Pergamon

Polyhedron Vol. 14, No. 19, pp. 2767–2769, 1995
Elsevier Science Ltd
Printed in Great Britain
0277-5387/95 \$9.50+0.00

0277-5387(95)00277-4

$[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(\eta^2\text{-}CH_2{=}CH_2)]PF_6$, A RHODIUM(IV) ETHYLENE COMPLEX*

ZHI-QIANG WANG, MICHAEL L. TURNER, BRIAN F. TAYLOR and
PETER M. MAITLIS†

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

Abstract—The rhodium(IV) ethylene complex $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(\eta^2\text{-}CH_2{=}CH_2)]PF_6$ was prepared in quantitative yield by the reaction of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]PF_6$ with ethylene. Variable temperature ^1H NMR spectra showed that the η^2-ethylene ligand did not exchange with free ethylene and rotated ($\Delta G\ddagger = 52$ kJ mol^{-1}). The complex decomposed on heating to give methane and ethylene, together with small amounts of higher olefins.

We have, over the past few years, synthesized many dinuclear complexes of the type $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)_2]$ (**A**), $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(X)_2]$ (**B**), $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)(X)]$ (**C**) and $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(R)(L)]PF_6$ (**D**) (R = alkyl, aryl, vinyl, etc, X = halide, etc, and L = CO, MeCN, etc).[1] These all have the intriguing feature of having the rhodium in the formal oxidation state of +4, and yet being quite robust and kinetically surprisingly inert. Thus, most of them are stable to air and to many reagents; the only consistent way we have found of decomposing them under mild conditions is with a one-electron oxidizer such as Ag^+ or iridium(IV). Under these conditions, complexes **A**, **C** and **D** decompose to give chiefly $RCH{=}CH_2$. These C—C—C coupling reactions have been applied as models for the methylene polymerization steps of the Fischer–Tropsch reaction over heterogeneous catalysts. A new mechanism has been proposed for this process based on the interaction of surface vinyls (or alkenyls) with surface CH_2.[2]

The proposed mechanism has been tested under actual Fischer–Tropsch conditions (carbon monoxide and hydrogen, 1 : 2, 1 atm, 225°C, over a rhodium–ceria–silica catalyst) and found to be consistent with the experimental observations.[3] It was found that ^{13}C-labelled vinyl bromide ($^{13}C_2H_3Br$) was an efficient source of C_2 initiator for hydrocarbon chain growth, when added to the H_2+CO gas feed; by contrast, ethylene was found to be a much poorer initiator. To try and use our model complexes to shed some further light on the individual steps, we have now synthesized the ethylene complex, $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(\eta^2\text{-}CH_2{=}CH_2)]PF_6$ (**1**), and have examined its decomposition.

$$[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]PF_6 + C_2H_4 \longrightarrow [\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(\eta^2\text{-}CH_2{=}CH_2)]PF_6$$

1

Reaction of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]PF_6$ (**2**)[4] with ethylene (1 atm) in dry acetone at −78°C gave the η^2-ethylene complex **1** in quantitative yield. The new complex was characterized by ^1H and ^{13}C NMR and IR spectroscopy, mass spectrometry and elemental analysis. The stability of complex **1** is very dependent on temperature: solid samples can be stored below −10°C under nitrogen for several weeks and solutions in acetone or dichloromethane saturated with ethylene are stable below −20°C.

The ethylene complex **1** was shown to be a single isomer by ^1H NMR spectroscopy. By contrast, a

---

*With all good wishes to Prof. E. W. Abel on his retirement.

† Author to whom correspondence should be addressed.

low temperature ^{1}H NMR study (-78°C) in acetone-d_6 showed that the acetonitrile complex **2** exists as a mixture of two isomers (*cis* and *trans*, 1 : 2).[4] We have previously suggested a "rule-of-thumb", that for *trans*-isomers of the type **A** or **B**, the difference in chemical shift between the two methylene resonances in the ^{1}H NMR spectrum is <0.5 ppm, while for *cis*-isomers it is >0.5 ppm. However, it is not clear whether this always holds for asymmetric isomers such as **C** or **D**. If it does, then **1** is *cis*, since the ethylene complex **1** dissolved in CD_2Cl_2 showed two μ-CH_2 resonances at δ 8.60 and 9.75 at -80°C. On raising the temperature, the resonances due to the coordinated ethylene (which

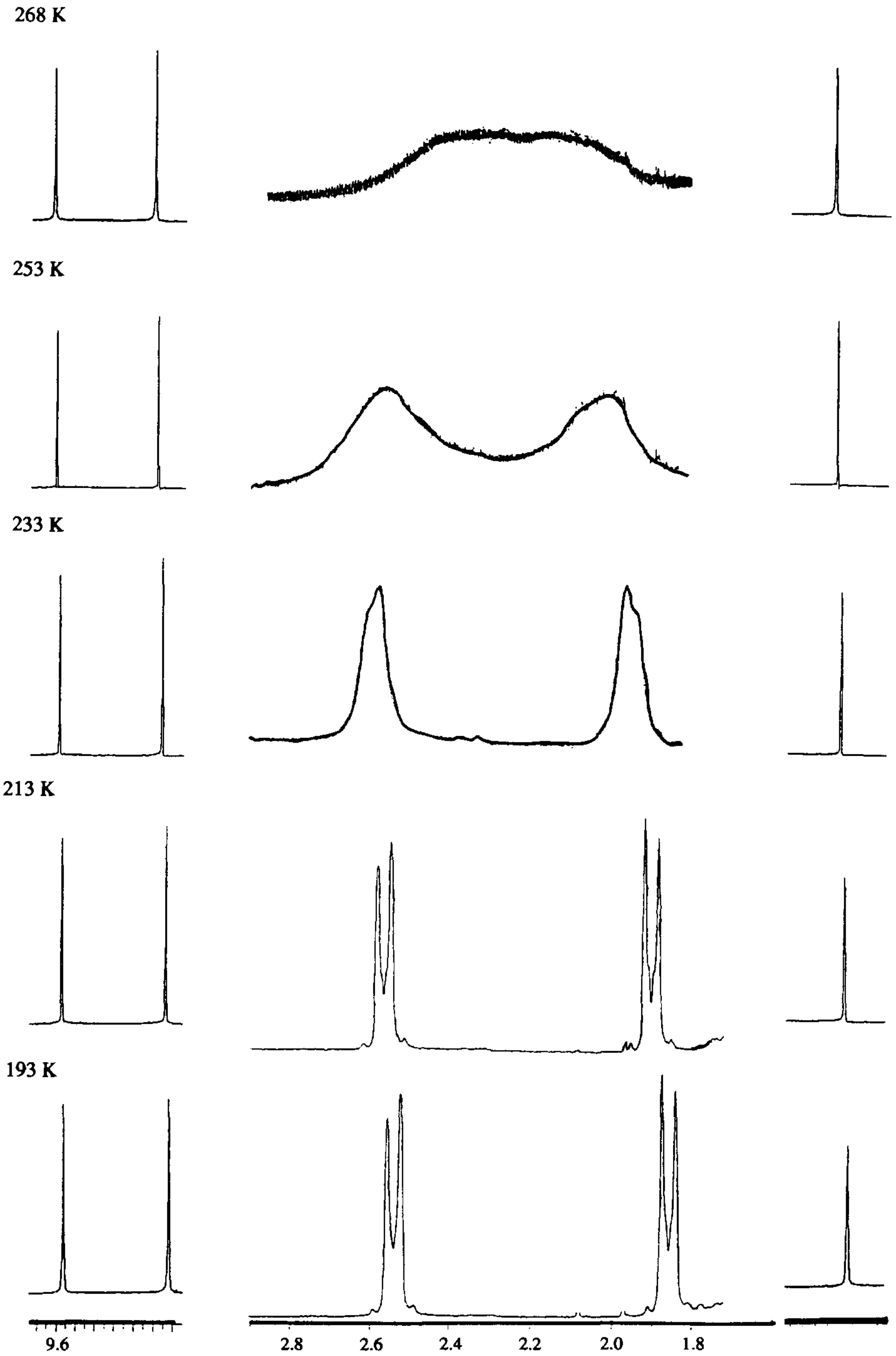

Fig. 1. The variable temperature ^{1}H NMR spectra of complex **1** in CD_2Cl_2; from bottom to top, at 193, 213, 233, 253 and 268 K; three regions, μ-CH_2 (left), η^2-C_2H_4 (middle) and Me–Rh (right), are observed.

give rise to an $[AX]_2$ spin system at 400 MHz, δ 1.88 and 2.57, at −80°C) slowly broadened and then collapsed into a broad singlet at *ca* −5°C (Fig. 1). None of the other resonances were affected and thus we propose that the dynamic behaviour arises from a rotation of the C_2H_4 about its bond to the rhodium. There was no sign of any isomerization of the complex nor was there any evidence of exchange coordinated with free ethylene in solution (δ 5.3). The coalescence temperature of the signals for the ethylene ligand was −5°C, leading to an estimated $\Delta G\ddagger$ 52 ± 2 kJ mol^{-1}. This value is close to that found for the mononuclear cyclopentadienyl complexes $[(C_5H_5)Rh(C_2H_4)(L)]$ ($L = C_2H_4$, SO_2, C_2F_4; $\Delta G\ddagger$ 50–65 kJ mol^{-1}),[5] but is significantly smaller than for the mononuclear pentamethylcyclopentadienyl rhodium complex $[(C_5Me_5)Rh(C_2H_4)_2]$ ($\Delta G\ddagger \geqslant 70$ kJ mol^{-1}).[6] We suggest that the binding of the ethylene in the dimeric **1** is significantly looser than in the mononuclear $[(C_5Me_5)Rh(C_2H_4)_2]$; this may be due to weaker back-bonding from the metal or because of greater steric congestion in the dimer.

Complex **1** reacted rapidly with HCl gas in acetone saturated with ethylene to give the dichloro dirhodium complex, $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Cl)_2]$. It also reacted with nucleophiles such as sodium methoxide to give $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)_2]$, a reaction similar to that which the acetonitrile complex **2** undergoes with bases.[4]

Complex **1** rapidly decomposed on warming above room temperature under nitrogen and it could also be decomposed at low temperature (below −20°C) by addition of an oxidant, such as basic iron sulphate, Na_2IrCl_6 or $AgBF_4$. Thermal decomposition (solid, under nitrogen, 80°C) gave mainly methane (51%) and ethylene (34%), together with small amounts (3–5%) of ethane, propylene and but-1-ene, as well as traces of but-2-enes and pentene (identified by GC–MS and quantified by GC). The complex decomposed very readily in acetone in the presence of $AgBF_4$ (25°C, 6 h) to give again largely methane (26%) and ethylene (67%), plus a small amount of propylene. There was some evidence for higher hydrocarbon formation when the decomposition of the solid was carried out at higher temperature (160°C), but in general these reactions showed little sign of ready C—C bond formation. This is in qualitative agreement with the observations that ethylene is not a good initiator of methylene polymerization during the Fischer–Tropsch reaction over rhodium catalysts.

EXPERIMENTAL

Ethylene was bubbled slowly through the red solution of the acetonitrile complex $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]PF_6$ (**2**) (0.040 g, 0.056 mmol) dissolved in acetone (3 cm^3; −78°C; 2 h); the colour of the solution changed to orange–red. Diethyl ether (20 cm^3) saturated with ethylene at room temperature was slowly added to the solution at −78°C, causing the precipitation of orange–red crystals of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(C_2H_4)]PF_6$ (**1**) (0.038 g, 100%). The crystals were filtered off and were dried *in vacuo* below −20°C; they could be kept under an ethylene atmosphere below −10°C for some weeks.

Found: C, 43.25; H, 6.1. Calc. for $C_{25}H_{41}F_6PRh_2$: C, 43.4; H, 6.0. Mass spectrum (FAB): *m*/*z* 664 ($M^+ - 28$). IR (KBr): 841 cm^{-1} (PF_6). ^1H NMR (Bruker AMX 400; CD_2Cl_2, −80°C): δ 1.55 (s), 1.64 (s, C_5Me_5); 0.60(d, $J = 3$ Hz, CH_3); 8.52 (sb), 9.58 (sb, CH_2); 2.57 (m), 1.88 (m, $CH_2{=\!=}CH_2$). ^{13}C NMR (CD_3COCD_3): δ 10.2 (s), 10.6 (s, $C_5\mathit{Me}_5$); 99.3 (s), 100.5 (s, C_5Me_5); 44.1 (d, J(Rh–C) = 14 Hz, $CH_2{=\!=}CH_2$), 180.6 (t, $J = 30$ Hz, CH_2).

Acknowledgements—We thank the S.E.R.C. and the Royal Society for support.

REFERENCES

1. P. M. Maitlis, *J. Organomet. Chem.* 1995, **500**, in press.
2. P. M. Maitlis, *Pure Appl. Chem.* 1989, **61**, 1747; I. M. Saez, D. G. Andrews and P. M. Maitlis, *Polyhedron* 1989, **7**, 827; J. Martinez, J. B. Gill, H. Adams, N. A. Bailey, I. S. Saez, G. J. Sunley and P. M. Maitlis, *J. Organomet. Chem.* 1990, **394**, 583; G. J. Sunley, I. M. Saez and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* 1990, 2193.
3. M. L. Turner, P. K. Byers, H. C. Long and P. M. Maitlis, *J. Am. Chem. Soc.* 1993, **115**, 4417; M. L. Turner, H. C. Long, A. Shenton, P. K. Byers and P. M. Maitlis, *Chemistry—A European Journal* 1995, in press.
4. S. Okeya, N. J. Meanwell, B. F. Taylor, K. Isobe, A. Vázquez de Miguel and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* 1984, 1453.
5. R. Cramer, *J. Am. Chem. Soc.* 1972, **94**, 5681; R. Cramer, J. B. Kline and J. D. Roberts, *J. Am. Chem. Soc.* 1969, **91**, 2519.
6. K. Moseley, J. W. Kang and P. M. Maitlis, *J. Chem. Soc.* (*A*) 1970, 2875; R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta* 1971, **5**, 528.