^+$ (2a) in $(CD_3)_2CO$–$CD_3CN$: (*a*) Rh–Me region (high field) and (*b*) $Rh(\mu\text{-}CH_2)_2Rh$ region (low field)

(by a factor of *ca.* 10) than the alkyl cations (9)—(11). The fact that other alkyl groups also migrate, and faster than methyl, is at first surprising. However, we suggest that this is because the bulk of ethyl, propyl, or butyl is bigger than that of methyl; this makes the MeCN more labile in the higher alkyl complexes than in the methyl complex (2a).

The ambient-temperature $^{13}C$-{$^1$H} spectra were much simpler and showed a *triplet* ($J$ = 15 Hz) at δ 13.6 for (9), 23.5 for (10), or 20.7 for (11) arising from the coupling of the α-$CH_2$ of the alkyl chain to two rhodiums, equivalent on the n.m.r. time-scale. [For comparison, $J$(Rh–C) for a terminal methyl is usually *ca.* 30—35 Hz.] The ambient-temperature $^1$H spectrum of the n-propyl complex was sufficiently clear to show that the β-$CH_2$ is diastereotopic. Since this would not have been expected if there had been free rotation about the C–C bonds of the alkyl chain, it implies severe restriction to rotation, and supports the proposal that there is substantial steric crowding in the transition state for the higher alkyl cations.

Overall then, in the processes described, the alkyl group moves between the two rhodiums. Although there are many examples of alkyl transfer both inter- and intra-molecularly in compounds of the main group elements,[4] rather fewer examples are known among transition metal complexes and these all seem to be intermolecular.[5] There appear to have been no prior reports of alkyl migration from one transition metal atom to another within a di- or poly-nuclear cluster. On the other hand, a number of transition metal complexes are known in which the methyl bridges two metal atoms in a stable ground state;[6] some of these have been very carefully characterised, and shown to have M–H–C bridges. We have no evidence whether such a form of bonding plays a part in either the transition state (A), or the paths leading to or from it, for the present complexes. It would, however, seem logical for it to do so since this would imply that the movement involves Rh–C–H–Rh (or possibly even Rh–H–C–H–Rh) which would be expected to be energetically more favourable, since smaller movements of nuclei are required, than one in which the only transition state was one of the type Rh–C–Rh, and the methyl hydrogens were not involved at all. The process described here also offers a homogeneous model for alkyl migrations on metal surfaces.[7] Such situations must arise very frequently on surfaces during catalytic reactions; for example, during hydrocarbon cracking or Fischer–Tropsch processes.

This picture is also consistent with the intermolecular migration of methyl involved in the base-promoted reaction of (2a) to give (1) and, in view of the larger bulk of the higher alkyls, with their failure to undergo that migration.

The complexes (2b)—(2f) behaved rather similarly to (2a), and were therefore only examined briefly. The two other nitrile complexes, (2b) and (2c), showed the same pattern of resonances as (2a) in the $^1$H n.m.r. at ambient temperature, corresponding to the high-temperature limit of the migration.

However, the pyridine complex (2d) was both more stable than (2a) (*e.g.* in acetone solution) and less dynamic; for example, the $^1$H n.m.r. spectrum in hexadeuterioacetone even at +22 °C showed four $C_5Me_5$ and two Me–Rh signals, indicating that any migration of methyl was very slow on the n.m.r. time scale. Broadening of the signals was observed on heating the acetone solution to 56 °C or on heating a pentadeuteriopyridine solution of (2d) to 100 °C. Clearer evidence for dynamic behaviour came from the sharp $C_5Me_5$ singlet observed in the $^{13}C$ spectrum at +83 °C in $C_5D_5N$, just below the decomposition point.

By contrast, but not surprisingly in view of the greater bulk

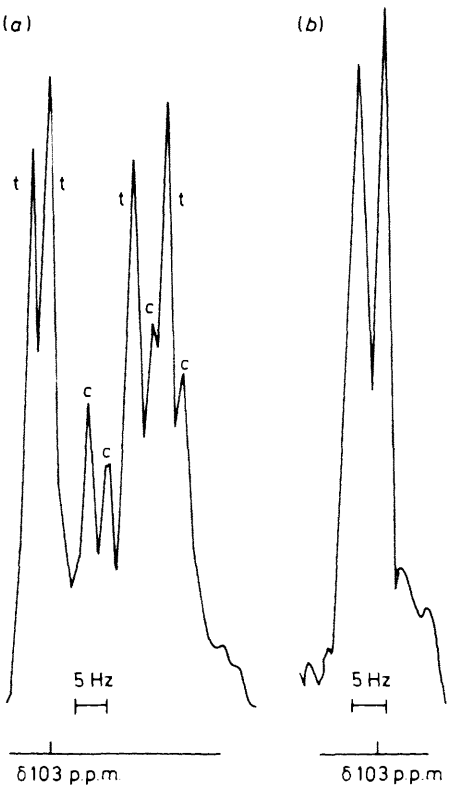


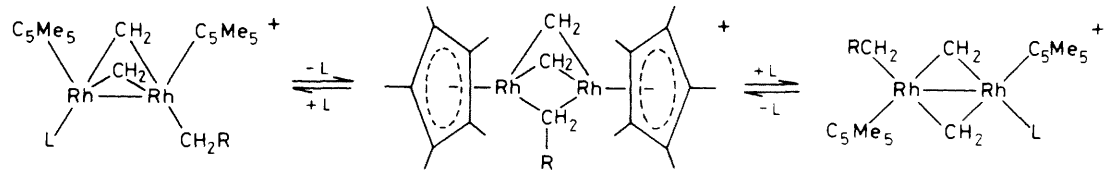

**Figure 2.** Variable-temperature (°C) $^{13}C$ n.m.r. spectra (25 MHz) of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Me)(MeCN)]^+$ (2a) in $(CD_3)_2CO$: $C_5Me_5$ region (*a*) at −85 °C and (*b*) at −40 °C; c, doublets [*J*(Rh C)] due to *cis* isomer; t, doublets due to *trans* isomer

in the site available here, more so than nitriles (RCN). This could be due in part to a small steric effect, but we feel that the π-acid properties of the ligand must also be important since this would also account for the greater difficulty that methyl has in migrating in the pyridine complex (2d).

These conclusions are reinforced by the i.r. spectrum of (2f) which shows two carbonyl stretches (2 042 and 2·059 $cm^{-1}$, corresponding to the two isomers), the frequencies of which suggest that substantial back-bonding from the metal onto CO is occurring. Although the carbonyl complex (2f) is stable enough to be isolated, it slowly decomposes in solution over *ca.* 2 h at ambient temperature.

The neutral asymmetric methyl–chloro- (3), methyl–iodo- (4), and ethyl–chloro-complexes (12) also gave unusual n.m.r. spectra. The proton spectrum of (3) in deuteriobenzene at 20 °C indicated the complex to be present as a single static *cis* isomer. This was clear from an analysis of the chemical shifts and couplings of the μ-methylene protons. The higher field resonance, which we assign to $H_{ax}$, is a double doublet. One of these doublets arises from the geminal H–H coupling [*J*(H–H) = 2 Hz] while the other arises from coupling to only one of the two rhodiums, *J*(Rh–H) = 2 Hz. The lower field resonance, assigned to $H_{eq}$, consists of three doublets, one again being assigned to the geminal *J*(H–H). The two others are due to coupling to two different rhodiums [*J*(Rh–H) = 2 and 4 Hz]. This illustrates yet again how very dependent is $^3J$(Rh–H) on the geometry, in other words on the size of the angle Rh–C–H, since this is presumably quite different for the two different rhodiums. A very similar pattern was clearly observed for the ethyl–chloro-complex in the higher field methylene resonance which showed one geminal coupling (3 Hz) and two $^3J$(Rh–H) couplings of 2 and 3 Hz respectively.

However, even in only slightly more polar solvents such as deuteriodichloromethane, much more complex behaviour was




*cis* -(2a) R = H
*cis* -(9) R = Me
*cis* -(10) R = Et
*cis* -(11) R = $Pr^n$

*trans* -(2a) R = H
*trans* -(9) R = Me
*trans* -(10) R = Et
*trans* -(11) R = $Pr^n$

**Scheme 3.**

of the ligand, the α-picoline (2-methylpyridine, 2Me-py) complex (2e) is much less stable and much more dynamic than the pyridine complex (2d). For example, the $^1H$ n.m.r. spectrum in dichloromethane (containing some picoline to minimise decomposition) showed fully dynamic behaviour even at +35 °C. At −50 °C it exhibited the spectrum characteristic of the mixture of *cis* and *trans* isomers. For both this complex and the pyridine complex (2d) we estimate the *trans*–*cis* ratio to be about 2 : 1. The $^{13}C$ n.m.r. spectra of both (2d) and (2e) confirmed the conclusions, even though that of (2e) was complicated due to decomposition products which formed during the time needed to accumulate the spectra.

The $^1H$ n.m.r. spectrum of the methyl–carbonyl complex (2f) at +22 °C showed the presence of both *cis* and *trans* isomers (through the *trans* form predominated in a freshly made up solution) and any dynamic process was very slow. We take this to imply that CO binds rather strongly to rhodium observed, which probably arises from the ability of the solvent to ionise the halide, thus permitting methyl migration again to occur. For example, the methyl–chloro-complex (3) at −70 °C showed the presence of both *cis* and *trans* isomers (ratio 2 : 1) as indicated by the μ-methylene resonances at δ 8.67 and 9.75 (*cis*) and 8.62 and 9.06 (*trans*). At higher temperatures broadening was observed, indicating the onset of coalescence.

## Experimental

All reactions were carried out under nitrogen even though not all the complexes were appreciably air-sensitive. Typical preparations are given below; yields, microanalyses* (carried out by the University of Sheffield Microanalytical Unit), and

* Some of the complexes showed unexpectedly poor analytical data; we suspect difficulties in combustion as the cause since all the other properties agree with the postulated structures. See also ref 2.

**Table 3.** $^{13}C$-{$^1H$} N.m.r. spectra (δ/p.p.m.) [a]

| Complex | $C_5Me_5$ | $C_5Me_5$ | μ-$CH_2$ | Alkyl group C[1] | C[2] | C[3] | C[4] | Temp. (°C), solvent |
|---|---|---|---|---|---|---|---|---|
| (2a) | 9.6 | 103.0d [5] | n.o. | n.o. | | | | −40, $(CD_3)_2CO$ [b] |
| | 9.2 | 102.2d [5] | | | | | | −85, $(CD_3)_2CO$ [c] |
| | 9.6 | 102.7d [3] | | | | | | |
| | 9.3 | 102.3d [5] | 168.4t [26] | 5.9d [34] | | | | |
| | 9.6 | 103.1d [3] | | | | | | |
| (2d) | 9.1 | 103.2d [3] | 174.2t [28] | n.o. | | | | +22, $C_5D_5N$ |
| | 9.8 | 101.9d [5] | | | | | | |
| | 8.9 | 101.9d [5] | 177.2t [27] | 6.1t [31] | | | | |
| | 9.6 | 103.0d [3] | | | | | | |
| (2e) | 8.3 | 100.9d [5] | n.o. | 1.1d [34] [d] | | | | −60, $CD_2Cl_2$ |
| | 9.5 | 102.4 | | 3.9d [33] | | | | |
| | 8.8 | 100.8 | n.o. | 5.8d [32] | | | | |
| | 9.0 | 102.4 | | | | | | |
| *cis*-(7) | 9.8 | 100.7 | 161.1t [31] | 20.0m | 19.0 | 26.0 | | +22, $CDCl_3$ |
| *trans*-(7) | 9.8 | 101.0 | 163.1t [33] | 17.3m | 18.6 | 26.3 | | |
| *cis*-(8) | 9.8 | 101.0 | 163.2t [31] | 14.2m | 27.5 | 35.8 | 14.1 [e] | |
| *trans*-(8) | 10.1 | 100.8 | 161.1t [30] | 17.2m | 27.8 | 35.5 | 14.0 [e] | |
| (9) | 9.9 | 103.6d [5] | 176.4t [28] | 13.6t [15] | 17.8 | | | +20, $CD_3CN$ |
| (10) | 9.8 | 103.5d [4] | 176.0t [28] | 23.5t [15] | 26.9 | 19.0 | | +22, $(CD_3)_2CO$ |
| (11) | 9.8 | 103.6d [5] | 176.0t [28] | 20.7t [15] | 28.2 | 36.3 | 14.2 [e] | |

[a] $J$(Rh−C) values are in square brackets. n.o. = not observed. [b] MeCN, δ 3.3 p.p.m. [c] MeCN, δ 3.2 and 126.4 p.p.m. [d] This resonance may be due to a decomposition product. [e] Assignments of the alkyl carbons not certain.

i.r. data are collected in Table 1; $^1H$ and $^{13}C$ n.m.r. data are given in Tables 2 and 3. $^1H$ N.m.r. spectra were run at 60 (PE R-12B), 220 (PE R-34), and 400 MHz (Bruker WH-400); 100-MHz $^1H$ and 25-MHz $^{13}C$ n.m.r. spectra were run on a JEOL PFT-100 and 100-MHz $^{13}C$ spectra on the Bruker WH-400 spectrometer.

[{$(C_5Me_5)Rh$}$_2$(μ-$CH_2$)$_2$(Me)(MeCN)]$PF_6$ (2a).—A solution of *p*-toluenesulphonic acid monohydrate (0.38 g, 2 mmol) in acetonitrile (4 $cm^3$) was added dropwise to a vigorously stirred solution of the dimethyl complex (1) (1 g, 1.9 mmol) in dichloromethane (10 $cm^3$) at 0 °C containing a suspension of finely ground $KPF_6$ (0.42 g, 2.3 mmol). The suspension was stirred a further 15 min, the residue was filtered off and washed with more acetonitrile (1 $cm^3$). Diethyl ether (100 $cm^3$) was then slowly added to the combined red filtrates to give thin red plates of complex (2a) (total yield, 1.2 g, 91%). The complex was soluble, but very unstable, in solvents of moderate polarity (acetone, dichloromethane, *etc.*); it was more stable in acetonitrile but even such solutions decomposed slowly.

When triethylamine (0.1 $cm^3$) was added to a suspension of (2a) (87 mg, 0.12 mmol) in methanol (0.5 $cm^3$) the suspension and the solution darkened and a red precipitate slowly formed; this was filtered off, washed and dried and shown to contain a 10 : 1 mixture of (1) and its *cis* isomer (yield 30 mg, 45%) by n.m.r. spectroscopy.

[{$(C_5Me_5)Rh$}$_2$(μ-$CH_2$)$_2$(Me)(py)]$PF_6$ (2d).—Complex (2a) (35 mg) was dissolved in a solution of pyridine (py) (0.05 $cm^3$) in dichloromethane (0.03 $cm^3$) and the solution allowed to stand (30 min at 20 °C). Diethyl ether (2 $cm^3$) was added and the resultant suspension slowly produced red plates of complex (2d) (22 mg, 60%).

[{$(C_5Me_5)Rh$}$_2$(μ-$CH_2$)$_2$(Me)(CO)]$PF_6$ (2f).—A solution of complex (2a) (0.5 g, 0.7 mmol) in acetone (3 $cm^3$) at 0 °C saturated with CO was stirred under an atmosphere of CO [3.5 atm (3.5 × $10^{-5}$ Pa), 5 min, 0 °C]. The pressure was then released and diethyl ether (50 $cm^3$) was added to the solution. This slowly produced brown plates of complex (2f) (0.43 g, 87%).

[{$(C_5Me_5)Rh$}$_2$(μ-$CH_2$)$_2$(Me)Cl] (3).—A solution of tetraphenylarsonium chloride (0.2 g, 0.5 mmol) in acetonitrile (5 $cm^3$) was added to a vigorously stirred solution of complex (2a) (0.35 g, 0.5 mmol) in acetonitrile (3 $cm^3$). After a few minutes the solution deposited a dark violet crystalline complex, which was filtered off and recrystallised from benzene–hexane to give violet crystals of (3) (0.17 g, 61%). Occasionally the product from this reaction contained some (1) and (5), formed by a disproportionation, and from which it was not possible to purify (3). The ethyl–chloro-complex (12) did not show this behaviour.

[{$(C_5Me_5)Rh$}$_2$(μ-$CH_2$)$_2$$Pr^n_2$] (7).—A solution of n-propylmagnesium bromide in diethyl ether (5 mmol in 5 $cm^3$) was added slowly by syringe to a toluene solution of [{$(C_5Me_5)Rh$}$_2$(μ-$CH_2$)$_2$$Cl_2$] (5) (0.4 g, 0.7 mmol). The colour lightened from the deep wine-red of (5) to a light, brighter red. The solution was stirred a further 15 min; acetone (2 $cm^3$) was added to neutralise the excess Grignard reagent giving a white precipitate. All the solvent was then removed *in vacuo* and the residue was extracted with diethyl ether (3 × 30 $cm^3$); removal of the solvent followed by addition of cold methanol (5 $cm^3$) gave red crystals of (7) (0.3 g, 72%). Integration of the $^1H$ n.m.r. spectrum showed the presence of *cis* and *trans* isomers in the ratio 2 : 1. When the mixture of isomers was dissolved in dichloromethane and chromatographed using a Z module reversed-phase h.p.l.c. $C_{18}$ column (Waters system) and eluted with 100% methanol (flow rate 4 $cm^3$ $min^{-1}$), a clean separation was obtained: retention times, *cis* 3.5 min, *trans* 4.5 min.

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