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Formation of a Novel Yttrium Hydride with Bridging 1,2,3,4-Tetramethylfulvene and Hydride Ligands

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Thermolysis of $[(C_5Me_5)_2YH]_2$ in *n*-octane or benzene yields $(C_5Me_5)_2Y(\mu-H)Y(\eta^5-C_5Me_4CH_2)(C_5Me_5)$, a bis-yttrium-monohydride in which a tetramethylfulvene ligand bridges in a $\sigma-\eta^5$ manner between the yttrium atoms; the hydride bridge is asymmetric showing two yttrium-hydrogen coupling constants in the 1H n.m.r. spectrum.

Hydrogen abstraction from a pentamethylcyclopentadienyl group to give a tetramethylfulvene ligand probably plays a crucial role in processes like H-D-exchange and C-H-activation with permethylmetallocene derivatives of early transition metals and f elements.¹ The tetramethylfulvene ligand is interesting since it can bond in several ways: as a 'tucked in' cyclopentadienyl-alkyl (I),² as a six-co-ordinate fulvene (II),³ and also as a bridging η^5 -cyclopentadienyl- σ -alkyl (III).⁴

As part of a project on permethyltrocene derivatives we tried to prepare yttrium-fulvene systems. We followed an approach that proved to work well for titanium, *e.g.* thermolysis of compounds $(C_5Me_5)_2TiR$ ($R = H$ or alkyl).⁵ By analogy with $(C_5Me_5)_2TiH$, we expected that reaction (1) would occur.

However on thermolysis of $[(C_5Me_5)_2YH]_2$ (**1**)⁶ at 100 °C only half of the expected amount of hydrogen was liberated. A red crystalline organo-yttrium compound compatible with the stoichiometry $(C_5Me_5)_2YH(C_5Me_5)Y(CH_2C_5Me_4)$ was isolated. Spectroscopic evidence (1H and ^{13}C n.m.r., i.r.) identified the compound as compound (**2**), the proposed structure for which is illustrated. The n.m.r. spectra[†] espe-

cially provide conclusive evidence on the bonding of the ligands.

Both 1H and ^{13}C n.m.r. data[†] show the C_5Me_5 ligand resonances at normal positions; the coupling constants ($^1J_{CH}$) of the methyl groups are as expected for sp^3 C-H bonds. The intensity ratio of the 1H resonances indicates the presence of a $(C_5Me_5)Y$ and a $(C_5Me_5)_2Y$ unit.

The resonances of the tetramethylfulvene ligand are compatible with a mirror plane perpendicular to the five-membered ring, including the methylene carbon atom, the two yttrium atoms, and the hydride ligands. The methyl groups show two 1H n.m.r. singlets at δ 2.02 and 2.04 (intensity ratio 1 : 1). The methylene group at δ 1.19 has the correct intensity and is split into a doublet by second-order coupling to the yttrium atom to which it is bonded ($^2J_{Y-H}$ 4.10 Hz). In the $^{13}C\{^1H\}$ n.m.r. spectrum the ring carbon resonances are found at δ 114.14, 118.07, and 148.03. The methyl carbons show two signals at δ 11.40 and 14.07 with normal sp^3 C-H bond coupling constants, $^1J_{CH}$. The methylene carbon resonance, δ 35.97, is split into a double triplet by coupling with two equivalent protons ($^1J_{C-H}$ 120.17 Hz) and one yttrium nucleus ($^1J_{Y-C}$ 35.60 Hz), and there is a second-order coupling with the bridging hydride ($^2J_{CH}$ 6.51 Hz). The yttrium-carbon coupling constant is virtually the same as found in $(C_5Me_5)_2YCH(SiMe_3)_2$,⁶ and is indicative of a normal Y-C σ bond.

The bridging hydride resonates at δ 3.77 and is split into a double doublet by interaction with two inequivalent yttrium nuclei ($^1J_{Y-H}$ 47.80 and 29.45 Hz). It seems reasonable to assign the larger coupling constant to a more or less regular Y-H σ -bond although the value is somewhat low. For the terminal Y-H in the monomeric $(C_5Me_5)_2YH \cdot THF$, $^1J_{Y-H}$ is 81.74 Hz.⁷ The observation of two different Y-H couplings is

[†] Compound (**2**), 1H n.m.r. (360 MHz, C_6D_6 , 25 °C, J values in Hz): δ 1.19 (d, 2H, $^2J_{YH}$ 4.10, Y-CH₂), 1.92 (s, 15H, C_5Me_5Y), 2.02 (s, 6H, $2 \times \alpha-C_5Me_4CH_2$), 2.04 (s, 6H, $2 \times \beta-C_5Me_4CH_2$), 2.10 [s, 30H, $(C_5Me_5)_2Y$], and 3.77 (dd, 1H, $^1J_{YH}$ 47.80 and 29.45, Y-H-Y); ^{13}C n.m.r. (50.3 MHz, C_6D_6 , 25 °C, J values in Hz): δ 11.40 (q, $^1J_{CH}$ 126.33, $\beta-C_5Me_2Me_2$), 11.52 (q, $^1J_{CH}$ 124.56, C_5Me_5Y), 11.74 [q, $^1J_{CH}$ 125.40, $(C_5Me_5)_2Y$], 14.07 (q, $^1J_{CH}$ 125.23, $\alpha-C_5Me_2Me_2$), 35.97 (ddt, $^1J_{CH}$ 120.17, $^2J_{CH}$ 6.51, $^1J_{YC}$ 35.60, Y-CH₂), 114.14 (s, ring- $\beta-C_5Me_4$), 116.19 [s, $(C_5Me_5)_2Y$], 118.07 (s, ring- $\alpha-C_5Me_4$), 119.88 (s, C_5Me_5Y), and 148.03 (d, $^2J_{YC}$ 3.97, ring-CH₂-C).

Scheme 1

in full agreement with an asymmetric 3-centre-2-electron hydrogen bridge.

The i.r. spectrum[‡] shows two Y-H absorptions at 1240 and 660 cm⁻¹, which shift on deuteration to 885 and 470 cm⁻¹ respectively in agreement with the theoretical shift (calc. ν_{Y-H}/ν_{Y-D} 1.41; found 1.401 and 1.404 respectively). The high energy vibration is identical to that found in [(C₅H₄Me)₂-YH·THF]₂.⁸

The reactivity of complex (2) is interesting. A solution of (2) in [2H₆]benzene shows at room temperature a gradual decrease of the hydride resonance at δ 3.77 and a concomitant increase of the residual proton signal of [2H₆]benzene at δ 7.16. All other resonances remain at exactly the same positions with no changes in multiplicity or intensity. This form of H/D exchange, which is limited to solvent sp² C-D and complex Y-H bonds, and does not occur with the sp³ C-H bonds of the C₅Me₅ and C₅Me₄CH₂, can be explained by σ -bond metathesis following a [2s + 2s + 1a₁]₁₀ mechanism⁹ as has been proposed for Sc and Lu compounds.

A similar mechanism also presents a plausible explanation for the formation of (2) from (1) (Scheme 1, route A). If route B were followed, interaction with the solvent would be expected and, e.g. in benzene (C₅Me₅)₂YPh would be formed. However, no trace of this compound was detected when the thermolysis of (1) was carried out in benzene (75 °C). Only (2) was isolated.

[‡] I.r. (KBr, Nujol, cm⁻¹) 2720w, 1335w, 1240m br., 1155w, 1045w, 1020m, 920s, 810s, 795m, 660m, 640w, 590s, and 570w.

The formation of (2) provides the first example of a bis-yttrium-monohydride, a type of species which has never been observed in organo group 3 and f element complexes before. It is also the first example of an isolated compound with a C₅Me₄CH₂ ligand for these elements, obviously in a bridging position.

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