Carbon–Carbon Activation by Rhodium in Solution; sp^2–sp^3 is Preferred Over sp^3–sp^3 Bond Cleavage

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Reaction of the ethyl-aromatic phosphine **1** with $PhRh(PPh_3)_3$ results in C–H activation, yielding complex **2**, which upon treatment with H_2 undergoes selective cleavage of the sp^2–sp^3 hybridized C–C bond forming ethane and complex **3**; Ar–C cleavage is also observed upon reaction of **1** with H_2 and $[RhCl(C_8H_{14})_2]_2$.

Activation of carbon–carbon single bonds by transition metal complexes in solution is a topic of considerable current interest.[1–7] C–C Bonds are normally unreactive towards metal complex insertion, except when activated by strain,[1,2] by a functional group, such as a carbonyl[3,4] or by the drive to aromaticity in pre-aromatic systems[1,5].

Following our recent findings of Rh^I insertion into a strong aryl–methyl bond in solution[7] and its use in methylene transfer chemistry,[7] we now address the question of sp^2–sp^3 *vs* sp^3–sp^3 hybridised C–C bond cleavage. For this purpose, the aromatic phosphine **1** was synthesised from 2-bromo-*m*-xylene by lithiation, coupling with ethyl bromide, bromination and coupling with Ph_2PLi.

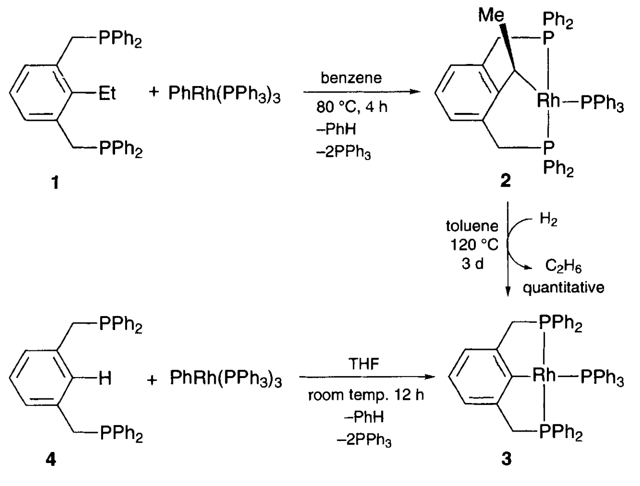
Upon reaction of **1** with $PhRh(PPh_3)_3$, phosphine exchange takes place, followed by C–H activation to give complex **2**[†] in 66% yield (Scheme 1). A similar reaction takes place with $HRh(PPh_3)_4$, although compound **2** is obtained in a lower yield.

Complex **2** was unambiguously characterised by $^{31}P\{^1H\}$, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{13}C\{^1H\}$ DEPT-135 and two-dimensional $^{31}P\{^1H\}$–$^{31}P\{^1H\}$, ^1H–^1H, ^1H–$^{13}C\{^1H\}$ NMR correlations in C_6D_6 at room temperature. Since the carbon atom bound to Rh is chiral, three different phosphorus atoms are observed. The PPh_2 groups *trans* to each other exhibit ddd splitting patterns in $^{31}P\{^1H\}$ NMR at δ 66.9 and 63.6, with J_{PP} (*trans*) = 247.4 Hz, one showing J_{RhP} = 199.7 Hz, J_{PP} (*cis*) = 31.2 Hz and the other, J_{RhP} = 207.9 Hz, J_{PP} (*cis*) = 30.3 Hz. The PPh_3 group exhibits an AA′MX pattern (essentially two dd), with J_{RhP} = 145.7 Hz, J_{PP} (*cis*) = 31.2, 30.3 Hz. ^1H NMR shows a quartet of three methyl protons at δ 1.86, which becomes a doublet with J_{HH} = 6.7 Hz upon phosphorous decoupling. The C*H*–Rh is hidden in the region of C*H*$_2$PPh$_2$ protons and its chemical shift of δ 3.57 is deduced from two-dimensional ^1H–^1H NMR. $^{13}C\{^1H\}$ NMR exhibits the methyls at δ 23.9 (dm, J_{PC} = 17.6 Hz). The Rh–C appears at δ 27.0 [dm, J_{PC} (*trans*) = 42.0 Hz]. These assignments are further confirmed by two-dimensional ^1H–$^{13}C\{^1H\}$ NMR and $^{13}C\{^1H\}$ DEPT-135 NMR (positive peaks). The carbon atoms of the CH_2P groups are inequivalent and appear as doublets at δ 42.9 and 44.7 (J_{PC} = 24.0 and 16.6 Hz, respectively). This is also confirmed by $^{13}C\{^1H\}$ DEPT-135 NMR (negative peaks). FD-MS of complex **2** exhibits the calculated molecular weight of 867.

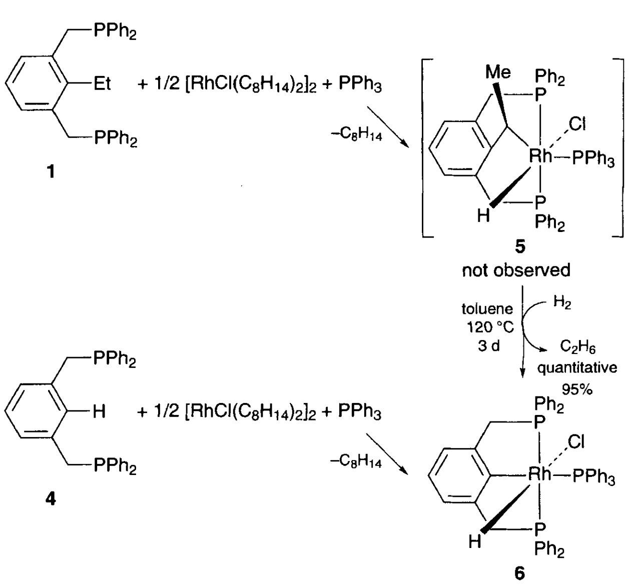
Upon heating a toluene solution of complex **2** at 120 °C under 20 psi of hydrogen for 3 d, selective sp^2–sp^3 C–C cleavage took place, quantitatively yielding complex **3** and ethane. The ethane was collected by a standard vacuum line technique and was quantitatively determined by GC. Significantly, methane was not detected in this experiment. Complex **3** was characterised spectroscopically[†] and independently synthesised by a reaction of 1,3-bis(diphenylphosphino)phenylene **4** with $PhRh(PPh_3)_4$ or $HRh(PPh_3)_4$.

Similarly, reaction of **1** with $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) at 120 °C under 20 psi H_2 results in, after 3 d, formation of ethane in 95% yield and the hydrido complex **6** was also quantitatively formed (Scheme 2). Again, methane was not detected. The presumed C–H activation complex **5** was not observed in this case. Complex **6** was fully characterised spectroscopically[†] and by independent synthesis from **4** and the rhodium dimer.

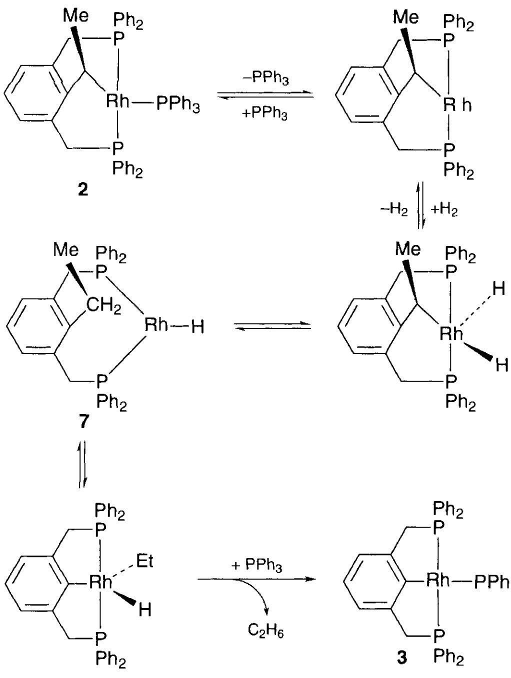
The proposed mechanism for the hydrogenolysis of **2** (Scheme 3) is similar to the one postulated for the hydrogenolysis of the analogous benzyl complex.[7] Of particular interest is the issue of rhodium insertion into C–C of the postulated intermediate **7**. Although the Ar–CH_2CH_3 is substantially stronger than $ArCH_2$–CH_3 [compare BDE Ph–CH_2CH_3 = 96.3 ± 1 *viz* BDE $PhCH_2$–CH_3 = 71.8 ± 1 kcal mol^{-1},[8] (1 cal = 4.184 J)] selective insertion into the Ar–C bond takes place. This is undoubtedly driven to a large extent by the formation of a relatively strong Ar–Rh bond[9] and the more stable five-membered chelating system. However, a pathway involving consecutive sp^3–sp^3, sp^2–sp^3 bond cleavages, generating methane and complex **3** would have been thermodynamically much more favourable.[‡] Thus, the reason for the preference of ethane formation is probably kinetic. Since both



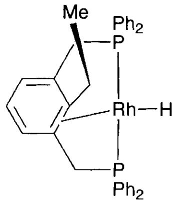
Scheme 1



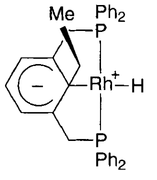
Scheme 2



Scheme 3



A



B

C–C bonds in question are easily accessible to the metal, it can be suggested that the main reason for the preference of Ar–C cleavage is associated with the aromatic system. As in Ar–H oxidative addition, an η^2-arene intermediate **A** may be involved here. Another possibility may involve nucleophilic attack of the metal *via* a Meisenheimer-type intermediate **B**.

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Footnotes

† *Spectroscopic data* for **2**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 66.9 [ddd, left part of AB_q, J_{PP} (*trans*) = 247.4, J_{RhP} = 199.7 Hz, J_{PP} (*cis*) = 31.2 Hz, 1 P, PPh_2], 63.6 [ddd, right part of AB_q, J_{PP} (*trans*) = 247.4, J_{RhP} = 207.9 Hz, J_{PP} (*cis*) = 30.3 Hz, 1 P, PPh_2] and 36.5 (2 dd, J_{RhP} = 145.7, J_{PP} (*cis*) = 31.2, 30.3 Hz, 1 P, PPh_3); ^1H NMR (C_6D_6) δ 7.95 (m, 6 H, PPh_3), 7.55 (m, 8 H, PPh_2), 7.12 (m, 9 H, PPh_3), 7.05 (m, 12 H, PPh_2), 6.98 (distorted t, J_{PH} = 1.0 Hz, 3 H, ArH), 3.75 (d, left part of AB_q, J_{HH} = 13.0 Hz, 1 H, CH_2PPh_2), 3.58 (d, left part of AB_q, J_{HH} = 13.8 Hz, 1 H, CH_2PPh_2), 3.57 [m, hidden, characterised by ^1H–^1H 2D NMR, 1 H, $CH(CH_3)Rh$], 3.47 (dm, right part of AB_q, J_{HH} = 13.0 Hz, 1 H, CH_2PPh_2), 3.45 (dm, right part of AB_q, J_{HH} = 13.8 Hz, 1 H, CH_2PPh_2), 1.86 [q (dt), J_{HH} = 6.7 Hz (characterised by $^1H\{^{31}P\}$ NMR), 3H, $CH(CH_3)Rh$]; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 148.3 (m, J_{PC} = 6.7 Hz, Ar), 140.5 (m, J_{PC} = 4.2, 1.8 Hz, Ar), 140.2 (m, J_{PC} = 7.8, 1.8 Hz, Ar), 138.6 (dvt, J_{PC} = 2.7 Hz, PPh_3), 138.3 (dvt, J_{PC} = 2.5 Hz, PPh_3) 138.0 (d, J_{PC} = 12.0 Hz, PPh_2), 135.1 (br d, J_{PC} = 14.8 Hz, PPh_2), 134.4 (d, J_{PC} = 12.7 Hz, PPh_2), 133.4 (d, J_{PC} = 18.7 Hz), 132.4 (d, J_{PC} = 10.4 Hz), 131.7 (d, J_{PC} = 8.1 Hz), 131.5 (m, Ar), 130.3 (s, PPh_3), 129.3 (d, J_{PC} = 1.3 Hz), 129.0 (s, PPh_2), 128.6 (d, J_{PC} = 6.3 Hz) 128.5 (d, J_{PC} = 6.4 Hz), 117.7 (d, J_{PC} = 1.3 Hz, Ar), 44.7 (d, J_{PC} = 16.6 Hz, CH_2PPh_2), 42.9 (d, J_{PC} = 24.0 Hz, CH_2PPh_2), 27.0 [dm, J_{PC} (*trans*) = 42.0 Hz, $CH(CH_3)Rh$], 23.9 [dm, J_{PC} = 17.6 Hz, CH $(CH_3)Rh$]. FD-MS: calc. *m/z* 867, found *m/z* 867.

For **3**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 50.7 (dd, J_{RhP} = 161.6, J_{PP} = 30.6 Hz, 2 P, PPh_2), 38.9 (dt, J_{RhP} = 121.6, J_{PP} = 30.6 Hz, 1 P, PPh_3); ^1H NMR (C_6D_6) δ 7.60–7.50 (m, 14 H, PPh_2 and PPh_3), 6.90–6.70 (m, 21 H, PPh_2 and PPh_3), 6.34 (br s, 3 H, ArH) and 3.94 (vt, J_{PH} = 3.1 Hz, 4 H, CH_2PPh_2); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 178.4 [ddt, J_{PC} (*trans*) = 78.8, J_{PC} (*cis*) = 7.7, J_{RhC} = 31.9 Hz, Ar, *ipso*-C], 148.3 (ddvt, J_{PC} = 11.2, 1.0, J_{RhC} = 2.3 Hz, Ar), 139.5 (dt, J_{PC} = 30.0, 2.2 Hz, PPh_3), 138.0 (td, J_{PC} = 16.8, 1.7 Hz, PPh_2), 134.7 (d, J_{PC} = 13.5 Hz, PPh_2), 133.6 (dt, J_{PC} = 6.2 Hz, PPh_3), 128.6 (d, J_{PC} = 7.4 Hz, PPh_3), 128.5 (s, PPh_3), 128.4 (d, J_{PC} = 1.5 Hz, PPh_2), 127.4 (d, J_{PC} = 8.8 Hz, PPh_2), 124.1 (s, Ar), 121.5 (dvt, J_{PC} = 9.7, 2.8 Hz, Ar), 49.9 (ddvt, J_{PC} = 13.7, 7.7, J_{RhC} = 2.8 Hz, CH_2PPh_2).

For **6**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 48.9 (dd, J_{RhP} = 111.3, J_{PP} = 24.2 Hz, 2 P, PPh_2) and 18.5 (dt, J_{RhP} = 82.5, J_{PP} = 24.2 Hz, 1 P, PPh_3); ^1H NMR (CD_2Cl_2) δ 7.50–6.80 (m, 38 H, PPh_2 and PPh_3), 4.55 (dvt, left part of ABX_2 pattern, J_{HH} = 15.2, J_{PH} = 3.8 Hz, 2 H, CH_2PPh_2, 3.74 (dvt, right part of ABX_2 pattern, J_{HH} = 15.2, J_{PH} = 4.6 Hz, 2 H, CH_2PPh_2) and −16.9 [m, (ddt), J_{PH} = 12.8, 12.3, J_{RhH} = 22.7 Hz, 1 H, H–Rh]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 166.7 [ddt, J_{PC} (*trans*) = 99.3, J_{PC} = 3.6, J_{RhC} = 25.8 Hz, Ar, *ipso*-C], 144.6 (dvt, J_{PC} = 8.3, 1.5 Hz, Ar), 135.5 (distorted m), 134.4 (d, J_{PC} = 11.2 Hz), 133.9 (t, J_{PC} = 5.2 Hz), 133.6 (distorted t, J_{PC} = 5.2 Hz), 130.0 (d, J_{PC} = 7.3 Hz), 129.2 (d, J_{PC} = 1.8 Hz), 128.8 (br s), 128.2 (dt, J_{PC} = 5.9, 4.7 Hz), 127.8 (d, J_{PC} = 8.9 Hz), 124.4 (s), 122.3 (dt, J_{PC} = 8.8, 4.7 Hz), 47.5 (ddvt, J_{PC} = 16.8, 7.5, J_{RhC} = 2.2 Hz, CH_2PPh_2); IR (film)/cm^{-1} 2107 (ν_{RhH})

‡ Comparing processes (*a*) and (*b*) below, the latter is calculated to be more exothermic by approximately 28 kcal mol^{-1}.

$$(a)\ HRh + PhCH_2CH_3 \rightarrow Ph\text{–}Rh + C_2H_6$$

$$(b)\ HRh + PhCH_2CH_3 + H_2 \rightarrow Ph\text{–}Rh + 2CH_4$$

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