Silole-Metal Complexes: 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene and its Tricarbonylruthenium Complex; Synthesis and X-Ray Structure

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Summary The synthesis and structure of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadienetricarbonylruthenium are reported, along with the structure of the uncomplexed ligand.

Silole complexes of transition metals have been synthesized only recently.[1-3] We ourselves have prepared silole complexes of molybdenum, cobalt, iron, and ruthenium. For example, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (I) and dodecacarbonyltriruthenium react in toluene under reflux to form the yellow complex $\overline{\mathrm{CH{:}CPh{\cdot}SiMe_2{\cdot}CPh{:}C}}\mathrm{HRu(CO)_3}$ (II), m.p. 122 °C.

To date, there has been no information upon the geometry of the silole ring system. Accordingly, we have determined the crystal structures of (I) and (II) by *X*-ray diffraction. Thus, besides establishing the structure of an uncomplexed silole ring, this work also permits assessment of the changes in structure and bonding which occur when such a ring is bonded to a transition metal.

Crystal data: (I), $M = 262{\cdot}4$, orthorhombic, $a = 15{\cdot}669$, $b = 7{\cdot}500$, $c = 6{\cdot}548$ Å; $Z = 2$; space group $Pmn2_1$. (II), $M = 447{\cdot}5$, monoclinic, $a = 11{\cdot}112$, $b = 8{\cdot}013$, $c = 27{\cdot}455$ Å; $\beta = 97{\cdot}22°$, $Z = 8$; space group $I2/c$ (C^6_{2h}, No. 15). MoK_α *X*-rays, $\lambda = 0{\cdot}71069$ Å.

Both structures were solved by the heavy-atom method, using for (I) 828 and for (II) 3363 diffractometric intensity data. Full-matrix least-squares refinement led to $R = 0{\cdot}034$ for (I) and $0{\cdot}049$ for (II). In the Figure views are shown of the discrete molecules from which crystals of (I) and (II) are respectively built.

Molecules of (I) possess exact C_s symmetry. The mirror plane passes through the silicon atom and is normal to the plane of the silole ring. The bond lengths within this ring

[Si–C(1) 1·878(3), C(1)–C(2) 1·345(4), and C(2)–C(2′) 1·466(6) Å] are consistent with complete localization of the double bonds. The butadiene unit [C(1)C(2)C(2′)C(1′)] is exactly planar. The silicon atom is displaced from this plane by 0·08 Å, so that the SiC(1)C(1′)-butadiene dihedral angle is 3·7°. The phenyl rings are nearly coplanar with the butadiene unit, the small dihedral angle of 14° being sufficient to relieve the overcrowding between the *ortho* hydrogen atoms and those on C(2) and C(2′).

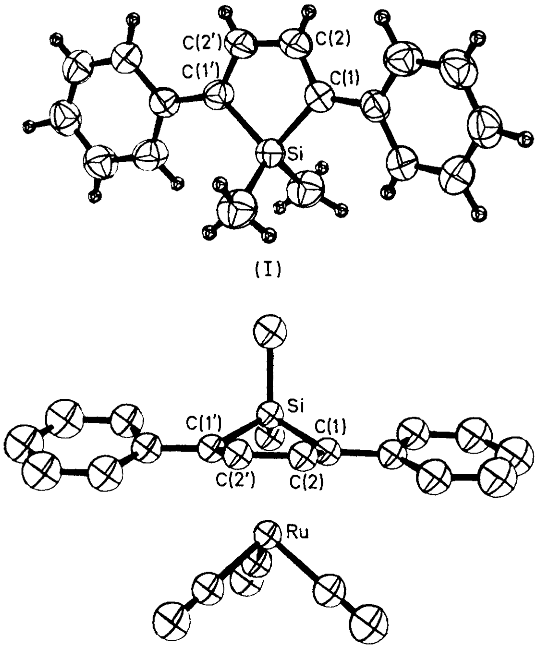

FIGURE. Perspective views of the molecules of (I) and (II).

Approximate C_s symmetry is retained in (II). The metal atom is π-bonded to the butadiene unit within the silole ring, with mean Ru–C(1) and Ru–C(2) bond lengths of 2·293(4) and 2·189(3) Å. Its co-ordination, which may be described as octahedral, with three facial sites occupied by carbonyl ligands, and a further three by C(1), C(1′), and the midpoint of the C(2)–C(2′) bond, bears a striking similarity to that of the ruthenium atom in [$(C_8H_8)Ru(CO)_3$].[4] The presence of the metal atom causes considerable perturbation of the bond lengths in the silole ring: C(1)–C(2) increases by 0·108(6) to 1·453(4), C(2)–C(2′) decreases by 0·060(9) to 1·406(7), whereas the mean Si–C(1) distance of 1·880(7) Å is unaltered.

There is one further major difference in geometry between the silole rings in (I) and (II). The SiC(1)C(1′)-butadiene dihedral angle in (II) has opened up to 32°, so that the silicon atom lies 0·72 Å from the butadiene plane on the side opposite to that of the metal atom. As a consequence, the Ru–Si distance is 2·992(2) Å. This excludes any possibility of normal bonding between these atoms, since the length of a Ru–Si covalent bond is known to be 2·43 Å.[5] In [(C_5H_5)-Co{$(CF_3)_4C_4PO{\cdot}OH$}] and [{$(CF_3)_4C_4SC_6F_5$}$Mn(CO)_3$], where again there is no direct bond between the metal and the ring hetero-atoms, the tetrahapto rings are also folded about the line through the terminal carbon atoms of the butadiene. The dihedral angle, respectively 32 and 31°,[6] agree well with the corresponding angle in (II). In all three molecules the non-bonded separation between the metal and the heteroatom appears surprisingly small, since subtraction of the van der Waals radius of the hetero-atom suggests that the contact radii of the metal atoms are in the range 0·8—1·0 Å.

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