Activation of Linear and Cyclic Saturated Hydrocarbons involving Arene–Rhenium Compounds: Crystal Structure of μ-Dihydrido-μ-neopentylidene-bis(η-benzene)-dirhenium

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Co-condensation of rhenium atoms with a mixture of benzene and an alkane, RH = ethane, propane, butane, 2-methylpropane, neopentane, tetramethylsilane, cyclopentane, or cyclohexane gives the compounds $[(\eta\text{-}C_6H_6)Re(\mu\text{-}H)_2(\mu\text{-}CR'R'')Re(\eta\text{-}C_6H_6)]$, where CR′R″ = CHMe, CHEt and CMe_2, $CHPr^n$ and CMeEt, $CH(CHMe_2)$, $CHBu^t$, $CHSiMe_3$, cyclopentylidene, or cyclohexylidene respectively: the crystal structure of the compound where CR′R″ = $CHBu^t$ has been determined.

The ability of transition metals to insert into carbon–hydrogen bonds of alkanes has been demonstrated, mostly in recent reports, for compounds of iridium,[1,2] rhenium,[3] rhodium,[2] and lutetium.[4] Here we describe a quite general reaction in which two C–H bonds of alkanes are caused to add oxidatively to two rhenium atoms.

We recently observed that co-condensation of rhenium atoms with certain alkylbenzenes gave binuclear compounds containing bridging alkylidene groups of the general type $[(\eta\text{-arene})Re(\mu\text{-}H)_2(\mu\text{-}CHAr)Re(\eta\text{-arene})]$.[5] It appeared that the bridging alkylidene and two bridging hydrido ligands derived from a single CH_2 or CH_3 group. When rhenium atoms were co-condensed with benzene alone then no tractable products could be isolated at room temperature. It was, therefore, decided to co-condense rhenium atoms with benzene in the presence of saturated hydrocarbons in order to find whether in these circumstances it would be possible to form a μ-alkylidene and two μ-hydrido groups from the alkanes.

When rhenium atoms are co-condensed with a *ca.* 1:1 mixture of benzene and neopentane then volatile, yellow-brown crystals of (**1**) may be isolated from the reaction mixture. Microanalysis and detailed n.m.r. studies† indicated a binuclear structure, and so an *X*-ray structure analysis was undertaken.‡

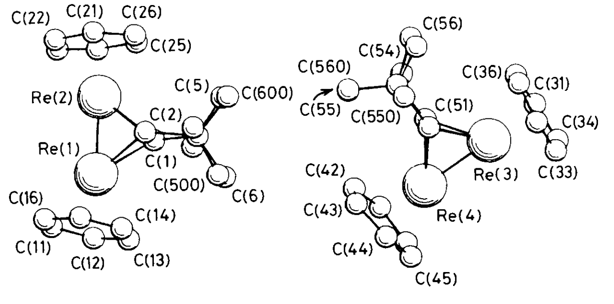

Figure 1. Crystal structure of (**1**). Selected distances (Å) and angles (°): Re(1)–Re(2) 2.436(1), Re(3)–Re(4) 2.442(1), Re(1)–C(1) 2.13(3), Re(3)–C(51) 2.11(3), Re(1)–C(2) 2.13(5), Re(3)–C(52) 2.12(4), Re(2)–C(1) 2.13(3), Re(4)–C(51) 2.19(3), Re(2)–C(2) 2.06(5), Re(4)–C(52) 2.09(3), Re(1)–C(1)–Re(2) 69.7(8), Re(3)–C(51)–Re(4) 69.2(9), Re(1)–C(2)–Re(2) 71.1(14), Re(3)–C(52)–Re(4) 70.8(10), $\eta\text{-}C_6H_6$–Re(1) 1.73, $\eta\text{-}C_6H_6$–Re(2) 1.74, $\eta\text{-}C_6H_6$–Re(3) 1.76, $\eta\text{-}C_6H_6$–Re(4) 1.75. Angle between the normals to the planes of the benzene rings for Re(1)–Re(2) 13.5 and for Re(3)–Re(4) 13.6°.

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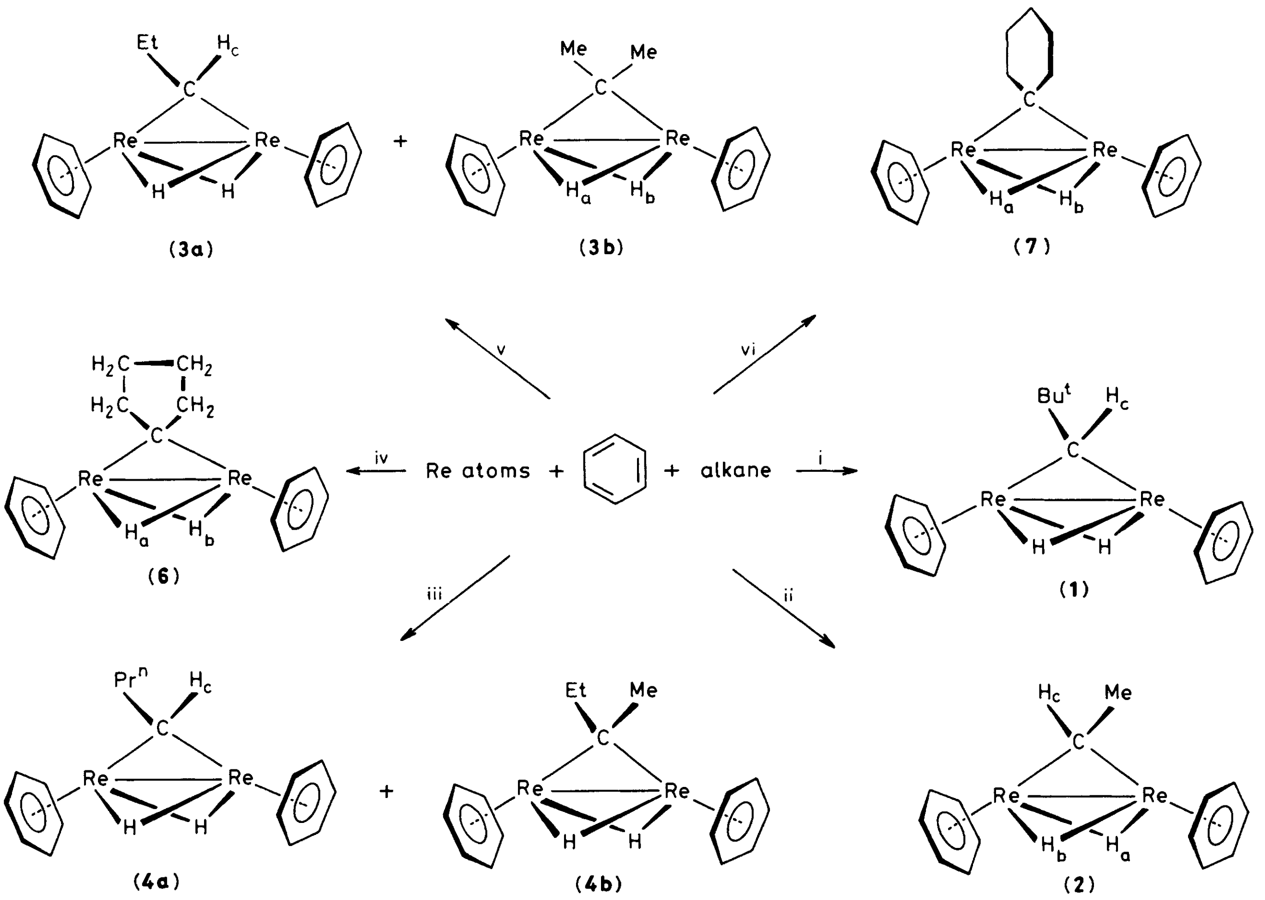
† N.m.r data for (**1**), *J* in Hz. ^1H n.m.r. in C_6D_6: δ 13.65 [dd, 1H, $J(H_a\text{–}H_c)$ 6, $J(H_b\text{–}H_c)$ 2, μ-CH], 4.31 (s, 12H, 2 × $\eta\text{-}C_6H_6$), 1.37 (s, 9H, CMe_3), −4.26 (br. s, 1H, H_a), −5.13 (br. s, 1H, H_b); ^{13}C n.m.r. in C_6D_6: δ 193 [d, *f*(C–H) 135, μ-C], 70.36 [d, *J*(C–H) 172, $\eta\text{-}C_6H_6$], 55.35 (s, C of *C*Me_3), 35.0 p.p.m. [q, *J*(C–H) 124, 3 × Me].

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



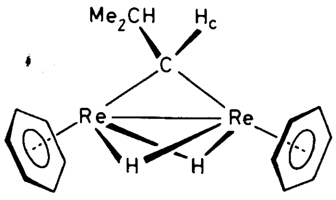
Scheme 1. Rhenium atoms (*ca.* 1–3 g), generated from a positive hearth gun supplied by G. V. Planer Ltd., were co-condensed with the indicated substrates: i, neopentane; ii, ethane; iii, butane [ratio of (**4a**):(**4b**) is *ca.* 2:1]; iv, cyclopentane; v, propane [ratio of (**3a**):(**3b**) is *ca.* 8:6]; vi, cyclohexane.

Crystal data: (**1**), $C_{17}H_{24}Re_2$, $M = 600.78$, orthorhombic, space group *Pbca*, $a = 30.034(3)$, $b = 17.284(3)$, $c = 12.353(2)$ Å, $U = 6417.53$ Å^3, $D_c = 2.49$ g cm^{-3}, $Z = 16$ (2 molecules in the asymmetric unit), $\mu(\text{Mo-}K_\alpha) = 159.35$ cm^{-1}, $F(000) = 4416.0$, $R = 3.67\%$ ($R_w = 5.77\%$) for 2782 observed reflections [$I > 3\sigma(I)$].

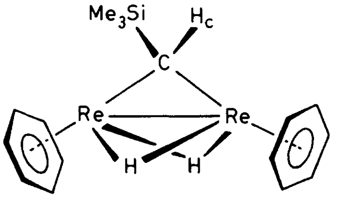
Data were collected on an Enraf–Nonius CAD-4F diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). The structure was solved using Patterson and direct methods and the non-hydrogen atoms refined, first isotropically and then anisotropically for rhenium atoms and benzene ring carbon atoms, by full-matrix least squares. Hydrogen atoms were located around the benzene rings but included in calculated positions which were modified between successive cycles of refinement.

The crystal structure analysis shows that (**1**) has the expected binuclear structure, shown in Figure 1, with relevant distances and angles. The bridging CHBu^t groups of both molecules in the asymmetric unit exhibit disorder and have been resolved into components involving a common C(3) in one molecule and C(53) in the other.

The ^{1}H n.m.r. spectrum of (**1**) shows two high field bands assignable to two different hydrogens directly bonded to one or more rhenium atoms. The crystallographic data do not allow unequivocal location of the Re-hydrogens. We assume that the solution structure is the same as that in the crystal. In which case, the occurrence of non-equivalent Re-hydrogens whilst there is only one band assignable to the two, equivalent η-arene groups in the ^{1}H and ^{13}C n.m.r. spectra can only be understood in terms of the presence of two bridging hydrogens rather than two terminal Re–H groups.



(**5**)



(**8**)

The proposed structures are shown in Scheme 1 and the 18-electron formalism requires that these triply bridged molecules also have a formal single Re–Re bond. The observed mean Re–Re distance is 2.436(1) Å which is most consistent with there being only a single bond.[6]

It appears that the ability of the rhenium–benzene system to activate alkanes is quite general. We have co-condensed rhenium atoms with alkane:benzene mixtures using the

Table 1. Selected n.m.r. data for compounds (**1**)—(**8**).[a]

		δ_H						
Alkane	CR'R''	H_a	H_b	H_c[b]	η-C_6H_6	μ-C[b]	$J(H_a–H_c)$[c]	$J(H_b–H_c)$
Neopentane	$CHBu^t$	−4.26	−5.13	13.65	4.3	193.0	6.0	2.0
Ethane	CHMe	−5.3	−5.57	12.49	4.2	165.1	2.0	4.0
Propane	CHEt	−5.38	−5.4	12.7	4.19	176.0	2.0	6.0
	CMe_2	−5.7	−5.7	—	4.15	175.3	—	—
Butane	$CHPr^n$	−5.26	−5.26	12.7	4.24	172.9	3.0	4.0
	CEtMe	−5.45	−5.66	—	4.19	181.6	—	—
2-Methylpropane	$CH(CHMe_2)$	−5.04	−5.34	13.38	4.24	185.3	5.0	2.0
Cyclopentane	$C[CH_2]_4$	−5.6	−5.6	—	—	187.2	—	—
Cyclohexane	$C[CH_2]_5$	−5.47	−5.47	—	4.27	189.0	—	—
Tetramethylsilane	$CHSiMe_3$	−3.3	−4.1	12.8	4.19	162.9	5.0	3.0

[a] ^1H N.m.r. data determined on a Bruker WH 300 instrument. All assignments were confirmed by double resonance experiments. ^{13}C N.m.r. data determined on a Bruker AM 250 instrument. [b] δ_c in p.p.m. The low field chemical shifts are characteristic for alkylidene carbons and hydrogens, ref. 7. [c] All coupling constants given in Hz.

alkanes ethane, propane, butane, 2-methylpropane, neopentane, tetramethylsilane, cyclopentane, and cyclohexane. Sublimation from the less volatile reaction products gave yellow–brown compounds in 10–20% yield (based on rhenium) for which the characteristic ^1H n.m.r. data unambiguously show the compounds to have μ-alkylidene structures analogous to that of (**1**) (see Scheme 1). Selected n.m.r. data are given in Table 1.

The mechanism of the formation of the compounds (**1**)–(**8**) is not known but it is interesting that the oxidative addition of the alkane C–H bonds has occurred in the presence of an excess of benzene and that the product has the binuclear μ-alkylidene moiety. During the formation of the co-condensate it was continuously exposed to the radiation from the molten rhenium sample (*ca.* 3600 °C), which is approximately equivalent to the radiation from a 500 W tungsten lamp. Thus photochemical steps cannot be excluded from the mechanism.

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