Activation of sp^3 Carbon–Hydrogen Bonds of Alkylbenzenes by Rhenium Forming Binuclear μ-Arylidene Derivatives

F. Geoffrey N. Cloke,[a] Andrew E. Derome,[b] Malcolm L. H. Green,[a]* and Dermot O'Hare[a]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.*
[b] *The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.*

Co-condensation of rhenium atoms with the arenes 1,3,5-$R_3C_6H_3$, R_3 = MeH_2 or Me_3, or 1,4-$Me_2C_6H_4$ gives the compounds [{(η-arene)Re}$_2$(μ-CHR′)(μ-H)$_2$], where R′ = Ph, 3,5-$Me_2C_6H_3$, or 4-MeC_6H_4 respectively, which contain a μ-arylidene group; the structurally related compounds [{(η-arene)Re}$_2$(μ-CR^1R^2)(μ-H)$_2$], where R^1,R^2 = Me, Ph or H, CH_2Ph, are formed from rhenium atoms and ethylbenzene.

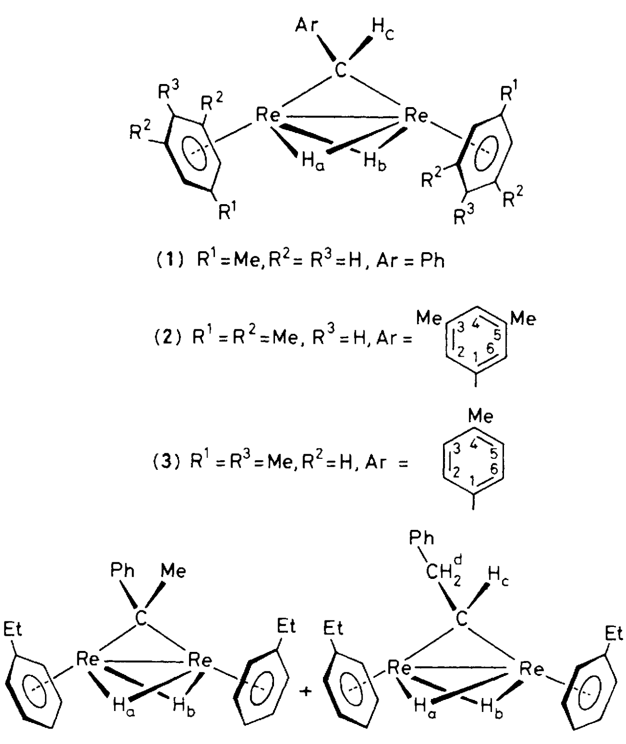
Co-condensation of transition metal atoms with arenes such as benzene and toluene is well known to form bis-arene-metal derivatives.[1] However, in many such reactions the yields based on the metal atoms are less than *ca.* 40%. Evidence that competing reactions such as carbon–hydrogen activation can occur is provided by the isolation of non-metal-containing products such as biaryl derivatives.[2,3] The reactions between hafnium or zirconium atoms with pure toluene gave deep red solutions but no bis-arene-metal derivatives could be isolated. However, when the same atoms were co-condensed with a mixture of toluene and trimethylphosphine then the compounds M(η-MePh)$_2$(PMe$_3$), M = Zr or Hf, were formed.[3] We have previously suggested that the red solution from the toluene reaction might contain derivatives formed by the insertion of initially formed bis-arene-metal compounds into the C–H bonds of toluene.[3]

We now report striking examples of metal atom reactions in which the product has been formed *via* activation of aliphatic C–H bonds of alkyl substituents attached to the arene ring.

Rhenium atoms (*ca.* 1.0 g), generated from a positive-hearth electron-gun furnace operating at 3200 °C in a 'bell-jar' metal atom reactor,[2,3] were co-condensed in separate experiments with an excess of toluene, mesitylene, or *p*-xylene, forming the air-sensitive, deep red compounds [{(η-PhMe)Re}$_2$(μ-CHPh)(μ-H)$_2$] (**1**), [{(η-$C_6H_3Me_3$)Re}$_2${μ-CH(3,5-$C_6H_3Me_2$)}(μ-H)$_2$)] (**2**), and [{(η-1,4-$C_6H_4Me_2$)Re}$_2${μ-CH(4-C_6H_4Me)}(μ-H)$_2$] (**3**), respectively in *ca.* 15% yields. The compounds readily sublime at *ca.* 90—100 °C, 10^{-4} mbar.

The structures of the compounds (**1**)—(**3**) are shown in Scheme 1 and they are proposed on the basis of microanalytical, mass spectral [(**2**), M^+-2, *m/z* 730] and, especially, detailed n.m.r. data.† A rhenium–rhenium bond is invoked to account for the observed diamagnetism and is in accordance with the eighteen-electron rule.

The ^{1}H n.m.r. spectra show a characteristic low-field resonance at δ *ca.* 12.0 assignable to the μ-alkylidene hydrogen and two high-field resonances at δ *ca.* −5 assignable to the two chemically different bridging hydrogens; coupling is observed between these three hydrogens. The ^{13}C n.m.r. spectra show *inter alia* resonances at 165—170 p.p.m. in the region characteristic for μ-alkylidene carbon systems.[4] Comparison of the i.r. spectra of (**1**) and of its perdeuteriated analogue (prepared by reaction between rhenium atoms and



Scheme 1. Structures proposed for compounds (**1**)—(**5**), showing the labelling scheme for assignment of the n.m.r. spectra.

† N.m.r. data were determined at probe temperature on Bruker AM250 and WH300 instruments; all assignments have been confirmed where possible by double resonance experiments. Coupling constants are given in Hz; data are for ^{1}H n.m.r. (δ relative to internal solvent) unless otherwise stated, in solutions in C_6D_6; η- refers to assignment to the η-arene rings. Compound (**2**): 12.45 [1H, dd, $J(H_b-H_c)$ 1.1, $J(H_a-H_c)$ 4.4, H_c], 8.2 (1H, s, H^4), 6.79 (1H, s, H^2 or H^6), 6.74 (1H, s, H^6 or H^2), 4.0 (6H, s, 6 × η-H), 2.49 (3H, s, Me^3 or Me^5), 2.26 (21H, s, 6 × η-Me + Me^5 or Me^3), −5.03 [1H, dd, $J(H_b-H_a)$ 4.0, $J(H_a-H_c)$ 4.4, H_a or H_b], and −5.25 [1H, dd, $J(H_a-H_b)$ 4.0, $J(H_b-H_c)$ 1.2, H_b or H_a]; ^{13}C n.m.r., gated decoupling (p.p.m.): 170.7 (s, mesityl C^1), 167.0 [d, J(C–H) 139, μ-CH], 137.0 (s, mesityl C^3 or C^5), 136.1 (s, mesityl C^5 or C^3), 135.0 [d, J(C–H) 150, mesityl C^4], 126.0 [d, J(C–H) obscured by solvent, mesityl C^2 or C^6], 124.0 [d, J(C–H) 153, mesityl C^6 or C^2], 86.2 (s, 6 × η-mesitylene *C*–Me), 71.0 [d, J(C–H) 166, 6 × η-mesitylene *C*–H], 21.8 [quartet, J(C–H) 123.5, Me^3 or Me^5], 20.7 [quartet, J(C–H) 127.7, 6 × η-mesitylene Me], and 18.7 [quartet, J(C–H) 125.1, Me^5 or Me^3].

Partial ^{1}H data for (**3**) in C_6D_{12}: 12.1 [1H, dd, $J(H_b-H_c)$ 3.9, $J(H_c-H_a)$ 1.3, H_c], −5.4 [1H, dd, $J(H_a-H_b)$ 3.4, $J(H_a-H_c)$ 1.3, H_a or H_b], and −5.5 [1H, dd, $J(H_b-H_a)$ 3.4, $J(H_b-H_c)$ 3.9, H_b or H_a].

Compound (**4**): 7.33—7.0 (complex bands due to slowly fluxional μ-CPh group), 4.1, 4.0, and 3.86 (complex, 2 × η-*Ph*Et), 3.11 (3H, s, μ-C*Me*), 2.36 (4H, quartet, *J* 7.5, 2 × C*H*$_2$Me), 1.1 (6H, t, *J* 7.5, 2 × CH$_2$*Me*), −5.13 (1H, d, *J* 4.5, H_a or H_b), and −5.43 (1H, d, *J* 4.5, H_b or H_a).

Compound (**5**): 12.5 [1H, tdd, $J(H_c-H_d)$ 7, $J(H_c-H_a)$ 1.2, $J(H_c-H_b)$ 4, H_c], 7.33—7.0 (complex bands due to slowly fluxional *Ph*CH$_2$ system), 4.55 [2H, d, $J(H_c-H_d)$ 7, 2 × H_d], 4.43 (2H, t, *J* 6), 4.31 (2H, d, *J* 6), 4.25 (2H, d, *J* 6), 4.0 (2H, t, *J* 6), and 3.86 (2H, d, *J* 6, 2 × η-*Ph*Et), 2.36 (4H, quartet, *J* 7.0, 2 × η-PhC*H*$_2$Me), 1.1 (6H, t, *J* 7.5, 2 × η-PhCH$_2$*Me*), −5.26 [1H, dd, $J(H_a-H_c)$ 1.2, $J(H_a-H_b)$ 4, H_a or H_b], and −5.36 [1H, dd, $J(H_c-H_b)$ 4.0, $J(H_b-H_a)$ 4.0, H_b or H_a].

$C_6D_5CD_3$) showed no bands assignable to terminal or bridging hydrogen modes. However, the non-equivalence of the two Re-hydrogens and the equivalence of the two η-arene ligands is compatible only with the structure containing non-equivalent Re–H–Re bridges.

The room temperature ^1H n.m.r. spectrum of (**3**) showed that the 2-, 3-, 5-, and 6-hydrogens of the C_6-ring of the μ-CH(aryl) moiety are chemically different. As the temperature is raised to 45 °C the bands assignable to the 2- and 6-hydrogens and to the 3- and 5-hydrogens coalesce. This fluxional behaviour may be attributed to the rotation of the C_6-ring about the μ-CH–C(of Ph) axis. As expected, the barrier to rotation of the bulky 3,5-dimethylphenyl group of (**2**) is larger than for (**3**) as indicated by the higher temperature (*ca.* 75 °C) required for coalescence of the 2- and 6-hydrogens. The data indicate that $\Delta G^{\ddagger}$ for (**2**) is *ca.* 15 kJ mol^{-1} greater than for (**3**).

Co-condensation of rhenium atoms with ethylbenzene gives two red, air-sensitive compounds in approximately equal proportions. These could be only partially separated by successive recrystallisations. However, the n.m.r. data† of the mixtures may be readily assigned in terms of the two isomers (**4**) and (**5**) shown in Scheme 1. It is interesting that there seems to be little selectivity between the activation of the methylene and methyl C–H bonds.

In conclusion, the compounds (**1**)—(**5**) contain rare[5] examples of a bridging μ-CH(aryl) moiety which it can be envisaged are formed *via* a sequential oxidative-addition of two carbon–hydrogen bonds to two rhenium centres of an η-arene–rhenium species.

We thank the Petroleum Research Fund administered by the American Chemical Society for partial support and the British Petroleum Company and the Department of Education of Northern Ireland for supporting a C.A.S.E. award (to D. O'H.).

Received, 28th July 1983; Com. 1012

References

1 J. R. Blackborow and D. Young, 'Metal Vapour Synthesis in Organometallic Chemistry,' Springer Verlag, Berlin, 1979.
2 M. L. H. Green, *J. Organomet. Chem.*, 1980, **200**, 119; M. L. H. Green, 'Frontiers of Chemistry,' I.U.P.A.C., ed. K. J. Laidler, Pergamon Press, Oxford and New York, 1982.
3 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.
4 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159.
5 W. A. Herrmann, *J. Organomet. Chem.*, 1983, **250**, 319.