Synthesis and Crystal Structures of *cis*- and *trans*-Dimethyl-di-μ-methylene-bis(pentamethylcyclopentadienyl)dirhodium(IV) †

Kiyoshi Isobe, Amelio Vázquez de Miguel, Pamela M. Bailey, Seichi Okeya, and Peter M. Maitlis *
Department of Chemistry, The University, Sheffield S3 7HF

Reaction of $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$ (1) with Li_4Me_4 or Al_2Me_6 gives, after air-oxidation, *cis*- or *trans*-$[\{Rh(C_5Me_5)Me\}_2(\mu\text{-}CH_2)_2]$ [(2a) (28%) and (2b) (15%) respectively] which are formally of Rh^{IV}. The structures were elucidated spectroscopically and were confirmed by a single-crystal *X*-ray determination of the *cis* isomer (2a). This showed a dinuclear complex with each rhodium bound to one methyl and one η^5-C_5Me_5, and with two bridging methylenes about a rhodium–rhodium bond [2.620(1) Å]. The two hydrogens on each methylene bridge are inequivalent as can be seen from the ^1H n.m.r. spectrum. Nuclear Overhauser effect experiments, interpreted in the light of the *X*-ray structure, showed that it was only the equatorial hydrogen which was coupled to the rhodiums. The *cis* isomer (2a) was converted into *trans*-(2b) on reaction with Lewis acids (*e.g.* Al_2Me_6); (2b) also reacted with Al_2Et_6 to give *trans*-$[\{Rh(C_5Me_5)Et\}_2(\mu\text{-}CH_2)_2]$ suggesting a common pathway for substitution and isomerisation. When the yellow solution obtained by reaction of (1) and Al_2Me_6 in hydrocarbons was reacted with acetone at −78 °C the *cis* isomer (2a) was obtained in good yield; if the reaction was carried out at higher temperature the *trans* isomer (2b) was isolated in 89% yield. The results of experiments when perdeuterio-(1) was reacted with Al_2Me_6 and the reactions quenched (*a*) with air and (*b*) with acetone are discussed.

There is considerable interest in the chemistry of complexes in which two metal atoms are linked by one or more bridging methylene groups. One reason is because of their relation to heterogeneous Fischer–Tropsch reactions, one proposed mechanism for which involves the formation and polymerisation of methylenes bridging surface metal atoms.[1,2] While a large and varied number of such complexes are now known and have been extensively reviewed,[3] the two complexes *cis*-$[\{Rh(C_5Me_5)Me\}_2(\mu\text{-}CH_2)_2]$ (2a) and *trans*-$[\{Rh(C_5Me_5)Me\}_2(\mu\text{-}CH_2)_2]$ (2b) described in this paper[4] are representative of a most unusual type and their synthesis poses an interesting mechanistic problem.

The complexes were first isolated during an examination of the reaction of methyl-lithium or hexamethyldialuminium with the dimeric complex, $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$ (1), whose chemistry and related complexes have been reviewed.[5] These reactions seemed likely to yield novel results as the immediate product, '$Rh(C_5Me_5)Me_2$', is co-ordinatively unsaturated and would have either to dimerise or, more probably, to undergo hydrogen migration in order to arrive at a stable structure. Such reactions have been extensively studied amongst complexes of the lighter transition metals[6] but, with some notable exceptions,[7] are less common amongst Group 8 metal complexes.

Results and Discussion

Characterisation of cis-(2a) *and* trans-(2b).—Initial experiments were carried out by reacting the dimeric rhodium chloride complex (1) with methyl-lithium in diethyl ether–benzene or Al_2Me_6 in benzene. It was observed that the characteristic red colour of *cis*-(2a) or *trans*-(2b) developed only on exposing the reactant solution to air. Reaction with methyl-lithium gave the *cis* complex (2a) as the main hydrocarbon-soluble product after removal of solvent and of lithium compounds. With care, yields of (2a) as high as 28%, after crystallisation, could consistently be obtained.

The reaction with Al_2Me_6 was carried out similarly, but gave only *ca.* 15% yield of the *trans* isomer (2b). The reason for the difference in reaction became apparent when it was discovered that *cis*-(2a) was isomerised to *trans*-(2b) by a variety of Lewis acids. As indicated below, the initial product is the *cis* isomer which is then isomerised by the aluminium compounds in a subsequent step. Lithium compounds, being poorer Lewis acids, do not promote the isomerisation and hence the *cis* isomer is isolated.

The complexes were characterised initially by microanalysis, mass spectrometry, and n.m.r. spectroscopy; subsequently the proposed structures were confirmed by single-crystal *X*-ray studies.

The ^{13}C-$\{^1H\}$ n.m.r. spectra of (2a) and (2b) were very similar and consisted of four signals; two were due to the C_5Me_5 rings (δ 9.7 and 100.0), the third one was at lower field [δ 156.0 for (2a) and 161.5 for (2b)] and the fourth at higher field [δ −0.4 for (2a) and −4.0 for (2b)], the high-field signal in both cases was a doublet due to coupling to ^{103}Rh (100%, $I = \frac{1}{2}$) and arose from a methyl bound to one rhodium. The low-field resonance was a triplet, arising from coupling to two rhodiums, and, by analogy to related systems,[8] it is assigned to bridging methylenes.

The ^1H n.m.r. spectrum of *trans*-(2b) showed a C_5Me_5 resonance at δ 1.70 and a terminal methyl at −0.87; both had the form of a triplet arising from 'virtual coupling' to both rhodiums (N[9] = 0.6 and 3.0 Hz respectively). In addition, it showed another triplet at δ 8.03, coupled normally to two rhodiums, J = 1.8 Hz.

The ^1H n.m.r. spectrum of *cis*-(2a) was very similar in the higher-field region [δ 1.70 (t, C_5Me_5, N[9] = 0.6 Hz) and −0.46 (t, Me, N = 2.4 Hz)]. However at low field it showed two resonances, one a doublet at δ 6.96 (J = 1.8 Hz), and the other a doublet of triplets at 8.10 (J = 1.8 and 2.6 Hz).

The *cis* complex (2a) still retains planes of symmetry through (*i*) the two methylene carbons and the midpoint of the Rh–Rh bond, and (*ii*) the two metal atoms, the methyls and the midpoints of the C_5Me_5 rings, but it lacks the centre

---

† *Supplementary data available* (No. SUP 23618, 47 pp.): structure factors, thermal parameters, full bond distances and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

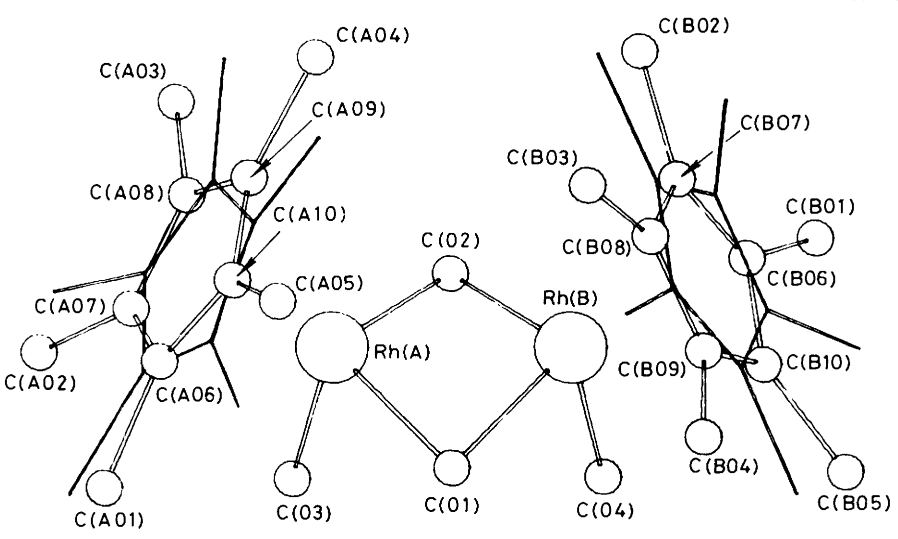
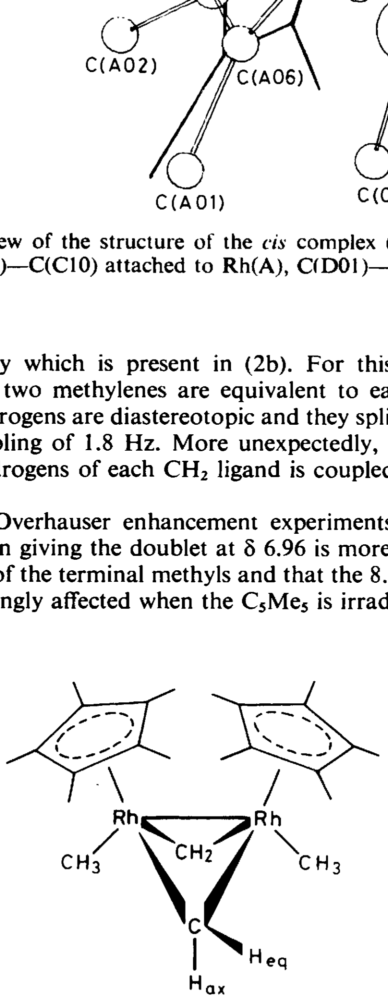


Figure. A view of the structure of the *cis* complex (2a). Hydrogens are omitted for clarity; outlines show the lower population C_5Me_5 rings [C(C01)—C(C10) attached to Rh(A), C(D01)—C(D10) attached to Rh(B)] and indicate the nature of the disorder found

of symmetry which is present in (2b). For this reason although the two methylenes are equivalent to each other in (2a) the hydrogens are diastereotopic and they split each other with a coupling of 1.8 Hz. More unexpectedly, only one of the two hydrogens of each CH_2 ligand is coupled to the two rhodiums.

Nuclear Overhauser enhancement experiments show that the hydrogen giving the doublet at δ 6.96 is more affected by irradiation of the terminal methyls and that the 8.10 multiplet is more strongly affected when the C_5Me_5 is irradiated.

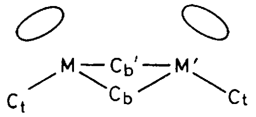


(A)

As the representation (A) of (2a) indicates, the *X*-ray crystal-structure determination shows the $Rh_2(CH_2)_2$ unit to be puckered with the CH_2 bridges bent downwards *away* from the C_5Me_5 rings [angle between the planes Rh(A)C(1)-C(2) and Rh(B)C(1)C(2) is 32°]. From this structure it must be the equatorial hydrogens H_{eq} which are more nearly in the RhC(1)C(2) planes and which are therefore closer to the C_5Me_5 ligands. Hence H_{eq} gives the resonance at δ 8.10 which shows coupling to both rhodiums. The other resonance (δ 6.96) must therefore arise from the axial hydrogens H_{ax} *which do not couple to rhodium.*

Neither in the ^1H nor in the ^{13}C spectra was there any sign of either of the molecules being other than completely rigid: no dynamic behaviour was detected over the temperature range −90 to +100 °C.

X-Ray Structure Determination of (2a).—As indicated in the Figure the structure determined for complex (2a) showed the *cis* arrangement of pentamethylcyclopentadienyl ligands on the two rhodiums. Each rhodium also had attached to it one methyl (again *cis* to each other) and the rhodiums were linked by two methylene bridges, to give a puckered Rh_2C_2 ring, as illustrated above. The rhodiums were 2.620(1) Å apart, which in dinuclear rhodium complexes is an indication of the presence of quite a strong metal–metal bond;[3,5,8] for example, in $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]^+$ it is 2.680(1) Å.[10] The existence of a Rh–Rh bond is also implied by the diamagnetism of (2a) since each Rh centre has the formal oxidation state +4 (d^5). The angle Rh–CH_2–Rh is very acute (79.9 and 80.7°), as has been found for other μ-methylene complexes,[3] and the angles of fold about the Rh ··· Rh and the $CH_2 \cdots CH_2$ axes are 28 and 32° respectively. The Rh–CH_2 bond lengths (mean, 2.032 Å) are very similar to those reported in other methylene-rhodium complexes[3,11] but interestingly enough, they are substantially shorter than the Rh–CH_3 bonds [2.102(16) and 2.135(16) Å]. It may be significant that the difference, *ca.* 0.09 Å, is very close to the difference in radius between an sp^2 and an sp^3 carbon atom (0.1 Å).



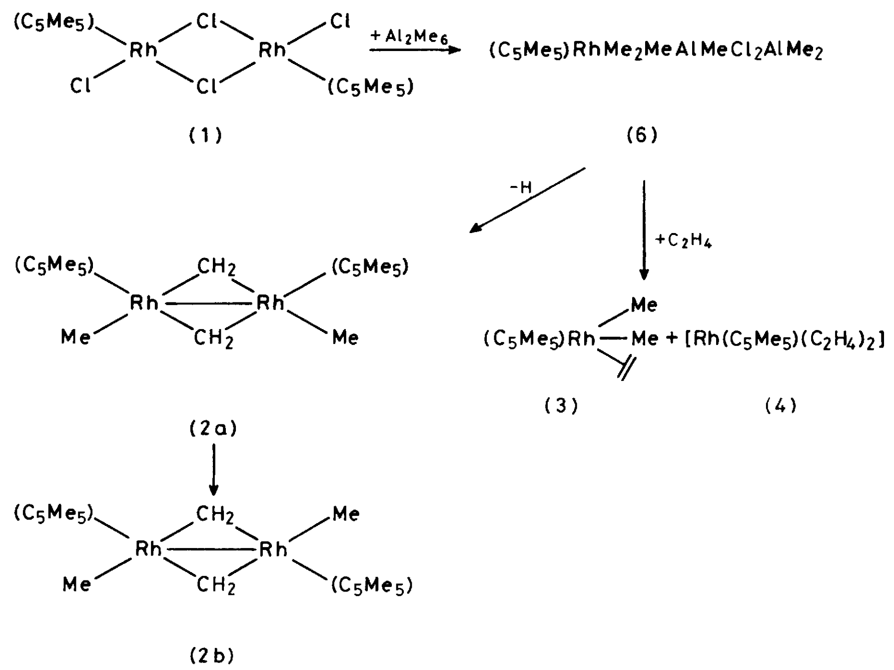
(B)

Related geometries have been reported for a variety of *cis*-dinuclear cyclopentadienyl complexes[12] but one of the most revealing is *cis*-$[\{Fe(C_5H_5)\}_2(\mu\text{-}CO)_2(CO)_2]$[13] the basic skeleton of which is remarkably similar to that of (2a). This can be seen in the close correspondence in bond angles between the $Rh_2(\mu\text{-}CH_2)_2(CH_3)_2$ and the $Fe_2(\mu\text{-}CO)_2(CO)_2$ cores (B) as illustrated by M–C_b–M′ 82.8, 82.4 (Fe), 80.7, 79.9 (Rh); C_b–M–C_b' 96.0, 96.0 (Fe), 95.6, 95.7 (Rh); and C_t–M–M′ 99.7, 101.3 (Fe) and 99.6, 101.9° (Rh). However, the M_2C_2 bridge is a little more puckered in (2a) than in *cis*-$[\{Fe(C_5H_5)\}_2(\mu\text{-}CO)_2(CO)_2]$; for example, the angle between the M_2C planes is 28° in (2a) and 16° in $[\{Fe(C_5H_5)\}_2(\mu\text{-}CO)_2(CO)_2]$.

Although crystals of the *trans* isomer (2b) apparently suitable for crystallographic analysis were obtained, upon refinement of the data they presented a serious problem, probably due to twinning, and which could not be resolved. Although the refinement was abandoned it was clear that (2b) had the expected centrosymmetric structure and the rhodiums were found to be 2.59 Å apart, again confirming the presence of a metal–metal bond.

Mode of Formation of (2a) *and* (2b).—The conversion of (1) into (2) involves at least a formal increase in oxidation state of the Rh from +3 to +4 coupled with a loss of two hydrogens from the coming together of two molecules of ' $Rh(C_5Me_5)Me_2$ ', the probable intermediate. In the original synthesis oxygen from the air acted as hydrogen acceptor.* From n.m.r. studies on the reaction of (1) and Al_2Me_6 under argon it was evident that a single species was produced initially in high yield (>95%, see below). This suggested that the hydrogen-transfer step was the inefficient one leading to low yields of (2).

A number of experiments were run in order to optimise the formation of (2) using a variety of hydrogen acceptors. Reaction of (1), Al_2Me_6, and ethylene, however, gave only a mixture of $[Rh(C_5Me_5)Me_2(C_2H_4)]$ (3) (57%) and $[Rh(C_5Me_5)(C_2H_4)_2]$ (4) (14%) (Scheme 1), and no complex (2). Cyclohexene was also ineffective as a hydrogen acceptor; (2b) was formed in 25% yield but it probably arose during work-up by exposure to air since no cyclohexane was detected.



Scheme 1.

Acetone, on the other hand, worked extremely well. On addition of acetone to the yellow solution formed by reaction of (1) and Al_2Me_6 in benzene the colour changed to the very characteristic red of (2). Upon work-up of the solution, the *trans* complex (2b) was obtained in 89% isolated yield of analytically pure red crystals.

The solvents and other volatiles were also examined by g.c.–mass spectrometry after hydrolysis. Isopropyl alcohol [*ca.* 0.6 mol per mol of (1)] and t-butyl alcohol (*ca.* 0.2 mol) were found. No isopropyl alcohol was found in a blank experiment when Al_2Me_6 was reacted with acetone. When a reaction mixture of (1) and Al_2Me_6 was quenched with $(CD_3)_2CO$ only $(CD_3)_2CH(OH)$ was found.

Other ketones (cyclohexanone, benzophenone) behaved similarly to acetone but propionaldehyde, methyl acetate, and nitrosobenzene did not give complex (2). Interestingly, addition of acetone to the reaction product from methyllithium (in diethyl ether) and (1) did not improve the yield of (2a).

If the reaction with acetone was carried out at −78 °C on the yellow toluene solution from (1) and Al_2Me_6, the colour again immediately became red; upon work-up this gave a 77% yield of mixed *cis* and *trans* complexes (2a) and (2b) in a 4 : 1 ratio. Clearly under these conditions the isomerising ability of the mixture has been largely quenched.

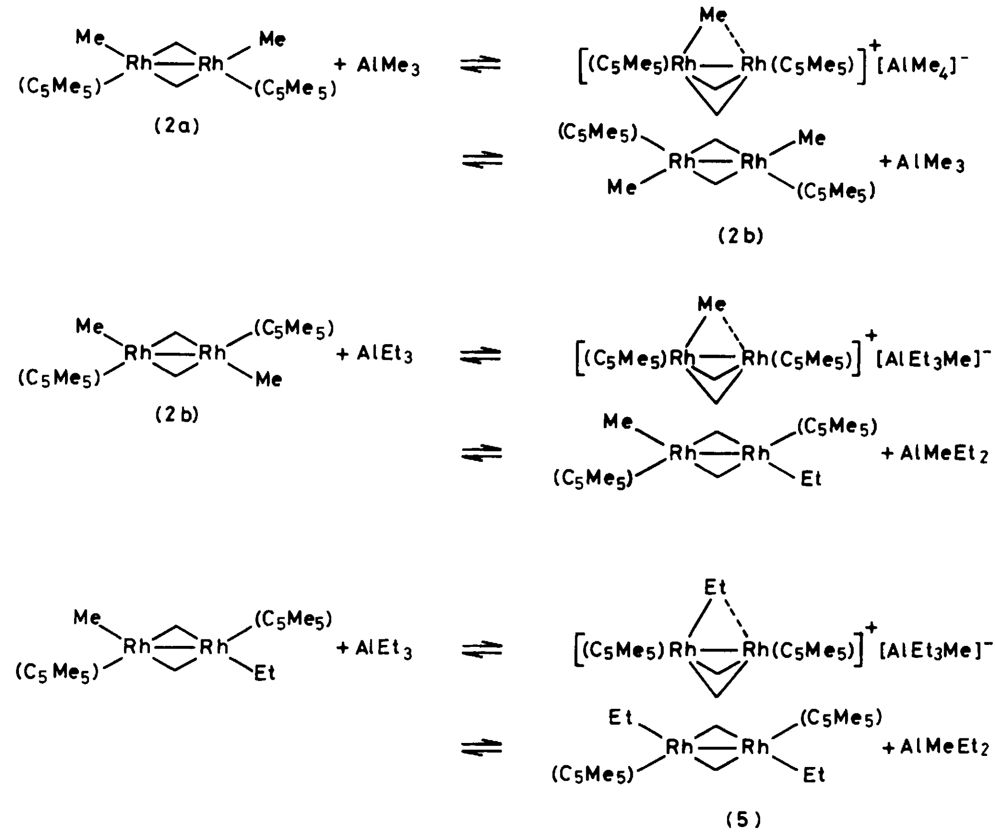
In a separate experiment designed to probe the nature of the isomerising species further a sample of *cis*-(2a) in $[^2H_8]$toluene was treated with Al_2Me_6 at +20 °C. The ^1H n.m.r. spectrum showed the presence of only the *trans* isomer (2b) and indicated that isomerisation had occurred within the time needed to prepare the solution and measure the spectrum.

Reaction of *trans*-(2b) with Al_2Et_6 in toluene gave a (isolated) yield of 45% of the pure *trans*-diethyl complex (5). We suggest that this exchange reaction and the *cis–trans* isomerisation probably proceed through similar ionic intermediates (which may be bridged) of the form shown in Scheme 2. Nucleophilic attack by AlR_4^- would always be expected to proceed at the least hindered site, thus giving the *trans* isomer in each case. In practice the equilibria will probably be on the side of (2) and Al_2R_6 rather than the ionic forms.

Full details of the low-temperature n.m.r. studies will be

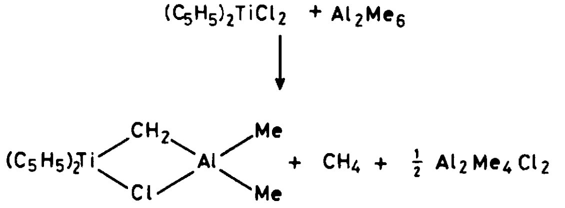
---

* Somewhat related processes have been reported.[14]



Scheme 2.

published in due course, but as has already been mentioned in a preliminary communication[4b] only one rhodium-containing species, ' $(C_5Me_5)RhMe_2MeAlMeCl_2AlMe_2$ ' (6), is formed at low temperature. No methane is produced nor is any carbene-, carbyne-, μ-methylidene-, or μ-methylidyne-containing complex formed under these conditions.* This is in contrast to the reactions described by Tebbe *et al.*[16] in the formation of (7).



(7)

When acetone was added to a solution of (6) at low temperatures only (2) and no further intermediates were detectable. This reaction is all the more surprising since carbene complexes of the lighter elements readily react with ketones to give olefins, for example, by complex (7).[16]

Further light on these reactions was shed by labelling studies. When a sample of highly deuteriated $[\{Rh[C_5(CD_3)_5]\}_2Cl_4]$ (1; D_{27}) was reacted with either methyl-lithium or Al_2Me_6 and the reaction worked-up with air as in the initial experiments, n.m.r. analysis of both the resultant *cis* and *trans* complexes (2) showed the D label to be approximately equivalently scrambled throughout the molecule including the Rh-bound methyls and μ-methylenes. By contrast, when (1; D_{27}) was reacted with Al_2Me_6 in benzene and the intermediate quenched with $(CD_3)_2CO$ [or $(CH_3)_2CO$] the product, *trans*-(2a), contained only very small amounts of deuterium in the rhodium methylene and methyl ligands. Essentially all the deuterium remained in the C_5Me_5 ring.

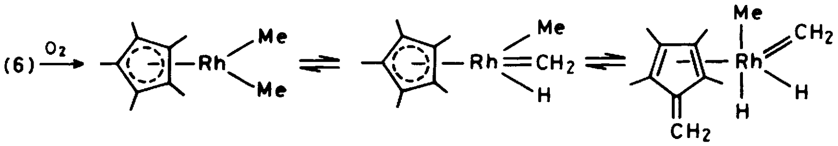
This suggests that the two hydrogen-transfer reactions from (6) to (2) occur *via* quite different intermediates depending on whether air or acetone is the acceptor. One possibility is that during the air-oxidation of (6), the monomeric species $Rh(C_5Me_5)Me_2$ may be released for long enough to allow hydrogen migration reactions such as (C) $\rightleftharpoons$ (D) $\rightleftharpoons$ (E) to occur. This sequence would allow complete H–D scrambling to proceed and formation of (C) could be induced by reaction of (6) with oxygen. Intermediates (D) and (E) have the rhodium formally in the (+5) oxidation state but we have recently shown that this is a viable (and indeed can be a stable) oxidation state.[17] Metal(v) complexes have been invoked previously as intermediates in H–D exchange reactions.[18]

A possible overall equation for the air-induced reaction could then be equation (i).

$$\underset{(6)}{2[(C_5Me_5)RhMe_2MeAlMeCl_2AlMe_2]} + \tfrac{7}{2}O_2 \longrightarrow \underset{(2)}{[\{Rh(C_5Me_5)Me\}_2(\mu\text{-}CH_2)_2]} + 2MeH + [(MeO)_6Al_4Cl_4O] \qquad (i)$$

---

* Under different conditions Al_2Me_6 and (1) do give methane and $[\{Rh(C_5Me_5)\}_2(CH)_2]$.[15]



(C) (D) (E)

$$\underset{(6)}{2[(C_5Me_5)RhMe_2MeAlMeCl_2AlMe_2]} + Me_2CO + 4H_2O \longrightarrow \underset{(2)}{[\{Rh(C_5Me_5)Me\}_2(\mu\text{-}CH_2)_2]} + Me_2CHOH + 8MeH + 2Al_2(OH)_4Cl_2 \qquad \text{(ii)}$$

The high yield, the absence of detectable intermediates, and the formation of the *cis* complex (2a) on reaction of (6) with acetone, together with the absence of significant H-D scrambling suggests a fast synchronous reaction. The overall process, neglecting side reactions (and assuming that only two methyls in each Al_2Me_6 are available for alkylation)[19] appears to be equation (ii). Since the reaction of Al_2Me_6 with acetone and other aliphatic ketones is greatly complicated by aldol condensations and similar reactions,[19] it is not surprising that the amount of isopropyl alcohol found was somewhat lower than expected.

Experimental

All reactions were carried out in carefully dried Schlenk tubes under pure argon; manipulations were carried out using hypodermic syringes or fine cannulae through Suba-seals. Solutions of trimethylaluminium (Ethyl Corporation) in various solvents were also made up in this way. Solvents were AnalaR grade which had been dried and distilled under argon prior to use. Microanalyses were carried out by the University of Sheffield Microanalytical Service; n.m.r. spectra were run on Perkin-Elmer R-12B (^1H, 60 MHz), Bruker WH-400 (^1H, 400 MHz; ^{13}C, 100 MHz), and JEOL PFT-100 (^{13}C, 25 MHz) spectrometers.

cis-*Dimethyl-di-*μ*-methylene-bis(pentamethylcyclopentadienyl)dirhodium* (2a).—*Method A*. A solution of methyl-lithium in diethyl ether (10 cm³, 16.7 mmol, low in halide, from Aldrich) was added to a suspension of $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$ (1) (0.5 g, 0.8 mmol) in benzene (40 cm³) at 20 °C. The solid dissolved to give a dark brown solution which was stirred magnetically (1 h at 20 °C). Air was then carefully admitted to the reaction vessel, **CAUTION**,* and the stirring continued for 2 h at 20 °C. The colour changed to red. The solution was evaporated *in vacuo* and the residue extracted with pentane (200 cm³); this gave essentially pure *cis*-(2a) on evaporation, which was crystallised from methanol–pentane as brown-red crystals (yield 0.12 g, 28%). One of these crystals was suitable for *X*-ray crystallography (see below) [Found: C, 53.85; H, 7.35%; *M* (mass spectrometry), 534. $C_{24}H_{40}Rh_2$ requires C, 53.95; H, 7.55%, *M*, 534]. ^1H N.m.r. ($CDCl_3$): δ −0.46 [t, *N*(Rh–H)[9] 2.4 Hz, Me–Rh], 1.70 [t, *N*(Rh–H)[9] 0.6 Hz, C_5Me_5], 6.96 [d, *J*(H–H) 1.8 Hz, H_{ax}], and 8.10 [dt, *J*(H–H) 1.8 *J*(Rh–H) 2.6 Hz, H_{eq}]. ^{13}C-{^1H} N.m.r. ($CDCl_3$): δ −0.4 [d, *J*(Rh–C) 30.5 Hz, CH_3], 9.7 (s, C_5*Me*$_5$), 100.0 (s, *C*$_5Me_5$), and 156.0 [t, *J*(Rh–C) 28.0 Hz, *C*H_2]. When a sample of $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$ (1) containing 27 ± 0.5 deuteriums (and 3 ± 0.5 hydrogens)[20] was reacted with methyl-lithium, as described above, the product *cis*-(2a) contained 27.5 ± 0.5 deuteriums and 12.5 ± 0.5 hydrogens. Of these, 23.5 ± 0.5 deuteriums were on the C_5Me_5 rings, 2.0 ± 0.5 on the two methyls, and 2.0 ± 0.5 on the two methylene groups, *i.e.* complete scrambling had occurred within the accuracy of the determination. Two different samples were prepared from (1; D_{27}) and were analysed by careful integration of the intensities of the ^1H n.m.r. signals of weighed amounts dissolved in C_6D_6 against the intensity of signal of a known amount of hexamethylbenzene, C_6Me_6. The analytical results in the two samples agreed to within ±0.5 D.

Method B. This method gives a higher yield of (2a) but the product also contains some (2b); purification can be achieved by high-pressure liquid chromatography. A freshly prepared 10% solution of Al_2Me_6 in toluene (25 cm³, 6.3 mmol) was added dropwise to a stirred suspension of complex (1) (0.45 g, 0.73 mmol) in toluene (5 cm³) at −70 °C. The brown-orange suspension rapidly gave a clear pale yellow solution. After stirring for 10 min at *ca.* −78 °C, acetone (10 cm³) was very slowly added and the resultant deep red solution was allowed to warm up slowly. After 18 h at 20 °C the solvent was removed *in vacuo* and the red residue extracted with pentane (3 × 30 cm³) to yield, after further purification from pentane, 0.202 g (77%) of a mixture containing (analysis by ^1H n.m.r. spectroscopy) 81% *cis*-(2a) and 19% *trans*-(2b).

trans-*Dimethyl-di-*μ*-methylene-bis(pentamethylcyclopentadienyl)dirhodium* (2b).—*Method A*. A 10% solution of Al_2Me_6 in benzene (10 cm³, 6.3 mmol) was added to a suspension of complex (1) (0.5 g, 0.8 mmol) in benzene (40 cm³) at 20 °C. The reaction proceeded and was worked-up in the same manner as described above for the preparation of (2a) by method A to give red crystals of (2b) (0.07 g, 15%) [Found: C, 53.90; H, 7.20%; *M* (mass spectrometry), 534. $C_{24}H_{40}Rh_2$ requires C, 53.95; H, 7.55%; *M*, 534]. ^1H N.m.r. (CD_2Cl_2): δ −0.87 [t, *N*(Rh–H)[9] 3.0 Hz, Me–Rh], 1.70 [t, *N*(Rh–H)[9] 0.6 Hz, C_5Me_5], and 8.03 [t, *J*(Rh–H) 1.8 Hz, CH_2]. ^{13}C-{^1H} n.m.r. ($CDCl_3$): δ −4.0 [d, *J*(Rh–C) 33.6 Hz, Rh–Me], 9.7 (s, C_5*Me*$_5$), 100.0 (s, *C*$_5Me_5$), and 161.5 [t, *J*(Rh–C) 28.0 Hz, CH_2].

When a sample of $[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$ containing 27.3 ± 0.5 deuteriums (and 2.7 ± 0.5 hydrogens) was reacted with Al_2Me_6 as described here, the product, *trans*-(2b), contained 27.2 ± 1.0 deuteriums of which 24 ± 1 were on the C_5Me_5 ring, 1.0 ± 0.5 on the two methyls, and 2.0 ± 0.5 on the two methylenes. Again, substantial scrambling of the label (confirmed by D n.m.r.) had occurred. Analysis was carried out as before on two different samples.

Method B. A freshly prepared 11% solution of Al_2Me_6 in toluene (3.6 cm³, 2.0 mmol) was slowly injected into a sus-

---

* *Considerable caution needs to be excercised in carrying out these oxidations of solutions containing organo-aluminium or organo-lithium compounds.* Occasionally the mixtures catch fire and can burn quite violently. All experiments should be carried out in a fume hood behind a safety screen and the operator should be suitably protected. We do not counsel working with larger quantities than are indicated.

Table 1. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex (2a)

Rh(A)–Rh(B)	2.620(1)		
Rh(A)–C(01)	2.029(13)	Rh(B)–C(01)	2.017(13)
Rh(A)–C(02)	2.036(12)	Rh(B)–C(02)	2.045(12)
Rh(A)–C(03)	2.102(16)	Rh(B)–C(04)	2.135(16)
Rh(A)–C(A06)	2.215(9)	Rh(B)–C(B06)	2.175(9)
Rh(A)–C(A07)	2.230(9)	Rh(B)–C(B07)	2.286(9)
Rh(A)–C(A08)	2.317(9)	Rh(B)–C(B08)	2.375(9)
Rh(A)–C(A09)	2.356(9)	Rh(B)–C(B09)	2.324(9)
Rh(A)–C(A10)	2.294(9)	Rh(B)–C(B10)	2.199(9)
Mean	2.282	Mean	2.272
Rh(A)–ring centre	1.960	Rh(B)–ring centre	1.936
Rh(A)–C(C06) *	2.319(18)	Rh(B)–C(D06) *	2.315(18)
Rh(A)–C(C07)	2.396(18)	Rh(B)–C(D07)	2.202(18)
Rh(A)–C(C08)	2.331(18)	Rh(B)–C(D08)	2.202(18)
Rh(A)–C(C09)	2.209(18)	Rh(B)–C(D09)	2.315(18)
Rh(A)–C(C10)	2.201(18)	Rh(B)–C(D10)	2.382(18)
Mean	2.291	Mean	2.283
Rh(A)–ring centre	1.948	Rh(B)–ring centre	1.951
Rh(A)–C(01)–Rh(B)	80.7(5)	Rh(A)–Rh(B)–C(04)	99.6(4)
Rh(A)–C(02)–Rh(B)	79.9(4)	Rh(B)–Rh(A)–C(03)	101.9(4)
C(01)–Rh(A)–C(02)	95.6(5)	C(01)–Rh(A)–C(03)	86.7(6)
C(01)–Rh(B)–C(02)	95.7(5)	C(01)–Rh(B)–C(04)	86.5(5)
		C(02)–Rh(A)–C(03)	87.6(6)
		C(02)–Rh(B)–C(04)	84.7(5)

Angles (°) between planes: C(01)–Rh(A)–C(02) and C(01)–Rh(B)–C(02) = 32° Rh(A)–C(01)–Rh(B) and Rh(A)–C(02)–Rh(B) = 28°

* For notation see Figure.

Table 2. Atomic parameters (× 10^4) for complex (2a)

Atom	*x*	*y*	*z*
Rh(A) *	38 423(9)	16 357(2)	28 420(7)
Rh(B) *	43 665(9)	9 641(2)	25 398(6)
C(01)	4 664(14)	1 388(3)	1 695(9)
C(02)	4 369(13)	1 242(3)	3 796(9)
C(03)	5 996(18)	1 836(4)	3 128(12)
C(04)	6 722(17)	960(4)	2 792(12)
C(A01)	3 591(33)	2 383(8)	1 605(23)
C(A02)	4 047(24)	2 454(6)	3 839(16)
C(A03)	2 085(25)	1 887(6)	4 850(17)
C(A04)	153(30)	1 477(7)	3 400(20)
C(A05)	971(43)	1 767(10)	1 218(28)
C(B01)	4 964(31)	188(7)	3 602(21)
C(B02)	1 558(34)	559(8)	3 651(23)
C(B03)	708(29)	814(7)	1 468(19)
C(B04)	3 352(29)	668(7)	241(19)
C(B05)	5 911(29)	285(7)	1 447(20)
C(C01)	1 169(64)	1 723(15)	4 491(43)
C(C02)	−101(50)	1 531(12)	2 197(33)
C(C03)	1 880(42)	1 952(10)	847(28)
C(C04)	4 126(59)	2 484(14)	2 103(40)
C(C05)	3 719(70)	2 363(17)	4 291(47)
C(D01)	1 823(82)	804(20)	698(55)
C(D02)	5 219(80)	442(19)	720(53)
C(D03)	5 824(69)	140(16)	2 811(46)
C(D04)	3 281(66)	340(16)	4 152(44)
C(D05)	725(59)	677(14)	3 062(39)
C(A06)	2 770(11)	2 133(2)	2 324(6)
C(A07)	3 108(10)	2 169(2)	3 310(7)
C(A08)	2 217(11)	1 931(3)	3 791(5)
C(A09)	1 329(9)	1 749(2)	3 103(7)
C(A10)	1 670(11)	1 873(3)	2 196(6)
C(B06)	4 051(10)	404(3)	2 819(6)
C(B07)	2 617(10)	545(3)	2 824(6)
C(B08)	2 220(9)	665(3)	1 897(7)
C(B09)	3 409(11)	599(3)	1 319(5)
C(B10)	4 541(8)	437(3)	1 889(7)
C(C06)	1 684(21)	1 850(5)	3 461(11)
C(C07)	1 275(19)	1 773(5)	2 502(14)
C(C08)	2 155(22)	1 979(5)	1 922(9)
C(C09)	3 108(19)	2 183(5)	2 523(14)
C(C10)	2 817(21)	2 103(5)	3 474(11)
C(D06)	2 695(20)	642(5)	1 573(12)
C(D07)	4 134(20)	503(5)	1 579(12)
C(D08)	4 516(17)	383(5)	2 509(14)
C(D09)	3 313(22)	447(5)	3 077(10)
C(D10)	2 187(16)	607(5)	2 498(14)

* × 10^5.

pension of complex (1) (0.5 g, 0.8 mmol) in toluene (6 cm³) at −40 °C. The solid dissolved to give a yellow solution which was stirred for 60 min at 40 °C, and then warmed to 0 °C (external ice-bath). Acetone (3 cm³) was then slowly injected and the resultant red solution was allowed to warm up and was kept at 20 °C, with stirring for at least 8 h. The solution was cooled again to 0 °C and 0.1 cm³ of water was added with rapid stirring. After 1 h the solvent was removed *in vacuo* and the residue extracted with pentane (4 × 35 cm³) to yield, after further purification from pentane, 0.39 g (89%) of pure *trans*-(2b).

The above reaction was also carried out using different potential hydrogen acceptors. Butan-2-one, cyclohexanone, and benzophenone were all approximately as effective as acetone when used in very large excess [70—80% yields of (2b)], acetophenone gave a somewhat poorer yield (*ca.* 50%), but all were rather less convenient to use than acetone. Virtually zero yields of (2a) were obtained when methyl acetate, propionaldehyde, or nitrosobenzene were added.

When a sample of complex (1) containing 27.5 ± 0.5 deuteriums (and 2.5 hydrogens) was reacted with Al_2Me_6 and the mixture quenched with $(CD_3)_2CO$ and then D_2O, the product (2b) contained 28 ± 0.5 deuteriums of which a maximum of 0.4 was in the two Rh-methyls and a maximum of 0.4 in the methylenes. The virtual absence of H–D scrambling was confirmed by D n.m.r. spectroscopy and by a variety of experiments in which the CH_3 and CH_2 groups were released as methane, ethylene, or ethane. Only very low levels of deuterium were found in these gases by mass spectrometry.

Reaction of Complex (1) *and* Al_2Me_6 *with Ethylene to give* $[Rh(C_5Me_5)(C_2H_4)_2]$ (4) *and* $[Rh(C_5Me_5)Me_2(C_2H_4)]$ (3).—A solution of Al_2Me_6 (3 mmol) in benzene (6 cm³) was injected dropwise into a stirred suspension of complex (1) (0.25 g, 0.4 mmol) in benzene (50 cm³) saturated with ethylene and through which a slow stream of ethylene was being passed. The solid dissolved to give a yellow solution; the stream of ethylene was stopped, the solution was exposed to air and the solvent removed *in vacuo* to give a residue. The residue was extracted with pentane to give a yellow-orange solid (0.17 g) which was shown by n.m.r. spectroscopy to contain $[Rh(C_5Me_5)Me_2(C_2H_4)]$ (3; 0.46 mmol, 57%) and $[Rh(C_5Me_5)(C_2H_4)_2]$ [21] (4; 0.11 mmol, 14%). ^1H N.m.r. (CD_2Cl_2 at −50 °C); δ for (4), 1.2 (m, C_2H_4, H_i) and 1.69 (overlapping H_0 of C_2H_4 and C_5Me_5); δ for (3), −0.11 (d, *J* 2.4 Hz, RhMe), 1.55 (s, C_5Me_5), and 2.13 (m, C_2H_4). ^{13}C-$\{^1H\}$ n.m.r. (CH_2Cl_2): δ for (4), 9.2 (s, $C_5\mathit{Me}_5$), 48.3 (d, *J* 12.2 Hz, C_2H_4), and 96.5 (d, *J* 4 Hz, C_5Me_5); δ for (3), 3.9 (d, *J* 27.5 Hz, $RhMe_2$), 7.8 (s, $C_5\mathit{Me}_5$), 57.3 (d, *J* 10.7 Hz, C_2H_4), and 98.8 (d, *J* 3 Hz, C_5Me_5).

trans-*Diethyl-di-μ-methylenebis(pentamethylcyclopentadienyl)dirhodium* (5).[22]—Al_2Et_6 (0.5 mmol) in toluene (1.4 cm^3) was added dropwise to a solution of (2b) (0.13 g, 0.25 mmol) in toluene (2 cm^3) at -70 °C with stirring. The solution became a darker red in colour. Acetone (0.5 cm^3) was then added and the solvent was removed *in vacuo*. Extraction of the residue with pentane gave 63 mg (45%) of the *trans*-diethyl complex (5) after purification [Found: C, 56.25; H, 7.95%; *M* (mass spectrometry), 562. $C_{26}H_{44}Rh_2$ requires C, 55.50; H, 7.90%; *M*, 562]. ^1H N.m.r. (C_6D_6): δ 0.29 [qt, *J*(H–H) 7.6, *J*(Rh–H) 1.5 Hz, $RhCH_2Me$], 1.03 [t, *J*(H–H) 7.6 Hz, $RhCH_2CH_3$], 1.67 (s, C_5Me_5), and 8.33 [t, *J*(Rh–H) 1.0 Hz, $Rh_2(CH_2)_2$]. ^{13}C-{^1H} N.m.r. ($CDCl_3$): δ 6.9 [d, *J*(Rh–C) 6.9 Hz, $-CH_2CH_3$], 9.8 (s, C_5Me_5), 17.8 (s, $-CH_2CH_3$), 101.1 (s, C_5Me_5), 164.3 [t, *J*(Rh–C) 31 Hz, $Rh(CH_2)Rh$].

X-*Ray Structure Determination of Complex* (2a).—*Crystal data*. *cis*-$C_{24}H_{40}Rh_2$, $M = 534.4$, Monoclinic, $a = 9.023(5)$, $b = 37.79(2)$, $c = 13.962(10)$ Å, $\beta = 93.12(1)°$, $U = 4\,754$ Å^3, $Z = 8$, $D_c = 1.49$ g cm^{-3}, $F(000) = 2\,192$, space group $B2_1/c$ (C^5_{2h}, no. 14) (from systematic absences), Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 13.72 cm^{-1}.

Single-crystal *X*-ray data in the range $6.5 < 2\theta < 50°$ were collected on a Stoe STADI-2 diffractometer with the crystal mounted along the *c* axis, in the stationary-counter-moving-crystal mode. 2 760 Reflections were collected with intensity $I > 3\sigma(I)$ and background difference $\Delta < 4\sigma(B)$ were corrected for Lorentz and polarisation, but not for absorption or extinction. The structure was solved by Patterson and Fourier methods; block-diagonal matrix least-squares refinement reduced *R* to 0.080 at which stage disorder was noticeable in the region of the cyclopentadienyl rings. A model was constructed such that each of the pentamethylcyclopentadienyl rings was disordered about the C_5 axis with relative proportions of 2 : 1. Further refinement with fixed geometry and isotropic thermal parameters for the cyclopentadienyl carbon atoms reduced *R* to 0.059 (unit weights were applied to all reflections).

Significant bond angles and lengths are collected in Table 1 and atomic co-ordinates in Table 2. A view of the molecule is given in the Figure.

Acknowledgements

We thank the S.E.R.C. for supporting this work, the Spanish Ministry of Education for an award (to A. V. de M.), the University of Sheffield for the award of a Junior Research Fellowship (to P. M. B.), Mr. G. A. Wright for expert technical help, Drs. B. E. Mann and B. F. Taylor for n.m.r. spectra, and Mr. J. T. Gauntlett and Miss M. E. Daniels for help with early experiments. We also acknowledge gifts of hexamethylbicyclohexadiene (from Chemische Werke, Hüls) and aluminium alkyls (from Ethyl Corporation, Houston).

References

1 R. C. Brady and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 1681; 1981, **103**, 1287.

2 W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 117.

3 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 160; *Pure Appl. Chem.*, 1982, **54**, 65.

4 Preliminary communications: (*a*) K. Isobe, D. G. Andrews, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 809; (*b*) A. Vásquez de Miguel, K. Isobe, B. F. Taylor, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 758.

5 P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

6 See, for example, R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98; P. R. Sharp, S. J. Holmes, R. R. Schrock, M. R. Churchill, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1981, **103**, 964; R. R. Schrock, *ibid.*, 1982, **104**, 1710.

7 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

8 W. A. Herrmann, J. Plank, D. Riedel, M. L. Ziegler, K. Weidenhammer, E. Guggolz, and B. Balbach, *J. Am. Chem. Soc.*, 1981, **103**, 63; W. A. Herrmann, C. Bauer, G. Kriechenbaum, H. Kimkely, M. L. Ziegler, D. Speth, and E. Guggolz, *Chem. Ber.*, 1982, **115**, 878.

9 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.

10 A. Nutton, P. M. Bailey, and P. M. Maitlis, *J. Organomet. Chem.*, 1981, **213**, 313.

11 W. A. Herrmann, J. Plank, C. Bauer, M. L. Ziegler, E. Guggolz, and R. Alt, *Z. Anorg. Allg. Chem.*, 1982, **487**, 85.

12 See, for example, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 861; M. Cooke, D. L. Davies, J. E. Guerchais, S. A. R. Knox, K. A. Mead, J. Roué, and P. Woodward, *ibid.*, 1981, 862.

13 R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 1970, 3068.

14 A. J. Shortland and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 872; A. L. Galyer and G. Wilkinson, *ibid.*, 1973, 2235.

15 A. Vásquez de Miguel, K. Isobe, P. M. Bailey, N. J. Meanwell, and P. M. Maitlis, *Organometallics*, 1982, **1**, 1604.

16 F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.

17 M-J. Fernandez and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 310; *Organometallics*, 1983, **2**, 164; see also, K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 808.

18 C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 1654.

19 K. Ziegler, 'Organometallic Chemistry,' ed. H. Zeiss, A.C.S. Monograph No. 147, 1960, p. 236 *et seq.*; T. A. Mole and E. A. Jeffery, 'Organoaluminium Compounds,' Elsevier Publishing Co., Amsterdam, 1972.

20 J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **30**, 127.

21 K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc. A*, 1970, 2875.

22 See also K. Isobe, P. M. Bailey, P. Schofield, J. Y. Gauntlett, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 425.

Received 12*th November* 1982; *Paper* 2/1899