Synthesis of η-Arene Rhenium Compounds using Rhenium Atoms. Crystal Structures of $[Re_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)_2(\mu\text{-}H)_2]$ and $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$ *

Malcolm L. H. Green and Dermot O'Hare
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The new compounds $[Re_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)_2(\mu\text{-}H)_2]$, $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$, $[Re(\eta\text{-}C_6H_6)(\eta^5\text{-}C_7H_7)]$, $[Re(\eta\text{-}C_6H_6)(\eta^5\text{-}C_7H_9)]$, and $[Re(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_9H_8)]$ are described, including the determination of the crystal structures of the first two compounds. The new compounds have been made by co-condensation of rhenium atoms with benzene–cyclohexene, benzene–cyclohexa-1,3-diene (or cyclohexene), benzene–cycloheptatriene, benzene–cycloheptatriene, and pure indene, respectively. Co-condensation of rhenium atoms with benzene–cyclopentadiene yields a mixture of $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]$ and $[Re(\eta\text{-}C_5H_5)_2H]$. Characterisation of the η-cycloheptatriene and η-indene derivatives required two-dimensional (^1H–^1H) COSY and (^{13}C–^1H) correlation n.m.r. spectroscopy. Co-condensation of rhenium atoms with cyclohexane–trimethylphosphine gives $[Re(\eta\text{-}C_6H_6)(PMe_3)_2H]$ where the η-benzene ligand derives from the cyclohexane.

Metal atoms have been shown to be useful and versatile intermediates for the synthesis of highly reactive organotransition metal compounds.[1] The positive hearth, electron-gun furnace is a convenient source of atoms of all the transition metals.[2] Recently we have shown that rhenium atoms can be used for the preparation of binuclear μ-alkylidene (R) derivatives $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}R)(\mu\text{-}H)_2)]$.[3,4] An interesting feature of these reactions is the activation of alkanes by the rhenium atoms, giving the μ-alkylidene groups, in the presence of an excess of benzene. This quite unexpected selectivity warranted further exploration. Therefore, we have studied the reaction between rhenium atoms and mixtures of benzene and cyclic olefins. A part of this work has been communicated.[5,6]

Results and Discussion

Co-condensation of rhenium atoms with a mixture of benzene and cyclohexene (1 : 1) gives, after fractional crystallisation from pentane, the less soluble, and minor component $[Re_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)_2(\mu\text{-}H)_2]$ (**1**) as bright red platelets, and the major component is orange crystalline $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$ (**2**). The crystal structures of (**1**) and (**2**) have been determined. The molecular structure of (**1**) is shown in Figure 1 and selected distances and angles are given in Table 1. The molecule possesses a non-crystallographic C_2 symmetry axis along the Re(1)–Re(2) vector which equivalences the η-cyclohexa-1,3-diene (C_6H_8) ligands.

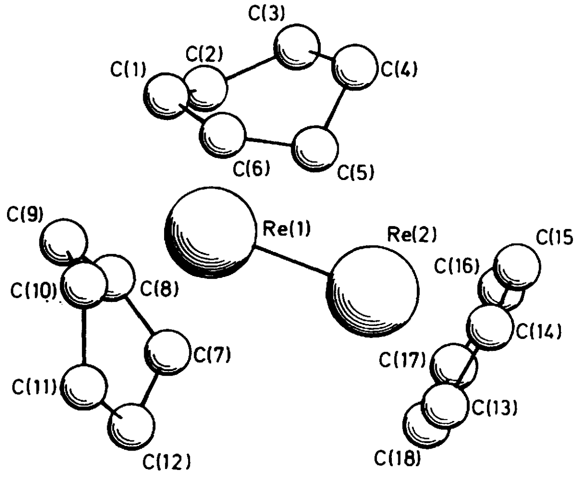

Figure 1. Molecular structure of (**1**)

The observed geometries of the η-cyclohexa-1,3-diene ligands are analogous to those found in other structurally characterised cyclohexadiene compounds.[7] The C(2)–C(1), C(1)–C(6), C(6)–C(5), C(7)–C(8), C(8)–C(9), and C(9)–C(10) bond lengths are closely similar (Table 1) which suggests that there is delocalisation of the electrons within the 1,3-diene entity. The η-cyclohexadiene ligands are folded along the C(2)–C(5) and C(7)–C(10) vectors by 41.9 and 44.9° respectively. The Re(1)–Re(2) bond length of 2.555(1) Å is typical of dirhenium complexes with a formal metal–metal single bond and two bridging ligands. An analysis of the structure and bonding in related dirhenium complexes has been presented in the preceding paper.[8]

Although there is some evidence in the final difference map for 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 data do not allow their unequivocal location.

Compound (**1**) is unusual in that electron-counting considerations[9] lead to the conclusion that it is formally a mixed-valence compound in which Re(1) is d^4 and Re(2) is d^6.

The room-temperature ^1H n.m.r. spectrum of (**1**) shows it to be fluxional (the characterising data for all new compounds are given in Table 2 and will only be discussed when interpretation is not straightforward). The only resonances observed at this temperature were a sharp singlet at δ 4.85 assignable to $\eta\text{-}C_6H_6$ hydrogens, and a rhenium–hydride resonance at δ −8.61. A two-dimensional (^1H–^1H) COSY-45 n.m.r. spectrum at −60 °C, together with extensive $^{13}C\text{-}\{^1H_{selective}\}$ n.m.r. experiments at −60 °C show that (**1**) has the same structure in solution as found for the crystalline state.

The molecular structure of (**2**) is shown in Figure 2 and

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* 1-(η-Benzene)-2,2-bis(η-cyclohexa-1′,3′-diene)-di-μ-hydrido-dirhenium (*Re–Re*) and (η-benzene)(η-cyclohexa-1,3-diene)hydridorhenium(I) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: Torr ≈ 133 N m^{-2}.

Table 1. Bond distances (Å) and angles (°) for $[Re_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)_2(\mu\text{-}H)_2]$ (**1**); estimated standard deviations are given in parentheses

Re(1)–Re(2)	2.555(1)	C(8)–C(9)	1.42(1)	C(17)–C(18)	1.37(1)	Re(1)–C(9)	2.215(7)
		C(9)–C(10)	1.42(1)	C(18)–C(13)	1.38(1)	Re(1)–C(10)	2.215(7)
C(1)–C(2)	1.44(1)	C(10)–C(11)	1.52(1)			Re(2)–C(13)	2.185(7)
C(2)–C(3)	1.52(1)	C(11)–C(12)	1.52(1)	Re(1)–C(1)	2.209(7)	Re(2)–C(14)	2.185(7)
C(3)–C(4)	1.53(1)	C(12)–C(7)	1.52(1)	Re(1)–C(2)	2.224(7)	Re(2)–C(15)	2.175(8)
C(4)–C(5)	1.55(1)	C(13)–C(14)	1.38(1)	Re(1)–C(5)	2.276(6)	Re(2)–C(16)	2.202(8)
C(5)–C(6)	1.45(1)	C(14)–C(15)	1.40(1)	Re(1)–C(6)	2.152(6)	Re(2)–C(17)	2.168(8)
C(6)–C(1)	1.41(1)	C(15)–C(16)	1.39(1)	Re(1)–C(7)	2.235(6)	Re(2)–C(18)	2.166(7)
C(7)–C(8)	1.42(1)	C(16)–C(17)	1.38(1)	Re(1)–C(8)	2.201(6)		

C(13)–C(14)–C(15)	119.6(4)	C(18)–C(13)–C(14)	112.0(4)	C(4)–C(5)–C(6)	114.1(6)	C(9)–C(10)–C(11)	120.9(7)
C(14)–C(15)–C(16)	119.4(4)	C(2)–C(1)–C(6)	115.4(7)	C(5)–C(6)–C(1)	113.8(6)	C(10)–C(11)–C(12)	108.9(6)
C(16)–C(17)–C(18)	119.8(4)	C(1)–C(2)–C(3)	119.0(7)	C(7)–C(8)–C(9)	113.0(7)	C(11)–C(12)–C(7)	110.9(6)
C(15)–C(16)–C(17)	120.7(4)	C(2)–C(3)–C(4)	109.8(7)	C(8)–C(9)–C(10)	114.1(6)	C(12)–C(7)–C(8)	120.3(7)
C(17)–C(18)–C(13)	120.3(4)	C(3)–C(4)–C(5)	110.2(6)				

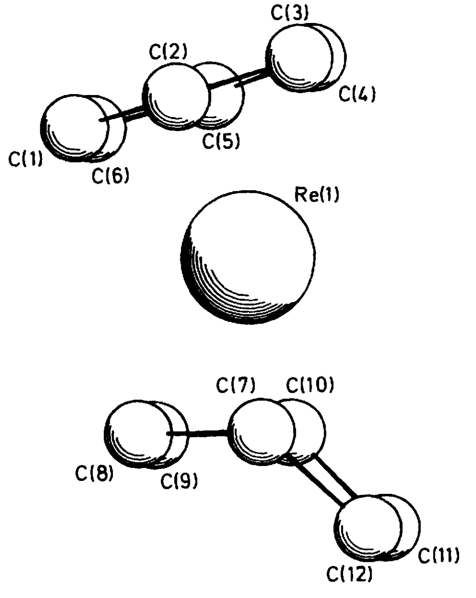


Figure 2. Molecular structure of (**2**)

selected distances and angles are given in Table 3. The $\eta\text{-}C_6H_6$ and $\eta\text{-}C_6H_8$ rings [taking the $\eta\text{-}C_6H_8$ ring plane to be that defined by C(7)—C(10)] are tilted by an angle of 17°, creating a site on the same side as the atoms C(7), C(10), C(11), and C(12) for the (unobserved) hydride ligand. The atoms C(7), C(8), C(9), and C(10) are symmetrically located with respect to Re(1), with the Re(1)–C(7) and Re(1)–C(10) distances being similar.

Compound (**2**) has been characterised in solution by ^1H and ^{13}C n.m.r. and by i.r. spectroscopy. The ^{13}C n.m.r. data strongly support the diene structure for the cyclohexadiene ligand. Further, there is a broad band at 1 960 cm^{-1} in the i.r. spectrum assignable to ν(Re–H). We conclude that the rhenium hydride is located symmetrically between the two ring systems and there is no Re $\leftarrow$ H–C interaction.

Brookhart *et al.*[10] have shown that in solution the isoelectronic agostic compound tricarbonyl(η^3-cyclohexenyl)manganese is in equilibrium with tricarbonyl(η-cyclohexa-1,3-diene)hydridomanganese. However, there is no evidence in the n.m.r. spectra of (**2**) for a corresponding equilibrium. This observation supports the hypothesis that in equilibria between a metal–olefin–hydride and the corresponding metal–agostic η-alkenyl system, the olefin–hydride is more favoured in the sequence 5*d* > 4*d* > 3*d* transition metals.[11]

Co-condensation of rhenium atoms with a mixture of benzene and cyclohexa-1,3-diene yields an orange microcrystalline solid which the ^1H n.m.r. spectrum shows to be *ca.* 95% $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$ (**2**) and *ca.* 2% $[Re_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)_2(\mu\text{-}H)_2]$ (**1**). The almost exclusive formation of (**2**) in this reaction suggests that hydrogen abstraction from cyclohexene is the crucial step in the synthesis of (**1**).

Rhenium atoms were co-condensed with pure cyclohexene giving a yellow-orange solid, the ^1H n.m.r. spectrum of which could be interpreted as that of an approximately equimolar mixture of at least three compounds containing the $(\eta\text{-}C_6H_6)ReH$ moiety, including $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$. The other components could not be separated and their identity could not be elucidated due to the complexity of the spectra. However, we note that (**2**) could not be detected in the reaction products.

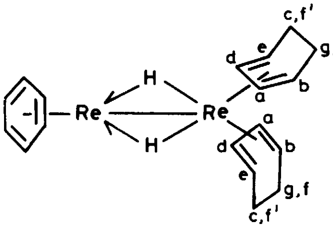
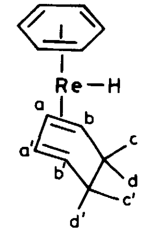
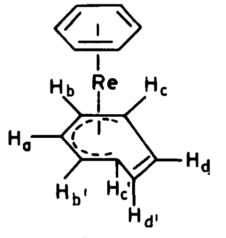
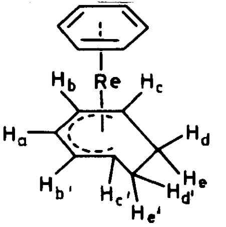
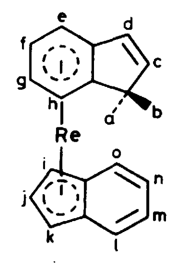
Co-condensation of rhenium atoms with a mixture of benzene and cycloheptatriene (1:1, w/w) gave a bright red microcrystalline solid. The ^1H n.m.r. spectrum showed there to be a mixture of two $\eta\text{-}C_6H_6$ rhenium complexes. The characterisation of the component compounds in the mixture was made possible by the two-dimensional (^1H–^1H) COSY-45 and two-dimensional (^{13}C–^1H) correlation n.m.r. spectra.[12] Analysis of the ^1H–^1H and ^1H–^{13}C connectivity unambiguously determines the two compounds to be $[Re(\eta\text{-}C_6H_6)(\eta^5\text{-}C_7H_7)]$ (**3**) and $[Re(\eta\text{-}C_6H_6)(\eta^5\text{-}C_7H_9)]$ (**4**), in the ratio 4:3, respectively. These formulations are supported by the mass spectral and microanalytical data (Table 2). Further, chromatography of the mixture on alumina separates (**3**) in high purity, but destroys (**4**). We were unable to obtain (**4**) free from (**3**). High-temperature magnetisation transfer experiments have shown that, surprisingly, the $\eta^5\text{-}C_7H_7$ ring in (**3**) does not undergo ring-shift processes at temperatures up to 90 °C, which puts a lower limit on $\Delta G^{\ddagger}$ of *ca.* 75 kJ mol^{-1}.

Co-condensation of rhenium atoms with a mixture of benzene and freshly distilled cyclopentadiene (4:1, w/w) gave yellow microcrystals. The ^1H n.m.r. spectrum shows the product to be a mixture of two complexes: $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]$ (**5**)[13] and the well known $[Re(\eta\text{-}C_5H_5)_2H]$ (**6**)[14] (ratio 3:2). Compound (**5**) could be separated from (**6**) by chromatography on alumina, in 8% yield.

Co-condensation of rhenium atoms with a mixture of cyclopentene and benzene (1:1) also gave a mixture of the known compounds $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]$ (**5**) and $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}C[CH_2]_4)]$[3,4] which were identified by comparison of the ^1H n.m.r. spectrum with those of authentic samples.

Co-condensation of rhenium atoms with pure indene yields, after removal of the volatile compounds, work-up and crystallisation, orange crystals of $[Re(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_9H_8)]$ (**7**). The modes of bonding of the ligands were determined by extensive ^1H and ^{13}C n.m.r. experiments. All the hydrogens and

Table 2. Analytical and spectroscopic data for the new compounds[a]

Compound	N.m.r. data[b] ^{1}H	^{13}C
 (1)[c] (red)	[d] 4.85 [6 H, s, η-C_6H_6], 1.70 [4 H, br, η-C_6H_8], −8.61 [2 H, s, 2 Re–H] [e] At −60 °C: 5.2 [2 H, dd, $J(H_a–H_b)$ 7, $J(H_a–H_d)$ 5, H_a], 4.8 [6 H, s, η-C_6H_6], 3.7 [2 H, br, m, H_b], 2.6 [2 H, dt, $J(H_c–H_g)$ 13, $J(H_{f'}–H_c)$ 7, $J(H_f–H_c)$ 7, H_c], 2.4 [2 H, dd, $J(H_d–H_a)$ 5, $J(H_d–H_e)$, 6, H_d], 2.2 [2 H, d, $J(H_d–H_e)$ 6, H_e], 2.0 [4 H, t, $J(H_f–H_c)$ 7, $J(H_f–H_g)$ 7, $H_{ff'}$], 1.6 [2 H, br m, H_g], −8.6 [2 H, s, 2 Re–H]	[e] 70.0 [vbr, η-C_6H_8], 62.5 [s, η-C_6H_6], 30.5 [br, η-C_6H_8] [e] At −60 °C: 75.4 [d, J(C–H) 172, C_a], 67.8 [d, J(C–H) 173, C_d], 62.6 [d, J(C–H) 174, η-C_6H_6], 47.1 [d, J(C–H) 155, C_e], 36.0 [d, J(C–H) 151, C_b], 30.2 [t, J(C–H) 129, $C_{c,f'}$ or $C_{g,f}$], 29.6 [t, J(C–H) 129, $C_{g,f}$ or $C_{c,f'}$]
 (2)[f] (orange)	[d] 4.55 [2 H, m (4 lines), $H_{aa'}$], 4.27 [6 H, d, $J(H–H_{Re})$ 1.3, η-C_6H_6], 3.45 [2 H, m (13 lines), $H_{bb'}$], 2.38 [2 H, m (17 lines), $H_{cc'}$ or $H_{dd'}$], 2.08 [2 H, m (15 lines), $H_{dd'}$ or $H_{cc'}$], −6.10 [1 H, br, s, Re–H]	[d] 73.5 [d, J(C–H) 171, C_a], 72.6 [d, J(C–H) 172, η-C_6H_6], 48.3 [d, J(C–H) 151, C_b], 30.7 [t, J(C–H) 131, $C_{c,d}$]
 (3)[g] (red)	[e] 6.05 [1 H, tt, $J(H_a–H_b)$ 5.3, $J(H_a–H_c)$ 0.5, H_a], 5.80 [2 H, ddd, $J(H_b–H_a)$ 5.3, $J(H_b–H_c)$ 6.0, $J(H_b–H_d)$ 1.0, H_b], 5.30 [2 H, m (6 lines), H_d], 4.60 [6 H, s, η-C_6H_6], 3.9 [2 H, m (15 lines), H_c]	[e] 135.5 [d, J(C–H) obscured by solvent, C_d], 95.3 [d, J(C–H) 161, C_a], 82.6 [d, J(C–H) 162, C_b], 73.0 [d, J(C–H) 172, η-C_6H_6], 52.8 [d, J(C–H) 152, C_c]
 (4)[h] (red)	[e] 5.7 [1 H, t, $J(H_a–H_b)$ 5.1, H_a], 5.3 [2 H, dd, $J(H_b–H_a)$ 5.1, $J(H_b–H_c)$ 6.4, H_b], 4.54 [6 H, s, η-C_6H_6], 4.16 [2 H, m (13 lines), H_c], 1.71 [4 H, d, $J(H_{d/e}–H_c)$ 22, H_d + H_e]	[e] 98.8 [d, J(C–H) 163, C_a], 80.0 [d, J(C–H) 160, C_b], 70.7 [d, J(C–H) 173, η-C_6H_6], 54.0 [d, J(C–H) 143, C_c], 37.0 [t, J(C–H) 130, $C_{d/e}$]
 (7)[i] (orange)	[d] At 500 MHz: 6.91 [1 H, dq, $J(H_l–H_m)$ 7.5, $J(H_l–H_n)$, $J(H_l–H_o)$, $J(H_l–H_k)$ 1.0, H_l], 6.75 [1 H, ddd, $J(H_m–H_n)$ 8.5, $J(H_m–H_l)$ 7.5, $J(H_m–H_o)$ 1.0, H_m], 6.61 [1 H, dq, $J(H_o–H_n)$ 7.5, $J(H_o–H_m)$, $J(H_o–H_l)$, $J(H_o–H_i)$ 1.0, H_o], 6.58 [1 H, ddd, $J(H_n–H_m)$ 8.5, $J(H_n–H_o)$ 7.5, $J(H_n–H_l)$ 1.0, H_n], 5.84 [2 H, m (16 lines), H_c + H_d], 5.53 [1 H, m (4 lines), H_i], 5.40 [1 H, m (4 lines), H_k], 5.25 [1 H, t, $J(H_j–H_k)$, $J(H_j–H_i)$ 3, H_j], 5.23 [1 H, dd, $J(H_g–H_h)$ 5, $J(H_g–H_e)$ 1, H_g], 4.91 [1 H, dd, $J(H_e–H_g)$ 1, $J(H_e–H_f)$ 5, H_e], 4.72 [1 H, t, $J(H_f–H_g)$, $J(H_f–H_e)$ 5, H_f], 4.55 [1 H, t, $J(H_h–H_g)$, $J(H_h–H_f)$ 5, H_h], 1.81 [1 H, dt, $J(H_{a/b}–H_{a/b})$ 21, $J(H_{a/b}–H_c)$, $J(H_{a/b}–H_d)$ 1, H_a or H_b], 0.75 [1 H, dt, $J(H_{a/b}–H_{a/b})$ 21, $J(H_{a/b}–H_c)$, $J(H_{a/b}–H_d)$ 1, H_b or H_a]	[d] At 125.6 MHz: 131.6 [dq, ^{1}J(C–H) 166, $^{2}J(C–H_a)$, $^{2}J(C–H_b)$, $^{3}J(C–H_d)$ 3, C_c], 127.6 [ddt, ^{1}J(C–H) 168, $^{3}J(C–H_a)$, $^{3}J(C–H_b)$ 3, $^{2}J(C–H_c)$ 1.5 C_d], 126.8 [dd, ^{1}J(C–H) 167, ^{3}J(C–H) 3.7, C_l], 126.4 [dd, ^{1}J(C–H) 170, ^{3}J(C–H) 3.7, C_o], 121.2 [d, ^{1}J(C–H) 168, C_n], 120.1 [d, ^{1}J(C–H) 161, C_m], 92.7 [s, C], 92.2 [s, C], 84.4 [s, C], 79.4 [s, C], 74.9 [d, ^{1}J(C–H) 176, C_j], 66.6 [d, ^{1}J(C–H) 177, C_k], 66.1 [d, ^{1}J(C–H) 178 C_i], 59.9 [d, ^{1}J(C–H) 170, C_e], 58.9 [d, ^{1}J(C–H) 165, C_f], 57.9 [d, ^{1}J(C–H) 172, C_g], 57.6 [d, ^{1}J(C–H) 169, C_h], 35.5 [t, ^{1}J(C–H) 129, $C_{a/b}$]

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[a] Mass spectra are given for ^{187}Re, P^+ indicates the parent ion. Infrared spectra are for Nujol mulls on KBr plates, ν/cm^{-1}. ^{1}H N.m.r. and ^{13}C n.m.r. were recorded at 300 and 62.8 MHz respectively, and at r.t. unless otherwise stated. [b] Given as: chemical shift (δ) [relative intensity, multiplicity, coupling (J/Hz), assignment]; s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sxt = sextet, spt = septet, m = multiplet, vt = virtual triplet, br = broad, vbr = very broad. [c] M/e 614 [P^+]. [d] In [$^{2}H_6$]benzene. [e] In [$^{2}H_8$]toluene. [f] M/e 346 [P^+]. I.r.: ν(Re–H) 1 960m cm^{-1}. [g] M/e 356 [P^+]. Microanalysis [mixture of (3) and (4); required values in parentheses]: C, 45.6 (44.0); H, 3.9 (3.7)%. [h] M/e 358 [P^+]. Microanalysis: C, 45.6 (43.7); H, 3.9 (4.2)%. [i] M/e 428 [P^+]. Microanalysis: C, 51.6 (51.8); H, 3.5 (3.6)%.

Table 3. Bond distances (Å) and angles (°) for [Re(η-C_6H_6)(η-C_6H_8)H] (**2**); estimated standard deviations are given in parentheses

Re(1)–C(1)	2.24(1)	C(1)–C(2)	1.36(2)
Re(1)–C(2)	2.24(1)	C(2)–C(3)	1.42(2)
Re(1)–C(3)	2.23(1)	C(3)–C(4)	1.39(3)
Re(1)–C(4)	2.22(1)	C(4)–C(5)	1.39(3)
Re(1)–C(5)	2.22(2)	C(5)–C(6)	1.36(3)
Re(1)–C(6)	2.23(1)	C(6)–C(1)	1.41(2)
Re(1)–C(7)	2.21(1)	C(7)–C(8)	1.43(1)
Re(1)–C(8)	2.186(8)	C(8)–C(9)	1.42(1)
Re(1)–C(9)	2.190(6)	C(9)–C(10)	1.45(1)
Re(1)–C(10)	2.227(8)	C(10)–C(11)	1.51(1)
		C(11)–C(12)	1.53(1)
		C(12)–C(7)	1.52(1)
C(1)–C(2)–C(3)	118.7(13)	C(10)–C(9)–C(8)	114.6(7)
C(2)–C(3)–C(4)	119.1(12)	C(9)–C(8)–C(7)	113.6(7)
C(3)–C(4)–C(5)	121.8(15)	C(8)–C(7)–C(12)	117.8(9)
C(4)–C(5)–C(6)	118.3(14)	C(7)–C(12)–C(11)	110.8(7)
C(5)–C(6)–C(1)	121.0(13)	C(12)–C(11)–C(10)	110.5(6)
C(6)–C(1)–C(2)	120.9(12)	C(11)–C(10)–C(9)	117.2(7)

carbons in the molecule are chemically inequivalent, and complete assignment of all hydrogens and all proton-bearing carbons was achieved by a combination of two-dimensional (^1H–^1H) phase-sensitive COSY[15] and heteronuclear (^1H–^{13}C) shift-correlation,[15] and heteronuclear (^1H–^{13}C) *J*-resolved experiments.[16]

Since the hydrogens H_c and H_d could not be separately resolved at 500 MHz, shift-correlation experiments could not assign their attached carbons. It was however possible to assign C_c and C_d by examining the fully ^1H-coupled ^{13}C n.m.r. spectrum with particular emphasis on observing the long-range ^1H–^{13}C couplings. This assignment was achieved by recording a two-dimensional heteronuclear (^1H–^{13}C) *J*-resolved n.m.r. spectrum under high-resolution conditions. From this experiment we were able to resolve $^2J(CH)$ and $^3J(CH)$ couplings of magnitude <1 Hz. The carbon assigned as C_c appears as a doublet of quartets [$^1J(C_c–H_c) = 166$, $^2J(C_c–H_d) = {}^2J(C_c–H_a) = {}^2J(C_c–H_b) = 3$ Hz] while C_d appears as a doublet of doublets of triplets [$^1J(C_d–H_d) = 168$, $^2J(C_d–H_c) = 1.5$, $^2J(C_d–H_a) = {}^3J(C_d–H_b) = 3$ Hz]. Co-condensation of rhenium atoms with a 5% solution of trimethylphosphine in cyclohexane (spectroscopic grade) gives after work-up and sublimation, a mixture of the known compounds [Re(η-C_6H_6)(PMe_3)$_2$H] (**8**)[17] and [Re(PMe_3)$_4H_3$] (**9**).[18] The compound [Re(η-C_6H_6)(PPh_3)$_2$H], analogous to (**8**), has been described.[19] Elution of the product mixture on alumina (6% H_2O) with acetone–water (1 : 1, v/v) produces a brown, quickly moving band which, upon addition of ammonium hexafluorophosphate, gives a yellow precipitate of [Re(η-C_6H_6)(PMe_3)$_2H_2$]PF_6 (**10**).[18] This cation can be deprotonated to the neutral [Re(η-C_6H_6)(PMe_3)$_2$H] by KH.

Co-condensation of rhenium atoms with a 5% solution of trimethylphosphine in cycloheptane gives, after work-up and sublimation, [Re(PMe_3)$_4H_3$]. No other compounds could be detected by ^1H n.m.r. spectroscopy. Chromatography of the product on alumina (eluting with acetone) gives a pale yellow band which upon addition of ammonium hexafluorophosphate gives pure [Re(PMe_3)$_4H_4$]PF_6 (**11**).[17]

The reactions and the proposed structures of the products are shown in the Scheme. The detailed mechanisms for the formation of many of the products are unknown; however, it is clear that abstraction of hydrogen is a common reaction. It also appears that inter-ring hydrogen transfer occurs, as exemplified in the isomerisation reaction of [Mo(η-C_7H_8)$_2$] to [Mo(η-C_7H_7)(η^5-C_7H_9)].[20]

The activation of cyclohexane by rhenium has a parallel in the formation of [Ir(η-C_6H_6)(PPh_3)$_2$]$^+$ from [IrH_2(PPh_3)$_2$(Me_2CO)$_2$]$^+$ and cyclohexane.[21] The co-condensation of rhenium and a mixture of cyclohexane and trimethylphosphine giving the η-arene compound [Re(η-C_6H_6)(PMe_3)$_2$H] must proceed by a multi-step ligand-to-metal hydrogen transfer which, remarkably, proceeds in the presence of an excess of PMe_3. We assume that this reaction is driven by the stability of the Re–(η-C_6H_6) bond. The role of the PMe_3 in this reaction is not clear, yet it is essential since no reaction is observed between rhenium atoms and cyclohexane alone. It appears that some highly unsaturated intermediates such as {Re(PMe_3)$_n$} (n = 2—4) may be required to initiate attack on a C–H bond of cyclohexane. We note that [Re(PMe_3)$_4H_3$] is not formed when rhenium atoms are co-condensed with pure trimethylphosphine.[22] In contrast to cyclohexane, the reaction of rhenium atoms with a cycloheptane–trimethylphosphine mixture results in only hydrogen abstraction, giving [Re(PMe_3)$_4H_3$].

It seems probable that most of the reactions shown in the Scheme are essentially homogeneous; for example, there is a large excess of potential ligand substrate compared with rhenium.

Experimental

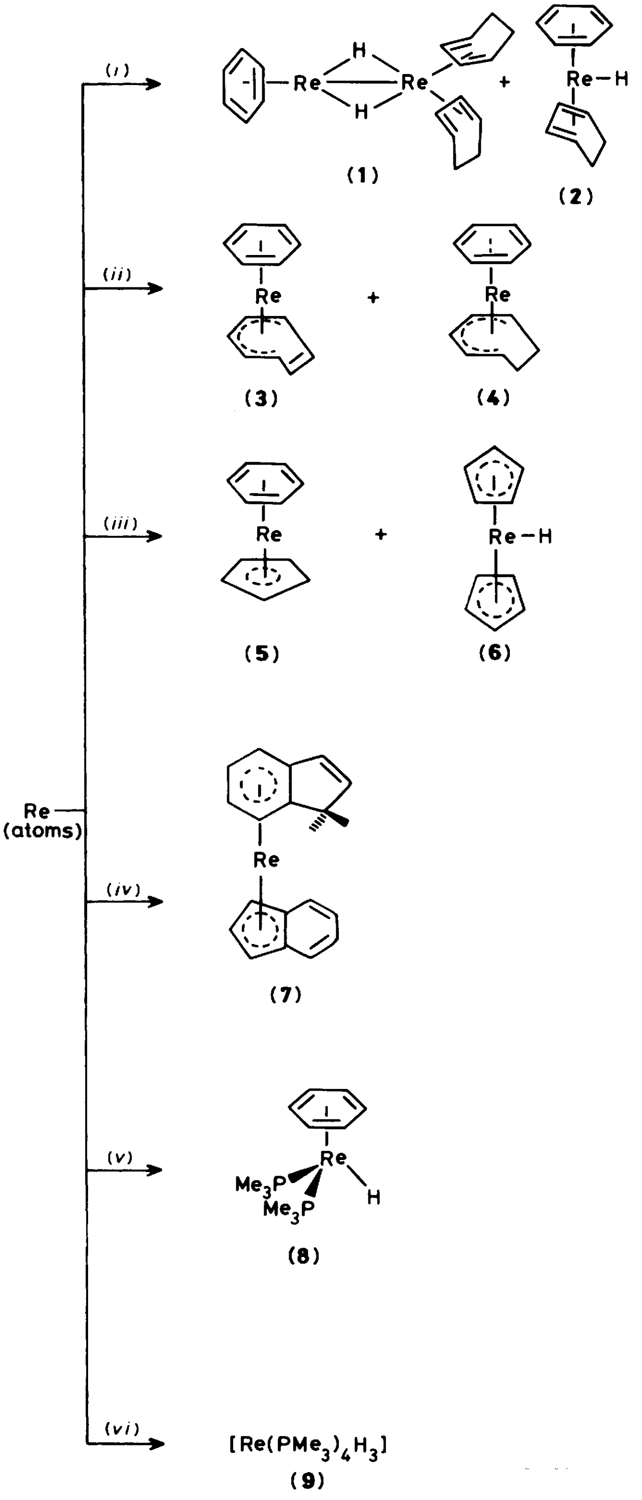
All preparations and reactions described were carried out under an atmosphere of nitrogen (< 10 p.p.m. oxygen or water) using standard Schlenk-tube and vacuum-line techniques or in a dry-box. Nitrogen was purified by passage through a gas drying column containing BASF catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of nitrogen. Solvents were pre-dried over molecular sieves and then distilled from potassium [toluene, benzene, tetrahydrofuran (thf), cyclohexane], sodium–potassium alloy [pentane, light petroleum (b.p. 40—60 °C throughout), diethyl ether], or phosphorus pentoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for n.m.r. were stored in Rotaflo ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation.

Elemental analyses were performed by the Analysis Department in this laboratory, or in the case of very air-sensitive materials, by Analytische Laboratorien, 5270 Gummersbach, 1 Elbach, West Germany.

Infrared spectra were recorded on a Pye Unicam SP2000 double-beam, grating spectrophotometer, or on a Perkin-Elmer 1510 FT interferometer. ^1H N.m.r. spectra were obtained using Bruker WH-300 (300 MHz) and AM-500 (500 MHz) spectrometers; ^{13}C n.m.r. using Bruker AM-250 (62.8 MHz) or AM-500 (125.6 MHz) instruments. Spectra were referenced internally using the solvent resonance (^1H, ^{13}C) relative to $SiMe_4$ (δ 0 p.p.m.), or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts are quoted as δ (p.p.m.), and coupling constants *J* are in Hz. All multiple-pulse and two-dimensional n.m.r. experiments were acquired using standard Bruker software, and processed using either ASPECT 2000 or ASPECT 3000 computers.

Metal vapour synthesis (m.v.s.) experiments were performed using both the 10-kW metal atom reactor[23] and the 3.5-kW twin-hearth machine.[24] Both machines were operated in the positive-hearth mode. M.v.s. reactions were carried out using a pre-melted ingot of the appropriate metal. A pre-melted ingot is required to minimise outgassing during the m.v.s. reaction which would lead to deterioration of the vacuum. In a typical reaction, the electron gun furnace was turned on when a vacuum better than 10^{-5} Torr was achieved. Ligand (*ca.* 10 cm^3)



Scheme. Co-condensation of rhenium atoms at −196 °C with a mixture of: (*i*) benzene and cyclohexene (1 : 1, w/w) or pure cyclohexa-1,3-diene, or pure cyclohexene for (**2**) only; (*ii*) benzene and cycloheptatriene (1 : 1, w/w); (*iii*) benzene and cyclopentadiene (4 : 1, w/w), or benzene and cyclopentene (1 : 1, w/w) for (**5**); (*iv*) indene; (*v*) cyclohexane and trimethylphosphine (20 : 1, w/w); (*vi*) cycloheptane and trimethylphosphine (20 : 1, w/w)

was condensed onto the walls of the vessel (maintained at liquid nitrogen temperature) prior to evaporation of the metal sample. The metal was evaporated using the appropriate power and the rate of ligand entry adjusted so that a vacuum better than 10^{-4} Torr was maintained. Over the period of the co-condensation (typically 3—4 h) a matrix formed on the wall of the vessel which varied in appearance from pale yellow to dark red, depending upon the metal and ligand. At the end of the reaction the apparatus was isolated from the cryopump and the cooling shroud of liquid nitrogen was emptied. The apparatus was filled with dinitrogen and allowed to warm to room temperature (r.t.). The matrix melted and the product collected in the gutter at the bottom of the bell-jar reactor. It was then washed from the gutter with the appropriate solvent into a flask.

*(η-Benzene)bis(η-cyclohexa-*1,3*-diene)-di-μ-hydrido-dirhenium,* (**1**), *and* *(η-Benzene)(η-cyclohexa-*1,3*-diene)hydridorhenium*(I), (**2**).—*Method A, for* (**1**) *and* (**2**)*: from benzene and cyclohexene.* Rhenium atoms (1.0 g, 5.3 mmol), generated from a molten ingot (*ca.* 5.0 g), were co-condensed with a mixture of benzene and cyclohexene (100 cm^3, 1 : 1 w/w) over 4 h using the 3.5-kW twin-hearth reactor. The input power was maintained at 5 kV and 300 mA throughout. After warming to r.t., the red-brown mixture was washed out of the machine with thf (500 cm^3), filtered through a bed of Celite and the volatiles removed under reduced pressure at 70 °C giving a brown oil. The oil was extracted with light petroleum (2 × 100 cm^3), filtered through Celite and the volatiles removed under reduced pressure giving a brown oil. Sublimation at 130 °C (10^{-4} Torr) using a water-cooled probe gave a bright red, oily sublimate. The sublimate was washed from the probe with pentane (2 × 50 cm^3), giving a bright red solution which was filtered and concentrated to *ca.* 10 cm^3 under reduced pressure. Cooling to −20 °C gave orange crystals of $[Re_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)_2(\mu\text{-}H)_2]$. Yield *ca.* 10 mg, 1%.

The mother-liquor was concentrated under reduced pressure and cooled to −80 °C overnight, giving orange crystals of $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$. Yield 200 mg, 11%.

Crystals suitable for single-crystal *X*-ray analysis for both compounds were grown by slow cooling of a saturated solution of the pure compound in pentane.

Method B, for (**2**) *only: from benzene and cyclohexa-*1,3*-diene.* In a typical experiment, rhenium atoms (1.0 g, 5.3 mmol) were co-condensed with a mixture of benzene and cyclohexa-1,3-diene (90 cm^3, 2 : 1 w/w) for 3 h. After warming to r.t., the red-brown mixture was washed out of the reactor with thf (500 cm^3), filtered through a bed of Celite and the volatiles removed under reduced pressure at 70 °C giving a brown oil. The oil was extracted with light petroleum (2 × 100 cm^3), filtered through Celite, and the volatiles removed under reduced pressure giving a red-brown oil. Sublimation of the residue onto a liquid nitrogen cooled probe at 120 °C (10^{-4} Torr) afforded a dark orange, waxy solid.

The waxy solid was washed off the probe with light petroleum (2 × 50 cm^3), giving an orange solution, which was concentrated to *ca.* 20 cm^3 and cooled initially to −20 °C, and then to −80 °C overnight, yielding orange crystals of $[Re(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)H]$ (200 mg, 11%).

Method C, for (**2**) *only: from rhenium atoms and cyclohexene.* Rhenium atoms (1.4 g, 7.5 mmol), generated from a molten ingot (*ca.* 7.8 g) were co-condensed with pure cyclohexene (100 cm^3) over 4 h. After warming to r.t. the red-brown matrix was washed out of the machine with thf (500 cm^3), filtered through a bed of Celite and the volatiles removed under reduced pressure at 60 °C giving a red oil. The oil was extracted with light petroleum (2 × 100 cm^3), filtered through Celite and concentrated to *ca.* 10 cm^3 under reduced pressure, giving a deep red solution. The red solution was adsorbed onto a chromatography column (neutral alumina, 6% water w/w, 50 × 2 cm). Elution with toluene gave a pale yellow band which, upon removal of the toluene under reduced pressure, gave a pale yellow oil. The ^{1}H n.m.r. spectrum of the yellow oil showed [Re(η-C_6H_6)(η-C_6H_8)H] as the major component. Two other unknown η-benzene rhenium hydride species were observed by ^1H and ^{13}C n.m.r. spectroscopy.

(η-*Benzene*)(η^5-*cycloheptatrienyl*)*rhenium*(I), (**3**), *and* (η-*Benzene*)(η^5-*cycloheptadienyl*)*rhenium*(I), (**4**).—In a typical experiment rhenium atoms (1.4 g, 7.5 mmol), evaporated from a molten ingot (*ca.* 7.8 g), were co-condensed with a mixture of benzene and cycloheptatriene (90 cm^3, 1:1 w/w) over 4 h. After warming to r.t. the red-brown matrix was extracted from the reaction vessel with thf (500 cm^3), filtered through a bed of Celite and the volatiles removed under reduced pressure at 80 °C, yielding a red-brown oily residue. The residue was extracted with light petroleum (2 × 100 cm^3), filtered through Celite and concentrated to *ca.* 10 cm^3 under reduced pressure giving a deep red solution. Cooling the solution, initially to -20 °C and then to -80 °C overnight, yielded a red microcrystalline solid (200 mg, 7.5%), consisting of a mixture of (**3**) and (**4**) (4:3 mol ratio).

Chromatography of a light petroleum solution of the red microcrystalline solid on alumina (neutral, 6% water w/w, 50 × 2 cm), eluting with toluene affords [Re(η-C_6H_6)(η^5-C_7H_7)] (**3**) in high purity.

(η-*Benzene*)(η-*cyclopentadienyl*)*rhenium*(I), (**5**), *and Bis*(η-*cyclopentadienyl*)*hydridorhenium*(III), (**6**).—In a typical experiment, rhenium atoms (1.0 g, 5.3 mol) were evaporated from a pre-melted ingot at a power of 1.5 kW (5 kV × 300 mA) and co-condensed with an excess of a mixture of benzene and freshly cracked cyclopentadiene (110 cm^3, 4:1) over a period of 4 h. After completion of metal evaporation and warming to ambient temperature, the products were washed from the reactor walls with thf (500 cm^3). The extract was filtered through a bed of Celite and the volatiles removed under reduced pressure at 70 °C giving a red-brown oil. The residue was extracted with light petroleum (2 × 150 cm^3), filtered, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure giving a deep red solution. The red solution was adsorbed onto a chromatography column (neutral alumina, 6% water w/w, 50 × 2 cm). Elution with toluene gave a pale yellow band, which upon concentration and cooling to -80 °C, gave yellow crystals of [Re(η-C_6H_6)(η-C_5H_5)] (150 mg, 8%).

Further elution with acetone gave a very pale yellow band, which upon concentration under reduced pressure, and cooling to -80 °C, gave pale yellow crystals of [Re(η-C_5H_5)$_2$H].

Reaction of Rhenium Atoms with Benzene and Cyclopentene: Synthesis of (**5**) *and* [{Re(η-C_6H_6)}$_2$(μ-H)$_2$(μ-C[CH_2]$_4$)].—Rhenium atoms (1.0 g, 5.3 mmol) were co-condensed with a mixture of benzene and cyclopentene (90 cm^3, 1:1 w/w) for 3 h. After extraction from the reactor jar, and following the work-up described above for (**5**), yellow crystals of (**5**) were obtained in low yield (50 mg, 3%). The ^1H n.m.r. spectrum of the reaction mixture also showed the presence of a trace of [{Re(η-C_6H_6)}$_2$(μ-H)$_2$(μ-C[CH_2]$_4$)].

(η^6-*Indene*)(η^5-*indenyl*)*rhenium*(I), (**7**).—Rhenium atoms (1.3 g, 6.9 mmol) were evaporated from a molten ingot (*ca.* 7.8 g) and were co-condensed with pure indene (80 cm^3) over 4 h. The subsequent work-up was identical to that described previously for (**3**). Crystallisation of the light petroleum extract gave, after cooling to -80 °C overnight, orange crystals of (**7**). Yield 150 mg, 6%.

Reaction of Rhenium Atoms with Cyclohexane and Trimethylphosphine: Synthesis of [Re(η-C_6H_6)(PMe_3)$_2$H], (**8**).—Rhenium atoms (1.4 g, 7.5 mmol) were co-condensed with a mixture of cyclohexane (spectroscopic grade, >99.99% purity) and trimethylphosphine (20:1 mol ratio, 80 cm^3) over 4 h. After warming to r.t. the red-brown matrix was extracted from the reactor with thf (500 cm^3). The extract was filtered through a bed of Celite and the volatiles removed under reduced pressure at 70 °C giving a red-brown oil. The residue was extracted with light petroleum (2 × 150 cm^3), filtered, and the filtrate reduced to a red oil under reduced pressure. After the light petroleum extract had been adsorbed onto an alumina column (neutral, 6% water w/w), neither elution with toluene nor diethyl ether yielded any organometallic products. However, further elution with aqueous acetone (1:1) gave a quickly moving brown band. Removal of the acetone under reduced pressure, followed by the addition of excess ammonium hexafluorophosphate, produced an orange precipitate, which was collected and dried *in vacuo*. Recrystallisation from acetone (10 cm^3) gave yellow microcrystals of [Re(η-C_6H_6)(PMe_3)$_2$$H_2$]$PF_6$ (100 mg, 2%).

Reaction of Rhenium Atoms with Cycloheptane and Trimethylphosphine: Synthesis of [Re(PMe_3)$_4$$H_3$], (**9**), *and* [Re($PMe_3$)$_4$$H_4$]$PF_6$, (**11**).—Rhenium atoms (1.0 g, 5.3 mmol) were co-condensed with a 20:1 molar mixture of cycloheptane (deolefinised) and trimethylphosphine (20:1 mol ratio, 80 cm^3) for 3 h. After warming to r.t., the red-brown matrix was washed from the reactor with toluene (750 cm^3), filtered through a bed of Celite and the volatiles were removed under reduced pressure at 50 °C. The resulting brown oil was extracted with light petroleum (2 × 100 cm^3), filtered through Celite, and reduced in volume to 20 cm^3 giving a deep red solution. The red solution was adsorbed onto a chromatography column (neutral alumina, 6% water w/w, 50 × 2 cm).

Elution with aqueous acetone (1:1) gave a quickly moving brown band. Removal of the acetone under reduced pressure, followed by addition of excess ammonium hexafluorophosphate, produced a colourless precipitate of [Re(PMe_3)$_4$$H_4$]$PF_6$ which was collected and dried *in vacuo*. Yield 100 mg, 3%. The ^1H n.m.r. spectrum of an aliquot of the reaction mixture, after extraction with light petroleum, showed it to contain [Re(PMe_3)$_4$$H_3$] as the major component.

Crystal Structure Determination.—Crystals of compounds (**1**) and (**2**) were sealed under nitrogen in Lindemann glass capillaries and mounted on an Enraf-Nonius CAD4F diffractometer; cell dimensions were obtained by least-squares methods from the positions of 25 carefully centred reflections. During data collection three intensity control reflections were measured every hour and four orientation controls checked after each 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout data collection.

Lorentz and polarisation corrections were applied together with an empirical absorption correction.[25] Equivalent reflections were merged and only those for which $I > 3\sigma(I)$ were included in the refinement [where $\sigma(I)$ is the standard deviation based on counting statistics].

The rhenium atomic co-ordinates were determined using Patterson methods; subsequent electron-density difference syntheses revealed the location of all non-hydrogen atoms. The rhenium atoms and the non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares methods. Hydrogen atoms were located around the benzene and cyclohexa-1,3-diene rings, but included in calculated positions (C–H 1.0 Å) which were modified between successive cycles of refinement. Refinements converged at $R = 0.0207$ ($R' = 0.0272$) for (**1**) and $R = 0.0718$ ($R' = 0.0912$) for (**2**); the final electron density difference synthesis showed no peaks > 9.66 e Å^{-3} for both structures, the largest peaks lying in close proximity to the rhenium atom positions.

Corrections for anomalous dispersion and isotropic extinc-

Table 4. Crystal data for (**1**) and (**2**)

	(**1**)	(**2**)
Formula	$C_{18}H_{24}Re_2$	$C_{12}H_{15}Re$
M	612.79	345.45
T/K	295	295
a/Å	8.534(1)	10.208(2)
b/Å	11.957(2)	6.282(2)
c/Å	9.496(1)	16.476(5)
α/°	94.256(9)	—
β/°	116.147(9)	110.22(2)
γ/°	109.06(1)	—
U/Å^3	794.51	991.42
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
D_c/g cm^{-3}	2.56	2.31
μ/cm^{-1}	160.92	129.12
F(000)	564.0	648.0
Crystal size (mm)	0.28 × 0.28 × 0.08	0.87 × 0.18 × 0.5
θ limits	1.0—29.0	1.0—33.0
Scan mode	ω—2θ	ω—2θ
Scan angle (°)	0.90 + 0.35 tan (θ)	1.0 + 0.35 tan (θ)
Total data collected	5 588	5 806
Merging *R*	0.015	0.0293
No. of observations	2 927	3 057
No. of parameters	187	122
No. of restraints	26	0
Observations/ parameters	15.65	24.9
Weighting scheme (Chebyshev)	4-term	3-term
coefficients	26.27, 36.32, 15.38, 2.95	3 036.0, 3 927.3, 887.0
Max. shift/e.s.d. at convergence	0.44	0.45
Max. peak in final difference map (e Å^{-3})	1.27	9.6
Final residuals* *R*	0.0207	0.0718
R′	0.0272	0.0912
Extinction	12.19	46.78

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{\frac{1}{2}}$.

Table 5. Fractional atomic co-ordinates for (**1**) ($\times 10^4$); estimated standard deviations are given in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	1 828.8(3)	2 588.4(2)	−1 995.3(2)
Re(2)	2 697.3(3)	2 543.3(2)	935.5(3)
C(1)	3 616(10)	2 611(7)	−3 119(9)
C(2)	2 658(11)	1 364(8)	−3 141(10)
C(3)	3 786(13)	776(8)	−1 948(13)
C(4)	5 348(12)	1 745(8)	−373(10)
C(5)	4 888(9)	2 888(7)	−248(8)
C(6)	4 689(10)	3 456(6)	−1 584(9)
C(7)	−1 119(9)	2 331(6)	−2 555(9)
C(8)	−1 144(10)	1 844(8)	−3 982(8)
C(9)	−16(12)	2 739(9)	−4 433(8)
C(10)	986(11)	3 919(8)	−3 334(9)
C(11)	−25(12)	4 500(7)	−2 742(11)
C(12)	−1 322(11)	3 538(7)	−2 335(9)
C(13)	2 975(17)	3 631(7)	3 051(10)
C(14)	4 624(12)	3 427(9)	3 523(9)
C(15)	4 494(15)	2 228(13)	3 207(12)
C(16)	2 715(22)	1 254(8)	2 476(13)
C(17)	1 092(14)	1 481(9)	1 974(11)
C(18)	1 215(12)	2 653(11)	2 261(10)

Table 6. Fractional atomic co-ordinates for (**2**) ($\times 10^4$); estimated standard deviations are given in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	2 290.9(3)	2 631.4(5)	3 815.4(2)
C(1)	889(14)	5 347(20)	3 860(11)
C(2)	72(11)	3 706(26)	3 434(8)
C(3)	204(14)	1 709(24)	3 856(15)
C(4)	1 185(23)	1 478(31)	4 680(15)
C(5)	2 067(18)	3 131(45)	5 093(10)
C(6)	1 899(13)	5 055(27)	4 692(11)
C(7)	2 703(12)	2 531(11)	2 584(7)
C(8)	3 203(9)	4 494(13)	3 024(6)
C(9)	4 222(7)	4 224(12)	3 857(6)
C(10)	4 558(9)	2 019(14)	4 113(6)
C(11)	4 862(9)	570(15)	3 473(6)
C(12)	3 774(9)	871(15)	2 570(6)

tion[26] were made in the final cycles of refinement, a Chebyshev weighting scheme[27] was used with parameters as in Table 4. The final positional parameters are recorded in Tables 5 and 6. All calculations were performed on the VAX 11/750 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system[28] and plotted using the CHEMGRAF package.[29] Atomic scattering factors and anomalous dispersion coefficients were taken from International Tables.[30]

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