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A BULKY LIGAND AND ITS ORGANOMETALLIC COMPOUND: SYNTHESIS OF HEPTAMETHYLINDENE AND A FERROCENE-TYPE COMPLEX, $Fe(\eta^5\text{-}C_9Me_7)_2$

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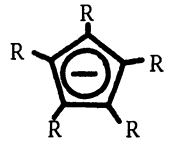
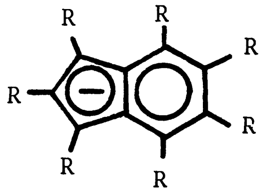
A bulky new indene, 1-H-1,2,3,4,5,6,7-heptamethylindene, has been synthesized and its application to organometallic chemistry is suggested.

A variety of η^5-pentamethylcyclopentadienyl(C_5Me_5, **1b**)-transition metal complexes have been used for the activation of small molecules such as N_2 or CO.1)-3) The advantages of **1b** are that it makes greater steric requisition than $\eta^5\text{-}C_5H_5$(**1a**), while giving greater solubility and crystallizability. An additional point is that methyl $C(sp^3)$-H bonds of **1b** are more inert with respect to scission than ring $C(sp^2)$-H bonds. Though coordination is formally analogous to **1a**, the indenyl ligand(**2a**) exerts great steric demands as seen on the crystal structure of Sm(indenyl)$_3$.4) It is highly probable that permethylation on indenyl ring, i.e., **2b**, will lead to the heavy steric congestion around metal ions. In analogy with the ligand **1b**, the methyl substituents will also afford the great kinetic stability to the resulting η^5-heptamethylindenyl(**2b**)-metal bonds. These speculations stimulated us to investigations in the synthetic routes to **2b**. We now wish to announce the successful synthesis of heptamethylindene **3**, a valuable precursor of **2b**.



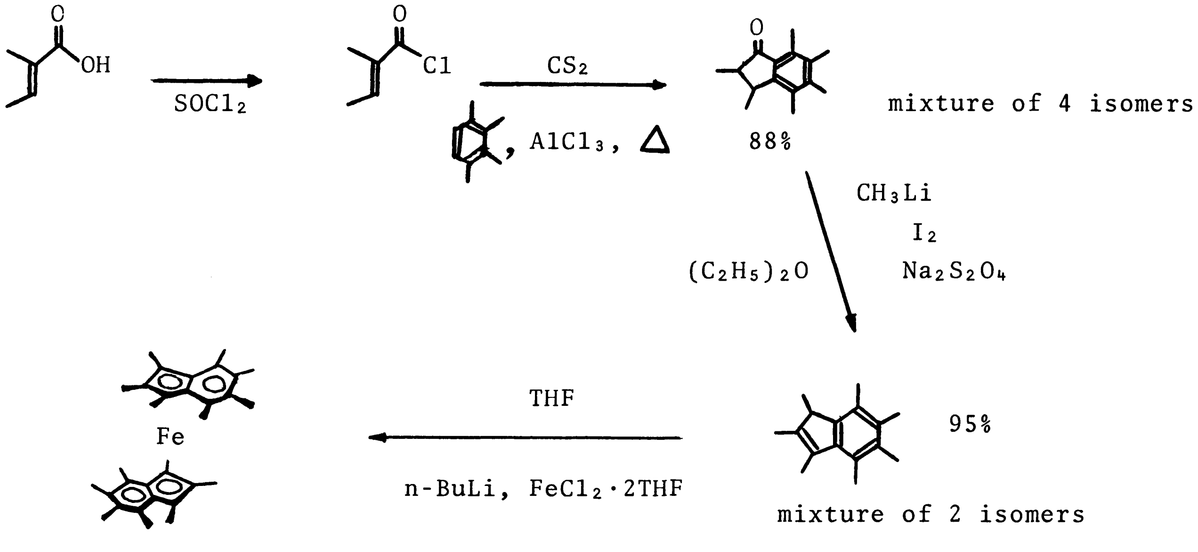
1a, R=H
b, R=Me,



2a, R=H
b, R=Me, (Abbr. hmi)

A new indene **3**, 1-H-1,2,3,4,5,6,7-heptamethylindene(HMI), was prepared as a mixture of two isomers by the Friedel-Crafts reaction and the subsequent methylation-(scheme). The pale yellow crystalline product is stable under inert atmosphere over a half year, and its formulation was supported by elemental analysis and the characteristic patterns of mass and NMR spectra.5)

The practical application of **3** was made to the synthesis of the ferrocene-type complex. The new indene **3** was converted to the lithium indenide by treatment with n-butyllithium, and the subsequent reaction with $FeCl_2 \cdot 2THF$ gave a black solid product in quantitative yield. The product **4** was purified by soxhlet extraction with hexane to give the glittering black crystals which were formulated as $Fe(hmi)_2$



4

3

(Abbr. HMI)

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based on elemental analysis. The NMR spectrum$^{6)}$ shows four singlet bands consistent with the structure of the hmi anion 2b. It seems likely that hmi(2b) is linked to the iron atom in a pentahapto manner.

In this way, applicability of heptamethylindenyl(hmi) is supported by the isolation of the ferrocene-type complex. The organometallic synthesis with the aid of hmi is now in progress in our laboratories.

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5) Anal. Calcd. for $C_{16}H_{22}$: C, 89.66; H, 10.34. Found: 89.70; H, 10.26. m.p., 58.5 ~ 59.0°C. IR(nujol): 1680(m), 1300(w), 1297(w), 1262(w), 1182(w), 1167(w), 1103(w), 1060(w, br), 1025(m, br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 1.2(doublet, J=7Hz, CH_3), 1.9(singlet, CH_3), 2.2(multiplet, $3CH_3$), 2.3(singlet, CH_3), 2.5(singlet, CH_3), 3.0(quartet, J=7Hz, 1H). Mass Spectrum(15eV): 214(intensity 76), 199(100), 84(28). UV: in EtOH; 215(ε=3.9 x 10^4), 265 nm(9.7 x 10^3). in hexane; 223(2.1 x 10^4), 265 nm(1.0 x 10^4).

6) IR(nujol): 1600(m), 1300(m), 1105(m), 1035(s), 1020(s) cm^{-1}. Anal. Calcd. for $C_{32}H_{42}Fe$: C, 79.65; H, 8.77; Fe, 11.57. Found: C, 79.95; H, 8.87; Fe, 11.42. m.p., 250°C. UV in hexane: 230(ε=1.1 x 10^4), 284 nm(2.1 x 10^4). Visible Spectrum in THF: 425(ε=9.7 x 10^1), 555 nm(5.8 x 10^2). ^1H NMR in C_6H_6: 1.7(singlet, CH_3), 1.9(singlet, $2CH_3$). 2.1(singlet, $2CH_3$), 2.3(singlet, $2CH_3$). The black crystals **4** are fairly stable to air.

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