Bridging Cycloheptatrienyl Complexes: X-Ray Crystal Structure of $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$

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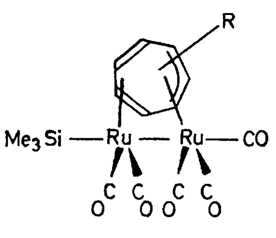
Summary Cycloheptatrienes, $7\text{-}RC_7H_7$, react with $[Ru(CO)_4(SiMe_3)]_2$ to afford *inter alia* fluxional complexes $[Ru_2(CO)_5(SiMe_3)(C_7H_6R)]$ ($R = H$, Me, Ph, C_6F_5); an X-ray structural study on a minor product from C_7H_8 reveals ring substitution by a trimethylsilyl group.

COMPLEXES in which a C_7-ring forms a bridge between two metal atoms bonded together are rare. The ruthenium–ruthenium bonded complex $[Ru(CO)_4(SiMe_3)]_2$ (I) seemed ideally suited as a precursor,[1] and we report a general synthesis of the species $[Ru_2(CO)_5(SiMe_3)(C_7H_6R)]$ (II; $R = H$, Me, Ph, C_6F_5) from reactions with cyclohepta-1,3,5-triene or its 7-substituted derivatives. Due to the removal of a trimethylsilyl ligand from one of the ruthenium atoms during the course of reaction, these species establish a mode of bonding of a C_7-ring to two metal atoms different from the symmetrical attachment recently reported.[2]



(II) $R = H$, Me, Ph, C_6F_5

Compound (II; $R = H$) [ν_{max}(CO) 2063s, 2007s, 2003s, 1984w, and 1958m cm^{-1}; $(M-n\text{CO})^+$, $n = 0$—5; ^{1}H n.m.r. τ 6·14 (7H, s, C_7H_7) and 9·66 (9H, s, $SiMe_3$)] is formed as orange crystals, m.p. 137°, from cycloheptatriene and (I) in heptane under reflux. The singlet signal for the seven ring protons persists at −90° corresponding to a low energy rearrangement process. In contrast, the ^{1}H n.m.r. spectrum of (II; $R = Ph$) is highly temperature dependent between +60° and −90°.

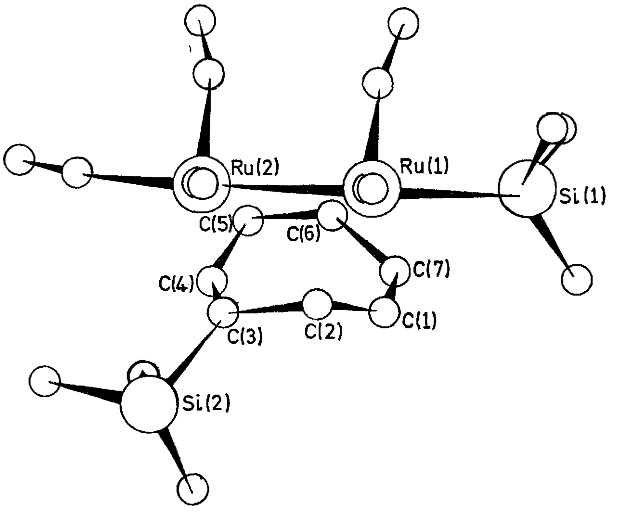


FIGURE.

A single crystal X-ray study believed to be on (II; $R = H$) revealed the structure shown in the Figure, establishing the existence of a minor product (II; $R = SiMe_3$), since isolated as orange crystals m.p. 92° [ν_{max}(CO) 2060s, 2005s, 1999s, 1980w, and 1955m cm^{-1}; $(M-n\text{CO})^+$, $n = 0$—5; $(C_7H_6\text{-}SiMe_3)^+$].

Crystals of (II; R = $SiMe_3$) are orthorhombic, $P2_12_12_1$, with 4 molecules per unit cell (a = 10·35, b = 12·38, c = 17·58 Å). The structure was solved by direct methods from data collected on a Syntex $P2_1$ four-circle diffractometer with Mo-K_α monochromatised radiation to $2\theta = 50°$; current R = 0·049. Within the OC–Ru–Ru–$SiMe_3$ chain Ru–Ru = 2·937(2) and Ru–Si = 2·456(4) Å, while the angle Ru–Ru–Si is 172·8(1)° with the silyl group bent away from the C_7-ring. The ruthenium–carbon distances of the C_7-ring [Ru(1)–C(2) = 2·38(1), Ru(1)–C(1) = 2·21(1), Ru(1)–C(7) = 2·23(1), Ru(1)–C(6) = 2·29(1), Ru(2)–C(2) = 2·90(1), Ru(2)–C(3) = 2·26(1), Ru(2)–C(4) = 2·19(1), and Ru(2)–C(5) = 2·30(1) Å] show that Ru(1) is effectively bonded to a diene system C(2), C(1), C(7), and C(6), whereas Ru(2) is bonded to an allyl grouping, C(3)–C(5). The interplanar angle between the diene and allyl fragments is 57°. The Ru(2)–C(2) distance is effectively non-bonding, but significantly Ru(1)–C(2) is the longest of the "bonded" distances. The overall situation therefore tends very slightly away from the idealised diene–allyl system (II) towards the symmetrical structure recently found in $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$.[2] The trimethylsilyl substituent in the ring occupies a position at one end of the allyl group but it does not necessarily follow that the other substituents R are similarly located in the solid state.

Formation of (II; R = $SiMe_3$) corresponds to transfer of a trimethylsilyl group from ruthenium to the ring. In contrast, reactions of (I) with 7-RC_7H_7 (R = CN, OBu^t) afford the parent complex (II; R = H), presumably *via* loss of Me_3SiR.

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[1] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559.

[2] R. Bau, J. C. Burt, S. A. R. Knox, R. M. Laine, R. P. Phillips, and F. G. A. Stone, preceding communication.