Trimethylsilyl and Trimethylgermyl Group Migration from Ruthenium to Cycloheptatriene: Crystal Structure of [Ru(SiMe$_3$)(CO)$_2$C$_7$H$_7$(C$_6$F$_5$)(SiMe$_3$)]

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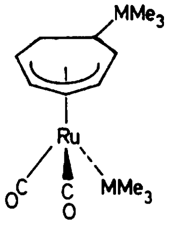
Summary Cycloheptadienyl complexes [Ru(MMe$_3$)(CO)$_2$(C$_7$H$_8$MMe$_3$)] (M = Si or Ge) are formed on reaction of Ru(MMe$_3$)$_2$(CO)$_4$ with cycloheptatriene; an *X*-ray diffraction study on [Ru(SiMe$_3$)(CO)$_2$C$_7$H$_7$(C$_6$F$_5$)(SiMe$_3$)] has established an *exo*-configuration for the migrant SiMe$_3$ group.

Initially it was thought that reaction between triphenyltin(pentacarbonyl)manganese and tetraphenylcyclopentadienone afforded a complex with a tin-manganese bond,[1] but subsequently it was realised[2] that the product is a cyclopentadienyl complex [Mn(CO)$_3$(C$_5$H$_4$OSnPh$_3$)]. We now describe reactions which suggest that migration of organosilicon and -germanium ligands from transition metals to co-ordinated hydrocarbons can occur very readily.

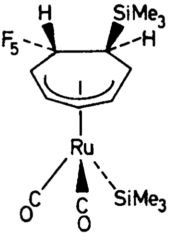
The compounds [Ru(MMe$_3$)$_2$(CO)$_4$] (M = Si, Ge) react with cycloheptatriene in heptane at reflux to give in high yield liquid cycloheptadienyl complexes [Ru(MMe$_3$)(CO)$_2$(C$_7$H$_8$MMe$_3$)] (I). The proton-coupled ^{13}C n.m.r. spectrum of (I; M = Ge) supports the formulation. Quartet resonances at $-4·19$ p.p.m. (upfield of Me$_4$Si) and 4·67 p.p.m. (downfield of Me$_4$Si) are assigned to the methyl carbons of GeMe$_3$ groups attached to ring carbon and ruthenium atoms respectively. The carbon atom carrying the GeMe$_3$ group appears as a doublet at 24·54 p.p.m. with the ring methylene carbon showing as a triplet at 46·35 p.p.m. The resonances of the remaining five essentially *sp*^{2} carbons of the cycloheptadienyl ligand occur as the expected doublets at 80·97, 88·37, 90·43, 102·78, and 104·99 p.p.m. The ^{1}H n.m.r. spectra of the complexes support the assignment; for (I; M = Ge) τ 4·80 (2H, m), 5·27 (2H, m), 6·12 (1H, m), 7·57 (2H, m), 9·47 (1H, m), 9·83 (9H, s), 10·02 (9H, s).

An *X*-ray diffraction study on a crystalline derivative (II) [m.p. 165°; ν_{CO} (hexane) 2021s, 1971s cm^{-1}; τ 4·72 m (3H), 5·16 m (1H), 6·40m (1H), 7·29m (2H), 9·90s (9H), 10·38s (9H)], prepared from Ru(SiMe$_3$)$_2$(CO)$_4$ and 7-C$_6$F$_5$C$_7$H$_7$, has confirmed the MMe$_3$ migration.

Crystals of [Ru(SiMe$_3$)(CO)$_2$C$_7$H$_7$(C$_6$F$_5$)(SiMe$_3$)] are monoclinic, *Cc*, with four molecules in a unit cell: $a = 6{\cdot}798\,(2)$, $b = 17{\cdot}057(5)$, $c = 21{\cdot}157(6)$ Å, $\beta = 91{\cdot}61(2)°$. The structure was solved by conventional heavy-atom methods from data collected on a Syntex $P2_1$ four-circle diffractometer to $2\theta = 50°$ (Mo-K_α *X*-radiation); *R* 0·070.



(I)



(II)

In the 7-membered ring (Figure), five of the atoms C(1,2,3,4,5) are substantially coplanar and are π-bonded to the Ru atom at distances 2·25, 2·26, 2·19, 2·28, and 2·43 Å (all ± *ca.* 0·02 Å). The other two C atoms in the ring C(6,7) deviate from the C(1,2,3,4,5) plane to give a twisted configuration on the side away from the Ru atom; this ring twist is best seen from the torsion angles: C(1,2,3,4) = −4°, C(2,3,4,5) = + 2°, C(3,4,5,6) = −45°, C(4,5,6,7) = + 31°, C(5,6,7,1) = − 37°, C(6,7,1,2) = −89°, and C(7,1,2,3) = + 60°. The bond angles around C(6) and C(7) are close to tetrahedral with the SiMe$_3$ group in an *exo*-configuration and the C_6F_5 group in an *endo*-configuration with respect to the metal. The ruthenium atom carries one SiMe$_3$ group (Ru–Si = 2·43 Å) and two CO groups in an approximately orthogonal relationship. It is perhaps noteworthy that the longest Ru–C bond [to C(5)] lies *trans* to theSiMe$_3$ group.

The quantitative formation of the complexes (I) suggests that MMe$_3$ group migration is intramolecular, so that the migrant group would be expected to occupy a position on the hydrocarbon *endo* with respect to the metal, and not the *exo* configuration observed. In order to establish the nature of the reaction, an equimolar mixture of Ru(SiMe$_3$)$_2$(CO)$_4$ and Ru(GeMe$_3$)$_2$(CO)$_4$ was treated with cycloheptatriene and the ^{13}C n.m.r. of the products examined.

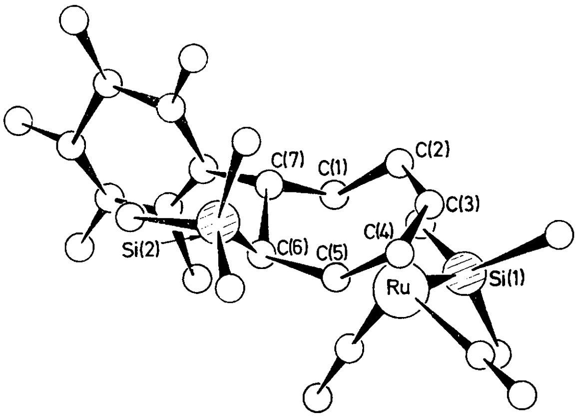


FIGURE. *X*-Ray crystal structure of Ru(SiMe$_3$)(CO)$_2$C$_7$H$_7$-(C$_6$F$_5$)(SiMe$_3$) (II).

The major products detected were (I; M = Si) and (I; M = Ge), with traces of Ru(MMe$_3$)(CO)$_2$(C$_7$H$_9$) (M = Si, Ge) and a species tentatively identified as Ru(GeMe$_3$)(CO)$_2$-(C$_7$H$_8$SiMe$_3$). It would thus appear that formation of "cross-over" products such as the latter reflects a minor reaction pathway, and that the migrations are essentially intramolecular.

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[1] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.

[2] R. D. Gorsich, *J. Organometallic Chem.*, 1966, **5**, 105.