

Platinum(0) Activation of Rhenium Polyhydride Complexes: Synthesis and X-Ray Crystal Structure of the Hydrido-ethylene Complex $[\text{ReH}_3(\text{C}_2\text{H}_4)_2(\text{PPhPr}^i)_2]$

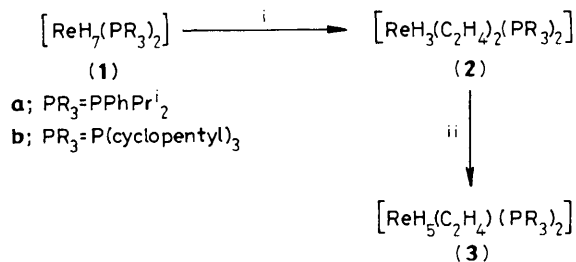
Nicholas J. Hazel, Judith A. K. Howard, and John L. Spencer

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

In the presence of $[\text{Pt}(\text{PPhBu}^t)_2]$ or $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPhPr}^i)_2]$ and ethylene (1 atm), $[\text{ReH}_7(\text{PR}_3)_2]$ [$\text{PR}_3 = \text{PPhPr}^i$ (**1a**); $\text{P}(\text{cyclopentyl})_3$ (**1b**)] reacts to give $[\text{ReH}_3(\text{C}_2\text{H}_4)_2(\text{PR}_3)_2]$ (**2**), which affords $[\text{ReH}_5(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ (**3**) on exposure to H_2 (1 atm).

Rhenium polyhydride complexes have recently been shown to be useful precursors for organorhenium chemistry¹ and to be capable of cleaving C–H bonds² in cyclic alkanes. Nevertheless, the complexes are not very reactive at 20 °C and are usually activated thermally or photochemically.^{3,4} We report here the activation of a transition metal polyhydride by platinum complex catalysts, and the synthesis of novel hydrido-ethylene complexes of rhenium.

The complex $[\text{ReH}_7(\text{PPhPr}^i)_2]$ (**1a**)⁵ does not react with ethylene (1 atm) at room temperature over a period of several days in hexane solution. However, in the presence of a platinum(0) complex such as $[\text{Pt}(\text{PPhBu}^t)_2]$ ⁶ or $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPhPr}^i)_2]$ ⁷ and ethylene a red colour develops which is subsequently discharged over 12–72 h depending on the relative proportions of Re and Pt. The new hydrido-ethylene complex $[\text{ReH}_3(\text{C}_2\text{H}_4)_2(\text{PPhPr}^i)_2]$ (**2a**) may be isolated from the solution as colourless crystals in 80% yield. When the reaction was followed by ³¹P n.m.r. spectroscopy a transient Pt–Re complex was observed but not isolated. The ultimate products of the reaction are ethane, (**2a**), and the regenerated Pt⁰ complex; no solid is deposited. It is evident that the Pt⁰ species functions as a catalyst as the reaction



Scheme 1. Reagents: i, C_2H_4 (1 atm), Pt(0), 20 °C; ii, H_2 (1 atm), 20 °C.

proceeds with Pt:Re ratios as low as 1:15. The complex $[\text{ReH}_3(\text{C}_2\text{H}_4)_2\{\text{P}(\text{cyclopentyl})_3\}_2]$ (**2b**) is prepared similarly from (**1b**), (80%).

Complexes (**2a**) and (**2b**) have been characterized by ¹H, ¹³C, and ³¹P n.m.r. spectroscopy,[†] elemental analysis, and by X-ray crystallography (**2a**)[‡] (Figure 1). The co-ordination environment of the Re atom is of approximate C_{2v} symmetry with parallel *cisoid* symmetrically bound ethylene ligands, an arrangement similar to that found in $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$. (Hacac = pentane-2,4-dione).⁸ The hydride ligands form a belt opposite, and in the plane bisecting, the ethylene ligands. The phosphine ligands are distorted from a *trans*-geometry, presumably as a result of steric interaction with the ethylene environments. The presence of three hydride ligands is further

[†] Selected n.m.r. data (25 °C; C_6D_6): (**2a**), ¹H, δ 7.7–7.13 (10 H, C_6H_5); 2.42 (m, 4 H, P–C–H) 1.42 (br. s, 8 H, C_2H_4), 1.23–0.96 (m, 24 H, CH_3), and –7.1 [t, 3 H, ReH, $J(\text{PH})$ 26 Hz]; ³¹P, δ 49.0 p.p.m. (**2b**), ¹H, δ 2.4–2.1 (6 H, P–C–H), 1.8–1.4 (56 H, $\text{CH}_2 + \text{C}_2\text{H}_4$), and –7.2 [t, 3 H, ReH, $J(\text{PH})$ 24 Hz]; ³¹P, δ 17.66 p.p.m. (**3a**), ¹H, δ 7.9–7.1 (10 H, C_6H_5), 2.26 (m, 4 H, P–C–H), 1.82 (s, 4 H, C_2H_4), 1.3–0.8 (m, 24 H, CH_3), and –6.1 [t, 5 H, ReH, $J(\text{PH})$ 19.7 Hz]; ³¹P, δ 49.0 p.p.m. (**3b**), ¹H, 2.11 (br. s, 4 H, C_2H_4), 1.68–1.3 (54 H, C_5H_9), and –6.86 [t, 5 H, ReH, $J(\text{PH})$ 19.7 Hz]; ³¹P, δ 44.25 p.p.m.

[‡] Crystal data for (**2a**): $\text{C}_{28}\text{H}_{49}\text{P}_2\text{Re}$, $M = 633.84$, monoclinic, $a = 8.779(4)$, $b = 26.33(12)$, $c = 12.197(7)$ Å, $\beta = 91.82(4)^\circ$ (190 K), $U = 2817.8(2.5)$ Å³, $Z = 4$, space group $P2_1/n$ (No. 14, non-standard setting), $F(000) = 1288$, Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 45.0$ cm⁻¹. 3880 Unique absorption-corrected data with $I > 2.5\sigma(I)$ were selected from 4953 recorded intensities: $R(R') 0.030$ (0.029). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

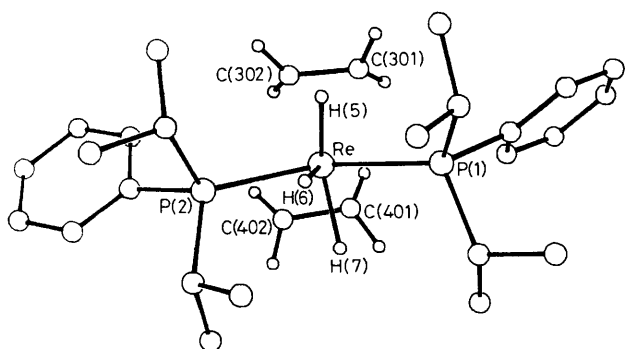


Figure 1. Molecular structure of (2a). Bond lengths: Re–P(1) 2.398(2), Re–P(2) 2.404(2), Re–C(301) 2.263(6), Re–C(302) 2.260(6), Re–C(401) 2.255(6), Re–C(402) 2.259(6), Re–H(5) 1.81, Re–H(6) 1.67(5), Re–H(7) 1.67(6) Å. Bond angles: P(1)–Re–P(2) 137.7(1), H(5)–Re–H(6) 54, H(6)–Re–H(7) 69°.

confirmed by the partially decoupled $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (2b) which shows a well resolved quartet.

The ^1H n.m.r. spectra of (2a) and (2b) are temperature dependent. At -60°C two hydride triplets are observed with intensity ratio 2:1 [for (2a); $\delta -7.73$, H(5) + H(7), $^2J(\text{PH})$ 20 Hz; -6.06 , H(6), $^2J(\text{PH})$ 29 Hz] and two ethylene resonances are also observed, corresponding to inner and outer hydrogen ligands. At ca. 45°C sharp single resonances are observed for both the hydride (triplet) and olefinic hydrogen, consistent with rapid ethylene rotation and hydride site exchange. At 70°C both resonances are broad and spin-saturation-transfer experiments⁹ confirm exchange between M–H and C_2H_4 protons, presumably through an ethyl intermediate. Similar dynamic behaviour has recently been observed¹⁰ in the complex $[\text{ReH}_3(\text{C}_5\text{H}_6)(\text{PPh}_3)_2]$ ($\text{C}_5\text{H}_6 = \text{cyclopentadiene}$).

Both (2a) and (2b) react with H_2 (1 atm) in hexane to produce the new mono-ethylene pentahydride complexes

$[\text{ReH}_5(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ (3a) and (3b)[†] which are formally analogous to the class of tris(tertiary phosphine) compounds $[\text{ReH}_5(\text{PR}_3)_3]$.¹¹

Metal–olefin–hydride complexes are rare and the new compounds (2) and (3) present an ideal and exciting opportunity for the study of olefin metal chemistry in a polyhydride environment.

We thank the S.E.R.C. for financial support.

Received, 29th August 1984, Com. 1230

References

- 1 D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 1982, **224**, 363.
- 2 D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1980, 1243; D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, *Tetrahedron Lett.*, 1984, **25**, 1283.
- 3 M. A. Green, J. C. Huffman, and K. G. Caulton, *J. Organomet. Chem.*, 1981, **218**, C39.
- 4 G. L. Geoffroy and D. A. Roberts, *J. Organomet. Chem.*, 1981, **214**, 221.
- 5 N. G. Connelly, J. A. K. Howard, J. L. Spencer, and P. K. Woodley, *J. Chem. Soc., Dalton Trans.*, 1984, 2003; J. A. K. Howard, K. A. Mead, and J. L. Spencer, *Acta Crystallogr., Sect. C*, 1983, **39**, 555.
- 6 S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, 1976, **98**, 5850.
- 7 M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1979, 1749 and references therein.
- 8 J. A. Evans and D. R. Russell, *Chem. Commun.*, 1971, 197.
- 9 J. L. M. Sanders and J. D. Marsh, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1982, **15**, 353.
- 10 W. D. Jones and J. A. Maguire, *J. Am. Chem. Soc.*, submitted for publication.
- 11 J. Chatt and R. S. Coffey, *Chem. Commun.*, 1966, 545.