Trimethylenemethane Complexes of Ruthenium *via* the Trimethylenemethane Dianion

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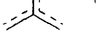
Reactions of $Li_2[C(CH_2)_3]$ or of $H_2C=C(CH_2SnMe_3)_2$ with (arene)ruthenium dichlorides **2** lead to trimethylenemethane ruthenium complexes; the structure of $Ru\{\eta^4\text{-}C(CH_2)_3\}(\eta^6\text{-}C_6H_6)$ **3** has been determined crystallographically.

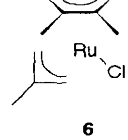
η^4-Trimethylenemethane (tmm) complexes of transition metals are of current interest,[1] especially since such species are postulated as reactive intermediates in metal assisted cycloaddition reactions.[2] Most synthetic strategies developed so far use organic precursors like alkylidene cyclopropanes, functionalised allylsilanes and dihalosubstituted methylpropenes.[1] Surprisingly, the ready availability of the dianion of trimethylenemethane (tmm^{2-})[3] **1** has rarely been exploited as a ligand source. Three complexes of Fe,[4] Co[5] and Rh[6] have been obtained in this way.

Herein we show that **1** can be used as a precursor to η^4-trimethylenemethane complexes of ruthenium having a mixed sandwich structure. Treating $[RuCl_2(arene)]_2$ (arene = C_6H_6 **2a**,[7] C_6Me_6 **2b**[8]) with $Li_2\cdot$**1** in tetrahydrofuran (thf) gives the compounds **3** and **4** in yields of 15 and 25%, respectively; light yellow cyrstals are obtained after filtration in pentane over basic alumina (7% H_2O). Higher yields of **4** (60% based on ruthenium) are obtained *via* the less reactive stannane $H_2C=C(CH_2SnMe_3)_2$ **5**.[9] Both sandwich complexes are volatile *in vacuo* and **3** undergoes sublimation at 40 °C (1 mbar). ^1H NMR spectra of **3** and **4** show singlets owing to the arene and trimethylenemethane ligands. ^{13}C NMR spectra show resonances for the central carbon of the tmm ligand of *ca.* δ 105;† the signals of the trimethylenemethane methylene carbons exhibit $^3J(CH)$ coupling constants of 10 Hz (*trans*) and 5 Hz (*cis*).† The hexamethylbenzene complex **4** is particularly sensitive to electrophilic attack at the tmm ligand. Exposure of a pentane solution to gaseous hydrogen chloride immediately precipitates the dihalide **2b** while upon dropwise addition of HCl in diethyl ether, the methallyl complex **6** is formed.



1

3; R = H
4; R = Me



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† All compounds gave satisfactory elemental analyses and mass spectra. Selected NMR data (C_6D_6). Compound **3**: ^1H (80 MHz), δ 1.51 [s, 6 H, $C(CH_2)_3$], 4.97 [s, 6 H, C_6H_6]; ^{13}C (68 MHz), δ 40.7 [ttt, $C(\mathit{C}H_2)_2$, $^1J(CH)$ 157, $^3J(CH\text{-}\mathit{trans})$ 10, $^3J(CH\text{-}\mathit{cis})$ 5 Hz], 80.8 [d, C_6H_6, $^1J(CH)$ 172 Hz], 103.5 [s, $\mathit{C}(CH_2)_3$]. Compound **4**: ^1H (80 MHz), δ 0.95 [s, 6 H, $C(CH_2)_3$], 2.03 [s, 18 H, C_6Me_6]; ^{13}C (68 MHz), δ 18.4 [q, $C_6\mathit{Me}_6$, $^1J(CH)$ 127 Hz], 40.2 [ttt, $C(\mathit{C}H_2)_2$, $^1J(CH)$ 155, $^3J(CH\text{-}\mathit{trans})$ 10, $^3J(CH\text{-}\mathit{cis})$ 5 Hz], 91.6 [s, C_6Me_6], 105.0 [s, $\mathit{C}(CH_2)_3$]. Compound **6** ($CDCl_3$): ^1H (80 MHz), δ 1.64 [s, 3 H, Me], 2.08 [s, 18 H, C_6Me_6], 2.46 [s, 2 H, CH_2], 3.11 [s, 2 H, CH_2]; ^{13}C (68 MHz), δ 15.9 [q, $C_6\mathit{Me}_6$, $^1J(CH)$ 128 Hz], 23.2 [q, $\mathit{Me}C(CH_2)_2$, $^1J(CH)$ 126 Hz], 53.0 [t, $MeC(\mathit{C}H_2)_2$, $^1J(CH)$ 159 Hz], 95.4 [s, C_6Me_6], 104.4 [s, $Me\mathit{C}(CH_2)_2$].

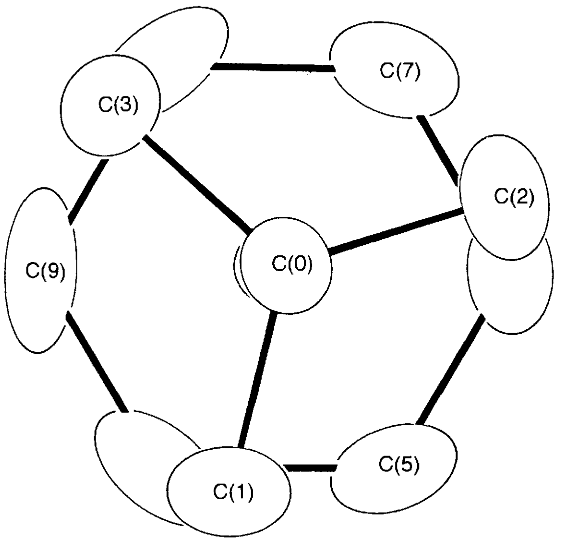

Fig. 1 Molecular structure of Ru{η^4-C(CH$_2$)$_3$}(η^6-C$_6$H$_6$) **3**, hydrogen atoms omitted. Interatomic distances: Ru–C(0) 2.029(3), Ru–C(1) 2.186(3), Ru–C(2) 2.175(4), Ru–C(3) 2.198(4), Ru–C(4) 2.198(5), Ru–C(5) 2.219(4), Ru–C(6) 2.204(4), Ru–C(7) 2.194(4), Ru–C(8) 2.200(4), Ru–C(9) 2.215(4), C–C$_{arene}$ 1.39 (av), C–C$_{tmm}$ (av) 1.43 Å. Angles: C(1)–C(0)–C(2): 115.2(5), C(1)–C(0)–C(3) 114.2(4), C(2)–C(0)–C(3) 114.1(4)°.

The crystal structure of **3** has been determined by X-ray diffraction.‡ It reveals a sandwich like structure with a planar η^6-benzene ring (within 0.01 Å) and the expected umbrella like η^4-tmm ligand (with the central C atom 0.34 Å above the plane of the terminal C atoms),[1] adopting a staggered conformation, as shown in Fig. 1. All ring C–C bond distances are in the range of 1.37–1.42 Å with an average value of 1.39 Å; no significant alternation is observed. The metal–carbon (ring) distances lie between 2.194 and 2.219 Å with a metal to the C$_6$ centre of gravity separation of 1.715 Å.

We are currently extending this work to substituted trimethylenemethane dianions and to the investigation of *e.g.* ring displacement reactions.

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‡ *Crystal data* for **3**: C$_{10}$H$_{12}$Ru, $M = 233.3$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 17.686(4)$, $b = 8.012(2)$, $c = 6.119(1)$ Å, $U = 867.1(4)$ Å^3, $Z = 4$, $D_c = 1.79$ g cm^{-3}; Mo-Kα X-radiation, $\lambda = 0.7093$ Å, μ(Mo-Kα) = 17.05 cm^{-1}; final $R = 0.019$ ($R_w = 0.026$) for 1199 independent reflections ($3 < \theta < 30°$) [$I \geq 1\sigma(I)$], collected at 293 K on an Enraf-Nonius CAD4 diffractometer.

Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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