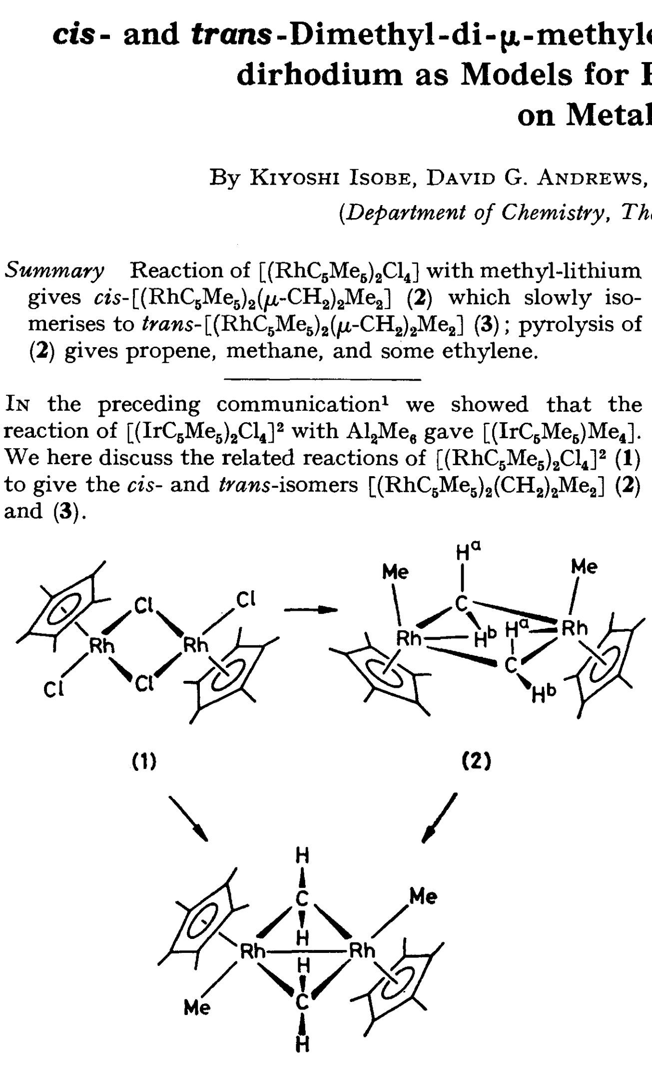
cis- and *trans*-Dimethyl-di-μ-methylene-bis(pentamethylcyclopentadienyl)-dirhodium as Models for Fischer–Tropsch Reactions on Metal Surfaces

By Kiyoshi Isobe, David G. Andrews, Brian E. Mann, and Peter M. Maitlis*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary Reaction of $[(RhC_5Me_5)_2Cl_4]$ with methyl-lithium gives *cis*-$[(RhC_5Me_5)_2(\mu\text{-}CH_2)_2Me_2]$ (**2**) which slowly isomerises to *trans*-$[(RhC_5Me_5)_2(\mu\text{-}CH_2)_2Me_2]$ (**3**); pyrolysis of (**2**) gives propene, methane, and some ethylene.

In the preceding communication[1] we showed that the reaction of $[(IrC_5Me_5)_2Cl_4]$[2] with Al_2Me_6 gave $[(IrC_5Me_5)Me_4]$. We here discuss the related reactions of $[(RhC_5Me_5)_2Cl_4]$[2] (**1**) to give the *cis*- and *trans*-isomers $[(RhC_5Me_5)_2(CH_2)_2Me_2]$ (**2**) and (**3**).



The *cis*-complex (**2**) was obtained (28% yield) from reaction of (**1**) with methyl-lithium as red-brown crystals from pentane. It was stable as the solid or in solution in the cold, but under some conditions the *cis*-isomer (**2**) was slowly converted into the *trans*-isomer (**3**). The latter was also obtained (15% yield) by reaction of (**1**) with Al_2Me_6.

Complexes (**2**) and (**3**) gave similar microanalyses and similar mass spectra, notably M^+ at *m/e* 534 corresponding to $(C_{24}H_{40}Rh_2)^+$.

The $^{13}C\{^1H\}$ n.m.r. spectra [100 MHz; $CDCl_3$ at −20 °C for (**2**), CD_2Cl_2 at +30 °C for (**3**)] showed four signals in each case, two of which arose from the η^5-C_5Me_5 ligand [δ 9·7 (C_5*Me*$_5$) and 100·0 p.p.m. (*C*$_5Me_5$) in both]. The other two signals were at very low and high field respectively [δ 156·0 for (**2**), 161·5 p.p.m. for (**3**); −0·4 for (**2**), −4·0 p.p.m. for (**3**)]. The low-field signals are in the characteristic positions for methylene ligands[3] and since they are seen as triplets (*J* 28 Hz) arising from coupling to ^{103}Rh ($I = \frac{1}{2}$, 100%) they must be methylene groups bridging two rhodium atoms. The high-field signals have the characteristic chemical shifts of metal-bonded methyl groups and since they are both doublets [*J*(Rh–C) 30·5 for (**2**) and 33·6 Hz for (**3**)] they arise from methyl groups bound to only one rhodium atom.

The ^1H n.m.r. spectrum of (**3**) (400 MHz, CD_2Cl_2) shows three signals [at δ −0·87 (t, *N*[4] 3·0 Hz), +1·70 (t, *N* 0·6 Hz), and +8·30 (t, *N* 1·8 Hz)] in the ratio of 3 : 15 : 2, and which are therefore due to the CH_3, C_5Me_5, and CH_2 groups respectively. Bearing in mind the multiplicity of the ^{13}C resonances we conclude that the couplings to the first two signals must arise from a 'virtual coupling' to the two rhodiums but that the coupling of the third lowest-field resonance arises from the CH_2 bridging the two metals.

The ^1H n.m.r. spectrum of complex (**2**) (400 MHz, $CDCl_3$) is very similar in the higher-field region [δ −0·46 (CH_3, t, *N* 0·6 Hz) and +1·70 (C_5Me_5, t, *N* 2·4 Hz)], but the low-field resonance is now a doublet (H^a, δ 6·96, *J* 1·8 Hz) and a doublet of triplets (H^b, δ 8·10, *J* 1·8, *J′* 2·6 Hz) each of relative intensity corresponding to one hydrogen. Decoupling showed that the smaller splitting arose from $J(H^a\text{–}H^b)$ while the larger triplet on the lowest-field resonance was due to coupling to the two rhodium atoms. These results show (a) that (**2**) and (**3**) are geometric isomers and that (**3**) is centrosymmetric,† (b) that in (**2**) the two

---

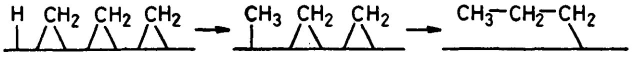
† Preliminary *X*-ray data on (**2**) and (**3**) confirm these structures.[5]

hydrogens (H^a and H^b) on the bridging methylene are not equivalent, and (c) that only one of these hydrogens (H^b) can couple to rhodium.‡

Although detailed structural studies are still in progress we may draw the analogy between the *cis*- and *trans*-complexes (**2**) and (**3**) and the well known *cis*- and *trans*-complexes $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2]$,[6] with the terminal CH_3 groups in (**2**) or (**3**) being formally equivalent to the terminal CO groups in these complexes and the bridging CH_2 groups equivalent to the bridging CO groups.

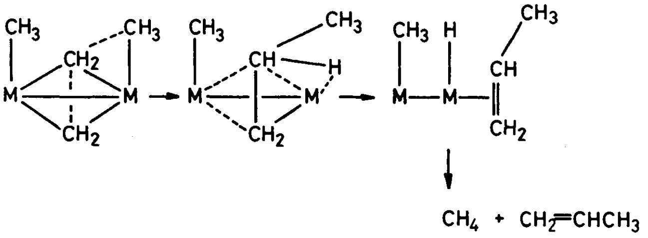
We have also studied the behaviour of (**2**), (**3**), and $[(IrC_5Me_5)Me_4]$ on heating. $[(IrC_5Me_5)Me_4]$ readily gave methane (97%) and small amounts of ethane (2%) and ethylene (1%) at temperatures between 250 and 350 °C. The *cis*-complex (**2**) was also easily pyrolysed; a typical product composition (pyrolysis at 350 °C) was methane (48%), ethylene (20%), ethane (2%), and propene (30%).§ Only trace amounts of propane and C_4 hydrocarbons were observed. The *trans*-complex (**3**) was more difficult to pyrolyse and gave about one-tenth of the amount of gas that (**2**) gave. The gas composition was similar to that from the *cis*-complex (**2**) except that less propene and more ethylene were formed. No cyclopropane was detected in any decomposition. Separate experiments using C_5Me_5Rh complexes *not* containing Rh-bonded CH_3 or CH_2 ligands gave only trace quantities of methane and no C_2–C_4 products, showing that breakdown of the C_5Me_5 ring was insignificant under these conditions.

Pettit and Brady[7] have recently reviewed and extended the original Fischer and Tropsch hypothesis on the mechanism of the formation of hydrocarbons from carbon monoxide and hydrogen. A key step in this mechanism was proposed to be a polymerisation of methylene groups on a metal surface initiated by a metal hydride (Scheme 1).



Scheme 1

The pyrolysis results described above lend support to this suggestion and a possible mechanism for the formation of methane and propene from *cis*-(**2**) is, by analogy, that given in Scheme 2.



Scheme 2

The production of propene rather than propane in the pyrolysis also agrees with the general view that the initial products of Fischer–Tropsch reactions are α-olefins.[8]

The fact that the *cis*-isomer (**2**) is so much more reactive than the *trans*-isomer (**3**) suggests that only certain arrangements of metal atoms, methylene groups, and hydride groups will facilitate the polymerisation reaction. Thus it should only take place on surfaces (of metal particles or crystallites, for example) where suitable sites are available.

We thank the S.R.C. for supporting this work.

(*Received*, 18*th May* 1981; *Com.* 595.)

‡ This phenomenon appears to have been observed before[3] but the point that ^3J(Rh–H) is highly directional has not previously been noted.

§ Percentages normalised to take account of the different numbers of carbon atoms in the various products; analysis by g.l.c. on Poropak Q (2 m) at 100 °C.

[1] K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, preceding communication.
[2] For recent reviews of the area see P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1; *Acc. Chem. Res.*, 1978, **11**, 301.
[3] W. A. Hermann, J. Plank, D. Riedel, M. L. Ziegler, K. Weidenhammer, E. Guggolz, and B. Balbach, *J. Am. Chem. Soc.*, 1981, **103**, 63.
[4] R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.
[5] P. M. Bailey, unpublished results.
[6] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 1970, 3068; R. F. Bryan and P. T. Green, *ibid.*, p. 3064.
[7] R. C. Brady and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 6181; *ibid.*, 1981, **103**, 1287.
[8] G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 136; see also 'Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen,' eds E. L. Kugler and F. W. Steffgen, A.C.S. Advances in Chemistry Series, 1979, p. 178.