Synthesis and Properties of Tetramethyl(η^5-pentamethylcyclopentadienyl)iridium(V), Dimethyl-di-μ-methylene-bis[(η^5-pentamethylcyclopentadienyl)iridium(IV)], and Related Complexes from Reactions of Di-μ-chloro-dichlorobis[(η^5-pentamethylcyclopentadienyl)iridium(III)] with Hexamethyldialuminium

Kiyoshi Isobe, Amelio Vázquez de Miguel, Andrew Nutton, and Peter M. Maitlis *
Department of Chemistry, The University, Sheffield S3 7HF

The intermediate $[\{(C_5Me_5)IrMe_3\}_2AlMe]$ (2b) from reaction of $[\{(C_5Me_5)Ir\}_2Cl_4]$ and Al_2Me_6 in pentane, reacted with ligands ($L = PPh_3$ or C_2H_4) to give $[(C_5Me_5)IrMe_2L]$, and with a hydrogen-acceptor (acetone) to give the dimethyl-di-μ-methylene complex $[\{(C_5Me_5)IrMe\}_2(\mu\text{-}CH_2)_2]$. The most unusual reaction of (2b) was the oxygenation to give a 40% yield of the iridium(V) complex $[(C_5Me_5)IrMe_4]$. Other complexes which were formed in these reactions in lower yields include the chloro(methyl)-di-μ-methylene complex $[\{(C_5Me_5)Ir\}_2Me(Cl)(\mu\text{-}CH_2)_2]$ and the trinuclear di-μ_3-methylidyne complex $[\{(C_5Me_5)Ir\}_3(\mu_3\text{-}CH)_2]$. The complexes have been characterised spectroscopically and by comparison with their rhodium analogues. Mechanisms for the reactions are proposed.

We have reported quite extensively, both in communications [1-3] and in full papers [3-6] on the reactions undergone by the (pentamethylcyclopentadienyl)rhodium complex $[\{(C_5Me_5)Rh\}_2Cl_4]$ (1a) with Al_2Me_6. In brief, this leads initially to a yellow solution containing $Al_2Me_4Cl_2$ and a single rhodium species which has now been formulated as $[\{(C_5Me_5)RhMe_3\}_2AlMe]$ (2a).[6] On reaction of (2a) with ligands, complexes of the type $[(C_5Me_5)RhMe_2L]$ (3a) ($L = PPh_3$, Me_2SO, *etc.*) are formed in excellent yield. However, when the solution containing (2a) is reacted with air or, better, with a hydride acceptor such as acetone, a smooth reaction takes place giving the dinuclear Rh^{IV} di-μ-methylene complex $[\{(C_5Me_5)RhMe\}_2(\mu\text{-}CH_2)_2]$ (4a).[2,5] The initially formed complex has the *cis* configuration but is very readily isomerised by Lewis acids, such as the aluminium compounds present in the reaction mixture, to the *trans* isomer, (5a); this is the normal product isolated from such reactions. In addition, a rather curious and less understood reaction takes place when (1a) and Al_2Me_6 are mixed in very concentrated solution to give methane and the trinuclear di-μ_3-methylidyne complex $[\{(C_5Me_5)Rh\}_3(\mu_3\text{-}CH)_2]$ (6a).[4]

The initial reaction of the iridium complex $[\{(C_5Me_5)Ir\}_2Cl_4]$ (1b) with Al_2Me_6 gives $[\{(C_5Me_5)IrMe_3\}_2AlMe]$ (2b),[6] precisely parallel to the reaction of (1a) to give (2a). Again, (2b) reacts with ligands such as dimethyl sulphoxide to give (3b) in high yield.[6] However, other reactions take a more surprising and more complex turn.[7,8] For example, the solution containing $Al_2Me_4Cl_2$ and (2b) is rather easily oxidised by air to give $[(C_5Me_5)IrMe_4]$, the first organoiridium(V) complex.[7] A detailed account of this and the other reactions undergone by (2b) is presented here.

Results and Discussion

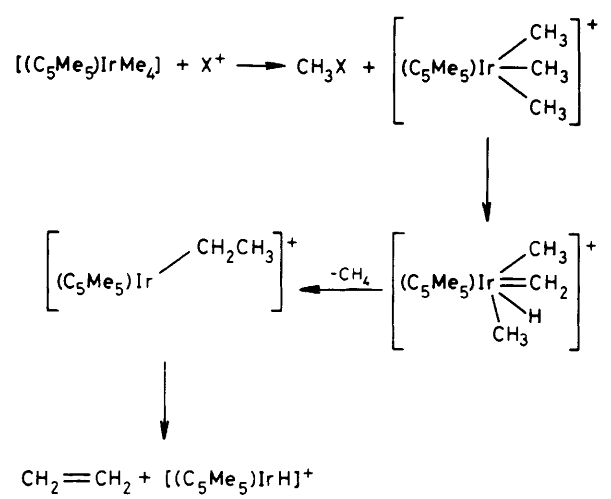
Tetramethyl(η^5-*pentamethylcyclopentadienyl*)*iridium*(V), (7). —The reactions in which (2b) is generated are best carried out under argon at low temperatures in aliphatic hydrocarbons such as n-pentane, cyclopentane, or 2-methylbutane. [The use of aromatic hydrocarbons (benzene or toluene) leads to further complications arising from the incorporation of phenyl (or tolyl) into the products.[8]] The pale orange-yellow solution of (2b) is then allowed to warm up to room temperature and stirred in air for some minutes; the colour changes through pale yellow to cloudy and the solution finally deposits a pale brown solid. The reaction is stopped at this point and on work-up of the clear supernatant solution, a 40% isolated yield of colourless crystals of $[(C_5Me_5)IrMe_4]$ (7) can reproducibly be obtained. A large number of variations on the synthetic procedure have been tried (for example, the use of other oxidants such as peroxides) but the method indicated gives the optimum yield.

The complex is purified by chromatography on Florisil or by vacuum sublimation. It is very soluble in less polar organic solvents and it appears reasonably stable to air and other reagents, both in solution and in the solid. In this it is quite different from other transition metal permethyls in high oxidation states which are often extremely sensitive and even explosive.[9,10]

The complex (7) was characterised by microanalysis, mass spectrum [which showed molecular ions at *m/e* 386 and 388 with the appropriate intensities for ^{191}Ir (37%) and ^{193}Ir (63%)], and the n.m.r. spectra. The ^1H n.m.r. spectrum showed two resonances in the ratio 5 : 4 (CD_2Cl_2, at δ 1.28 and 0.47) due to the C_5Me_5 and the $IrMe_4$ ligands; as expected, the ^{13}C n.m.r. spectrum showed three resonances (δ −3.4, 6.3, and 97.8) due to the $IrMe_4$, the $C_5\mathit{Me}_5$ and the C_5Me_5 carbons respectively. The structure was finally confirmed by a single-crystal *X*-ray determination which showed that the molecule has a 'four-legged piano stool' shape, with each of the methyls acting as a leg in the square base of the pyramid and the C_5Me_5 ring as the seat on top.[7]

Formally complex (7) has the metal in the -5 oxidation state. Although Ir^V is known in fluoro-complexes such as $[IrF_5]_n$ or $K[IrF_6]$ [11] and in the pentahydrides, $[Ir(PR_3)_2H_5]$,[12] this complex is the first organometallic compound in that oxidation state. In fact, photoelectron spectra show that although the first ionisation potentials increase in the direction expected in going from the Ir^I complex $[(C_5Me_5)Ir(CO)_2]$ (6.93 eV) through $[(C_5Me_5)IrMe_2(Me_2SO)]$ (7.01 eV) to the Ir^V complex (7) (7.31 eV), the differences are smaller than might have been anticipated.[13] One way qualitatively to explain this is in terms of a substantial electron flow from the C_5Me_5 ring into the nominally electron-poor metal in the higher oxidation states; this raises the energy of the highest occupied molecular orbital and thus reduces the energy needed to ionise the electron.

On heating, complex (7) begins to decompose above *ca.* 200 °C; the main product was methane (only traces of ethylene



Scheme 1.

and ethane were present). At 200 °C, 0.5 mol of methane was formed per mol of (7); about double this amount was formed at 350 °C.

However, other reagents, especially electrophiles, react rapidly at ambient temperature. For example, iodine in chloroform reacted readily to give gas [shown by g.c. to amount to 0.7 mol ethane, 0.1 mol ethylene, and a trace of methane per mol of (7)] plus a solution which contained methyl iodide [^{1}H n.m.r., δ 2.13; *ca.* 1.4 mol of CH_3I per mol of (7)]. The ^{1}H n.m.r. spectrum showed a number of lines in the C_5Me_5 region, indicating the presence of many other species. Iridium metal was also formed, but [$\{(C_5Me_5)Ir\}_2I_4$] appeared to be absent.

Acid (HBF_4) reacted very rapidly with (7) in benzene to liberate *ca.* 2 mol of methane, 0.5 mol of ethylene and traces of ethane per mol of (7). Silver tetrafluoroborate reacted immediately with (7) in benzene to give *ca.* 0.7 mol methane and 0.6 mol ethane per mol of (7).

Thus, decomposition is promoted by electrophiles (X) and gives primarily methane (or CH_3X). The secondary products are either ethane, formed by a reductive coupling promoted by the electrophile,[14] or ethylene. The origin of this last product is intriguing. One possible route is the one in Scheme 1 in which ' [$(C_5Me_5)IrMe_3]^+$ ', which arises from (7) by loss of one of its methyls through direct reaction with the electrophile, undergoes an α-hydride migration onto the metal, followed by (*i*) reductive elimination of methane and (*ii*) a methyl migration onto the carbene. A β-elimination from the ethyliridium thus created then gives rise to ethylene. This bears some resemblance to the paths mapped out by Cooper and Werner and their co-workers [15] wherein dimethyl-tungsten or -ruthenium complexes are converted into the respective ethylene-metal hydrides.

It may also be mentioned that in one reaction [in which complex (2b) was oxidised with di-t-butyl peroxide] a small amount (*ca.* 11%) of a compound tentatively identified as the ethylene-dimethyl complex [$(C_5Me_5)IrMe_2(C_2H_4)$] from its ^{1}H n.m.r. spectrum [singlets at δ 0.59 (Me_2), 1.38 (C_5Me_5), and 2.09 (C_2H_4), in C_6D_6] was isolated in addition to the tetramethyl complex (7) (20%). The co-ordinated ethylene presumably arises again from a coupling of two C_1 units.

When the yellow solution containing (2b) was treated with triphenylphosphine before work-up, the main product (39%) was the dimethyliridium triphenylphosphine adduct [$(C_5Me_5)IrMe_2(PPh_3)$]; a small amount of (7) (5%) was also isolated.

Dimethyl-di-μ-methylene-bis[(η^5-*pentamethylcyclopentadienyl*)*iridium*(IV)], (4b).—When the solution of (2b) was treated with acetone and then hydrolysed, the product was a mixture of the *cis*- and *trans*-dimethyl-di-μ-methylene complexes (4b) and (5b).* This reaction exactly paralleled that of (2a) with acetone, except for the yield which was only 35% in the case of the iridium complex. The two complexes could be separated by chromatography on Florisil in pentane and were identified by conventional methods. Separate experiments showed that the *cis* isomer (4b) was transformed into the *trans* isomer (5b) on reaction with Lewis acids such as Al_2Me_6. This reinforces the analogy to the rhodium complexes and suggests that also in the reaction of (2b) with acetone the *cis* isomer is formed first and is then isomerised into the *trans* in a second stage. One (not unexpected) contrast between these rhodium and iridium complexes is that the *cis* iridium complex (4b) is very much more slowly converted into the *trans* isomer (5b) and hence they can be separated by conventional column chromatography. The separation of (4a) from mixtures with (5a) is very difficult because of the ease with which it isomerises and can only be accomplished by reversed-phase h.p.l.c.

The mass spectra of the complexes (4b) and (5b) were very similar and showed three molecular ions, at *m/e* 710, 712, and 714 with the intensities expected for mixtures containing $^{191}Ir_2$, $^{191}Ir^{193}Ir$, and $^{193}Ir_2$. The ^{1}H n.m.r. spectra each showed a single C_5Me_5 resonance and a single methyl resonance to high field (Table). In the *trans* isomer (5b) all the methylene hydrogens are equivalent and they resonate slightly to higher field than those in the rhodium complex (5a). In the *cis* isomer (4b) the methylene hydrogens are now inequivalent; as in the case of the rhodium analogue,[5] one is axial (higher field) the other, equatorial (lower field).

Other Products.—Under some conditions, instead of the mixture of (4b) and (5b) normally produced by the above reaction, the chloro-methyl complex (8) was isolated and characterised by microanalysis, mass spectrum, and ^{1}H n.m.r. spectrum. The μ-methylene hydrogens are not equivalent in (8) and hence appear as an AB double doublet. The separation between the two resonances (1 p.p.m.) suggests [by analogy to (4b) and related Rh complexes [16]] that complex (8) has the *cis* configuration.

One further complex which was produced in the reaction was the iridium analogue of the di-μ_3-methylidyne trinuclear complex (6a). The complex (6b) was the main product (but even then only isolated in 16% yield) when the solution of Al_2Me_6 was added directly to solid complex (1b) at room temperature and the product hydrolysed with propan-2-ol. There are some similarities to the conditions used for the preparation of (6a), but no attempts were made to optimise this reaction. Again, complex (6b) was identified by the characteristic very low-field μ_3-methylidyne resonance at δ 11.99 in the ^{1}H n.m.r. spectrum.[4]

Mechanisms for the formation of (4b), (5b), (7), *and* (8).—The formation of the *cis*- and *trans*-dimethyl-di-μ-methylene complexes (4b) and (5b) has a close parallel in the analogous rhodium reactions. The two points of difference, the lower yield and the greater difficulty in isomerising the *cis* to the *trans* isomer, are probably both explained by the lower reactivity normally associated with reactions at Ir compared to those at Rh. [Typically, inorganic Rh^{III} complexes undergo substitution at least 100 times faster than Ir^{III}.[17]] The reader is referred to our earlier discussion for details of the possible route from (2a) to (4a).[6] The isomerisation (4b) to (5b) we

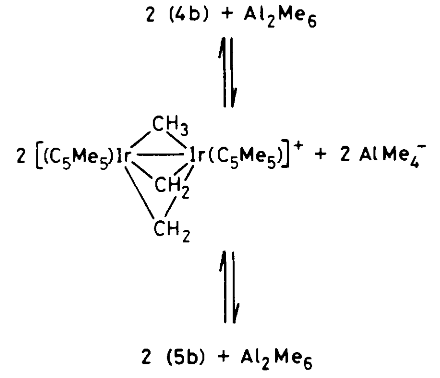
---

* For a review on μ-methylene complexes, see W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 160.

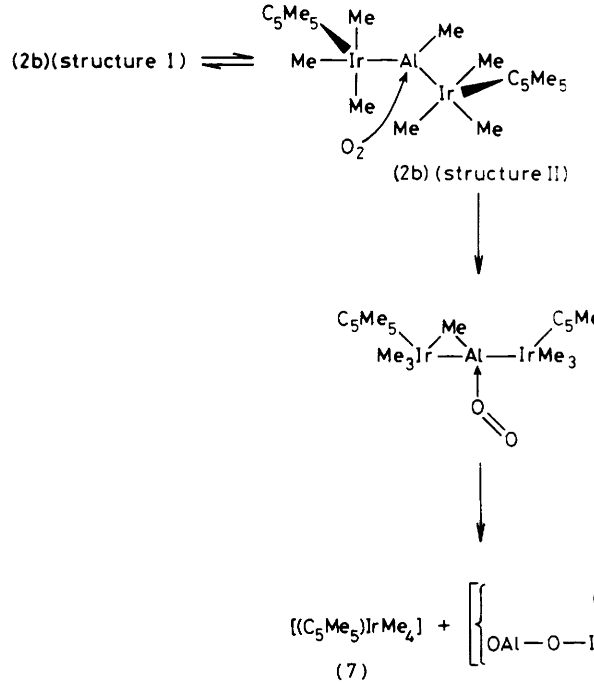
Table. Analytical, mass spectroscopic, and ^{1}H n.m.r. data

Complex	Analysis [a] (%) C	H	Mass spectrum M [b]	^{1}H N.m.r. (δ, C_6D_6) [c] C_5Me_5	Me	Other
$[(C_5Me_5)IrMe_2(PPh_3)]$ (3b)	57.8	5.8		1.37 d	0.49 d	Ph, 7.09 m
	(58.1)	(5.9)		[J(PH) = 1.7]	[J(PH) = 5]	7.42 m
cis-$[\{(C_5Me_5)IrMe\}_2(\mu\text{-}CH_2)_2]$ (4b)	40.7	5.6	710 (13) [14]	1.69	0.56	CH_2, 6.60
	(40.4)	(5.7)	712 (47) [47]			7.27
			714 (41) [39]			
trans-$[\{(C_5Me_5)IrMe\}_2(\mu\text{-}CH_2)_2]$ (5b)	40.5	6.0	710 (13) [14]	1.73	−0.02	CH_2, 7.44
	(40.4)	(5.7)	712 (47) [47]			
			714 (42) [39]			
$[\{(C_5Me_5)Ir\}_3(\mu_3\text{-}CH)_2]$ (6b)	39.4	4.9		1.96	—	CH, 11.99
	(38.1)	(4.7)				
$[(C_5Me_5)IrMe_4]$ (7)	43.0	6.8	386 (38) [37]	1.03	0.92	—
	(43.4)	(7.0)	388 (62) [63]			
cis-$[\{(C_5Me_5)Ir\}_2Me(Cl)(\mu\text{-}CH_2)_2]$ (8)	38.5	5.5 [d]	730 (25) [11]	1.79	−0.49	CH_2, 7.86 d
	(37.7)	(5.1)	732 (39) [39]	1.55		8.89 d
			734 (25) [41]			[J = 2]
			736 (8) [10]			

[a] Calculated values are in parentheses. [b] Relative intensities of molecular ions: observed values are in parentheses, calculated values in square brackets. [c] Coupling constants are in Hz. [d] Cl, 5.0 (4.8)%.



Scheme 2.

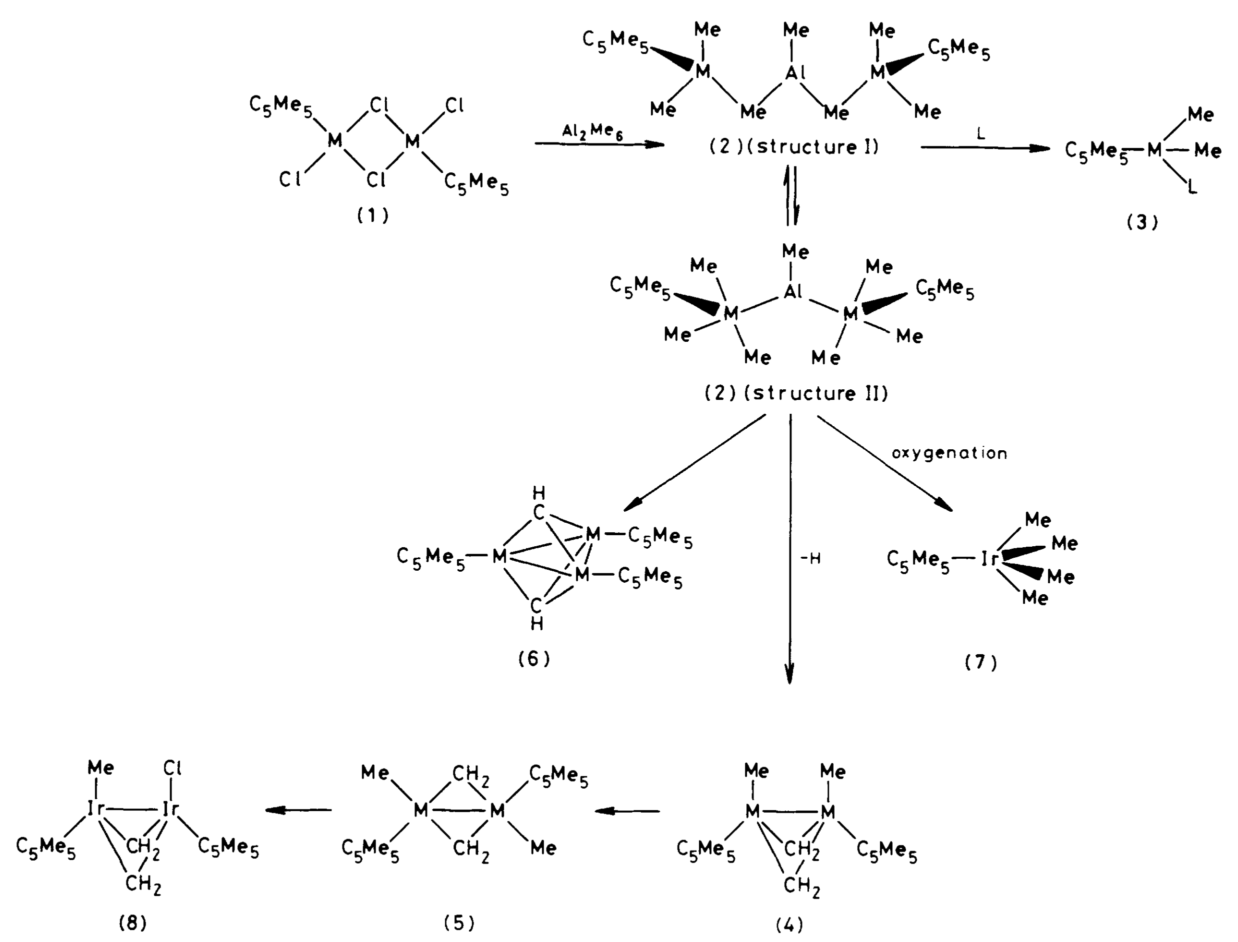


Scheme 3.

suggest occurs by the reversible transfer of Me^- from Ir to the Lewis acid. In the case of the reaction of (4b) with Al_2Me_6 the route proposed is shown in Scheme 2.

We have already noted that the dimethyl-di-μ-methylene-rhodium complexes, (4a) and (5a), readily lose the Rh-bound methyls under acid conditions. Thus, with HCl they give the *trans*-dichloro-di-μ-methylene complex $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}CH_2)_2]$;[3] under milder conditions the asymmetric complexes analogous to (8) are formed.[16] We therefore suggest that (8) itself arises during the hydrolytic work-up when significant amounts of HCl are allowed to come into contact with (4b) or (5b) for longer periods.

The most novel product from the reactions of (2b) is (7); while the metal in complex (1b) is in the +3 oxidation state, (7) formally has the iridium in the +5 state. The formation of higher oxidation state alkyls under what are formally reducing conditions is by no means unknown; for example, in the preparation of materials as diverse as $PbMe_4$[18] and WMe_6. In our preparation of complex (7) and also in the original synthesis of WMe_6[19] air (oxygen) was clearly implicated. The non-reductive methylation of WCl_6 used by Gayler and Wilkinson[9] to make WMe_6 is not practicable for the synthesis of (7) since no suitable Ir^V starting material is available, and the method given in the Experimental section is the best we presently have. As with the analogous rhodium reactions, no intermediates were detected either by n.m.r. or e.s.r. spectroscopy and we can only therefore propose the somewhat speculative route set out in Scheme 3. The essential feature here is contained in the representation (II) of the structure suggested for (2b) in which a trinuclear metal–metal bonded Ir–Al–Ir unit is present. We suggest that attack of the oxygen takes place at the Al concurrent with transfer of the methyl on the Al to one Ir, which then becomes (7) directly. The fate of the other iridium is not clear, but this proposal indicates that the maximum yield of (7) based on Ir could only be 50%; the attained yield of 40% is therefore 80% of that theoretically possible. Since the original discovery of (7) a number of (pentamethyl-



Scheme 4. M = Rh, compounds (*n*a); M = Ir, compounds (*n*b). L = PPh_3 or C_2H_4

cyclopentadienyl)iridium(V) hydride complexes have been prepared.[20,21]

Experimental

All reactions were carried out in carefully dried Schlenk tubes under dry argon using the methods already cited.[4-6] Microanalyses (carried out by the University of Sheffield Microanalytical Service), ^1H n.m.r. spectra (60 MHz), and mass spectra are collected in the Table. The preparative routes are summarised in Scheme 4.

Gases were determined by g.c. using a Pye 104 instrument fitted with a Poropak Q column and flame ionisation detector. In a typical experiment a sample (10 mg) of the complex in a 5-cm^3 flask fitted with a Suba-seal was treated with the reagent in a suitable solvent (usually benzene). The flask was then heated to 50 °C to complete the reaction, cooled to room temperature and a measured volume of the gas transferred by gas syringe to the gas chromatograph. For quantitative work the instrument was calibrated using samples of methane and the other gases.

Tetramethyl(η^5-*pentamethylcyclopentadienyl*)*iridium*(V), (7).—A freshly prepared solution of Al_2Me_6 (1 mmol) in pentane (1.8 cm^3) was injected, very slowly and without stirring, onto a suspension of complex (1b) (0.32 g, 0.4 mmol) in pentane (15 cm^3) at −78 °C contained in a Schlenk tube fitted with a Suba-seal. The suspension was allowed to stand (10 min) and was then stirred with a magnetic stirrer until all the solid had dissolved and a pale orange-yellow solution [of (2b)] was produced (1 h). The solution was allowed to warm up to −40 °C and was then recooled to −78 °C during the reaction; it was then left to warm slowly to room temperature where it was stirred a further 15 min. The Schlenk tube was then uncapped and the contents exposed to air, with stirring, for 45 min. (CAUTION: we have once or twice had small fires at this stage of the reaction. On the scale described, and using proper precautions, this is not a dangerous experiment. However, we *do not* advise working on a larger scale.) The solution changed, first to pale yellow and then to a milky colour; an orange oily solid and later a pale brown solid separated. At the end of this phase of the reaction the solution was colourless and a brown solid was left at the bottom of the Schlenk tube. The clear solution was decanted from the solid which was washed with more pentane (30 cm^3); the solutions were combined and evaporated to dryness and the resultant residue extracted with pentane and chromatographed on a Florisil column (7 × 100 mm) using pentane as eluant. Yield of pure (7) was 0.125 g (40%). ^{13}C N.m.r. spectrum (CD_2Cl_2; WH-400 spectrometer): δ −3.4 (Me), 6.26 and 97.84 (C_5Me_5).

cis- *and* trans-*Dimethyl-di-*μ*-methylene-bis*[(η^5-*pentamethylcyclopentadienyl*)*iridium*(IV)], (4b) *and* (5b).—A solution of complex (2b), made up as described above from (1b) (0.70 g, 0.88 mmol) and Al_2Me_6 (15 mmol) in pentane (45 cm^3), was treated with acetone (3 cm^3) and then with water (1 cm^3). This gave an orange-red solution and a brown oil which was discarded. The orange-red solution was taken to dryness. The residue was extracted with pentane and chromatographed carefully on Florisil in pentane to give two bands from which the *cis* isomer (4b) (0.11 g, 18%) and the *trans* isomer (5b) (0.11 g, 18%) were isolated and crystallised.

A solution of Al_2Me_6 (2 mmol) in benzene (2 cm^3) was added to a solution of the pure *cis* complex (4b) (28 mg, 0.04 mmol) in benzene (2 cm^3). The solution was stirred (18 h, 24 °C); acetone (1 cm^3) was then added and the solution worked-up as usual to give orange crystals (24 mg), shown by ^1H n.m.r. spectroscopy to be a 3 : 2 mixture of *trans* (5b) and *cis* (4b). Extended reaction times or higher temperatures increased the proportion of *trans* (5b).

Dimethyl(η^5-*pentamethylcyclopentadienyl*)(*triphenylphosphine*)*iridium*(III).—Triphenylphosphine (0.21 g, 0.81 mmol) dissolved in pentane (17 cm^3) was added to a solution of complex (2b) [prepared from complex (1b) (0.4 mmol) and Al_2Me_6 (1 mmol) in pentane (50 cm^3) as described above] at −78 °C. On work-up this gave 0.1 g of the product (39%) together with 5% of (7).

Chloro(*methyl*)-*di*-μ-*methylene-bis*[(η^5-*pentamethylcyclopentadienyl*)*iridium*(IV)], (8).—The solution of (2b) from (1b) (0.53 mmol) and Al_2Me_6 (2.6 mmol) in pentane was treated at −50 °C with acetone (2 cm^3) and the reaction worked-up as described above. Chromatography on Florisil in pentane eluted a colourless band composed of (7) (1%) and [$(C_5Me_5)IrMe_2(C_2H_4)$] (10%, identified by n.m.r.). When the column was then eluted with acetone a yellow-orange solution was obtained, which on crystallisation gave crystals of (8) (0.084 g, 23%).

Di-μ_3-*methylidyne-tris*[(η^5-*pentamethylcyclopentadienyl*)-*iridium*(III)], (6b).—The solution of (2b) from (1b) (0.5 mmol) and Al_2Me_6 (1.5 mmol) in pentane was hydrolysed at room temperature with propan-2-ol (1 cm^3). After normal work-up it was chromatographed on Florisil in pentane and benzene to separate the components; this gave the *cis*-dimethyl complex (4b) (0.03 g, 8%) and complex (6b) (0.05 g, 16%).

Acknowledgements

We thank the S.E.R.C. for support of this work, the Spanish Ministry of Education for a grant (to A. V. de M.), Ethyl Corporation for the aluminium trimethyl, Dr. W. Schaefer (Chemischewerke Huels) for organic starting materials, and Johnson Matthey for the loan of iridium trichloride. We are also grateful to Dr. J. C. Green for allowing us to quote the results of her photoelectron spectroscopic measurements ahead of publication.

References

1 K. Isobe, D. G. Andrews, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 809.
2 A. Vázquez de Miguel, K. Isobe, B. F. Taylor, A. Nutton, and P. M. Maitlis, *J. Chem Soc., Chem. Commun.*, 1982, 758.
3 K. Isobe, P. M. Bailey, P. Schofield, J. T. Gauntlett, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 425; K. Isobe, S. Okeya, N. J. Meanwell, A. J. Smith, H. Adams, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, in the press.
4 A. Vázquez de Miguel, K. Isobe, P. M. Bailey, N. J. Meanwell, and P. M. Maitlis, *Organometallics*, 1982, **1**, 1604.
5 K. Isobe, A. Vázquez de Miguel, P. M. Bailey, S. Okeya, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1983, 1441.
6 A. Vázquez de Miguel, M. Gómez, K. Isobe, B. F. Taylor, B. E. Mann, and P. M. Maitlis, *Organometallics*, 1983, **2**, 1724.
7 K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 808.
8 K. Isobe, A. Vázquez de Miguel, and P. M. Maitlis, *J. Organomet. Chem.*, 1983, **250**, C25.
9 A. L. Gayler and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 2235.
10 K. Mertis and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, 1976, 1488; J. F. Gibson, G. M. Lack, K. Mertis, and G. Wilkinson, *ibid.*, 1976, 1492.
11 W. P. Griffith, 'Chemistry of the Rarer Platinum Metals,' Interscience, London, 1967, p. 231; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, 1981, p. 907.
12 B. E. Mann, C. Masters, and B. L. Shaw, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2195.
13 N. Dudeney, O. N. Kirchner, J. C. Green, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, in the press.
14 A. Nutton, A. Vázquez de Miguel, K. Isobe, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1983, 166 and refs. therein.
15 J. C. Hayes and N. J. Cooper, *J. Am. Chem. Soc.*, 1982, **104**, 5570; H. Kletzin, H. Werner, O. Serhadli, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 46; see also D. L. Thorn and T. L. Tulip, *J. Am. Chem. Soc.*, 1981, **103**, 5984.
16 S. Okeya, B. F. Taylor, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1983, 971; S. Okeya, N. J. Meanwell, B. F. Taylor, K. Isobe, A. Vázquez de Miguel, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, in the press.
17 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, pp. 158, 164.
18 M. Baudler, 'Handbook of Preparative Inorganic Chemistry,' 2nd edn., ed. G. Brauer, Academic Press, New York, 1963, vol. 1, p. 763.
19 A. J. Shortland and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 872.
20 M-J. Fernandez and P. M. Maitlis, *Organometallics*, 1983, **2**, 164; *J. Chem. Soc., Dalton Trans.*, in the press.
21 T. M. Gilbert and R. G. Bergman, *Organometallics*, 1983, **2**, 1458.

Received 4*th July* 1983; *Paper* 3/1149