Synthesis of η-Benzene-η-cyclohexa-1,3-diene Derivatives of Rhenium *via* Reaction of Rhenium Atoms with Benzene and Cyclohexene: Crystal Structures of Re(η-C_6H_6)(η-C_6H_8)H and (η-C_6H_6)Re(μ-H)$_2$Re(η-C_6H_8)$_2$

Malcolm L. H. Green,[a] Dermot O'Hare,[a] Judith A. Bandy,[b] and Keith Prout[b]

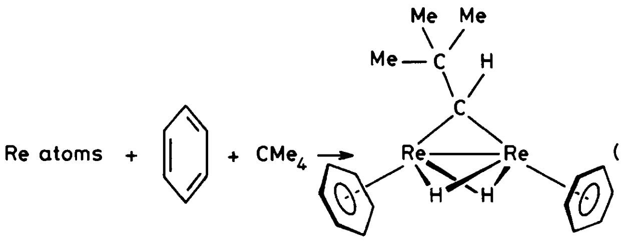
[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, U.K.*

The reaction between rhenium atoms, benzene, and cyclohexene gives the compound Re(η-C_6H_6)(η-C_6H_8)H and the mixed valency dimer (η-C_6H_6)Re(μ-H)$_2$Re(η-C_6H_8)$_2$.

When rhenium atoms are co-condensed with benzene in the presence of alkanes such as ethane and cyclohexane then binuclear compounds are formed in which CH_2 groups can undergo the loss of two hydrogens giving μ-alkylidene-di-μ-hydrido systems, *e.g.* equation (1).[1]

In order to investigate further the selectivity of the rhenium atom reactions towards hydrocarbon systems we have studied their co-condensation with a benzene–cyclohexene mixture (1 : 1). In a typical experiment, rhenium atoms (*ca.* 1 g) were co-condensed with a 1 : 1 mixture of benzene–cyclohexene (120 cm^3) over 4 h. The product was extracted with light petroleum and sublimation gave two compounds which were separated by fractional crystallisation from pentane.

The major component was the orange crystalline, air-sensitive compound Re(η-C_6H_6)(η-C_6H_8)H (**1**) and the minor product was a red crystalline compound (η-C_6H_6)Re-(μ-H)$_2$Re(η-C_6H_8)$_2$, (**2**). Compounds (**1**) and (**2**) have been characterised by ^1H and ^{13}C n.m.r. spectroscopy† and by crystal structure determinations.



(1)

Crystal data for (**1**): $ReC_{12}H_{15}$, $M = 345.45$, monoclinic, space group $P2_1/c$, $a = 10.208(2)$, $b = 6.282(2)$, $c = 16.476(5)$ Å, $\beta = 110.22(2)°$, $U = 991.42$ Å^3, $D_c = 2.31$ Mg m^{-3}, $Z = 4$, $\mu = 129.12$ cm^{-1}, $F(000) = 648.0$, $R = 7.18\%$, $R_w = 9.12\%$ for 3037 observed reflections $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

Crystal data for (**2**): $Re_2C_{18}H_{24}$, $M = 612.79$, triclinic, space group $P\bar{1}$, $a = 8.534(1)$, $b = 11.957(2)$, $c = 9.496(1)$ Å, $\alpha = 94.256(9)$, $\beta = 116.147(9)$, $\gamma = 109.06(1)°$, $U = 794.51$ Å^3, $D_c = 2.56$ Mg m^{-3}, $Z = 2$, $\mu = 160.92$ cm^{-1}, $F(000) = 564.00$, $R = 2.07\%$, $R_w = 2.72\%$ for 2927 observed reflections $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

Data were collected using an Enraf-Nonius CAD4 diffractometer [$2\theta_{max} = 66°$ for (**1**) and 58° for (**2**)]. The structures were solved by using Patterson and Fourier synthesis and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions which were modified between cycles of refinement. Crystallographic calculations were carried out using the Oxford CRYSTALS package.‡[3]

The crystal structures of (**1**) and (**2**) (Figures 1 and 2) show that the geometry of the η^4-1,3-cyclohexadiene ligands are analogous to those found in other structurally characterized

---

† N.m.r. data, *J* in Hz. Compound (**1**) in C_6D_6: δ_H −6.10 (1H, s, Re–H), 4.6 [2H, m(4 lines), AA′], 4.26 (6H, s, η-C_6H_6), 3.4 [2H, m(13 lines), BB′], 2.34 [2H, m(17 lines), XX′ or YY′], and 2.05 [2H, m(15 lines), YY′ or XX′]; δ_C 73.5 (*J* 171, 2C_A), 72.6 (*J* 172, η-C_6H_6), 48.3 (*J* 151, 2C_B), and 30.7 (*J* 131, 2C_{XY}); *m/z* 343 [P^+ − 1]. Compound (**2**) in $CD_3C_6D_5$: δ_H (room temp.) 4.88 (6H, s, η-C_6H_6), 1.75 (4H, br. s), and −8.5 [2H, s, 2×(Re−H)]; connectivity from COSY-45[2] at −65 °C, coupling constants from double resonance, δ_H (−65 °C) (only coupling constants greater than 3 Hz quoted) 5.2 [2H, dd, $J(H_aH_b)$ 7, $J(H_aH_d)$ 5, H_a], 4.8 (6H, s, η^6-C_6H_6), 3.7 (2H, br. m, H_b), 2.6 [2H, dt, $J(H_cH_g)$ 13, $J(H_cH_f)$ 7, H_c], 2.4 [2H, dd, $J(H_dH_a)$ 5, $J(H_dH_e)$ 6, H_d], 2.2 [2H, d, $J(H_dH_e)$ 6, H_e], 2.0 [4H, t, $J(H_fH_c)$ 7, $J(H_fH_g)$ 7, H_f], and 1.6 (2H, br. m, H_g);δ_c ($CD_3C_6D_5$, room temp.) 63.0 (η-C_6H_6) and 30.7 (C_g or C_f); δ_C (− 60 °C) [*J* refers to *J* (C−H)] 75.4 (2C, *J* 172, C_a), 67.8 (2C, *J* 173, C_d), 62.6 (6C, *J* 174, η-C_6H_6), 47.1 (2C, *J* 155, C_e), 36.0 (2C, *J* 151, C_b), 30.2 (2C, *J* 129, C_f or C_g), and 29.6 (2C, *J* 129, C_g or C_f); the ^{13}C assignments are from selective decoupling experiments at −65 °C. Compound (**3**) in C_6D_6: δ_H 4.97 (5H, s, η-C_5H_5) and 4.64 (6H, s, η-C_6H_6); δ_C 72.3 [*J*(C–H) 177, η-C_5H_5] and 60.85 [*J*(C–H) 175, η–C_6H_6].

‡ 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.

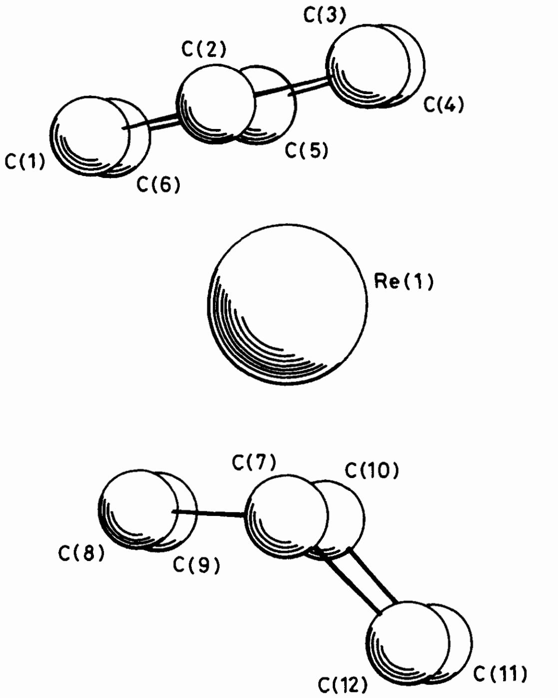


Figure 1. Molecular structure of Re(η-C_6H_6)(η-C_6H_8)H (**1**). Important interatomic distances (Å) and angles (°): Re(1)–C(7) 2.21(1), Re(1)–C(8) 2.186(8), Re(1)–C(9) 2.190(6), Re(1)–C(10) 2.227(8), C(7)–C(8) 1.43(1), C(8)–C(9) 1.42(1), C(9)–C(10) 1.45(1), C(10)–C(11) 1.51(1), C(11)–C(12) 1.53(1), C(12)–C(7) 1.52(1); C–C–C: (8)–(7)–(12) 117.8(9), (9)–(8)–(7) 113.6(7), (10)–(9)–(8) 114.6(7), (11)–(10)–(9) 117.2(7), (12)–(11)–(10) 110.5(6), (7)–(12)–(11) 110.8(7); Re–C_6H_6 plane 1.745; Re–C(7)C(8)C(9)C(10)-plane 1.78.

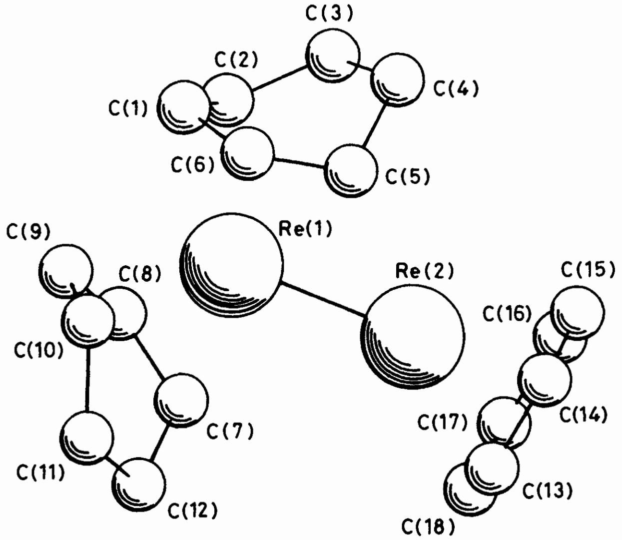
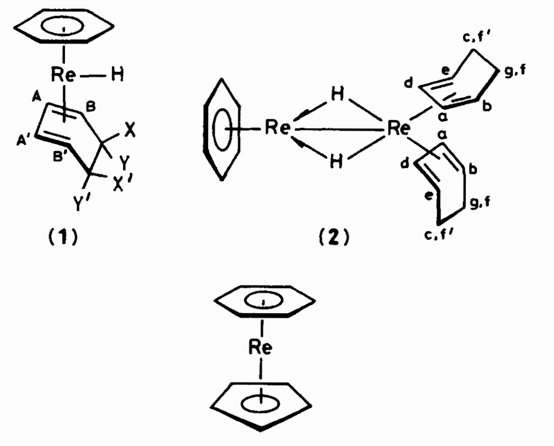


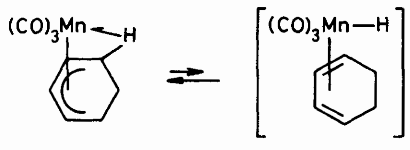
Figure 2. Molecular structure of Re(η-C_6H_6)(μ-H)$_2$Re(η-C_6H_8)$_2$ (**2**). Important interatomic distances (Å) and angles (°): C(1)–C(2) 1.44(1), C(2)–C(3) 1.52(1), C(3)–C(4) 1.53(1), C(4)–C(5) 1.55(1), C(5)–C(6) 1.45(1), C(6)–C(1) 1.41(1); C–C–C: (2)–(1)–(6) 115.4(7), (1)–(2)–(3) 119.0(7), (2)–(3)–(4) 109.8(6), (3)–(4)–(5) 110.2(6), (4)–(5)–(6) 114.1(6), (5)–(6)–(1) 113.8(6); Re(1)–Re(2) 2.555(1); Re(2)–C_6H_6-plane 1.68; Re(1)–C(1)C(2)C(5)C(6)-plane 1.80.

cyclohexadiene compounds.[4,5] The delocalization of the electrons within the butadiene entity tends to equalise the C(1)–C(2), C(1)–C(6), and C(6)–C(5) and C(7)–C(8), C(8)–C(9), and C(9)–C(10) bond lengths in (**2**) and C(7)–C(8), C(8)–C(9), and C(9)–C(10) bond lengths in (**1**). As expected the cyclohexadiene group is folded along the C(7)–C(10) vector in (**1**) and along the C(2)–C(5) and C(7)–C(10) vectors in (**2**) by 44.8, 41.9, and 44.9°, respectively. The structure of (**1**) shows that the η^6-C_6H_6 and η^4-C_6H_8 rings [taking the ring plane defined by C(7)–C(10)] are tilted by an angle of 17.0°, creating a site on the same side as C(7), C(10), C(11), and C(12) for the unobserved Re-hydrogen. The C(7), C(8), C(9), and C(10) carbon atoms are symmetrically located with respect to the Re(1) atom and the Re(1)–C(7) and Re(1)–C(10) distances are very similar. The n.m.r. data strongly support the diene structure for these carbon atoms. Further, there is a band at 1960 cm^{-1} in the i.r. spectrum assignable to a Re–H stretch. We conclude that a Re–H hydrogen group is located symmetrically between the two ring systems and there is not a Re–H–C interaction.



(**1**) (**2**) (**3**)

Figure 3



(A) (B)

In the crystal structure of (**2**) the molecule possesses a pseudo C_2 symmetry axis along the Re(1)–Re(2) vector which is consistent with the structure observed in solution. There is some evidence in the final difference map for the two bridging hydrogens which would be expected to lie in the plane defined by Re(1), Re(2), and the bisector of the lines joining the centroids of C(1), C(2), C(5), C(6) and C(7), C(8), C(9), C(10) to Re(2). The Re(1)–Re(2) bond length in (**2**) is 2.555(1) Å and is similar to the value of 2.436(1) Å found for [(η-C_6H_6)$_2$Re$_2$(μ-H)$_2$(μ-CHCMe$_3$)].[1]

Compound (**2**) is most unusual and electron counting considerations, using the approach previously outlined,[6] lead to the conclusion that compound (**2**) is, formally, a mixed valency compound in which Re(2) is d^4 and Re(1) is d^6, see Figure 3.

Brookhart has shown that in solution (η^4-cyclohexenyl)-tricarbonylmanganese, (A), is in equilibrium with the diene–hydride (B).[7] There is no evidence in the n.m.r. spectra† of (**1**) for a corresponding equilibrium. This observation supports the thesis that in equilibria between metal–olefin–hydride and the corresponding metal–agostic η-alkenyl system the latter moves towards the olefin–hydride in the sequence 5d > 4d >3d transition metals.[8]

Finally, co-condensation of rhenium atoms with a 1:1 mixture of benzene and cyclopentadiene gives the compound

Re(η-C_6H_6)(η-C_5H_5), (**3**),† in 17% yield, and the well-known Re(η-C_5H_5)$_2$H. Compound (**3**) has been previously described but the synthesis is lengthy and results in only 8% yield.[9]

We thank the British Petroleum Co. Ltd, the Northern Ireland Department of Education (D. O'H.), and S.E.R.C. (J. A. B.) for support and the donors of the Petroleum Research fund administered by the American Chemical Society for additional support.

Received, 29th March 1984; Com. 431

References

1 J. A. Bandy, F. G. N. Cloke, M. L. H. Green, D. O'Hare, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1984, 240.
2 A. Bax, '2D-N.M.R. in liquids,' Delft University Press, D. Reidel, London, 1982.
3 D. J. Watkin and J. R. Carruthers, 'CRYSTALS User Guide,' Chemical Crystallography Laboratory, University of Oxford, 1981.
4 C. Kruger and Yi-H. Tsay, *J. Organomet. Chem.*, 1971, **33**, 59.
5 M. R. Thompson, C. S. Day, V. W. Day, R. I. Mink, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 2979.
6 M. Berry, N. J. Cooper, M. L. H. Green, and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1980, 29.
7 M. Brookhart, W. Lamanna, and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **10**, 2117.
8 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.
9 E. O. Fischer and H. W. Werner, *Chem. Ber.*, 1968, **101**, 454.