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SYNTHESIS OF SILYL RUTHENIUM COMPLEXES, $RuH_3(SiR_3)(PPh_3)_3$

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Hydrosilanes react with $RuH_2(PPh_3)_4$ to give $RuH_3(SiR_3)(PPh_3)_3$, where R_3 = Et_3, $EtMe_2$, $PhMe_2$, $(EtO)_3$, $Et_2.H$, PhMe.H, $Ph_2.H$, $Ph.H_2$ and cyclo-$C_6H_{11}.H_2$. These apparently seven-coordinate silyl ruthenium(IV) complexes were characterized by i.r. and n.m.r. spectra.

The ruthenium-silicon bond has been reported [1] to be formed by the reaction of a triorganohydrosilane with dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$. Oxidative addition of hydrosilanes to phosphine complexes of the group VIII element such as nickel[2a], cobalt[2b], rhodium[2c], palladium[2d], iridium[2e], and platinum[2f] furnished an alternative method of preparing silyl-metal compounds. In all the cases the coordination numbers of the silyl complexes isolated were less than six and we now report the first synthesis of apparently seven-coordinate silyl complexes on the reaction of tetrakis(triphenylphosphine)ruthenium dihydride[3] with a variety of hydrosilanes.

$$RuH_2(PPh_3)_4 + R_3SiH \xrightarrow{-PPh_3} RuH_3(SiR_3)(PPh_3)_3$$

R_3= Et_3, $EtMe_2$, $PhMe_2$, $(EtO)_3$, $Et_2.H$, PhMe.H, $Ph_2.H$, $Ph.H_2$, and cyclo-$C_6H_{11}.H_2$.

In a typical example, $RuH_2(PPh_3)_4$ (0.30g) was sealed in an evacuated tube with methylphenylsilane(2 ml) and the tube was kept at room temperature for 3 hr. Evolution of any gas or heat was not observed throughout the reaction. A white solid product(0.21g) formed by adding 10 ml of n-hexane to the mixture was filtered off, washed with n-hexane repeatedly and dried in vacuo. The compound was characterized as $RuH_3(SiHMePh)(PPh_3)_3$, mp 110°C(decomp.), yield 80%, IR(KBr disk) : ν_{Si-H}, 2120 and 2000 cm^{-1}; ν_{Ru-H}, 1980 and 1948 cm^{-1}; $\nu_{C-H\ of\ SiMe}$, 2975 and 2925 cm^{-1}. Anal. Found: C, 72.1; H, 5.8%. Calcd for $C_{61}H_{57}P_3SiRu$: C, 72.4; H, 5.7%.

With other hydrosilanes such as Et_3SiH, $EtMe_2SiH$, $PhMe_2SiH$, $(EtO)_3SiH$, Et_2SiH_2, Ph_2SiH_2, $PhSiH_3$, and cyclo-$C_6H_{11}SiH_3$, the respective silyl ruthenium complex was obtained(61-94%). All the complexes gave satisfactory analyses and are stable in the solid phase, but in organic solvent gradually decomposed with changing color

from white to violet.

The infrared spectra of solid complexes(KBr disk) showed two bands due to ν_{Si-H}, i.e., an absorption at 2135-2030 cm^{-1} which presumably depends on crystalline forms and was not detectable in Nujol mull, and one at 2060-1996 cm^{-1}(sharp). The presence of ν_{Ru-H} at 2020-1880 cm^{-1}(strong or medium multiplets) was also indicated in the spectra. The assignment of Ru-H and Si-H stretching absorption bands was confirmed by the infrared measurements of $RuH_2D(SiDPh_2)(PPh_3)_3$, which exhibited characteristic absorption bands at 1970(broad, Ru-H), 1920(broad, Ru-H), 1472(sharp, Si-D), and 1418(sharp, Ru-D) cm^{-1}.

Immediate n.m.r. measurement in C_6D_6 afforded legitimate support for the seven-coordinate structure of the silyl ruthenium complexes. For example, the spectrum of $RuH_3[Si(OEt)_3](PPh_3)_3$ showed multiplet signals at τ 2.4-3.7(Phenyl protons of triphenylphosphine, 45H), a quartet at τ 6.2(methylene protons of triethylsilyl group, 6H), a triplet at τ 8.9(methyl protons of triethylsilyl group, 9H) and, in the high field, a poorly resolved signal at τ 20.1(Ru-H, 3H). Integration of the high field resonance of Ru-H confirmed the presence of three ruthenium hydride hydrogens in the complex.

Treatment of $RuH_3(SiMe_2Ph)(PPh_3)_3$ with excess carbon disulfide at room temperature gave a known compound, $Ru(S_2CH)_2(PPh_3)_2$[4], red orange crystals, mp 178-181°C, which decomposed above melting point with evolution of CS_2(lit. 196-200°C decomp.). Thus, this reaction can be elucidated in terms of the following equation:

$$RuH_3(SiMe_2Ph)(PPh_3)_3 \xrightarrow{-PhMe_2SiH} RuH_2(PPh_3)_3 \xrightarrow[2CS_2]{-PPh_3} Ru(S_2CH)_2(PPh_3)_2$$

These interesting apparently seven-coordinate silyl ruthenium(IV) complexes are the equivalence of $RuH_4(PPh_3)_3$ reported as a product of hydrogenation of $RuH_2(PPh_3)_4$[3] or $RuH_2(N_2)(PPh_3)_3$[5].

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