Activation of Alkanes involving Rhenium Atoms: Synthesis and Electronic Structure of Binuclear μ-Alkylidene Derivatives; Molecular Structure of $[\{Re(\eta-C_6H_6)\}_2(\mu-CHBu^t)(\mu-H)_2]$ *

Jennifer C. Green, Malcolm L. H. Green, Dermot O'Hare, and Rhuann R. Watson
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR
Judith A. Bandy
Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD

Co-condensation of rhenium atoms with a mixture of benzene and alkanes (neopentane, ethane, propane, butane, 2-methylpropane, tetramethylsilane, cyclopentane, cyclohexane, or cyclopropane) gives the compounds: $[\{Re(\eta-C_6H_6)\}_2(\mu-CHBu^t)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-CHMe)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-CHEt)(\mu-H)_2]$ and $[\{Re(\eta-C_6H_6)\}_2(\mu-CMe_2)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-CHPr^n)(\mu-H)_2]$ and $[\{Re(\eta-C_6H_6)\}_2(\mu-CMeEt)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-CHCHMe_2)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-CHSiMe_3)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-C[CH_2]_4)(\mu-H)_2]$; $[\{Re(\eta-C_6H_6)\}_2(\mu-C[CH_2]_5)(\mu-H)_2]$; and $[\{Re(\eta-C_6H_6)\}_2(\mu-CHCH{=}CH_2)(\mu-H)_2]$ and $[\{Re(\eta-C_6H_6)\}_2(\mu-CHEt)-(\mu-H)_2]$ respectively. The crystal structure of $[\{Re(\eta-C_6H_6)\}_2(\mu-CHBu^t)(\mu-H)_2]$ has been determined. Co-condensation of rhenium atoms with a mixture of $[^2H_6]$benzene and neopentane gives $[\{Re(\eta-C_6D_6)\}_2(\mu-CHBu^t)(\mu-H)_2]$. The He I and He II photoelectron spectra of $[\{Re(\eta-C_6H_6)\}_2(\mu-CHBu^t)(\mu-H)_2]$ are reported. Assignment of the photoelectron spectra and an analysis of the bonding in $[\{Re(\eta-C_6H_6)\}_2(\mu-CHBu^t)(\mu-H)_2]$ is described based on the results of extended-Hückel calculations.

Co-condensation of rhenium atoms with certain alkylbenzenes gives dirhenium compounds containing μ-alkylidene ligands of the general formulation $[Re_2(\eta-arene)_2(\mu-CHR)(\mu-H)_2]$ (R = aryl),[1,2] where the bridging alkylidene group and the bridging hydrido ligands are derived from CH_2 or CH_3 groups of the alkyl side-chain. In particular, with ethylbenzene and rhenium atoms, one product contained the $Re(\mu-CHCH_2Ph)(\mu-H)_2Re$ moiety in which the methyl group of the ethylbenzene had added across the two rhenium atoms. This methyl group must be considered to have properties closely similar to those in simple alkanes. Further, we had observed that when rhenium atoms are co-condensed with pure benzene, no tractable products could be isolated at room temperature. Therefore, we decided to co-condense rhenium atoms with benzene in the presence of saturated hydrocarbons, in the expectation that alkane activation would occur giving μ-alkylidene derivatives analogous to the dimers $[Re_2(\eta-arene)_2(\mu-CHR)(\mu-H)_2]$. A brief communication of this work has appeared.[3]

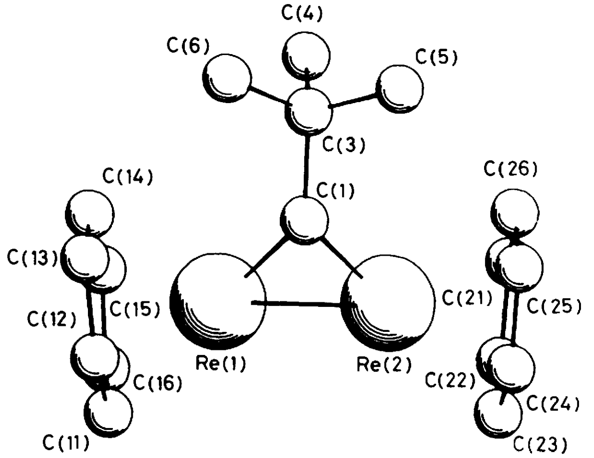

Figure 1. Molecular structure of (1) showing one orientation of one independent molecule in the asymmetric unit

Results and Discussion

Co-condensation of rhenium atoms with benzene–neopentane (*ca.* 1:1 w/w) yields volatile, red, air-sensitive crystals of $[\{Re-(\eta-C_6H_6)\}(\mu-CHBu^t)(\mu-H)_2]$, (1). Compound (1) crystallizes with two crystallographically independent molecules in the asymmetric unit, each having the expected dirhenium structure. The crystal structure has been determined and the molecular structure of one molecule is shown in Figure 1. The bond angles and distances are given in Table 1. The μ-$CHBu^t$ groups of both molecules in the asymmetric unit exhibit a two-fold disorder and have been resolved into two components involving a common C(3) in one molecule and C(53) in the other (Figure 2).

The 18-electron formalism requires that (1) has a single rhenium–rhenium bond, although the observed mean Re–Re distance of 2.439(1) Å is short for a bond order of one. However, a survey of structurally characterized dirhenium complexes (Table 2) suggests that, within a series of compounds of the same formal bond order, the presence of bridging ligands causes a shortening of the metal–metal distance. The data in Table 2, although rather limited, suggest that although each bridging hydride ligand introduced into a dirhenium fragment reduces the formal bond order by one, the Re–Re distance is only slightly lengthened in comparison to the unbridged fragment because of incomplete charge transfer from the metal–metal bonding orbitals to the bridging ligands.

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* μ-2,2-Dimethylpropylidene-di-μ-hydrido-bis(η-benzenerhenium) (*Re–Re*).

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

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, atm = 101 325 N m^{-2}.

Table 1. Bond distances (Å) and angles (°) for [{Re(η-C_6H_6)}$_2$(μ-CHBu^t)(μ-H)$_2$] (**1**), with estimated standard deviations in parentheses (atoms differing by 50 are for the other independent molecule, atoms differing by 100 show contributors to disorder)

Re(1)–Re(2)	2.436(1)	C(11)–C(12)	1.40(2)	Re(3)–C(31)	2.27(2)	C(41)–C(42)	1.38(2)
Re(3)–Re(4)	2.442(1)	C(11)–C(16)	1.40(2)	Re(3)–C(32)	2.20(2)	C(41)–C(46)	1.38(2)
		C(12)–C(13)	1.41(2)	Re(3)–C(33)	2.17(3)	C(42)–C(43)	1.38(2)
Re(1)–C(11)	2.20(2)	C(13)–C(14)	1.39(2)	Re(3)–C(34)	2.24(2)	C(43)–C(44)	1.40(2)
Re(1)–C(12)	2.24(2)	C(14)–C(15)	1.40(2)	Re(3)–C(35)	2.19(2)	C(44)–C(45)	1.41(2)
Re(1)–C(13)	2.25(2)	C(15)–C(16)	1.39(2)	Re(3)–C(36)	2.22(2)	C(45)–C(46)	1.38(2)
Re(1)–C(14)	2.21(3)			Re(3)–C(51)	2.11(3)		
Re(1)–C(15)	2.18(3)	C(21)–C(22)	1.41(2)	Re(3)–C(510)	2.12(4)	C(1)–C(3)	1.539(5)
Re(1)–C(16)	2.24(2)	C(21)–C(26)	1.43(2)			C(100)–C(3)	1.540(5)
Re(1)–C(1)	2.13(3)	C(22)–C(23)	1.37(2)	Re(4)–C(41)	2.18(2)	C(3)–C(4)	1.54(3)
Re(1)–C(100)	2.13(5)	C(23)–C(24)	1.41(2)	Re(4)–C(42)	2.23(2)	C(3)–C(5)	1.54(3)
		C(24)–C(25)	1.42(2)	Re(4)–C(43)	2.28(2)	C(3)–C(6)	1.54(3)
Re(2)–C(21)	2.26(2)	C(25)–C(26)	1.42(2)	Re(4)–C(44)	2.23(2)	C(3)–C(400)	1.55(3)
Re(2)–C(22)	2.25(2)			Re(4)–C(45)	2.22(2)	C(3)–C(500)	1.55(3)
Re(2)–C(23)	2.21(2)	C(31)–C(32)	1.39(2)	Re(4)–C(46)	2.24(2)	C(3)–C(600)	1.53(3)
Re(2)–C(24)	2.25(2)	C(31)–C(36)	1.41(2)	Re(4)–C(51)	2.19(3)		
Re(2)–C(25)	2.26(2)	C(32)–C(33)	1.38(2)	Re(4)–C(510)	2.10(3)	C(51)–C(53)	1.541(5)
Re(2)–C(26)	2.23(2)	C(33)–C(34)	1.39(2)			C(510)–C(53)	1.541(5)
Re(2)–C(1)	2.13(3)	C(34)–C(35)	1.39(2)	C(53)–C(540)	1.54(3)	C(53)–C(54)	1.52(3)
Re(2)–C(100)	2.06(6)	C(35)–C(36)	1.38(2)	C(53)–C(550)	1.55(3)	C(53)–C(55)	1.56(3)
				C(53)–C(560)	1.57(3)	C(53)–C(56)	1.56(3)
C(1)–Re(1)–Re(2)	55.1(9)	C(26)–C(21)–C(22)	120.1(8)	Re(2)–C(1)–Re(1)	69.7(9)	Re(4)–C(51)–Re(3)	69.2(9)
C(100)–Re(1)–Re(2)	53.1(17)	C(23)–C(22)–C(21)	120.7(8)	C(3)–C(1)–Re(1)	129.5(22)	C(53)–C(51)–Re(3)	128.8(23)
C(51)–Re(3)–Re(4)	56.8(10)	C(24)–C(23)–C(22)	120.6(8)	C(3)–C(1)–Re(2)	126.8(21)	C(53)–C(51)–Re(4)	124.2(22)
C(510)–Re(3)–Re(4)	54.2(10)	C(25)–C(24)–C(23)	120.0(8)	Re(2)–C(100)–Re(1)	71.1(14)	Re(4)–C(510)–Re(3)	70.8(10)
C(1)–Re(2)–Re(1)	55.2(9)	C(26)–C(25)–C(24)	119.4(8)	C(3)–C(100)–Re(1)	130(4)	C(53)–C(510)–Re(3)	128.3(26)
C(100)–Re(2)–Re(1)	55.8(16)	C(25)–C(26)–C(21)	118.8(8)	C(3)–C(100)–Re(2)	132(4)	C(53)–C(510)–Re(4)	130.2(25)
C(51)–Re(4)–Re(3)	53.9(9)			C(4)–C(3)–C(1)	112.7(23)	C(54)–C(53)–C(51)	108.3(25)
C(510)–Re(4)–Re(3)	55.0(11)	C(36)–C(31)–C(32)	120.0(8)	C(5)–C(3)–C(1)	107.9(25)	C(55)–C(53)–C(51)	116.4(26)
		C(33)–C(32)–C(31)	119.6(8)	C(5)–C(3)–C(4)	108.7(9)	C(55)–C(53)–C(54)	108.7(9)
C(16)–C(11)–C(12)	119.2(8)	C(34)–C(33)–C(32)	120.2(8)	C(6)–C(3)–C(1)	110.4(25)	C(56)–C(53)–C(51)	107.0(25)
C(13)–C(12)–C(11)	120.3(8)	C(35)–C(34)–C(33)	119.9(8)	C(6)–C(3)–C(4)	108.5(9)	C(56)–C(53)–C(54)	108.1(9)
C(14)–C(13)–C(12)	119.8(9)	C(36)–C(35)–C(34)	119.7(8)	C(6)–C(3)–C(5)	108.6(9)	C(56)–C(53)–C(55)	108.1(9)
C(15)–C(14)–C(13)	119.9(13)	C(35)–C(36)–C(31)	119.7(8)				
C(16)–C(15)–C(14)	120.1(9)			C(400)–C(3)–C(100)	99(4)	C(540)–C(53)–C(510)	112.7(27)
C(15)–C(16)–C(11)	120.1(8)	C(46)–C(41)–C(42)	120.5(8)	C(500)–C(3)–C(100)	111(4)	C(550)–C(53)–C(510)	108.2(28)
		C(43)–C(42)–C(41)	120.5(8)	C(500)–C(3)–C(400)	109.3(10)	C(550)–C(53)–C(540)	109.7(9)
		C(44)–C(43)–C(42)	119.2(8)	C(600)–C(3)–C(100)	120(4)	C(560)–C(53)–C(510)	108.5(25)
		C(45)–C(44)–C(43)	119.8(8)	C(600)–C(3)–C(400)	108.6(10)	C(560)–C(53)–C(540)	109.0(9)
		C(46)–C(45)–C(44)	119.5(8)	C(600)–C(3)–C(500)	109.0(10)	C(560)–C(53)–C(550)	108.9(9)
		C(45)–C(46)–C(41)	120.0(8)				

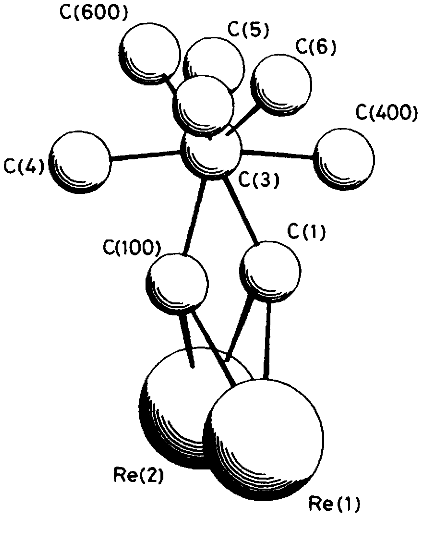


Figure 2. Molecular structure of (**1**) showing the disorder of the μ-CHBu^t ligand. Only one of the independent molecules in the asymmetric unit is shown and the η-C_6H_6 ligands have been removed for clarity

The internal angle α at the methylene carbon atoms C(1), C(100), C(51), or C(510) of compound (**1**) is very acute. The mean Re–C(*n*)–Re angle (*n* = 1, 100, 51, or 510) is 70.2(8)°. Prior to the structural characterisation of (**1**) the extreme range of the internal angle α was found to be 81 ± 7° (Table 3). The acute angle observed is due to the strong metal–metal interaction which is the dominant effect in determining the size of α.

In addition, the crystallographic data for (**1**) reveal that the benzene rings are tilted away from the μ-CHBu^t ligand, and the mean angle between the normals to the planes of the η-C_6H_6 ligands is 162.3°.

The ^1H n.m.r. spectrum of (**1**) (Figure 3) exhibits two high-field resonances at δ −4.27 and −5.15 assignable to two different hydrogens directly bonded to one or more rhenium atoms. The crystallographic data do not allow unequivocal location of the rhenium hydrides. If we assume that the solution structure is the same as that in the crystal, the occurrence of non-equivalent rhenium hydrogens (whilst there is only one resonance assignable to two equivalent η-C_6H_6 groups in both the ^1H and ^{13}C n.m.r. spectra) can only be understood in terms of the presence of two bridging hydrogens rather than two terminal hydrido ligands.

The resonance assignable to the μ-CH_c hydrogen of the μ-neopentylidene ligand occurs at δ 13.64 in the ^1H n.m.r.

Table 2. Examples of structurally characterized dirhenium complexes

Compound	Re–Re/Å	No. of μ-ligands	Formal bond order	Ref.
$[Re_2Cl_8]^{2-}$	2.241(7)	0	4	*a*
$[Re_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_3]$	2.411(1)	3	3	*b*
$[Re_2Cl_4(PEt_3)_4]$	2.22	0	3	*c*
$[Re_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)_2]$	2.557(1)	2	2	*d*
$[Re_2(\mu\text{-}H)_4(PEt_2Ph)_4H_4]$	2.597(1)	4	1	*e*
$[Re_2(\mu\text{-}H)_3H_4\{CCH_3(CH_2PPh_2)_3\}]^-$	2.597(1)	3	1	*f*
$[Re_2(CO)_8\{\mu\text{-}C(OMe)Ph\}]$	2.817(3)	1	1	*g*
$[Re_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CO)]$	2.957(1)	1	1	*h*
$[Re_2(\mu\text{-}\sigma,\eta^3\text{-}CHCHCMe_2)(CO)_3]$	3.058(1)	1	1	*i*
$[Re_2(CO)_{10}]$	3.040(1)	0	1	*j*
$[Re_2H(\mu\text{-}H)_3(PMe_2Ph)_4\{P(OCH_2)_3CEt\}_2]$	2.597(1)	3	0	*k*
$[Re_2H_2(\mu\text{-}H)_3(PPh_3)_4(CNBu^t)_2]^+$	2.604(2)	3	0	*l*
$[Re_2(CO)_8(\mu\text{-}H)_2]$	2.896(1)	2	0	*m*
$[Re_2(CO)_6(\mu\text{-}H)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$	2.893(2)	2	0	*n*

[a] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330. [b] J. K. Hoyano and W. A. G. Graham, *J. Chem. Soc., Chem. Commun.*, 1982, 27. [c] F. A. Cotton, B. A. Frenz, J. R. Ebner, and R. A. Walton, *Inorg. Chem.*, 1976, **15**, 1630. [d] M. Bochmann, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1797. [e] R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzele, *J. Am. Chem. Soc.*, 1977, **99**, 3872. [f] A. P. Ginsberg, S. C. Abrahams, P. Marsh, K. Ataka, and C. R. Sprinkle, *J. Chem. Soc., Chem. Commun.*, 1984, 1321. [g] E. O. Fisher, T. L. Lindner, H. Fisher, G. Huttner, P. Friedrich, and F. R. Kreibl, *Z. Naturforsch., Teil B*, 1977, **32**, 648. [h] A. S. Foust, J. K. Hoyano, and W. A. G. Graham, *J. Organomet. Chem.*, 1971, **32**, C65. [i] M. Green, A. G. Orpen, C. J. Schaverian, and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 1399. [j] N. I. Gapotchenko, N. V. Alekseev, N. E. Kolobova, K. N. Anisimov, I. A. Ponova, and A. A. Johansson, *J. Organomet. Chem.*, 1972, **35**, 319. [k] M. A. Green, J. C. Huffman, and K. G. Caulton, *J. Am. Chem. Soc.*, 1982, **104**, 2319. [l] J. D. Allison, F. A. Cotton, G. L. Powell, and R. A. Walton, *Inorg. Chem.*, 1984, **23**, 159. [m] M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, *J. Am. Chem. Soc.*, 1972, **94**, 6232. [n] M. J. Mays, D. W. Prest, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 171.

Table 3. Examples of metal–metal bond lengths and internal angles for μ-alkylidene complexes

Compound	M–M/Å	M–C–M′/°	M–C/Å	Ref.
$[Mn_2(\eta\text{-}C_5H_5)(CO)_4(\mu\text{-}CH_2)]$	2.799(1)	87.4(1)	2.02(4)	*a*
$[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CH_2)]$	2.661(1)	81.0(1)	2.05(4)	*b*
$[Ru_2(PMe_3)_6(\mu\text{-}CH_2)_3]$	2.650(1)	78.0(14)	2.10(13)	*c*
$[Fe_2(CO)_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CHMe)]$	2.520(1)	78.8(1)	1.98(3)	*d*
$[Rh_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CPh_2)_2]$	2.548(1)	75.1(2)	2.09(4)	*e*
$[Co_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$	2.320(1)	74.0(1)	1.90(9)	*f*

[a] D. A. Clemente, B. Rees, G. Bandol, M. C. Biagini, B. Reiter, and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 887. [b] F. Takusagawa, A. Fumagalli, T. F. Koetzele, and W. A. Herrmann, *Inorg. Chem.*, 1981, **20**, 3060. [c] M. B. Hursthouse, R. A. Jones, K. M. Abdul Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128. [d] A. F. Dyke, S. A. R. Knox, P. J. Naish, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1980, 441. [e] H. Ueda, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2250. [f] T. R. Halbert, M. E. Leonowicz, and D. J. Maydonovitch, *J. Am. Chem. Soc.*, 1980, **102**, 5101.

spectrum, and spin–spin coupling is resolvable to the two inequivalent rhenium hydrides. Homonuclear ^1H nuclear Overhauser effect (n.O.e.) experiments (Figure 3) revealed that H_a shows a large enhancement factor (5%) to H_c, while H_b showed only a negligible enhancement factor (0.3%). We conclude that H_c and H_a have adopted a cisoid conformation with respect to the rhenium–rhenium vector. The observation of a n.O.e. enhancement would be highly unlikely had the hydrogens adopted terminal positions. The ^{13}C n.m.r. spectrum shows, in addition to the resonances assignable to the Bu^t ligand, resonances at 70.3 and 193.8 p.p.m. assignable to the η-C_6H_6 ligands and the μ-*C*HBu^t moiety respectively.

The low-energy region of the He I photoelectron (p.e.) spectrum of (**1**) is shown in Figure 4, where the points are the experimental data and the solid line represents a least-squares fit to these points. The ionization energy (i.e.) and band intensity data are given in Table 4.

The broad features of the spectra can be assigned by comparison with other transition metal–arene complexes.[4,5] The upper regions of the spectrum (not shown here) are dominated by ionizations from orbitals localized on the arene ligands, also, from the ionization energy of band e, we conclude that this may be assigned to ionization from the upper π levels of the bound benzene.

In the lower region of the spectrum there are four main bands, a—d; the widths and intensities of bands b and d suggest that they result from more than one ionization process. Indeed a shoulder on the high i.e. side of d may be distinguished in the smoothed spectrum. The He II/He I intensity ratios are significantly larger for bands a, b, and c than for d and e, suggesting that the former arise from orbitals with high metal *d* character, whereas the latter are more ligand based. This confirms band e as the lowest ionization energy from the benzene orbitals, and suggests that band d may well be associated with bridge bonding. Further assignment is difficult without a more detailed bonding model for the bridged dimer, and is given below after the results of the molecular orbital (m.o.) calculation have been presented.

In order to model the electronic structure of (**1**), extended-Hückel calculations were carried out on both $[Re_2(\eta\text{-}C_6H_6)_2]$ and $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CH_2)(\mu\text{-}H)_2]$. To simplify the calculation the bridging alkylidene group was taken as CH_2; Herrmann[6b] has shown that the substitution of groups of the alkylidene hardly affects the geometry of the three-membered

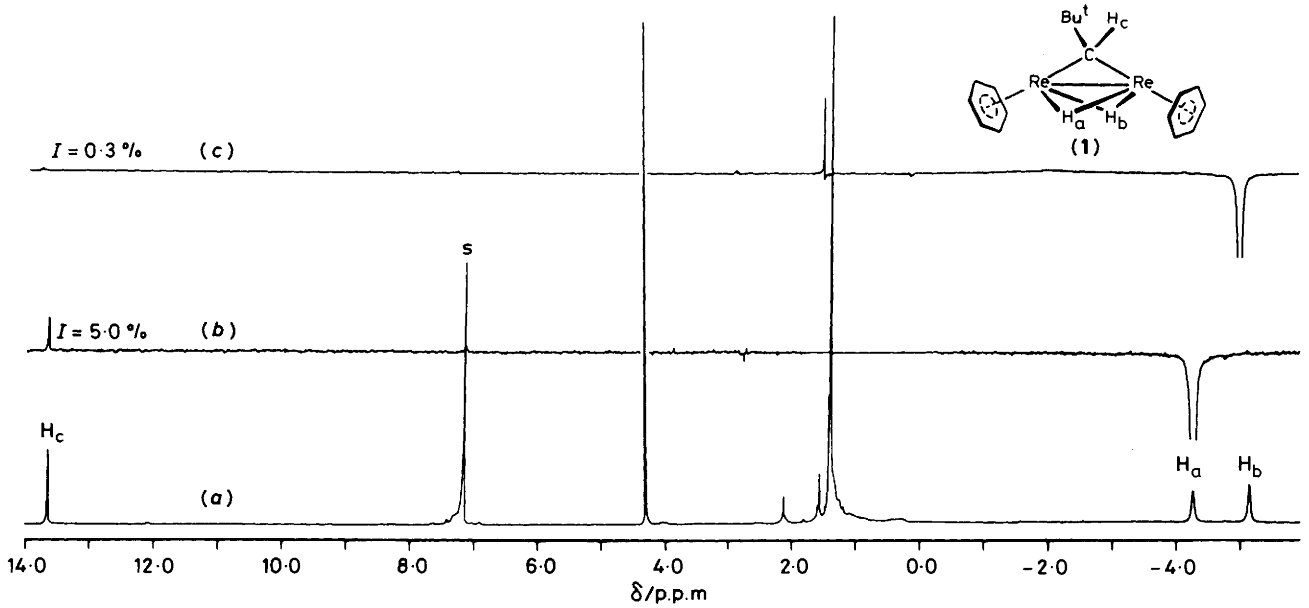


Figure 3. (*a*) ^{1}H N.m.r. spectrum of (**1**) in [^{2}H$_6$]benzene. Homonuclear ^{1}H n.O.e. difference spectra from selective irradiation of Re-H$_a$ (*b*) or Re-H$_b$ (*c*) (I = relative intensity)

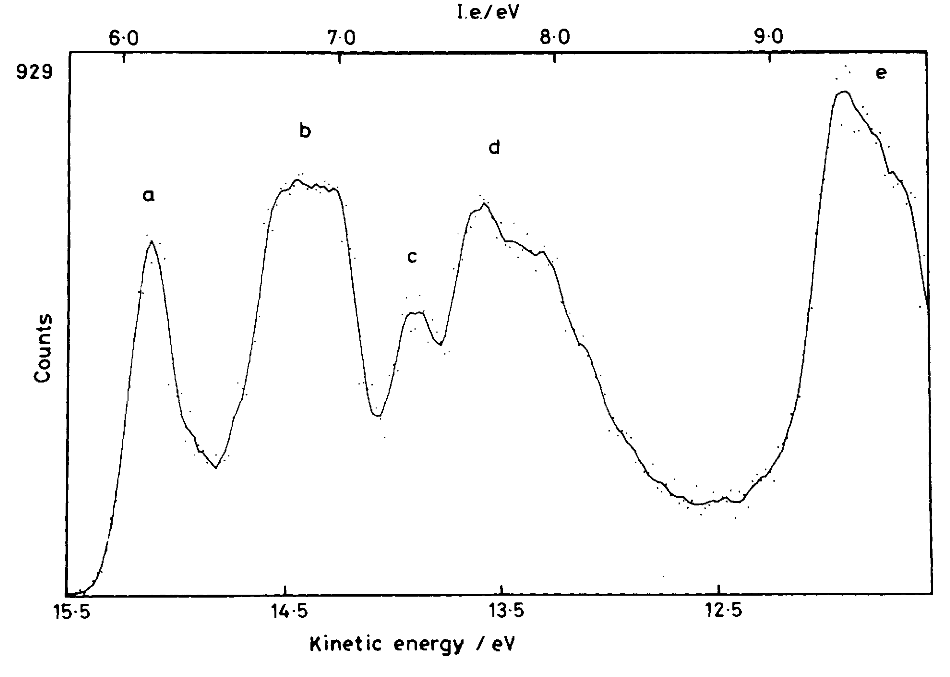


Figure 4. Low-ionization energy region of the He I photoelectron spectrum of [{Re(η-C$_6$H$_6$)}$_2$(μ-CHBu^t)(μ-H)$_2$] (**1**)

Table 4. Vertical ionization energies and band intensities of the p.e. spectrum of [{Re(η-C$_6$H$_6$)}$_2$(μ-CHBu^t)(μ-H)$_2$] (**1**)

Band	a	b	c	d	e
I.e./eV	5.91	6.55	7.11	7.65	9.15
He I intensity	8.2	21.7	7.0	30.9	32.1
He II intensity	13.4	23.5	11.7	25.0	26.5
He II/He I	1.63	1.08	1.67	0.84	0.82
Assignment	46	47—49	50	51—53	54—57

framework so that substitution of CHBu^t by CH$_2$ will not greatly affect the bridge bond under consideration. The parameters used were based on those obtained crystallographically for (**1**). Though the calculations on [Re$_2$(η-C$_6$H$_6$)$_2$] were for a parallel geometry for the benzene rings, for [{Re(η-C$_6$H$_6$)}$_2$(μ-CH$_2$)(μ-H)$_2$] a number of calculations were carried out with the benzene rings bent away from the μ-CH$_2$ group for angles between 0 and 20°, in order to investigate a possible electronic origin for the nature of this distortion.

The resulting m.o. schemes for [Re$_2$(η-C$_6$H$_6$)$_2$] and [{Re(η-C$_6$H$_6$)}$_2$(μ-CH$_2$)(μ-H)$_2$] are shown diagrammatically in Figure

5. The key bridging orbitals are represented pictorially in Figure 6. The hypothetical dimer $[Re_2(\eta\text{-}C_6H_6)_2]$ is predicted to have a formal triple bond between the metal atoms arising from the configuration $\sigma^2\delta^4\delta^{*4}\pi^4$ for the 14 metal electrons. As might be expected, both of the π orbitals of the dimer interact with the bridging ligands and the electrons occupying these metal–metal bonding orbitals in $[Re_2(\eta\text{-}C_6H_6)_2]$ are subsumed in to the bridge bonding orbitals in $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CH_2)(\mu\text{-}H)_2]$. Though the other metal m.o.s are modified on interaction with the bridging ligands there is a direct relation with the occupied m.o. of $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CH_2)(\mu\text{-}H)_2]$ so the metal–metal bond order in the alkylidene complex may be taken as one. This reduction of direct metal–metal bonding from a triple bond in $[Re_2(\eta\text{-}C_6H_6)_2]$ to a single bond in $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CH_2)(\mu\text{-}H)_2]$ is reflected in the calculated Re–Re reduced overlap population which goes from 1.3915 to 0.3837.

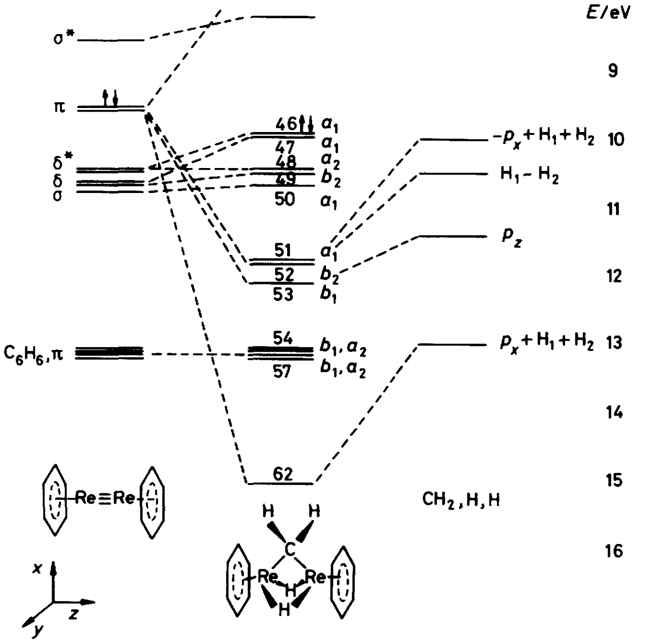


Figure 5. Molecular orbital diagram for $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CH_2)(\mu\text{-}H)_2]$ based on extended-Hückel calculations

The bridging ligands also interact significantly with the $d_{x^2-y^2}$ orbitals, which are consequently mixed with the d_{xz} orbitals; this results in a loss of degeneracy of the δ and δ* orbitals and a destabilization of the components built from the $x^2 - y^2$ orbitals. The highest occupied molecular orbital (h.o.m.o.) of $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CH_2)(\mu\text{-}H)_2]$ correlates with a δ orbital of $[Re_2(\eta\text{-}C_6H_6)_2]$.

Further assignments of the p.e. bands may be suggested on the basis of the m.o. calculations. Band a is assigned to the orbital $E(46)$ and band b, to the other δ orbital $E(49)$ and the two δ* orbitals $E(47)$ and $E(48)$. The highest i.e. metal band, c, is assigned to $E(50)$, the metal–metal σ-bonding orbital. Band d corresponds to the metal bridge bonds and the calculations suggest that the a_1 and b_2 orbitals [$E(51)$ and $E(52)$] lie higher in energy than the b_1 orbital $E(53)$ with a high component of C $2p_z$ character. The other a_1 bridging orbital $E(62)$ is predicted to be significantly more stable and ionization from this is expected in a different region of the spectrum.

As the rings were bent away from the alkylidene ligand the sum of the one-electron energies passed through a minimum at a value of θ of 10.5° (φ = angle between Re–Re axis and the perpendicular to the η-arene rings). Several of the bridge orbitals altered in energy to give an overall decrease of 0.18 eV. It was difficult to identify any particular electronic factor responsible for this very small stabilization and it may well be the case that the bending of the rings is due to the steric bulk of the μ-CHBu^t group.

In order to test the generality and selectivity of the reaction of rhenium atoms with alkanes, a systematic study with acyclic alkanes was carried out.

In a typical experiment rhenium atoms were co-condensed with a 1 : 1 (w/w) mixture of benzene and the desired alkane. In the case of gaseous alkanes, saturated solutions in benzene were

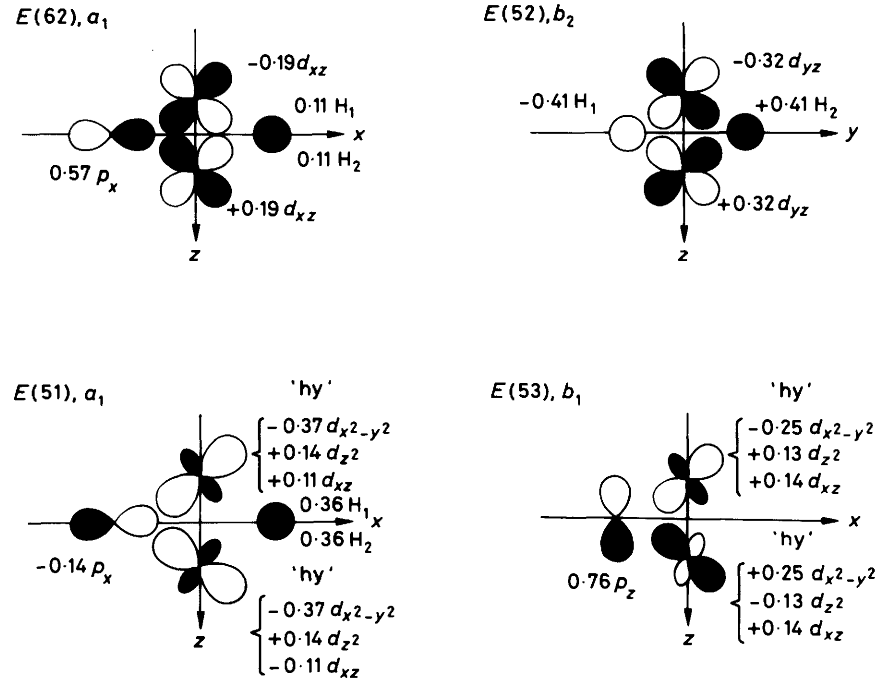
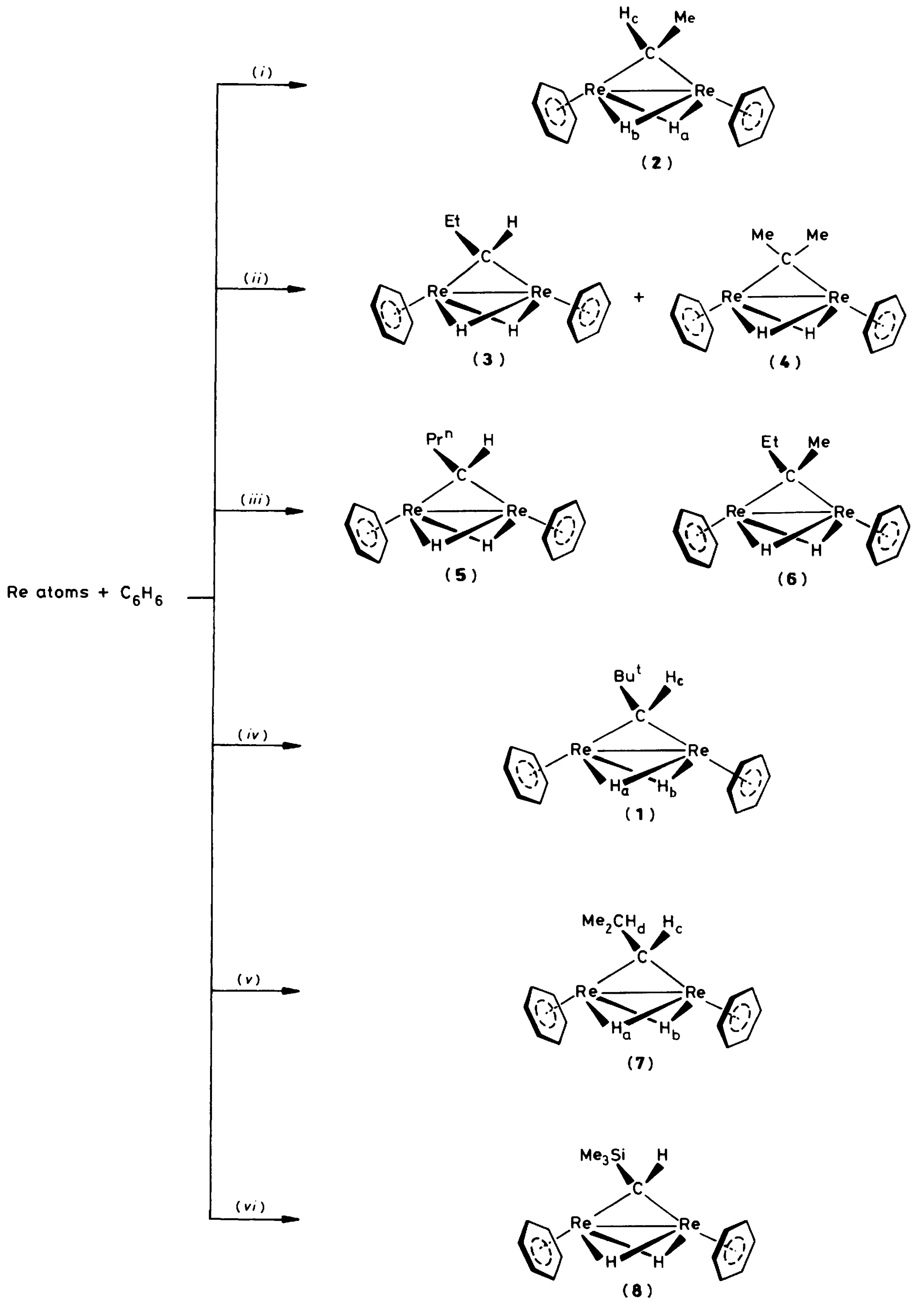


Figure 6. Representations of the orbitals binding the bridging alkylidene group



Scheme 1. Summary of the reactions of rhenium atoms with acyclic alkanes. Rhenium atoms were co-condensed with the indicated substrates at −196 °C. (*i*) Ethane, (*ii*) propane, (*iii*) n-butane, (*iv*) neopentane, (*v*) 2-methylpropane, (*vi*) tetramethylsilane

prepared under 10—30 atm pressure of the alkane and stored in a 150-cm^3 steel pressure vessel. After the co-condensation reaction, work-up and crystallization yielded compounds (**2**)—(**7**), whose proposed structures are shown in Scheme 1. All of these compounds have the dirhenium structure analogous to compound (**1**), and have been characterized by mass spectral

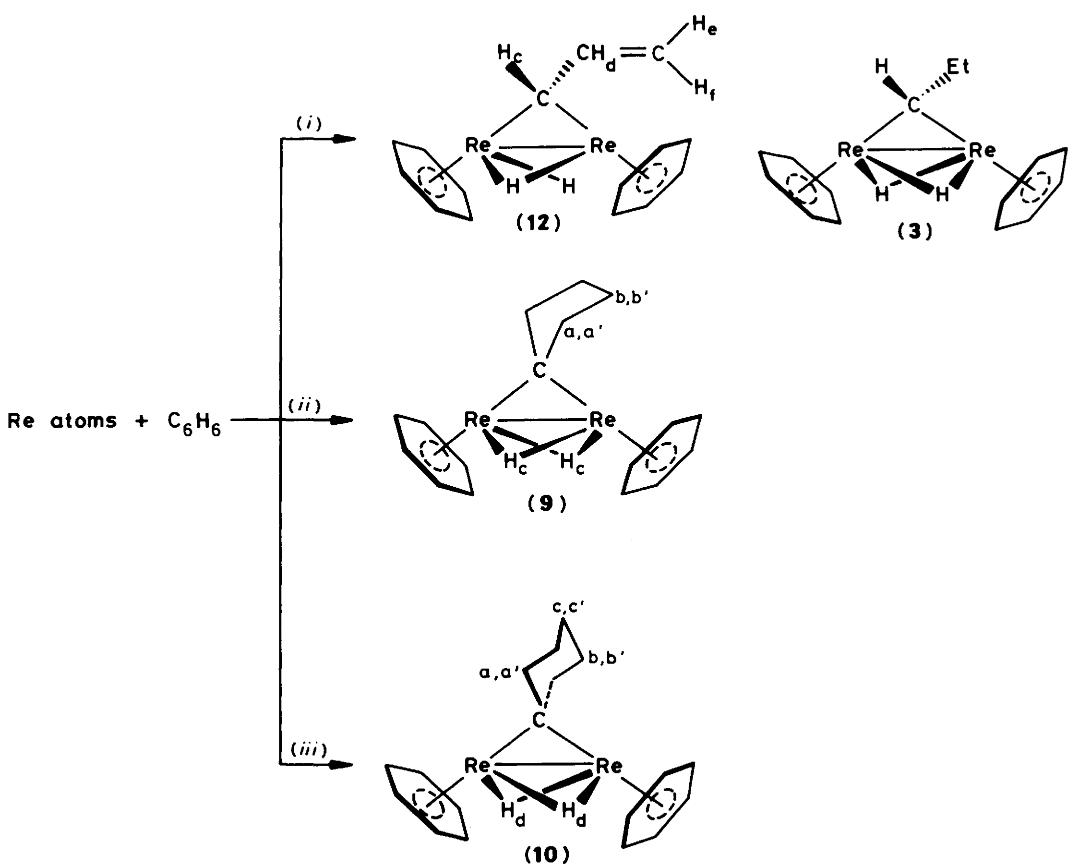
Table 5. Analytical and spectroscopic data

Compound, colour, analysis (%),[a] and mass spectrum[b]	N.m.r. data[c]	
	^{1}H	^{13}C
(1) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHBu^t)(\mu\text{-}H)_2]$ Red C, 33.8(33.9); H, 4.1(3.9) *m/e* = 600 [$P^+ - 2$]	13.64 [1 H, dd, $J(H_a - H_c)$ 5.1, $J(H_b - H_c)$ 1.5, H_c], 4.31 (12 H, s, 2 η-C_6H_6), 1.30 (9 H, s, Me), −4.27 (1 H, br, H_a), −5.15 (1 H, br, H_b)[d]	193.8 [d, J(C–H) 135, μ-CH], 70.3 [d, J(C–H) 170, 2 η-C_6H_6], 55.3 (s, *C*Bu^t), 35.0 [q, J(C–H) 120, Me][d]
(2) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHMe)(\mu\text{-}H)_2]$ Light green *m/e* = 558 [$P^+ - 2$]	12.5 [1 H, dd, $J(H_c - H_a)$ 2.2, $J(H_c - H_b)$ 4.4, $J(H_c - H_{Me})$ 6.2, H_c], 4.2 (12 H, s, 2 η-C_6H_6), 3.2 [3 H, d, $J(H_c - H_{Me})$ 6.2, Me], −5.3 [1 H, dd, $J(H_c - H_b)$ 4.4, $J(H_a - H_b)$ 4.0, H_b], −5.6 [1 H, dd, $J(H_c - H_a)$ 2.2, $J(H_a - H_b)$ 4.0, H_a][d]	165.1 [d, J(C–H) 145, μ-CH], 69.7 [d, J(C–H) 175, 2 η-C_6H_6], 52.1 [q, J(C–H) 128, Me][d]
(3) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHEt)(\mu\text{-}H)_2]$ Light green C, 31.2(31.4); H, 3.6(3.7) *m/e* = 573 [$P^+ - 1$]	12.7 [1 H, ddt, $J(H_a - H_c)$ 6, $J(H_b - H_c)$ 2.0, H_c], 4.2 (12 H, s, 2 η-C_6H_6), 3.1 [2 H, qnt, J(H–H) 7, CH_2CH$_3$], 1.3 [3 H, t, J(H–H) 7, CH$_2$CH_3], −5.4 (2 H, br, $H_a + H_b$)[e]	At 125.6 MHz: 176.0 [d, J(C–H) 125, μ-CH], 70.0 [d, J(C–H) 126, 2 η-C_6H_6], 47.6 [t, J(C–H) 128, *C*H$_2$CH$_3$], 20.2 [q, J(C–H) 120, CH$_2$*C*H$_3$][e]
(4) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CMe_2)(\mu\text{-}H)_2]$ Light green C, 31.2(31.4); H, 3.6(3.5) *m/e* = 573 [$P^+ - 1$]	4.1 (12 H, s, 2 η-C_6H_6), 2.8 (6 H, s, 2 Me), −5.8 (2 H, complex, $H_a + H_b$)[e]	175.3 (s, μ-C), 69.7 [d, J(C–H) 169, 2 η-C_6H_6], 60.3 [q, J(C–H) 129, Me][e]
(5) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHPr^n)(\mu\text{-}H)_2]$ Light green C, 32.6(32.7); H, 3.8(3.8) *m/e* = 587 [$P^+ - 1$]	12.76 [1 H, ddt, $J(H_c - H_a$ or $H_b)$ 3.0 or 4.0, $J(H_c - H_{Pr})$ 7, H_c], 4.24 (12 H, s, 2 η-C_6H_6), 3.15 [2 H, q, J(H–H) 6.6, CH_2CH$_2$CH$_3$], 1.60 [2 H, sxt, J(H–H) 7.0, CH$_2$CH_2CH$_3$], 1.11 [3 H, t, J(H–H) 7.0, CH$_2$CH$_2$CH_3], −5.26 (2 H, br, $H_a + H_b$)[d]	183.0 [d, J(C–H) 139, μ-CH], 69.7 [d, J(C–H) 177, 2 η-C_6H_6], 68.5 [t, J(C–H) 123, *C*H$_2$CH$_2$CH$_3$], 30.2 [t, J(C–H) 126, CH$_2$*C*H$_2$CH$_3$], 14.8 [q, J(C–H) 125, CH$_2$CH$_2$*C*H$_3$][d]
(6) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CMeEt)(\mu\text{-}H)_2]$ Light green C, 32.6(32.7); H, 3.8(3.8) *m/e* = 587 [$P^+ - 1$]	4.19 (12 H, s, 2 η-C_6H_6), 2.93 (3 H, s, Me), 2.50 [2 H, q, J(H–H) 7.0, CH_2CH$_3$], 1.41 [3 H, t, J(H–H) 7.0, CH$_2$CH_3], −5.41 (1 H, br, H_a or H_b), −5.81 (1 H, br, H_b or H_a)[d]	173.0 (s, μ-C), 69.4 [d, J(C–H) 178, 2 η-C_6H_6], 60.9 [q, J(C–H) 122, Me], 60.2 [t, J(C–H) 129, *C*H$_2$CH$_3$], 20.8 [q, J(C–H) 127, CH$_2$*C*H$_3$][d]
(7) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHCHMe_2)(\mu\text{-}H)_2]$ Red C, 32.7(32.7); H, 3.9(3.9) *m/e* = 584[$P^+ - 4$]	13.3 [1 H, ddd, $J(H_a - H_c)$ 4.5, $J(H_b - H_c)$ 1.5, $J(H_d - H_c)$ 3.5, H_c], 4.24 (12 H, s, 2 η-C_6H_6), 2.5 [1 H, d of spt, $J(H_c - H_d)$ 3.5, $J(H_d - H_{Me})$ 6.8, H_d], 1.43 [6 H, d, $J(H_d - H_{Me})$, 6.8, 2 Me], −5.04 (1 H, br, H_a), −5.34 (1 H, br, H_b)[d]	185.3 [d, J(C–H) 150, μ-CH], 70.9 [d, J(C–H) 174, 2 η-C_6H_6], 55.4 [d, J(C–H) 124, *C*HMe$_2$], 28.7 [q, J(C–H) 118, CH*Me*$_2$][d]
(8) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHSiMe_3)(\mu\text{-}H)_2]$ Dark green C, 31.0(31.1); H, 3.9(3.9) *m/e* = 617 [$P^+ - 1$]	12.86 [1 H, dd, $J(H_a - H_c)$ 5.0, $J(H_b - H_c)$ 3.0, H_c], 4.19 (12 H, s, 2 η-C_6H_6), 0.35 (9 H, s, SiMe$_3$), −3.33 (1 H, br H_a), −4.15 (1 H, br, H_b)[d]	162.9 [d, J(C–H) 122, μ-CH], 70.3 [d, J(C–H) 176, 2 η-C_6H_6], 4.38 [q, J(C–H) 118, SiMe$_3$][d]
(9) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}C[CH_2]_4)(\mu\text{-}H)_2]$ Light green C, 33.9(34.1); H, 3.7(3.7) *m/e* = 600 [P^+]	4.18 (12 H, s, 2 η-C_6H_6), 2.7 [4 H, m (7 lines), 2 $H_{a,a'}$], 1.36 [4 H, m (7 lines), 2 $H_{b,b'}$], −5.62 [2 H, br, 2 H_c][d]	188.2 (s, μ-C), 73.3 [t, J(C–H) 130, $(CH_2)_{a,a'}$], 69.9 [d, J(C–H) 174.1, 2 η-C_6H_6], 30.67 [t, J(C–H) 126, $(CH_2)_{b,b'}$] [d]
(10) $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}C[CH_2]_5)(\mu\text{-}H)_2]$ Green C, 39.3(35.3); H, 4.9(4.0) *m/e* = [$P^+ - 614$]	4.31 (12 H, s, 2 η-C_6H_6), 3.15 [4 H, m (5 lines), 2 $H_{a,a'}$], 1.48 [2 H, m (10 lines), $H_{c,c'}$], 1.56 [4 H, m (8 lines), 2 $H_{b,b'}$], −5.38 (2 H, br, 2 H_d)[d]	189.6 (s, μ-C), 70.2 [t, J(C–H) 132, $(CH_2)_{a,a'}$], 69.4 [d, J(C–H) 175, 2 η-C_6H_6], 28.3 [t, J(C–H) 127, $(CH_2)_{b,b'}$], 27.6 [t, J(C–H) 120, $(CH_2)_{c,c'}$][d]
(11) $[\{Re(\eta\text{-}C_6D_6)\}_2(\mu\text{-}CHBu^t)(\mu\text{-}H)_2]$ Red C, 34.1(34.0); H, 4.1(4.0) *m/e* = 612 [$P^+ - 2$]	13.66 [1 H, dd, $J(H_a - H_c)$ 5.1, $J(H_b - H_c)$ 1.5, H_c], 1.37 (9 H, s, 3 Me), −4.41 (1 H, br, H_a), −5.26 (1 H, br, H_b).[d] ^{2}H-{^{1}H} n.m.r. at 38.4 MHz:4.30 (s, 2 η-C_6D_6)[f]	193.8 (s, μ-CH), 70.5 [t, J(C–D) 27, 2 η-C_6D_6], 55.5 (s, *C*Bu^t), 34.9 (s, Bu^t)[d]

Table 5 (*continued*)

Compound, colour, analysis (%),[a] and mass spectrum[b]	N.m.r. data[c] ^1H	^{13}C
(**12**) $[\{Re(\eta-C_6H_6)\}_2(\mu-CHCH{=}CH_2)(\mu-H)_2]$ Red	12.3 [1 H, ddd, $J(H_c - H_a)$ 3.5, $J(H_c - H_b)$ 1.5, $J(H_c - H_d)$ 10.7, H_c], 7.3 [1 H, m (7 lines), H_d], 4.4 [1 H, m (10 lines), H_e], 4.2 [1 H, m (6 lines), H_f], 4.19 (6 H, s, 2 $\eta-C_6H_6$), −5.29 (1 H, br, H_a or H_b), −5.31 (1 H, br, H_b or H_a)[d]	

[a] Found (calc.). [b] Mass spectra are reported for *m/e* of the highest peak for the ^{187}Re isotope (assignment, P^+ indicates the parent ion). [c] Given as: chemical shift (δ/p.p.m.) [relative intensity, multiplicity, coupling (*J* in Hz), assignment]. ^1H N.m.r. spectra were determined at 300 MHz and ^{13}C spectra at 62.8 MHz, unless otherwise stated. All spectra were determined at room temperature. Assignments of Re–H_a, Re–H_b, and μ-CH_c are based on homonuclear ^1H n.O.e. experiments. H_a is defined as cisoid with respect to H_c. See Figure 3 and Schemes 1 and 2 for labelling. [d] In $[^2H_6]$benzene. [e] In $[^2H_8]$toluene. [f] In $[^1H_6]$benzene.



Scheme 2. Summary of the reactions of rhenium atoms with cyclic alkanes. Rhenium atoms were co-condensed with the indicated substrates at −196 °C. (*i*) Cyclopropane, (*ii*) cyclopentane, (*iii*) cyclohexane

and microanalytical data in addition to ^1H and ^{13}C n.m.r. spectroscopy (see Table 5).

It is interesting to note that for complexes (**1**) and (**3**)—(**12**) the lowest field hydride resonance in the ^1H n.m.r. spectrum is assignable to the hydrogen (H_a) *cis* to the μ-alkylidene hydrogen (H_c), whereas for compound (**2**) the order is reversed. However, in all cases the hydrogen H_a exhibits the largest homonuclear coupling to H_c.

As expected from the postulated molecular structures of compounds (**2**)—(**7**), when the bridging CRR′ ligand has R = R′, the molecule possesses a mirror plane along the Re–Re vector, which makes the rhenium–hydrides equivalent. When the alkane substrate is propane or any other higher homologue, isomers are formed which arise from oxidative addition involving all possible $-CH_2$ or $-CH_3$ groups. The relative ratios of the isomers appear to reflect an essentially statistical distribution, assuming that all C–H bonds are equally reactive.

Examples of dimetallaspiro complexes[6] are rare, due to the unavailability or instability of most alicyclic diazoalkanes (*e.g.* diazocyclobutane). We were interested in discovering if similar derivatives could be formed by the reaction of rhenium atoms with benzene and cyclic alkanes.

The reaction of rhenium atoms with benzene and cyclopentane or cyclohexane yielded compounds (**9**) and (**10**) respectively. These derivatives have been characterized by mass spectral and microanalytical data, together with ^1H and ^{13}C n.m.r. spectroscopy as the μ-cyclopentylidene and μ-cyclohexylidene derivatives, see Table 5.

Co-condensation of rhenium atoms with benzene and cyclopropane (2:1; w/w) yields, after work-up and sublimation, a mixture of two complexes. One component was identified as $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHEt)(\mu\text{-}H)_2]$, (**3**) by comparison of the ^1H n.m.r. spectrum with that of an authentic sample. The remaining component could not be isolated in a pure form, but ^1H n.m.r. spectra together with homonuclear ^1H decoupling experiments are consistent with the formulation $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHCH{=}CH_2)(\mu\text{-}H)_2]$, (**12**).

The structures proposed for the compounds (**9**), (**10**), and (**12**) are shown in Scheme 2: only one conformation is shown for the cyclopentane and cyclohexane rings. The equivalence of the geminal hydrogens in the ^1H n.m.r. spectra of (**9**) and (**10**) at −60 °C shows that rapid ring inversion is still occurring.

It is thought, regarding the reactions described previously, that sequential oxidative addition occurs at two carbon–hydrogen bonds of the alkane substrate, giving the two rhenium hydrides. In support of this proposal, it was found that the product of co-condensation of rhenium atoms with a 1 : 1 (w/w) mixture of C_6D_6 and neopentane gave the deuteriated complex $[\{Re(\eta\text{-}C_6D_6)\}_2(\mu\text{-}CHBu^t)(\mu\text{-}H)_2]$ (**11**) as the only observed product. No resonances attributable to Re–D or μ-CDBu^t could be detected by ^2H n.m.r. spectroscopy.

Compound (**1**) reacts with trimethylphosphine at room temperature over 2 h to give $[Re(\eta\text{-}C_6H_6)(PMe_3)_2H]$ (**13**) and $[Re(\eta\text{-}C_6H_6)(PMe_3)_2(CH_2Bu^t)]$ (**14**) as an inseparable mixture. Compound (**13**) was identified by comparison of the ^1H n.m.r. spectrum with that of an authentic sample.[7] The proposed formulation of (**14**) is strongly suggested by the ^1H and ^{31}P n.m.r. spectra (see Experimental section).

The mechanism of formation of the μ-alkylidene compounds is unknown. Photochemical steps cannot be excluded from any mechanism, since the total black body radiation from a molten rhenium sample (*ca.* 3 400 °C) is approximately equivalent to the radiation from a 1-kW tungsten lamp. It is interesting that the formation of compounds (**1**)—(**12**) *via* alkane activation takes place in the presence of an excess of benzene which is normally regarded as a much more reactive ligand than alkanes. Indeed, kinetic studies[8] have shown that the intermediate $[Rh(\eta\text{-}C_5Me_5)(PMe_3)]$ reacts 20 times faster with benzene than with cyclohexane.

This study reveals that an established ligand like benzene can be used as a solvent, or co-reactant, if the steric and electronic requirements favouring preferential alkane activation are fulfilled. In the rhenium atom experiments it seems that a requirement for isolation of a product is that at least one of the reactants possess a $-CH_2$ or $-CH_3$ group.

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 BTS 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, 40—60 °C light petroleum, diethyl ether), or phosphorus pentoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for n.m.r. studies were stored in Rotaflo ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation.

Liquid alkanes used in C–H activation studies were either of spectroscopic grade or were deolefinized by a mixture of concentrated HNO_3–H_2SO_4 (3:1 v/v), followed by washing with an aqueous solution of $NaHCO_3$, and distillation from 4-Å molecular sieves. Liquid alkenes were passed through a column containing activated Al_2O_3. Gaseous reactants were used as supplied (research grade) without further purification. Elemental analyses were performed by the Analytische Laboratorien, Elbach, West Germany.

Table 6. Orbital exponents and coulomb integrals used in the extended-Hückel calculation. H^* represents the bridging hydrogens

Atom	Re			C		H	H^*
Orbital	6*s*	6*p*	5*d*	2*s*	2*p*	1*s*	1*s*
Exponent	1.984	1.518	2.888	1.625	1.625	1.300	1.300
H_{ii}	−7.573	−3.828	−9.962	−21.40	−11.40	−13.60	−10.00

^1H N.m.r. spectra were determined using a 300-MHz Bruker WH-300 spectrometer. ^{13}C N.m.r. spectra were determined using 62.8-MHz Bruker AM-250 or 125.6-MHz Bruker AM-500 instruments. ^2H N.m.r. spectra were determined on a 38.4-MHz Bruker AM-250 spectrometer. Abbreviations used in multiplicities are: s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sxt = sextet, spt = septet, m = multiplet, vt = virtual triplet, and br = broad. Spectra were referenced internally using the solvent resonance (^1H, ^{13}C) relative to tetramethylsilane (δ = 0 p.p.m.), or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts are quoted in p.p.m., and coupling constants 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 experiments were carried out using both the 10-kW, bell-jar reactor[9] and the twin-hearth bell-jar reactor.[10] Both machines were operated in the positive hearth mode. Metal-vapour synthesis reactions were carried out using a pre-melted ingot of the appropriate metal. A pre-melted ingot is required to minimize outgassing during the reaction which would lead to deterioration of the vacuum. In a typical reaction, the electron gun furnace is turned on when a vacuum better than 10^{-5} Torr is achieved. Ligand (*ca.* 10 cm^3) was condensed onto the walls of the vessel (maintained at liquid nitrogen temperature) prior to evaporation of the metal sample. The metal is evaporated using the appropriate power and the rate of ligand entry adjusted so that a vacuum better than 10^{-4} Torr is maintained. Over the period of the co-condensation (typically 3—4 h) a matrix forms on the wall of the vessel which varies in appearance from pale yellow to dark red, depending upon the metal and ligand. At the end of the reaction the apparatus is isolated from the cryopump and the cooling shroud of liquid nitrogen emptied. The apparatus is filled with nitrogen and allowed to warm to room temperature (r.t.). As the matrix melts the product collects in the gutter and is washed out by the appropriate solvent under a positive pressure of nitrogen to a collection vessel.

Low-resolution mass spectra were recorded on an AEI M.S. 902 mass spectrometer, updated by a data handling system supplied by Mass Spectroscopy Services Ltd.

The photoelectron (p.e.) spectrum of (**1**) was obtained using a PES Laboratories 0078 spectrometer interfaced with a 380Z microprocessor which enabled digital collection of the data. Spectra were obtained using both He I and He II radiation and were calibrated with reference to Xe, N_2, and He.

Molecular orbital calculations were carried out using the extended-Hückel method in the form of the program ICON8.[11] The following distances were used: C–C 1.40, C–H 1.10, Re–ring centroid 1.74, Re–Re 2.44, Re–C(bridge) 2.13, and Re–H(bridge) 1.7 Å. Orbital exponents and coulomb integrals are given in Table 6.

Synthesis of μ*-2,2-Dimethylpropylidene-di-*μ*-hydrido-bis*(η*-benzenerhenium*), (**1**).—Rhenium atoms (0.6 g, 3.2 mmol), generated from a molten ingot (*ca.* 3.0 g), were co-condensed with a mixture of neopentane and benzene (120 cm^3, 1 : 1 w/w) over a period of 4 h. After warming to r.t., the red-brown solution was washed from the reactor with thf (500 cm^3), filtered through a bed of Celite, and volatiles removed under reduced pressure giving a red-brown oil. The residue was extracted with light petroleum (b.p. 40—60 °C, 2 × 150 cm^3), which was filtered through a Celite bed. Removal of the solvent and sublimation of the more volatile components at 120 °C, 10^{-4} Torr onto a liquid-nitrogen cooled probe yielded a red-brown waxy solid. The sublimate was washed from the probe with light petroleum (b.p. 40—60 °C, 2 × 50 cm^3) filtered, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C overnight, gave red crystals, which were collected and dried *in vacuo*. Yield: 300 mg, 15%.

Synthesis of μ*-Ethylidene-di-*μ*-hydrido-bis*(η*-benzenerhenium*), (**2**).—Rhenium atoms (1.2 g, 6.4 mmol) were evaporated from the twin-hearth metal-vapour synthesis machine over a period of 3.5 h, using a power of 6 kV and 300 mA throughout. Simultaneously, a saturated solution of ethane (6.0 g, 0.1 mol) in benzene (65 g, 0.75 mol) at 10 atm was condensed onto the walls of the reaction vessel. After warming to room temperature, the red-brown matrix was washed out of the machine with toluene (500 cm^3). The extract was filtered through a Celite bed and the volatiles removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60 °C, 2 × 100 cm^3) giving a red-brown solution which was filtered through a Celite bed. Removal of the solvent and sublimation at 120 °C, 10^{-4} Torr gave a dark green solid. The sublimate was washed off the sublimation probe with hot pentane (2 × 50 cm^3), filtered, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C overnight, gave feathery green crystals which were collected, and dried *in vacuo*. Yield: 40 mg, 2%.

*Synthesis of Di-*μ*-hydrido-*μ*-propylidene-bis*(η*-benzenerhenium*), (**3**) *and Di-*μ*-hydrido-*μ*-isopropylidene-bis*(η*-benzenerhenium*), (**4**).—Rhenium atoms (1.0 g, 5.3 mmol), generated from a molten ingot (*ca.* 5.0 g), were co-condensed with a saturated solution of propane (30 g, 0.34 mol) in benzene (80 g, 0.92 mol) at 30 atm onto the reactor wall over 4 h. The matrix was allowed to warm to r.t. and was washed from the reaction vessel with toluene (500 cm^3). The red-brown extract was filtered through a Celite bed and the volatiles removed under reduced pressure. The residue was extracted with light petroleum (b.p. 40—60 °C, 2 × 100 cm^3) giving a red-brown solution which was filtered through a Celite bed. Removal of the solvent under reduced pressure and sublimation at 120 °C, 10^{-4} Torr gave a dark red solid. The sublimate was washed off the sublimation probe with hot pentane (2 × 50 cm^3), filtered, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C and then to −80 °C gave light green crystals which were collected and dried *in vacuo*. Yield: 200 mg, 12%.

Synthesis of [{Re(η-C_6H_6)}$_2$(μ-CRR′)(μ-H)$_2$] [R,R′ = H,Pr^n (**5**); Me,Et (**6**); H,CHMe$_2$ (**7**); *or* H,SiMe$_3$ (**8**)].—The general preparation is described. Rhenium atoms (1.1 g, 5.9 mmol), generated from a molten ingot (*ca.* 5.0 g), were co-condensed simultaneously with a benzene–alkane mixture (100 cm^3, 1 : 1 w/w) onto the walls of the reactor over 4 h [alkane = butane for (**5**) and (**6**), 2-methylpropane for (**7**), and tetramethylsilane for (**8**)]. The matrix was allowed to warm to r.t. and extracted from the reaction vessel with toluene (500 cm^3). The extract was filtered through a Celite bed and the solvent and excess ligand removed under reduced pressure at 60 °C. The residue was extracted with light petroleum (b.p. 40—60 °C, 2 × 100 cm^3) giving a red-brown solution which was filtered through a Celite bed. Removal of the solvent and sublimation of the more volatile components at 120 °C, 10^{-4} Torr onto a liquid-nitrogen cooled probe yielded a red-brown, waxy solid. The sublimate was washed off the sublimation probe with light petroleum (b.p. 40—60 °C, 2 × 50 cm^3), filtered, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C overnight, gave red or dark green crystals which were collected, and dried *in vacuo*. Yield: typically 100—200 mg, *ca.* 10%.

Table 7. Crystal data and experimental conditions for [{Re(η-C_6H_6)}$_2$(μ-CHBu^t)(μ-H)$_2$] (**1**)

Formula	$C_{17}H_{24}Re_2$
M	600.78
Temp./K	295
a/Å	30.034(3)
b/Å	17.284(3)
c/Å	12.353(2)
U/Å^3	6 412.53
Crystal system	Orthorhombic
Space group	*Pbca*
Z	16 (2 molecules in asymmetric unit)
D_c/g cm^{-3}	2.49
μ/cm^{-1}	159.35
F(000)	4 416.0
Crystal size/mm	0.55 × 0.21 × 0.18
θ limits/°	1.0—25.0
Scan mode	ω–2θ
Total data collected	8 264
Merging *R* factor	0.051
No. of observations	2 782
No. of parameters	308
No. of restraints	132
Observations/parameters	9.03
Weighting scheme	3-term Chebyshev
Weighting coefficients	35.13, 34.64, 2.13
Maximum shift/e.s.d. at convergence	0.07
Maximum peak in final difference map/e Å^{-3}	1.66
Final residuals *R* (*R*′)*	0.0367 (0.0577)
Extinction parameter	16.34

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

Synthesis of [{Re(η-C_6H_6)}$_2$(μ-CRR′)(μ-H)$_2$] {R,R′ = H,Et (**3**); [CH_2]$_4$ (**9**); [CH_2]$_5$ (**10**); *or* H,CH=CH_2 (**12**)}.—The general preparation is described. Rhenium atoms (1.1 g, 5.9 mmol), generated from a molten ingot (*ca.* 5.0 g), were co-condensed simultaneously with a benzene–alkane mixture (100 cm^3, 1 : 1 w/w) onto the walls of the reactor over 4 h [alkane = cyclopropane for (**3**) and (**12**), cyclopentane for (**9**), or cyclohexane for (**10**)]. The matrix was allowed to warm to r.t. and extracted from the reaction vessel with toluene (500 cm^3). The remainder of the work-up is identical to that described above. Yield: typically 50—100 mg, *ca.* 5%.

Synthesis of [{Re(η-C_6D_6)}$_2$(μ-CHBu^t)(μ-H)$_2$], (**11**).—Rhenium atoms (0.6 g, 3.2 mmol), generated from a molten ingot (*ca.* 3.0 g), were co-condensed with a mixture of neopentane and perdeuteriobenzene (70 cm^3, 1 : 1 w/w) over a period of 4 h. After warming to r.t., the red-brown solution was washed from the reactor with thf (500 cm^3), filtered through a bed of Celite, and volatiles removed under reduced pressure giving a red-brown oil. The residue was extracted with light petroleum (b.p. 40—60 °C, 2 × 150 cm^3), which was filtered

Table 8. Fractional atomic co-ordinates for (**1**) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Re(1)	0.557 13(3)	0.087 46(4)	0.633 21(7)
Re(2)	0.518 17(4)	0.206 18(5)	0.584 94(7)
Re(3)	0.864 41(3)	0.402 94(5)	0.179 47(8)
Re(4)	0.828 09(3)	0.282 74(5)	0.234 22(7)
C(11)	0.537 7(6)	−0.035 1(13)	0.646 4(20)
C(12)	0.572 1(8)	−0.031 1(13)	0.570 4(15)
C(13)	0.612 8(7)	0.004 1(15)	0.597 6(22)
C(14)	0.618 5(8)	0.036 0(15)	0.699 8(28)
C(15)	0.584 4(11)	0.030 9(16)	0.776 2(17)
C(16)	0.545 2(9)	−0.008 5(13)	0.751 4(18)
C(21)	0.495 6(8)	0.319 6(14)	0.658 4(16)
C(22)	0.458 4(8)	0.271 0(14)	0.646 9(17)
C(23)	0.448 5(7)	0.237 9(13)	0.548 8(20)
C(24)	0.473 8(8)	0.255 8(14)	0.456 0(15)
C(25)	0.512 0(8)	0.304 2(15)	0.464 9(16)
C(26)	0.524 2(8)	0.334 0(12)	0.567 9(21)
C(31)	0.876 9(10)	0.530 3(13)	0.213 9(18)
C(32)	0.914 6(9)	0.486 7(14)	0.234 5(16)
C(33)	0.932 4(7)	0.441 2(15)	0.153 3(21)
C(34)	0.912 6(8)	0.439 6(14)	0.051 2(17)
C(35)	0.871 7(8)	0.475 2(14)	0.035 0(15)
C(36)	0.853 9(8)	0.521 5(14)	0.115 2(23)
C(41)	0.781 9(9)	0.196 0(13)	0.172 8(17)
C(42)	0.764 1(7)	0.222 0(14)	0.269 1(22)
C(43)	0.788 7(9)	0.218 3(14)	0.363 5(16)
C(44)	0.832 5(9)	0.190 5(15)	0.359 5(16)
C(45)	0.849 7(7)	0.161 2(14)	0.261 6(22)
C(46)	0.823 5(10)	0.161 5(13)	0.170 3(16)
C(1)	0.580 8(8)	0.171 2(18)	0.520(3)
C(100)	0.586 3(17)	0.197(4)	0.599(5)
C(3)	0.624 4(6)	0.218 1(11)	0.521 0(18)
C(4)	0.635 7(14)	0.250 5(21)	0.633 6(25)
C(5)	0.618 9(16)	0.286 2(20)	0.441 8(29)
C(6)	0.663 4(14)	0.167 6(23)	0.482(3)
C(400)	0.607 4(24)	0.176(3)	0.418(4)
C(500)	0.668 5(17)	0.181(4)	0.558(6)
C(600)	0.633 0(25)	0.303 2(22)	0.493(6)
C(51)	0.816 2(8)	0.397 3(20)	0.304(3)
C(510)	0.796 6(14)	0.390 7(21)	0.223 5(28)
C(53)	0.770 2(6)	0.436 5(10)	0.309 2(16)
C(54)	0.750 1(15)	0.436 3(20)	0.195 9(25)
C(55)	0.735 8(15)	0.400 2(26)	0.389(3)
C(56)	0.778 2(16)	0.522 4(18)	0.343 4(30)
C(540)	0.756 9(16)	0.517 7(20)	0.270(4)
C(550)	0.799 3(16)	0.443 2(29)	0.412(3)
C(560)	0.727 0(11)	0.389 9(21)	0.338(3)

through a Celite bed. Removal of the solvent and sublimation of the more volatile components at 120 °C, 10^{-4} Torr onto a liquid-nitrogen cooled probe yielded a red-brown waxy solid. The sublimate was washed from the probe with light petroleum (b.p. 40—60 °C, 2 × 50 cm^3), filtered, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C overnight, gave red crystals, which were collected and dried *in vacuo*. Yield: 200 mg, 10%.

Synthesis of $[\mathrm{Re}(\eta\text{-}C_6H_6)(PMe_3)_2H]$, (**13**) *and* $[\mathrm{Re}(\eta\text{-}C_6H_6)(PMe_3)_2(CH_2Bu^t)]$, (**14**).—$[\{\mathrm{Re}(\eta\text{-}C_6H_6)\}_2(\mu\text{-}CHBu^t)(\mu\text{-}H)_2]$ (50 mg, 0.08 mmol) in benzene (30 cm^3) was treated with trimethylphosphine (1 cm^3). The red solution was stirred at r.t. for 3—4 h. From the resulting orange solution, trimethylphosphine was removed under reduced pressure, affording an orange oily solid. The oily solid was sublimed at 100 °C, 10^{-4} Torr onto a water cooled probe giving a very pale yellow crystalline solid. The solid was found to be a *ca.* 1:1 molar mixture of $[\mathrm{Re}(\eta\text{-}C_6H_6)(PMe_3)_2H]$ and $[\mathrm{Re}(\eta\text{-}C_6H_6)(PMe_3)_2(CH_2Bu^t)]$ by ^1H n.m.r. spectroscopy. Total yield: 30 mg, 50%.

Crystal-structure Determination.—Crystals of compound (**1**) 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 every 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout data collection.

Lorentz and polarization corrections were applied together with an empirical absorption correction.[12] 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 and direct methods: subsequent electron-density difference syntheses revealed the location of all non-hydrogen atoms. The rhenium atoms and benzene ring carbons were refined anisotropically together with the remaining non-hydrogen atoms, which were refined with isotropic thermal parameters by full-matrix least squares. Hydrogen atoms were located around the benzene rings, but included in calculated positions (C–H, 1.0 Å) which were modified between successive cycles of refinement. Refinement converged at $R = 0.0367$ ($R' = 0.0577$) and the final electron-density difference synthesis showed no peaks > 1.66 e $Å^{-3}$, the largest peaks lying in close proximity to the rhenium atom positions.

Corrections for anomalous dispersion and isotropic extinction[13] were made in the final cycles of refinement, a Chebyshev weighting scheme[14] was used with parameters as in Table 7. The final positional parameters are recorded in Table 8. All calculations were performed on the VAX 11/750 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system[15] and plotted using the CHEMGRAF package.[16] Atomic scattering factors and anomalous dispersion coefficients were taken from International Tables.[17]

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References

1 F. G. N. Cloke, A. E. Derome, M. L. H. Green, and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, 1983, 1312.
2 M. L. H. Green and D. O'Hare, *J. Chem. Soc., Dalton Trans.*, 1986, 2469.
3 J. A. Bandy, F. G. N. Cloke, M. L. H. Green, D. O'Hare, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1984, 240.
4 S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J. Chem. Soc., Dalton Trans.*, 1974, 304.
5 F. G. N. Cloke, A. N. Dix, J. C. Green, R. N. Perutz, and E. A. Seddon, *Organometallics*, 1983, **2**, 203.
6 (*a*) W. A. Herrmann, Proceedings of the First Symposium of the Industry–University Cooperative Chemistry Program, Department of Chemistry, Texas Agriculture and Mining University, 1983; (*b*) W. A. Herrmann, *Adv. Org. Chem.*, 1982, **20**, 160.
7 R. A. Perlana and R. G. Bergman, *Organometallics*, 1984, **3**, 508.
8 M. L. H. Green, D. O'Hare, and J. M. Wallis, *J. Chem. Soc., Chem. Commun.*, 1984, 233.
9 F. G. N. Cloke, D.Phil. Thesis, Oxford, 1978.
10 J. M. Wallis, D.Phil. Thesis, Oxford, 1984.
11 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179.

12 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
13 A. C. Larson, *Acta Crystallogr.*, 1967, **23**, 664.
14 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.
15 J. R. Carruthers and D. J. Watkin, CRYSTALS User Manual, Oxford University Computing Centre, 1975.
16 E. K. Davies, CHEMGRAF User Manual, Chemical Crystallography Laboratory, Oxford, 1981.
17 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

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