Preparation and Crystal Structure of an η-Allyl Transition Metal Tetrahydride, Tetrahydrido[1,2-bis(diphenylphosphino)ethane](η^3-2-isopropylallyl)rhenium

Denise Baudry, Philip Boydell, Michel Ephritikhine, Hugh Felkin,* Jean Guilhem, Claudine Pascard,* and Elise Tran Huu Dau

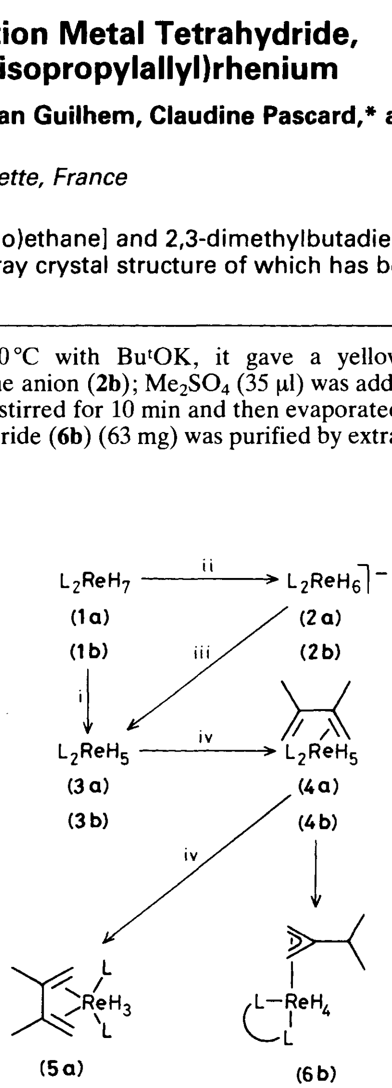
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

Treatment of a mixture of (dppe)ReH$_7$ [dppe = 1,2-bis(diphenylphosphino)ethane] and 2,3-dimethylbutadiene successively with Bu^{t}OK and Me$_2$SO$_4$ affords the title compound, the *X*-ray crystal structure of which has been determined.

Complexes with allyl ligands are ubiquitous in organo-transition metal chemistry, and η-allyl transition metal hydrides have been postulated as intermediates in a number of important catalytic reactions.[1] Not many such η-allyl hydrides have been isolated and characterised, the few that have are all monohydrides,[2] and only one crystal structure has been reported.[2b] Here we describe the preparation and *X*-ray crystal structure of an (η-allyl)rhenium tetrahydride (**6b**); we believe this to be the first example of a stable η-allyl transition metal complex containing more than one hydride ligand.

Bis(triarylphosphine)rhenium heptahydrides such as (**1a**)[3] are thermally labile and readily lose dihydrogen when heated in tetrahydrofuran (THF) (65 °C, 10 min); when the reaction is carried out in the presence of a diene, it leads to a bis(phosphine)(η-diene)rhenium trihydride, *e.g.*, (**5a**).[4] This reaction is thought to take place *via* the 16e pentahydride (**3a**) and the (η^2-diene)rhenium pentahydride (**4a**) (Scheme 1). The heptahydride (**1b**), with a chelating diphosphine ligand, is thermally much more stable[3] and does not react with dienes under the same conditions. The reasons for this difference are not understood.

We have found that both (**1a**) and (**1b**) can be made to react with dienes at room temperature by first converting them into the corresponding anions (**2**),† which are then methylated. In the presence of 2,3-dimethylbutadiene, the heptahydride (**1a**) affords the diene trihydride (**5a**) (15%), but the heptahydride (**1b**) leads to the (η-allyl)rhenium tetrahydride (**6b**) (37%). Thus, when a solution of the heptahydride (**1b**)[3] (145 mg) in THF (5 ml) containing 2,3-dimethylbutadiene (0.57 ml) was stirred at 20 °C with Bu^{t}OK, it gave a yellow solution containing the anion (**2b**); Me$_2$SO$_4$ (35 μl) was added and the mixture was stirred for 10 min and then evaporated *in vacuo*. The tetrahydride (**6b**) (63 mg) was purified by extraction with



Scheme 1. Postulated reaction paths. For (**a**), L = PPh$_3$ and (**b**), L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$. *Reagents:* i, L = PPh$_3$, THF, 65 °C, $-H_2$; ii, Bu^{t}OK, $-$Bu^{t}OH; iii, Me$_2$SO$_4$, $-CH_4$; iv, 2,3-dimethylbutadiene. Species (**3**) and (**4**) are postulated intermediates which have not been isolated or characterised.

---

† The anions (**2**) were formed in quantitative yield (by n.m.r.); they were not isolated. ^{1}H N.m.r., δ (60 MHz, THF): (**2a**), −7.5 [6 H, t, *J*(PH) 14 Hz, Re-H]; (**2b**), −8.0 [6 H, t, *J*(PH) 14 Hz, Re-H].

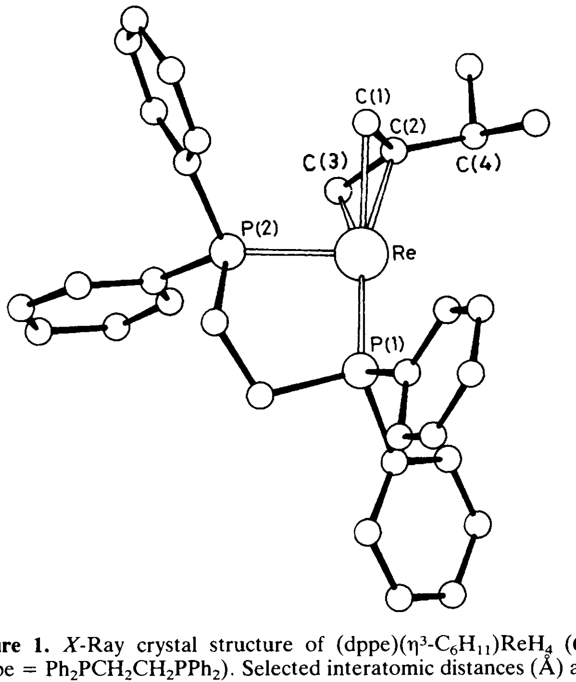


Figure 1. *X*-Ray crystal structure of (dppe)(η^3-C_6H_{11})ReH_4 (**6b**) (dppe = $Ph_2PCH_2CH_2PPh_2$). Selected interatomic distances (Å) and angles (°): Re–P(1) 2.377(1), Re–P(2) 2.421(1), Re–C(1) 2.305(19), Re–C(3) 2.261(10), Re–C(2) 2.214(14); P(1)–Re–P(2) 82.9(1), P(1)–Re–C(2) 165.4(3), P(2)–Re–C(2) 111.6(3), P(2)–Re–C(1) 90.4(5), P(2)–Re–C(3) 91.8(2), P(1)–Re–C(1) 145.6(5), P(1)–Re–C(3) 149.0(2), C(1)–Re–C(3) 64.4(5).

benzene followed by recrystallisation from methanol–THF, and isolated as colourless, air-stable, crystals.‡

Crystals of a benzene solvate of (**6b**) suitable for *X*-ray diffraction were obtained from benzene–hexane; the crystal structure is shown in Figure 1.§ The two phosphorus atoms, the rhenium atom, C(2), and C(4) lie in an approximate mirror plane of symmetry which is orthogonal to a second plane formed by P(1), Re, C(1), and C(3). The four hydride ligands (which appear as two inequivalent pairs in the ^1H n.m.r. spectrum) were not located; they probably lie in a plane containing P(2) and Re and orthogonal to the first plane, since a space-filling model shows a pronounced cleft running more than half-way around the rhenium atom on the side remote from P(2). The molecule may therefore most simply be regarded as a pentagonal bipyramid with the allyl ligand and P(1) at the apices, and P(2) and the four hydride ligands spaced around the equator.

Alkyl–transition metal bonds are much weaker than hydrogen–transition metal bonds,[5] and we imagine that the methylrhenium hexahydrides L_2ReH_6Me, formed by methylation of the anions (**2**), readily lose methane at 20 °C to form the 16e pentahydrides (**3**), which then react with the diene to give the η^2-diene pentahydrides (**4**). The divergent paths followed by (**4b**), which rearranges to the allyl tetrahydride (**6b**), and (**4a**), which undergoes further dehydrogenation to the diene trihydride (**5a**), are presumably related to the structures of the final products; (diene)rhenium trihydrides such as (**5a**) possess a distorted pentagonal bipyramidal structure, with P–Re–P *ca.* 145°,[6] which cannot accommodate a chelating ligand like dppe ('bite angle' typically *ca.* 85°).[7]

The isolation and characterisation of the η-allyl tetrahydride (**6b**) further illustrates the remarkable propensity of rhenium for simultaneously accommodating a hydrocarbon ligand and several hydride ligands in thermally stable, isolable compounds; other examples are bis(phosphine)(η^4-diene) trihydrides such as (**5a**),[4,6] a bis(phosphine)(η^5-cyclohexadienyl) dihydride,[8] and a tris(phosphine)(η^2-cyclopentene) trihydride.[9] With other transition metals, such 18e polyhydrides are, with a few exceptions, kinetically unstable and only exist as transient intermediates in catalytic cycles.

Received, 18th December 1984; Com. 049

---

‡ The complex (**6b**)·1/4THF gave satisfactory elemental analyses (C, H, P). *Selected spectroscopic data:* δ (^1H, 200 MHz, C_6D_6) 2.98 [1 H, septet, *J*(HH) 7 Hz, C*H*Me_2], 2.90 (2 H, br., *syn*-H), 1.57 [6 H, d, *J*(HH) 7 Hz, CH*Me*$_2$], 1.16 (2 H, deformed t, apparent *J* 8 Hz, *anti*-H), −5.8 (2 H, br., Re-H), −7.4 (2 H, br., Re-H); δ ($^{31}P\{ArH\}$, 80 MHz, C_6D_6) 45.3 (br.) and 43.2 p.p.m. (br.) (downfield from external 85% H_3PO_4); ν(mull) 1955 and 1925 cm^{-1} (Re–H stretch).

§ *Crystal data* for (**6b**): $C_{32}H_{39}P_2Re$, M = 671.15, monoclinic, space group *C*2/*c*, a = 35.630(17), b = 10.865(6), c = 17.869(9) Å, β = 111.98(7)°, U = 6415(14) Å^3, Z = 8, D_c = 1.39 g cm^{-3}, D_m = 1.47 g cm^{-3}, μ(Mo-K_α) = 40.89 cm^{-1}. The experimental data were collected with a Philips four-circle diffractometer, using Mo-K_α radiation ($\bar{\lambda}$ = 0.7107 Å). From 5823 measured reflections, 4833 were significant [$I > 3\sigma(I)$]. The structure was solved by analysis of the Patterson function. Lorentz, polarization, and empirical absorption[10] intensity corrections were made. The hydrogen atoms, apart from the four hydride ligands, were located from Fourier difference maps and fixed in the refinements. These latter were performed with anisotropic thermal parameters using the large-blocks least-squares method[11] to R = 0.044 (R_w = 0.051). In the final difference series, three peaks of intensity *ca.* 2 electrons per Å^3 appeared close to a binary axis; we assign these to a disordered molecule of benzene. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

1 For leading references, see: J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980, p. 133; S. G. Davies, 'Organotransition Metal Chemistry. Applications to Organic Synthesis,' Pergamon Press, Oxford, 1982, Ch. 7; G. W. Parshall, 'Homogeneous Catalysis,' Wiley, New York, 1980, Ch. 3.

2 (a) H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 736; J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Am. Chem. Soc.*, 1975, **97**, 3871; O. Howarth, C. H. McAteer, P. Moore, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1981, 506; E. O. Sherman and P. R. Schreiner, *ibid.*, 1978, 223; (b) T. H. Tulip and J. A. Ibers, *J. Am. Chem. Soc.*, 1979, **101**, 4201.

3 J. Chatt and R. S. Coffey, *J. Chem. Soc. (A)*, 1969, 1963.

4 D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 1982, **224**, 363.

5 J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 238.

6 D. Baudry, Y. Dromzee, M. Ephritikhine, H. Felkin, and Y. Jeannin, *J. Organomet. Chem.*, 1984, **272**, 403.

7 V. G. Albano and P. L. Bellon, *J. Organomet. Chem.*, 1972, **37**, 151.

8 D. Baudry, M. Ephritikhine, H. Felkin, Y. Jeannin, and F. Robert, *J. Organomet. Chem.*, 1981, **220**, C7.

9 M. H. Green, J. C. Huffman, K. G. Caulton, W. K. Rybak, and J. J. Ziolkowski, *J. Organomet. Chem.*, 1981, **218**, C39.

10 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

11 G. M. Sheldrick, SHELX76 Program for Crystal Structure Determination, University of Cambridge, England, 1976.