Formation of η-Benzene or η-Cyclohexa-1,3-diene Compounds of Chromium, Tungsten, and Rhenium from Cyclohexane and the Metal Atoms

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Co-condensation of atoms of tungsten, rhenium, and chromium with a mixture of cyclohexane and trimethylphosphine causes activation of the cyclohexane giving the compounds $W(\eta\text{-}C_6H_8)(PMe_3)_2H_4$, $W(\eta\text{-}C_6H_8)(PMe_3)_3H_2$, $W(\eta\text{-}C_6H_6)(PMe_3)_2H_2$, $W(PMe_3)_4H_4$, $Re(\eta\text{-}C_6H_6)(PMe_3)_2H$, and $Cr(\eta\text{-}C_6H_6)(PMe_3)_3$ respectively; when tungsten atoms react with a 3 : 1 mixture of cyclohexane and perdeuteriocyclohexane, together with PMe_3, then the absence of mixed H–D tungsten products indicates that the C–H activation processes are intramolecular.

The activation of cyclopentane giving η-cyclopentadienyl-metal compounds was first observed for rhenium and iridium compounds.[1,2] The dehydrogenation of cyclohexane, by polyhydride compounds $Re(PR_3)_2H_7$ giving cyclohexene,[3] and by $[IrH_2(PPh_3)_2(Me_2CO)_2]SbF_6$ giving $[Ir(\eta\text{-}C_6H_6)(PPh_3)_2]SbF_6$, has been observed.[4] We recently showed that tungsten atoms reacted with a mixture of cyclopentane and PMe_3 giving, *inter alia,* the pentahydride derivative $W(\eta\text{-}C_5H_5)(PMe_3)H_5$.[5] We were interested to investigate the generality of multistep C–H activation processes by transition metal atoms and here we describe the dehydrogenation of cyclohexane by several metals giving η-benzene and η-cyclohexa-1,3-diene compounds.

Co-condensation of tungsten atoms with a mixture of cyclohexane and PMe_3 gives a mixture of products. In a typical run 2.5 g of tungsten atoms were co-condensed with 60 cm^3 of cyclohexane (spectroscopic grade) and PMe_3 (10 : 1). The n.m.r. spectrum† of the less volatile product unambiguously shows the presence of the compounds $W(\eta\text{-}C_6H_8)(PMe_3)_2H_4$ (**1**), $W(\eta\text{-}C_6H_8)(PMe_3)_3H_2$ (**2**), $W(\eta\text{-}C_6H_6)(PMe_3)_2H_2$ (**3**), and $W(PMe_3)_4H_4$ (**4**). The compounds (**2**),[6] (**3**),[6] and (**4**)[7] have been prepared independently and characterised by microanalysis, their mass spectra, and detailed n.m.r. studies. The characterisation of (**1**) is based on detailed n.m.r. studies† since we were unable to separate a pure sample from the reaction mixture nor to find an independent synthesis. Co-condensation of tungsten atoms with cyclohexene and PMe_3 (10 : 1) gave only (**2**) and (**3**) and there was no evidence (n.m.r.) for (**1**) and (**4**).

Tungsten atoms were co-condensed with a mixture of cyclohexane and perdeuteriocyclohexane (3 : 1) and PMe_3. The ^1H n.m.r. spectrum (at 500 MHz) of the less volatile products showed that the complex bands assignable to tungsten–hydrogen groups were identical to those of (**1**)—(**4**).

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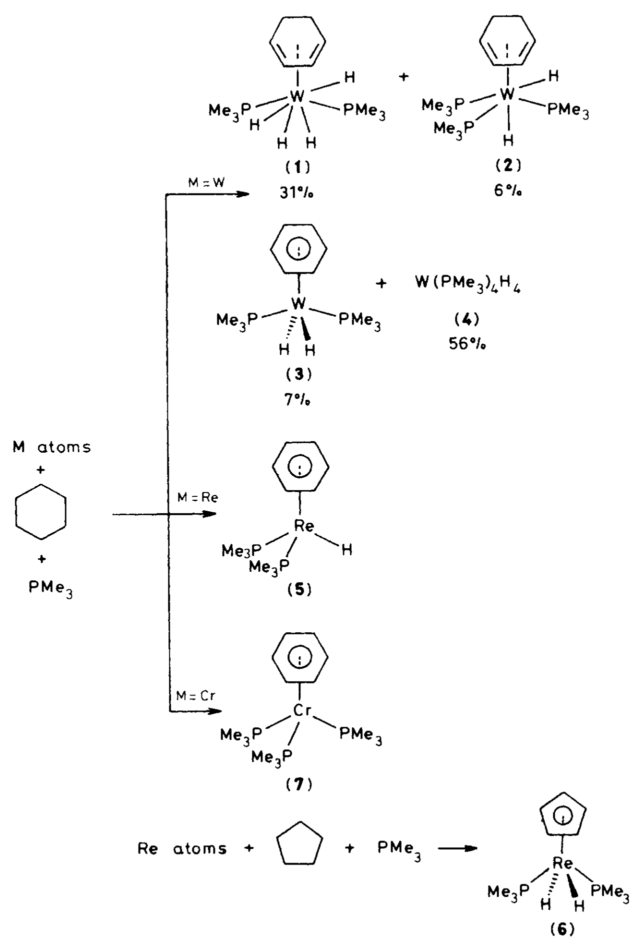
† N.m.r. data, in C_6D_6, δ values, *J* values in Hz. For (**1**), ^1H: 4.85 (2 H, br., 2H of $\eta\text{-}C_6H_8$), 3.16 (2 H, br., 2H of $\eta\text{-}C_6H_8$), 2.38 [2 H, d, *J*(H–H) 9, 2H of $\eta\text{-}C_6H_8$], 1.73 [2 H, d, *J*(H–H) 9, 2H of $\eta\text{-}C_6H_8$], 1.33 (18 H, virtually coupled triplet, *J′* 3.8, 2 PMe_3), and −2.89 [4 H, t, *J*(P–H) 37.5, *J*(W–H) 26, 4WH]; $^{31}P\{^1H\}$ n.m.r., rel. to $(MeO)_3PO$ (external): −21.5 p.p.m. [s, *J*(P–W) 132]. $^{31}P\{^1H\text{-}Me\}$: −21.5 p.p.m. (quintet). For (**2**), ^1H n.m.r.: −1.53 (complex, WH) and −5.55 (br., WH). For (**3**), ^1H n.m.r.: −6.15 [t, *J*(P–H) 48.1, *J*(W–H) 48.9, 2WH]. For (**4**), ^1H n.m.r.: −3.65 (complex, 4W–H). For (**6**), ^1H n.m.r.: 4.55 (5 H, s, $\eta\text{-}C_5H_5$), 1.52 [18 H, d, *J*(P–H) 9.5, 2 PMe_3], −12.13 [2H, t, *J*(P–H) 43.4, 2Re–H]; $^{31}P\{^1H\}$ n.m.r.: −39.84 p.p.m. (s); $^{31}P\{^1H\text{-}Me\}$: −39.84 p.p.m. (t); M^+, *m/z* 406 (^{187}Re). Full data for (**2**) and (**3**) will be published elsewhere.



Scheme 1

Further, the ^{2}H n.m.r. spectrum of the same sample showed bands expected for the deuteriated compounds $W(\eta\text{-}C_6D_8)(PMe_3)_2D_4$ (**1d**), $W(\eta\text{-}C_6D_8)(PMe_3)_3D_2$ (**2d**), $W(\eta\text{-}C_6D_6)(PMe_3)_2D_2$ (**3d**), and $W(PMe_3)_4D_4$ (**4d**). We conclude that there is no evidence for hydrogen–deuterium scrambling and this strongly suggests that (**1**)—(**4**) are formed by a process involving sequential intramolecular C–H activation of the cyclohexane.

Co-condensation of rhenium atoms with cyclohexane and PMe_3 (20 : 1) gives the previously described[8] compound $Re(\eta\text{-}C_6H_6)(PMe_3)_2H$ (**5**) in 5% yield. Similarly, rhenium atoms with cyclopentane and PMe_3 (10 : 1) give pale brown, crystalline $Re(\eta\text{-}C_5H_5)(PMe_3)_2H_2$ (**6**). The compound (**6**) has also been synthesised by treatment of rhenium pentachloride and PMe_3 in tetrahydrofuran with $LiAlH_4$ followed by treatment of the reaction products with cyclopentadiene.[†]

Co-condensation of chromium atoms with cyclohexane and PMe_3 (10 : 1) gives a small yield (*ca.* 1%) of the new compound $Cr(\eta\text{-}C_6H_6)(PMe_3)_3$ (**7**). The compound (**7**) has been prepared separately in *ca.* 50% yield (scale 2—3 g) from chromium atoms, benzene, and PMe_3.[9]

The activation of alkanes by atoms of the first-row transition metals Mn, Fe, and Cu has been demonstrated in matrices.[10—12] However, this is the first report of C–H activation by chromium and also isolation of an organometallic product. The structures proposed for compounds (**1**)—(**7**) are shown in Scheme 1. The n.m.r. data do not permit distinction between possible isomers.

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