η-Arene–Rhenium Chemistry: Activation of *sp*^{3} Carbon–Hydrogen Bonds of Alkylbenzenes by Rhenium; Formation of Binuclear μ-Alkylidene Derivatives

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

Co-condensation of rhenium atoms with arenes gives the binuclear compounds $[(\eta\text{-R})\text{Re}(\mu\text{-H})_2(\mu\text{-CHR}')\text{Re}(\eta\text{-R})]$, where R = toluene, *p*-xylene, or mesitylene and R′ = Ph, *p*-MeC_6H_4, or 3,5-$\text{Me}_2\text{C}_6\text{H}_3$ respectively. Similarly, rhenium atoms with ethylbenzene give a mixture of the isomers $[(\eta\text{-C}_6\text{H}_5\text{Et})\text{Re}(\mu\text{-H})_2(\mu\text{-CHCH}_2\text{Ph})\text{Re}(\eta\text{-C}_6\text{H}_5\text{Et})]$ and $[(\eta\text{-C}_6\text{H}_5\text{Et})\text{Re}(\mu\text{-H})_2(\mu\text{-CMePh})\text{Re}(\eta\text{-C}_6\text{H}_5\text{Et})]$. These μ-alkylidene compounds have been characterised *inter alia* by detailed n.m.r. studies. Variable-temperature n.m.r. data show the barriers to rotation of the aryl groups of the μ-CHR′ system to be $\Delta G^{\ddagger}$ = 55.1, 64.8, and 78.0 kJ mol^{-1} for R′ = Ph, *p*-MeC_6H_4, and 3,5-$\text{Me}_2\text{C}_6\text{H}_3$ respectively.

Co-condensation of transition-metal atoms with arenes has been shown to provide a general synthesis of bis(η-arene) compounds of many transition metals.[1–3] Here we describe a study of the reactions of rhenium atoms with benzene and a series of alkyl-substituted benzene derivatives. A brief communication of part of this work has been published.[4]

Results and Discussion

Co-condensation of rhenium atoms with pure benzene yields a red-brown material soluble in light petroleum. However, attempts to isolate a pure organometallic product were unsuccessful.[5] Previously, Fisher and co-workers [6] reported that reduction of $[\text{Re}(\eta\text{-C}_6\text{H}_6)_2]^+$ by sodium film gave a volatile orange product which decomposed above 77 K. We conclude that $[\text{Re}(\eta\text{-C}_6\text{H}_6)_2]$ is unstable at room temperature (r.t.).

Co-condensation of rhenium atoms with pure toluene yields dark red, air-sensitive crystals, which may be sublimed *in vacuo* at *ca.* 140 °C. The data given in Table 1 show the compound to be binuclear with a bridging μ-alkylidene group, $[(\eta\text{-C}_6\text{H}_5\text{Me})\text{Re}(\mu\text{-H})_2(\mu\text{-CHPh})\text{Re}(\eta\text{-C}_6\text{H}_5\text{Me})]$, (**1**). The proposed structure is shown in the Scheme and is based on detailed variable-temperature ^{1}H and ^{13}C n.m.r. studies, as described below.

Compound (**1**) exhibits a double doublet resonance at δ 12.45 in the ^{1}H n.m.r. spectrum of relative integral one and this lies in the region attributable to the hydrogen of alkylidene ligands.[7] Spin–spin coupling is observed between this low-field resonance and the two rhenium–hydrogen resonances observed at δ −5.09 and −5.14. Mutual coupling between the two Re hydrogens is resolvable. In addition, a set of five multiplets, each of relative integral two, are observed for two η-$\text{C}_6\text{H}_5\text{Me}$ ligands in the region δ 4.31—3.8. A connectivity was established between these five multiplets by homonuclear decoupling experiments.

We conclude that (**1**) is dimeric in nature with equivalent η-$\text{C}_6\text{H}_5\text{Me}$ ligands. The ring protons are diastereotopic as a consequence of the chiral rhenium centres. There is a broad resonance at δ 7.2 of relative integral four, and a well resolved triplet [*J*(H–H) 7.0 Hz] at δ 6.9 of relative integral one. On cooling to −60 °C, the ^{1}H n.m.r. spectrum (Figure 1) reveals that the broad resonance sharpens to four well resolved multiplets each of relative integral one. This behaviour is best accounted for by the presence of a μ-CHPh ligand, in which the phenyl group rotation is at the intermediate exchange limit at room temperature, but the slow exchange limit is reached at −60 °C and the five phenyl hydrogens are chemically inequivalent. The well resolved triplet at δ 6.9 remains sharp at all temperatures and is assignable to the *para* hydrogen of the phenyl group.

Measurement of the coalescence temperature from the variable-temperature ^{1}H n.m.r. data yields a value for $\Delta G^{\ddagger}$ of 55.1 kJ mol^{-1} for the rotation mechanism.

The fully coupled ^{13}C n.m.r. spectrum of (**1**) at r.t. exhibits a doublet resonance at 164.7 p.p.m., assignable to C_α of the μ-alkylidene ligand, which occurs typically in the range 150—200 p.p.m. (see Table 4 for selected examples). The *ipso* and *para* carbons of the μ-CHPh ligand are also observed as a singlet and doublet respectively, but the remaining carbon resonances appear as a broad band centred at 127.0 p.p.m. The ^{13}C n.m.r. spectrum also indicates that the two η-$\text{C}_6\text{H}_5\text{Me}$ ligands are equivalent, but for each η-$\text{C}_6\text{H}_5\text{Me}$ ligand the six ring carbon atoms are chemically inequivalent.

The observed equivalence of the η-$\text{C}_6\text{H}_5\text{Me}$ ligands together with the observation of resolvable homonuclear coupling between the inequivalent rhenium hydrides requires the hydrogens to be located in bridging positions. Homonuclear ^{1}H nuclear Overhauser enhancement (n.O.e.) experiments[8] show that only one of the hydride resonances (H_a) exhibits an enhancement effect to the μ-CH_c hydrogen. This indicates that H_a and H_c possess a mutual dipolar interaction, implying that they have adopted a cisoid configuration with respect to the rhenium–rhenium vector (Figure 2). It is unlikely that an n.O.e. enhancement would be observed if the hydrides were in terminal positions.

Bridging hydrogens are normally difficult to observe in i.r. spectra.[9] However, the i.r. spectrum of (**1**) exhibits *inter alia* a very weak reproducible band at 1 600 cm^{-1} which, in the absence of isotopic substitution studies, can tentatively be assigned to $\nu(\text{Re–H}_{\text{bridging}})$.

Co-condensation of rhenium atoms with *p*-xylene gives orange, feathery, air-sensitive crystals of $[(\eta\text{-C}_6\text{H}_4\text{Me}_2\text{-1,4})\text{Re}(\mu\text{-H})_2(\mu\text{-CHC}_6\text{H}_4\text{Me-}p)\text{Re}(\eta\text{-C}_6\text{H}_4\text{Me}_2\text{-1,4})]$, (**2**). The ^{1}H n.m.r. spectrum of (**2**) was very similar to that of (**1**). A low-field double doublet was observed at δ 12.1, together with two hydride resonances at δ −5.40 and −5.50. The coupling constants were also found to be similar to those observed for (**1**). In addition to the protons assignable to two η-$\text{C}_6\text{H}_4\text{Me}_2$-1,4 ligands, the r.t. ^{1}H and ^{13}C n.m.r. spectra exhibit four broad resonances assignable to the *ortho* and *meta* hydrogens of a μ-$\text{CHC}_6\text{H}_4\text{Me}$-*p* moiety in which rotation about the μ-C_c–C_{ipso} bond is at the intermediate exchange limit on the n.m.r. timescale. As the temperature is raised to 45 °C the resonances assigned to H_o and $\text{H}_{o'}$, and to H_m and $\text{H}_{m'}$ coalesce. Confirmation that the hydrogens were exchanging in a pairwise manner was obtained from magnetisation transfer experiments[10] at 25 °C. The coalescence temperature yields a barrier to rotation of the $\text{C}_6\text{H}_4\text{Me}$-*p* group in (**2**) of $\Delta G^{\ddagger}$ = 64.8 kJ

Table 1. Analytical and spectroscopic data

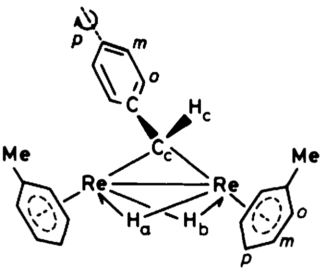
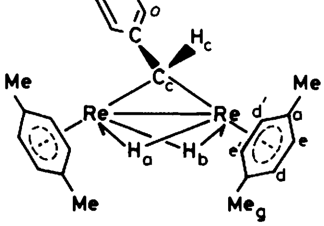
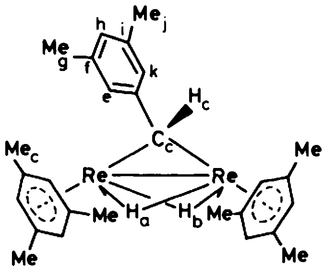
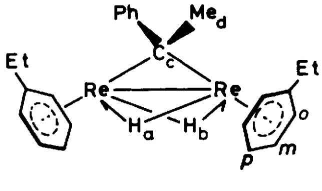
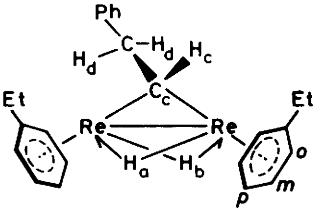
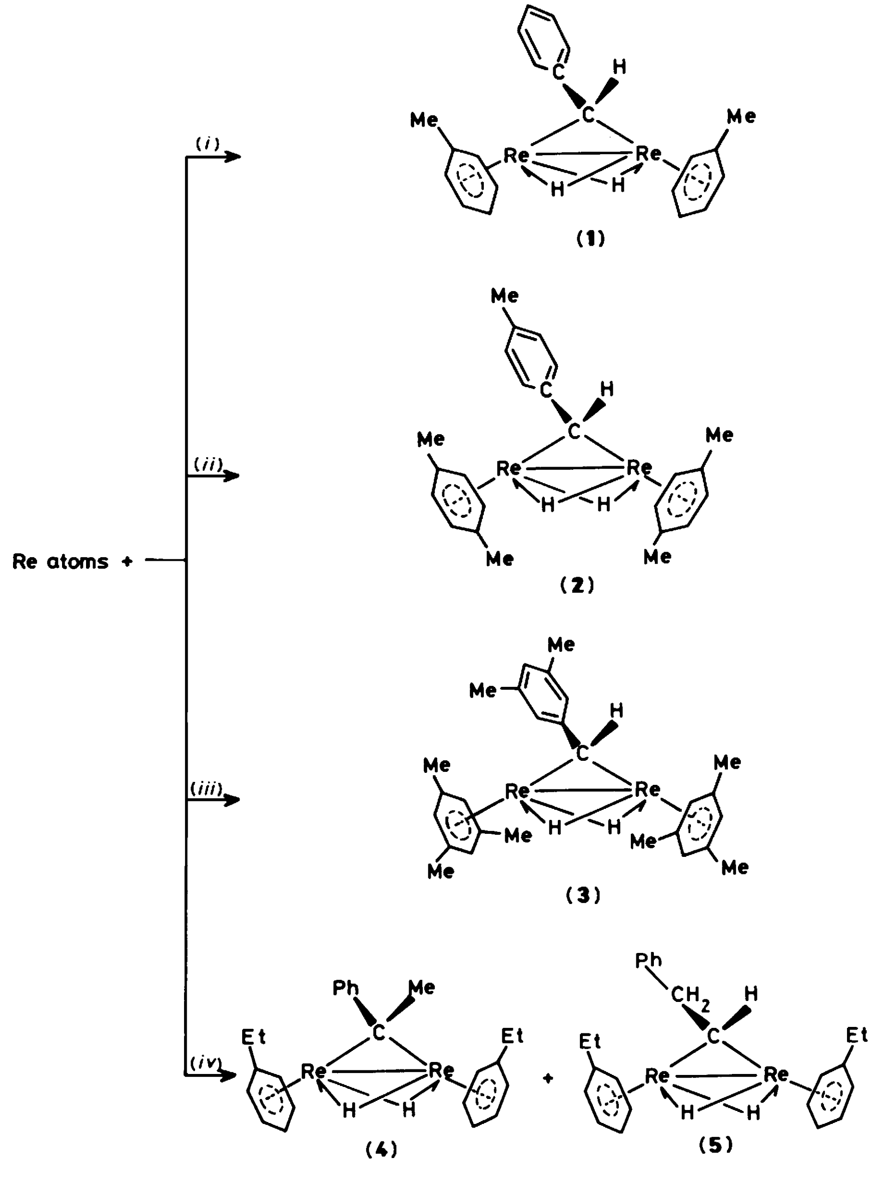
Compound, colour, and analysis[a]	N.m.r. data[b]	
	^{1}H	^{13}C
(**1**) [{Re(η-C$_6$H$_5$Me)}$_2$(μ-CHPh)(μ-H)$_2$] Red-brown C 38.3(38.8); H 3.7 (3.7)[c] 	12.45 [1 H, dd, J(H$_a$–H$_c$) 4.3, J(H$_b$–H$_c$) 1.3, H$_c$], 7.2 (4 H, br, Ph), 6.9 [1 H, t, J(H–H) 7.0, Ph, H$_p$], 4.31 [2 H, t, J(H–H) 6.9, η-C$_6$H$_5$Me, H$_m$], 4.13 [4 H, m (5 lines), η-C$_6$H$_5$Me, H$_o$ + H$_m$], 4.04 [2 H, t, J(H–H) 6.0, η-C$_6$H$_5$Me, H$_p$], 3.80 [2 H, d, J(H–H) 6.7, η-C$_6$H$_5$Me, H$_o$], 2.00 (6 H, s, 2 Me), −5.09 [1 H, t, J(H$_c$–H$_a$) = J(H$_b$–H$_a$) 4.3, H$_a$], −5.14 [1 H, dd, J(H$_c$–H$_b$) 1.3, J(H$_b$–H$_a$) 4.3, H$_b$][d] −30 °C and 250 MHz: 12.5 [1 H, dd, J(H$_a$–H$_c$) 4.3, J(H$_b$–H$_c$) 1.3, H$_c$], 8.2 [1 H, d, J(H–H) 7.1, Ph, H$_o$], 7.5 [1 H, t, J(H–H) 6.4, Ph, H$_m$], 7.2 [1 H, t, J(H–H) 7.0, Ph, H$_m$], 6.95 [1 H, t, J(H–H) 6.4, Ph, H$_p$], 6.8 [1 H, d, J(H–H) 6.9, Ph, H$_o$], 4.5 [2 H, t, J(H–H) 6.9, η-C$_6$*H*$_5$Me], 4.35 [2 H, t, J(H–H) 6.9, η-C$_6$*H*$_5$Me], 4.31 [2 H, t, J(H–H) 6.9, η-C$_6$*H*$_5$Me], 4.2 [2 H, t, J(H–H) 6.0, η-C$_6$*H*$_5$Me], 3.95 [2 H, d, J(H–H) 6.7, η-C$_6$*H*$_5$Me], 2.0 (6 H, s, 2 Me), −5.95 [1 H, t, J(H$_c$–H$_a$) = J(H$_b$–H$_a$) 4.3, H$_a$], −5.55 [1 H, dd, J(H$_c$–H$_b$) 1.3, J(H$_b$–H$_a$) 4.3, H$_b$][e]	75.4 MHz: 169.6 [s, Ph, C$_i$], 164.7 [d, J(C–H) 142, μ-CH], 130.0–125.0 (br, Ph), 124.0 [d, J(C–H) 152, Ph, C$_p$], 86.8 [s, η-*C*$_6$H$_5$Me], 72.9 [d, J(C–H) 177, η-*C*$_6$H$_5$Me), 72.4 [d, J(C–H) 174, η-*C*$_6$H$_5$Me], 71.8 [d, J(C–H) 175, η-*C*$_6$H$_5$Me], 70.3 [d, J(C–H) 174, η-*C*$_6$H$_5$Me], 68.3 [d, J(C–H) 175, η-*C*$_6$H$_5$Me], 20.9 [q, J(C–H) 128, 2 Me][d]
(**2**) [{Re(η-C$_6$H$_4$Me$_2$-1,4)}$_2$(μ-CHC$_6$H$_4$-Me-*p*)(μ-H)$_2$] Dark orange C 41.5(41.7); H 4.3(4.3)[f] 	400 MHz: 12.10 [1 H, dd, J(H$_a$–H$_c$) 3.9, J(H$_b$–H$_c$) 1.3, H$_c$], 8.1 (1 H, s, br, H$_o$), 6.9 (1 H, s, br, H$_m$), 6.8 (1 H, s, br, H$_m$), 6.7 (1 H, s, br, H$_o$), 4.25 [4 H, d, J(H$_e$–H$_d$) 5.5, 2 (H$_{dd'}$ or H$_{ee'}$)], 3.8 [4 H, d, J(H$_d$–H$_e$) 5.5, 2 (H$_{ee'}$ or H$_{dd'}$)], 2.2 (3 H, s, Me$_f$), 2.1 (12 H, s, 4 Me$_g$), −5.40 [1 H, dd, J(H$_a$–H$_b$) 3.4, J(H$_b$–H$_c$) 1.3, H$_b$], −5.50 [1 H, dd, J(H$_b$–H$_a$) 3.4, J(H$_a$–H$_c$) 3.9, H$_a$][g]	100.5 MHz: 166.6 (s, C$_i$), 164.3 [d, J(C–H) 157, μ-CH], 134.4 [d, J(C–H) 159, μ-*C*$_6$H$_4$Me-*p*], 131.8 (s, μ-*C*$_6$H$_4$Me-*p*), 128.7 [d, J(C–H) 155, μ-*C*$_6$H$_4$Me-*p*], 127.6 [d, J(C–H) 159, μ-*C*$_6$H$_4$Me-*p*], 126.3 [d, J(C–H) 156, μ-*C*$_6$H$_4$Me-*p*], 82.8 (s, η-*C*$_6$H$_4$Me$_2$), 72.4 [d, J(C–H) 170, η-*C*$_6$H$_4$Me$_2$], 71.1 [d, J(C–H) 170, η-*C*$_6$H$_4$Me$_2$], 20.9 [q, J(C–H) 124, Me$_f$], 20.0 [q, J(C–H) 130, 4 Me$_g$][g]
(**3**) [{Re(η-C$_6$H$_3$Me$_3$-1,3,5)}$_2$(μ-CHC$_6$-H$_3$Me$_2$-3,5)(μ-H)$_2$] Red-brown 44.0(44.3); H 4.9(4.9)[h] 	300 MHz: 12.45 [1 H, dd, J(H$_c$–H$_a$) 4.4, J(H$_c$–H$_a$) 0.9, H$_c$], 8.2 (1 H, s, H$_h$), 6.8 (1 H, s, H$_e$ or H$_k$), 6.7 (1 H, s, H$_k$ or H$_e$), 4.0 (6 H, s, η-C$_6$*H*$_3$Me$_3$), 2.5 [3 H, s, Me$_g$ or Me$_j$], 2.2 [18 H, s, 6 Me$_c$ + (Me$_g$ or Me$_j$)], −5.03 [1 H, dd, J(H$_a$–H$_c$) 4.4, J(H$_a$–H$_b$) 4.0, H$_a$], −5.25 [1 H, dd, J(H$_b$–H$_c$) 0.9, J(H$_b$–H$_a$) 4.0, H$_b$][d]	75.4 MHz: 170.7 (s, C$_i$), 167.0 [d, J(C–H) 139, μ-CH], 137.0 (s, C$_f$ or C$_i$), 136.1 (s, C$_i$ or C$_f$), 134.0 [d, J(C–H) 150, C$_h$], 127.1 [d, J(C–H) obscured by solvent, C$_e$ or C$_k$], 125.2 [d, J(C–H) 148, C$_k$ or C$_e$], 86.2 (s, η-*C*$_6$H$_3$Me$_3$), 71.0 [d, J(C–H) 166, η-*C*$_6$H$_3$Me$_3$], 21.8 [q, J(C–H) 126, Me$_g$ or Me$_j$], 20.7 [q, J(C–H) 125, 6 Me$_c$], 18.7 [q, J(C–H) 125, Me$_j$ or Me$_g$][d]
(**4**) [{Re(η-C$_6$H$_5$Et)}$_2$(μ-CMePh)(μ-H)$_2$] Red-brown[i] 	8.1 (br, Ph), 4.1 (2 H, m, 2 H$_p$), 4.0 (6 H, m, 2 H$_o$ + 4 H$_m$), 3.9 [2 H, d, J(H–H) 5.7, 2 H$_o$], 3.1 (3 H, s, Me$_d$), 2.3 [4 H, q, J(H–H) 7.5, 2 C*H*$_2$CH$_3$], 1.1 [6 H, t, J(H–H) 7.5, 2 CH$_2$C*H*$_3$], −5.10 [1 H, d, J(H$_a$–H$_b$) 4.5, H$_a$ or H$_b$], −5.40 [1 H, d, J(H$_b$–H$_a$) 4.5, H$_b$ or H$_a$][d]	125.6 MHz: 172.6 (C$_i$ or μ-C), 169.4 (s, μ-C or C$_i$), 127.1 [d, J(C–H) 150, CPh], 124.2 [d, J(C–H) 154, CPh], 73.7 (s, η-*Ph*Et), 73.3 [d, J(C–H) 171, η-*Ph*Et], 73.2 [d, J(C–H) 173, η-*Ph*Et], 69.9 [d, J(C–H) 175, η-*Ph*Et], 68.0 [d, J(C–H) 173, η-*Ph*Et], 67.0 [d, J(C–H) 172, η-*Ph*Et], 58.2 [q, J(C–H) 130, Me$_d$], 28.7 [t, J(C–H) 126, *C*H$_2$CH$_3$], 18.1 [q, J(C–H) 126, CH$_2$*C*H$_3$][d]

Table 1 (*continued*)

Compound, colour, and analysis[a]	N.m.r. data[b]	
	^{1}H	^{13}C
(5) $[\{Re(\eta-C_6H_5Et)\}_2(\mu-CHCH_2Ph)(\mu-H)_2]$ Red-brown[i] 	12.5 [1 H, ddt, $J(H_c-H_a)$ 4.0, $J(H_c-H_b)$ 1.2, $J(H_c-H_d)$ 7.0, H_c], 7.3—7.0 (complex bands, Ph), 4.5 [2 H, d, $J(H_c-H_d)$ 7.0, H_d], 4.4 [2 H, t, J(H–H) 5.7, H_p], 4.3 [2 H, d, J(H–H) 5.7, H_m], 4.25 [2 H, t, J(H–H) 5.7, H_m], 4.1 (2 H, m, obscured, H_o), 3.9 [2 H, d, J(H–H) 5.7, H_o], 2.3 [4 H, q, J(H–H) 7.5, CH_2CH_3], 1.1 [6 H, t, J(H–H) 7.5, CH_2CH_3], −5.2 [1 H, dd, $J(H_b-H_c)$ 1.2, $J(H_b-H_a)$ 4.5, H_b], −5.3 [1 H, dd, $J(H_a-H_c)$ 4.0, $J(H_a-H_b)$ 4.5, H_a][d]	125.6 MHz: 165.5 (d, μ-CH), 130.0—125.0 (Ph is not observed), 93.9 [t, J(C–H) 135, CH_2Ph], 73.7 (s, η-*Ph*Et), 71.7 [d, J(C–H) 171, η-*Ph*Et], 71.0 [d, J(C–H) 173, η-*Ph*Et], 70.9 [d, J(C–H) 175, η-*Ph*Et], 69.2 [d, J(C–H) 170, η-*Ph*Et], 67.9 [d, J(C–H) 172, η-*Ph*Et], 28.7 [t, J(C–H) 126, CH_2CH_3], 18.1 [q, J(C–H) 126, CH_2CH_3][d]

[a] Found (calc.) (%). [b] Given as chemical shift (δ) [relative intensity, multiplicity, coupling (J in Hz), assignment]; ^{1}H n.m.r. spectra determined at 500 MHz and all spectra at r.t., unless otherwise stated. [c] M/e = 648 [$P^+ - 2$], ν(Re–H–Re) at 1 600 m vbr cm^{-1}. [d] In [$^2H_6$]benzene. [e] In [$^2H_6$]acetone. [f] M/e = 690 [$P^+ - 2$], ν(Re–H–Re) at 1 600w vbr cm^{-1}. [g] In [$^2H_{12}$]cyclohexane. [h] M/e = 732 [$P^+ - 2$]. [i] M/e = 690 [$P^+ - 2$], ν(Re–H–Re) at 1 603w cm^{-1} (solution in pentane; microanalytical data not available due to mixtures of isomers).



Scheme. Co-condensation at −195 °C with (*i*) toluene, (*ii*) *p*-xylene, (*iii*) mesitylene, and (*iv*) ethylbenzene

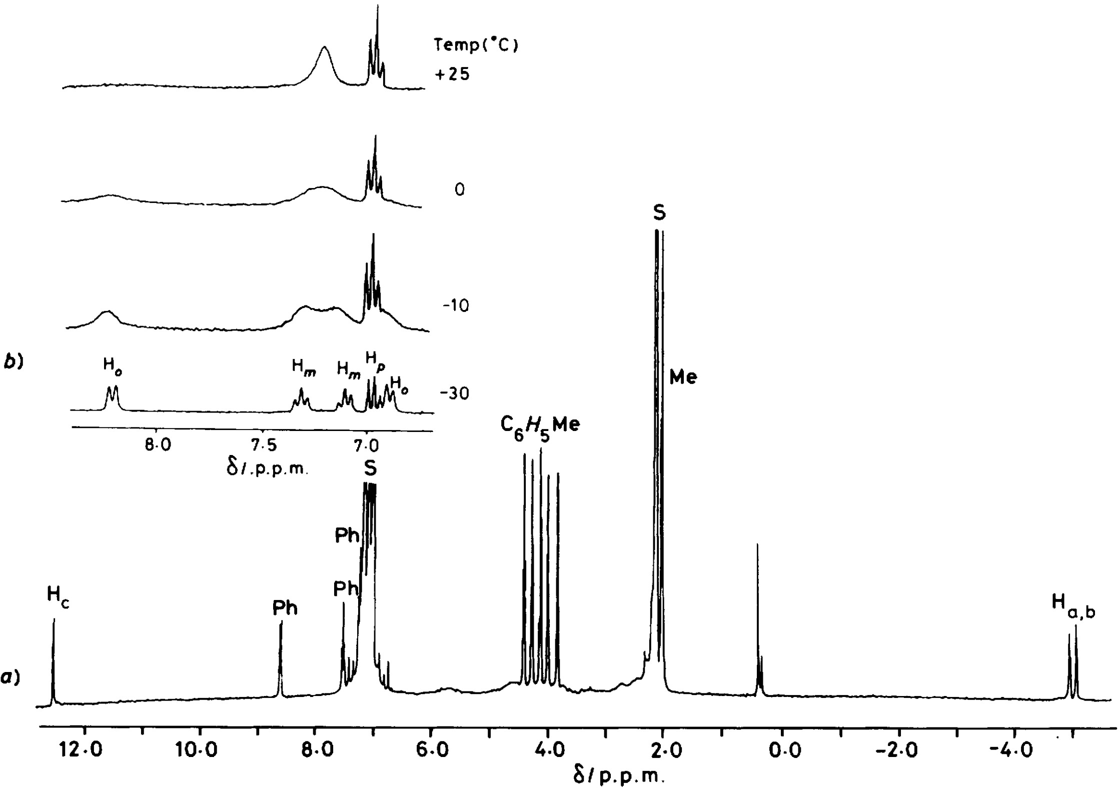


Figure 1. (*a*) 300-MHz ^1H n.m.r. spectrum of (**1**) in $[^2H_8]$toluene at − 60 °C (S = solvent). (*b*) Inset shows an expansion of the ^1H n.m.r. spectra of (**1**) between 25 and −30 °C at 250 MHz in $[^2H_6]$acetone

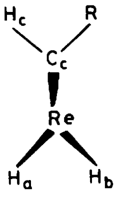


Figure 2. Relative conformation of H_a, H_b, and H_c about the Re–Re vector for compounds (**1**)—(**3**) and (**5**) (R = Ph, C_6H_4Me-*p*, $C_6H_3Me_2$-3,5, or CH_2Ph); the η-arene rings have been removed for clarity

mol^{-1}, which is slightly larger than the value found for (**1**). Again n.O.e. experiments established the relative conformation of the μ-CHC_6H_4Me-*p* and hydrido ligands.

An interesting point arises when interpreting the resonances due to the protons in the equivalent η-$C_6H_4Me_2$-1,4 ligands. Two doublets at δ 4.25 [*J*(H–H) 5.5] and 3.80 [*J*(H–H) 5.5 Hz] are observed in the ^1H spectrum at room temperature. Since the rhenium centres are chiral, the hydrogens H_d, $H_{d'}$ and H_e, $H_{e'}$ are diastereotopic and cannot be interchanged by rotation about the rhenium–ring centroid axis, rendering them chemically inequivalent.

Solutions of (**2**) in $(CD_3)_2CO$ show *ca.* 50% hydrogen–deuterium exchange of the solvent with the rhenium hydrides and the μ-CH_c hydrogen after 12 h at room temperature. The sample showed statistical exchange after 3 d at this temperature. When the exchange reaction is monitored by ^1H n.m.r. spectroscopy, we observe that the rates of hydrogen–deuterium exchange into the three sites are equal. In addition, during the exchange reaction, resonances are observed in the ^1H n.m.r. spectrum which are assignable to partially deuteriated compounds, indicating that the exchange at each site involves single hydrogen–deuterium exchange steps. Protonation reactions are common for complexes containing μ-alkylidene ligands.[7] Wilkinson and co-workers[11] have reported that the triply methylene-bridged ruthenium phosphine complex $[Ru_2(PMe_3)_6(\mu\text{-}CH_2)_3]$ rapidly undergoes protonation yielding mono- and di-positively charged μ-methyl species. It is possible that exchange reactions of (**2**) may be acid catalysed and proceed *via* initial D^+ attack at the bridging carbon atom giving a μ-$CHD(C_6H_4Me$-*p*) moiety (Figure 3) which subsequently undergoes H/D exchange with the bridging hydrogens.

Co-condensation of rhenium atoms with mesitylene gives red-brown, air-sensitive microcrystals of $[(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Re(\mu\text{-}H)_2(\mu\text{-}CHC_6H_3Me_2\text{-}3,5)Re(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$, (**3**). In contrast to the ^1H n.m.r. spectra of (**1**) and (**2**) only two sharp singlets were observed at δ 4.0 and 2.2 of relative integral 6 and 18 respectively for the ring and methyl hydrogens of the two η-$C_6H_3Me_3$-1,3,5 ligands. Although the rhenium centre is chiral as before, the methyl and ring hydrogens can be averaged by rapid rotation about the three-fold axis of the mesitylene rings.

As expected, the barrier to rotation of the bulky μ-$C_6H_3Me_2$-3,5 group of (**3**) is larger than for (**2**) as indicated by the higher temperature of *ca.* 80 °C required for coalescence of the H_e and H_k hydrogens. The data indicate that $\Delta G^{\ddagger}$ for the rotation in (**3**) is *ca.* 15 kJ mol^{-1} greater than for (**2**) (Table 2).

Co-condensation of rhenium atoms with ethylbenzene yields an air sensitive, red-brown microcrystalline product which the data show to be a mixture of the two isomers $[(\eta\text{-}C_6H_5Et)Re(\mu\text{-}H)_2(\mu\text{-}CMePh)Re(\eta\text{-}C_6H_5Et)]$ (**4**) and $[(\eta\text{-}C_6H_5Et)Re(\mu\text{-}H)_2(\mu\text{-}CHCH_2Ph)Re(\eta\text{-}C_6H_5Et)]$ (**5**) in approximately equal proportions. They could be partially separated by successive recrystallisation or sublimation.

The ^1H n.m.r. spectrum of the isomers (**4**) and (**5**) (see Figure 4) exhibited features similar to the toluene derivative (**1**). In the region δ 4.4—3.8, eight multiplets were observed assignable to two independent groups of ring hydrogens of the η-C_6H_5Et

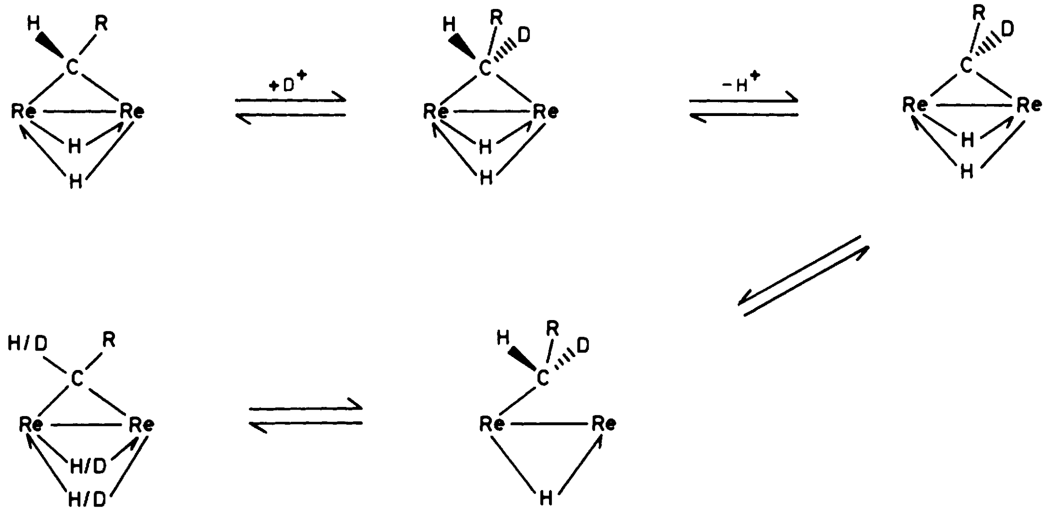


Figure 3. The proposed key steps in the H/D exchange reaction of (3) (R = $C_6H_3Me_2$-3,5); the η-arene rings have been removed for clarity

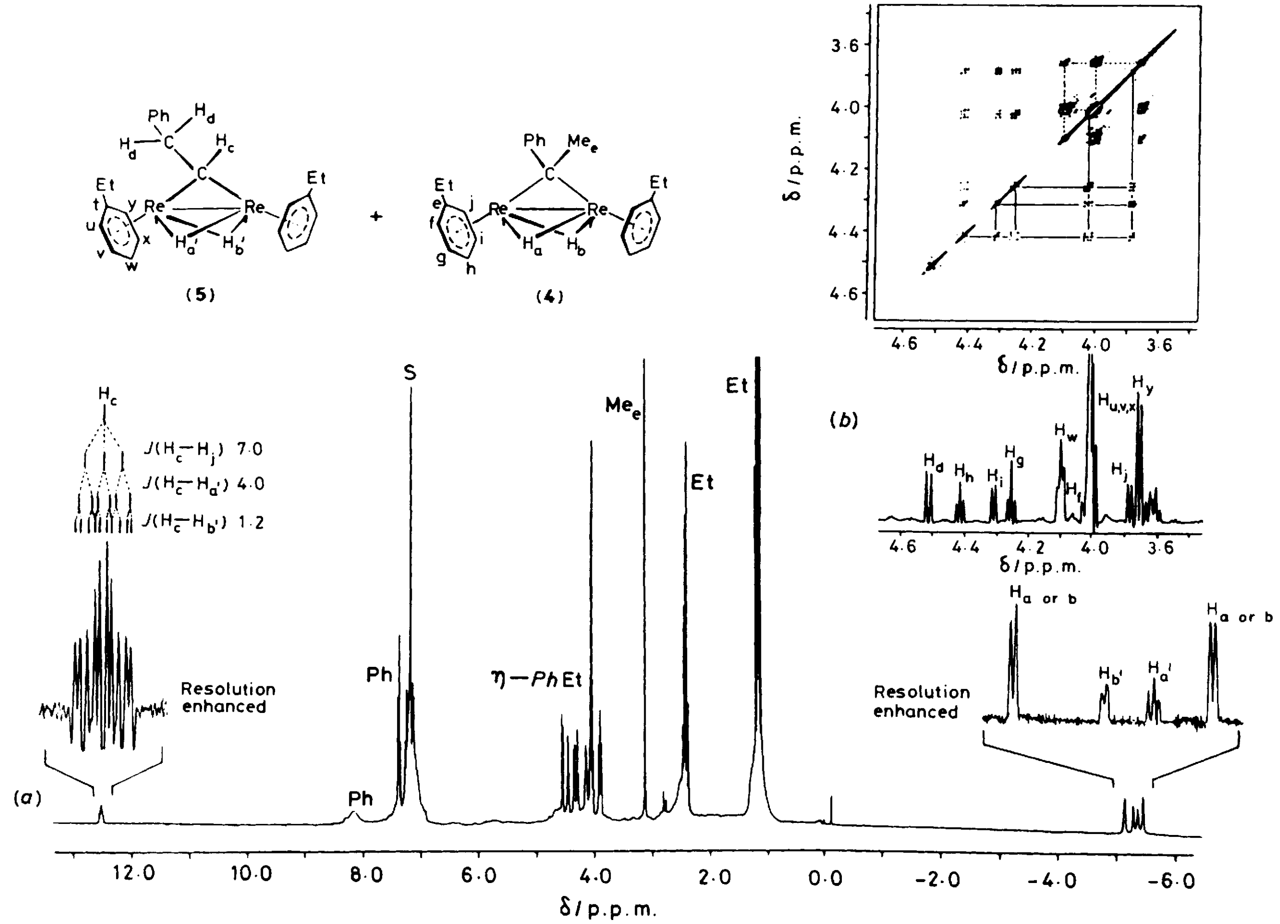


Figure 4. (a) 500-MHz ^1H n.m.r. spectrum of (4) and (5) in $[^2H_6]$benzene (S = solvent, J in Hz). (b) Inset shows the ($^1H-^1H$) COSY-45 spectrum of the regions 3.7—4.7 [connectivity given by (—) for (4), and (---) for (5)]

ligands for each of the two isomers (**4**) and (**5**). Assignment of the individual resonances for both isomers was possible by examination of the 500-MHz (^1H–^1H) COSY-45[12] two-dimensional n.m.r. spectrum. In addition, the aromatic region contained a complex set of sharp multiplets superimposed on broad featureless bands. Due to the complexity of this region, complete assignment of the phenyl hydrogens was not attempted. The n.m.r. data indicate that for isomer (**5**) the phenyl group of the μ-alkylidene ligand is undergoing fast rotation, whereas for (**4**) phenyl group rotation is at an intermediate rate on the n.m.r. time-scale at room temperature.

The relative orientation of the rhenium hydrides and the μ-CH_c hydrogen could only be determined for (**5**) by homonuclear ^1H n.O.e. experiments. Compound (**4**) has no μ-alkylidene hydrogen and as a result the hydride resonances appear as two doublets due to their mutual coupling.

Examination of Table 3 reveals that for compounds (**1**)—(**5**) the hydride–hydride coupling is typically 4.0 Hz, while the α-alkylidene hydrogen is characterised by two different hydride couplings, one typically 1.0 Hz, and the other *ca.* 4.5 Hz. It appears that the $J(H_a–H_c)$ is always the larger, where H_a has been determined by homonuclear ^1H n.O.e. measurements to be in a cisoid arrangement with respect to the μ-CH_c, *cf.* Figure 2.

There is extensive information on vicinal coupling constants and their relation to chemical structure in organic chemistry. The dependence of the vicinal coupling constants on the dihedral angle Φ was first theoretically predicted by Karplus.[13] In the case of a three-membered ring the dihedral angle for *cis* protons is 0° and for *trans* protons *ca.* 130°. It is always found experimentally that for a pair of *cis–trans* isomers of substituted cyclopropane rings, $^3J(H–H)(cis) > {}^3J(H–H)(trans)$.

The ability of metal atoms of Cu, Fe, Zn, Ag, and Mn to react oxidatively with sp^3 hybridised carbon–hydrogen bonds has been demonstrated recently.[14] It appears that the ability of rhenium atoms to react similarly, giving the μ-geminal arylidene dirhenium compounds (**1**)—(**5**) is a quite general reaction for alkyl-substituted benzenes. Compounds (**1**)—(**5**) provide rare examples of a μ-C(H)aryl moiety: a survey of previously reported examples is given in Table 4, together with ^1H and ^{13}C n.m.r. data for comparison. We conclude that rhenium atoms are reactive synthetic intermediates which are presently unpredictable and yet which can provide examples of new rhenium chemistry of contemporary interest.

Table 2. Summary of rate parameters for compounds (**1**)—(**3**)

Compound	T_c/°C	Rate at T_c/s^{-1}	$\Delta G_{T_c}^{\ddagger}$/kJ mol^{-1}
(**1**)	0	120.0	55.1
(**2**)	50	204.3	64.8
(**3**)	80	28.9	78.0

Table 3. Summary of the important chemical shifts and coupling constants for compounds (**1**)—(**5**)

Compound	$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$J(H_a–H_b)$/Hz	$J(H_a–H_c)$/Hz	$J(H_b–H_c)$/Hz
(**1**)	−5.09	−5.14	12.45	4.3	4.3	1.3
(**2**)	−5.50	−5.40	12.10	3.4	3.9	1.3
(**3**)	−5.03	−5.25	12.45	4.0	4.4	0.9
(**4**)	−5.10	−5.40	—	4.5	—	—
(**5**)	−5.30	−5.20	12.50	4.5	4.0	1.2

Table 4. Examples of μ-alkylidene dinuclear complexes and their characteristic ^1H and ^{13}C n.m.r. chemical shifts

Compound[a]	CRR′	δ(*C*RR′)	δ(C*H*R)	Ref.
$[Re_2(CO)_8\{\mu\text{-}C(OMe)Ph\}_2]$	C(OMe)Ph	217.5	—	*b*
$[Fe_2(CO)_8(\mu\text{-}CHPh)]$	CHPh	N.R.	6.96	*c*
$[Rh_2(cp)(\mu\text{-}CO)(\mu\text{-}CPh_2)_2]$	CPh_2	188.2	—	*d*
$[Rh_2(cp)_2(\mu\text{-}CPh_2)_2]$	CPh_2	156.0	—	*d*
$[Rh_2(\eta\text{-}C_5H_5N)_2(\mu\text{-}CO)(\mu\text{-}CPh_2)_2]$	CPh_2	185.2	—	*d*
$[WPt(PMe_3)_2(CO)_5\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	204.0	—	*e*
$[PtMn(PMe_3)_2(CO)_2(cp)\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	193.6	—	*f*
$[PtMn(cod)(CO)_2(cp)\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	198.0	—	*e*
$[PtW(cod)(CO)_5\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	197.9	—	*e*
$[PtW(CO)_4(PMe_3)_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	204.0	—	*g*
$[PtW(CO)_2(PMe_3)_3(cp)(\mu\text{-}CHC_6H_4Me\text{-}p)]^+$	$CHC_6H_4Me\text{-}p$	95.0	5.8	*h*
$[Mo_2(cp)_2(CO)_4\{\mu\text{-}C(C_6H_4Me\text{-}p)_2\}]$	$C(C_6H_4Me\text{-}p)_2$	174.9	—	*i*
$[Pt_2(CO)_2(PMeBu^t{}_2)_2\{\mu\text{-}C(OMe)Ph\}]$	C(OMe)Ph	N.R.	—	*j*
$[PtW(CO)_3(PMe_3)_2(cp)(\mu\text{-}CHC_6H_4Me\text{-}p)]^+$	$CHC_6H_4Me\text{-}p$	76.1	5.8	*h*
$[PtW(CO)_2(PMe_3)_2(\mu\text{-}H)(\mu\text{-}CHC_6H_4Me\text{-}p)]$	$CHC_6H_4Me\text{-}p$	105.3	6.5	*h*
$[CuW(CO)_5(cp)\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	231.5	—	*k*
$[AuW(CO)_2(PPh_3)(cp)(\mu\text{-}CHC_6H_4Me\text{-}p)]$	$CHC_6H_4Me\text{-}p$	228.9	—	*l*
$[PtW(CO)_5(\mu\text{-}dppm)\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}]$	$C(OMe)C_6H_4Me\text{-}p$	226.3	—	*m*

[a] cp = η-C_5H_5, cod = cyclo-octa-1,5-diene, dppm = $Ph_2PCH_2PPh_2$. [b] E. O. Fisher, T. L. Linder, H. Fisher, G. Hattner, F. Friedrich, and F. R. Kreibl, *Z. Naturforsch., Teil B*, 1977, **32**, 648. [c] E. O. Fisher, V. Kiener, and R. D. Fisher, *J. Organomet. Chem.*, 1969, **16**, P60. [d] T. Yamanoto, A. R. Garber, G. Wilkinson, C. B. Boss, W. E. Streib, and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, 1974, 354. [e] T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1615. [f] M. Berry, J. Martin-Gil, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1625. [g] W. A. Herrmann and I. Schweizer, *Z. Naturforsch., Teil B*, 1978, **33**, 911. [h] J. C. Jeffery, I. Moore, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1571. [i] L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 7789. [j] T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1979, 45. [k] G. A. Carreido, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1555. [l] G. A. Carriedo, J. A. K. Howard, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1984, 2545. [m] K. A. Mead, I. Moore, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2083.

Experimental

All preparations and reactions described were carried out under an atmosphere of nitrogen (< 10 p.p.m. oxygen or water) using standard Schlenk vessels, 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, cyclohexane), sodium–potassium alloy [pentane, light petroleum (b.p. 40—60 °C), 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 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 Fourier-transform interferometer. ^{1}H N.m.r. spectra were determined using Bruker AM-250 (250 MHz), Bruker WH-300 (300 MHz), Bruker WH-400 (400 MHz), or Bruker AM-500 (500 MHz) spectrometers. ^{13}C N.m.r. spectra were determined using Bruker AM-250 (62.8 MHz), Bruker WH-300 (75.4 MHz), Bruker WH-400 (100.5 MHz), or Bruker AM-500 (125.6 MHz) spectrometers.

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 performed using both the 10-kW metal atom[15] and the twin-hearth reactors,[16] which were both 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 minimise outgassing during the metal-vapour synthesis 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. A small quantity of 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 was evaporated using the appropriate power and the rate of ligand entry was adjusted such that a vacuum $> 10^{-4}$ 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 nitrogen and allowed to warm to room temperature. As the matrix melted the product was collected in the gutter and was washed out under a small positive pressure of nitrogen to a collection Schlenk vessel using an appropriate solvent.

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.

µ-*Benzylidene-di-*µ-*hydrido-bis*[(η-*toluene*)*rhenium*], (**1**).—Rhenium atoms (1.0 g, 5.3 mmol), generated from a molten ingot (*ca.* 5.0 g), were co-condensed with pure toluene (*ca.* 100 cm^3) 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 room temperature the red-brown matrix was washed out of the machine with toluene (500 cm^3), filtered through a bed of Celite, and the volatiles removed under reduced pressure at 70 °C to give a brown oil. The oil was extracted with light petroleum (b.p. 40—60 °C, 2 × 100 cm^3), filtered through Celite, and the volatiles removed under reduced pressure giving a brown oil. Sublimation at 120 °C (10^{-4} Torr) using a liquid-nitrogen cooled probe gave a red-brown sublimate. The sublimate was washed from the probe with light petroleum (b.p. 40—60 °C (2 × 50 cm^3), giving a dark red solution which was filtered and concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C, gave red-brown crystals, which were collected and dried *in vacuo*. Yield: 300 mg, 17%.

*Di-*µ-*hydrido-*µ-(p-*methylphenyl*)*methylidene-bis*[(η-1,4-*dimethylbenzene*)*rhenium*], (**2**).—Rhenium atoms (0.9 g, 4.8 mmol), generated from a molten ingot (*ca.* 3.8 g), were co-condensed with *p*-xylene (80 cm^3) over 3 h, using the 3.5-kW twin-hearth reactor. The input power was maintained at 5 kV and 300 mA throughout. After warming to room temperature the red-brown matrix was washed out of the machine with toluene (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 (40—60 °C, 2 × 50 cm^3), filtered through Celite, and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C, gave dark orange microcrystals. These were collected and dried *in vacuo*. Yield: 250 mg, 18%.

µ-(3,5-*Dimethylphenyl*)*methylidene-di-*µ-*hydrido-bis*[(η-1,3,5-*trimethylbenzene*)*rhenium*], (**3**).—Rhenium atoms (1.2 g, 6.4 mmol), generated from a molten ingot (*ca.* 7.8 g), were co-condensed with mesitylene (*ca.* 100 cm^3) over 3 h, using the 3.5-kW twin-hearth reactor. The input power was maintained at 5.5 kV and 300 mA throughout. After warming to room temperature the red-brown mixture was washed out of the machine with toluene (500 cm^3), filtered through a bed of Celite, and the volatiles removed under reduced pressure. The residue was extracted with pentane (2 × 250 cm^3), giving a dark red solution which was filtered through a Celite bed, and the filtrate concentrated to 10 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C, gave an amorphous red-brown solid. Re-extraction with pentane (2 × 50 cm^3) gave a dark red solution which was filtered, and the filtrate was concentrated to 10 cm^3 under reduced pressure. Cooling to −20 °C, and then to 80 °C, gave a red-brown solid. The solid was collected and dried *in vacuo* and was found to be analytically and spectroscopically pure. Yield: 350 mg, 15%.

*Di-*µ-*hydrido-*µ-*methylphenylmethylidene-bis*[(η-*ethylbenzene*)*rhenium*], (**4**), *and* µ-*Benzylmethylidene-di-*µ-*hydrido-bis*[(η-*ethylbenzene*)*rhenium*], (**5**).—Rhenium atoms (1.1 g, 5.9 mmol), generated from a molten ingot (*ca.* 5.3 g), were co-condensed with ethylbenzene (*ca.* 100 cm^3) over 3 h, using the 3.5-kW twin-hearth reactor. The input power was maintained at 5.0 kV and 300 mA throughout. After warming to room temperature the red-brown mixture was washed out of the machine with toluene (500 cm^3), filtered through a bed of Celite, and the volatiles removed under reduced pressure. The residue was extracted with pentane (2 × 100 cm^3) giving a dark red solution which was filtered through a Celite bed and the filtrate concentrated to 50 cm^3 under reduced pressure. Cooling to −20 °C, and then to −80 °C, overnight gave an oily brown solid. Re-extraction with pentane (2 × 50 cm^3) gave a dark red solution which was filtered and the filtrate was concentrated to 10 cm^3 under reduced pressure. Cooling to −20 °C, and then to 80 °C, gave a red-brown solid. The red-brown solid was found to be a mixture of the isomers $[\{Re(\eta\text{-}C_6H_5Et)\}_2(\mu\text{-}CHCH_2Ph)(\mu\text{-}H)_2]$ and $[\{Re(\eta\text{-}C_6H_5Et)\}_2(\mu\text{-}CMePh)(\mu\text{-}H)_2]$, which melted to a red oil on warming to room temperature. Yield: 100 mg, 5%.

Acknowledgements

We thank the Northern Ireland Department of Education for a grant (to D. O'H.) and the Donors of the Petroleum Research Fund for partial support.

References

1 P. L. Timms and T. W. Turney, *Adv. Organomet. Chem.*, 1977, **15**, 53.

2 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.

3 M. L. H. Green, *J. Organomet. Chem.*, 1980, **200**, 119.

4 F. G. N. Cloke, A. E. Derome, M. L. H. Green, and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, 1983, 1312.

5 F. G. N. Cloke, personal communication.

6 E. O. Fisher and H. O. Stahl, *Chem. Ber.*, 1956, **89**, 1805; E. O. Fisher and M. W. Schmidt, *ibid.*, 1966, **99**, 2206; 1969, **102**, 1954.

7 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159.

8 P. D. Kennewell, *J. Chem. Educ.*, 1970, **47**, 278; G. E. Bachers and T. Schaefer, *Chem. Rev.*, 1971, **71**, 617; C. L. Antwerp, *J. Chem. Educ.*, 1973, **50**, 638.

9 F. D. S. Moore and S. D. Robinson, *Chem. Soc. Rev.*, 1983, **12**, 412.

10 R. A. Hoffmann and S. Forsen, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1966, **1**, 173; G. Bodenhausen, R. Freeman, and G. A. Morris, *J. Magn. Reson.*, 1976, **23**, 171; J. Sandstrom, 'Dynamic N.M.R. Spectroscopy,' Academic Press, London, 1982.

11 R. A. Andersen, R. A. Jones, G. Wilkinson, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Chem. Commun.*, 1977, 865.

12 A. Bax, 'Two-Dimensional Nuclear Magnetic Resonance in Liquids,' Delft University Press, Delft, The Netherlands, 1982.

13 M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

14 W. L. Billups, M. M. Konarski, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, 1980, **102**, 7394; A. G. Ozin, D. F. McIntosh, and S. A. Mitchell, *ibid.*, 1981, **103**, 1574; J. J. Klabunde and Y. Tanaka, *ibid.*, 1983, **105**, 3544; A. G. Ozin and J. G. McCaffrey, *ibid.*, 1982, **104**, 7351.

15 F. G. N. Cloke, D.Phil. Thesis, Oxford, 1978.

16 J. M. Wallis, D.Phil. Thesis, Oxford, 1984.

Received 28th November 1985; *Paper* 5/2084