



Activation of the Si-H bond of Et₂SiH₂ on photochemical reaction with W(CO)₆: spectroscopic characterization of intermediate W–Si compounds and the revisited crystal structure of the bis{(μ-η²-hydridodiethylsilyl)tetracarbonyltungsten(I)} complex [W(μ-η²-H-SiEt₂)(CO)₄]₂.

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Streszczenie

The photochemical reaction of W(CO)₆ with diethylsilane has been used to generate new tungsten–silicon compounds varying in stability. The initially formed η²-silane intermediate complex [W(CO)₅(η²-H-SiHEt₂)], characterized by two equal-intensity doublets with ²J_{H-H} = 10 Hz at δ = 5.10 (¹J_{Si-H} = 217 Hz) and δ = -8.05 (¹J_{W-H} = 38 Hz, ¹J_{Si-H} = 93 Hz), was detected by the ¹H NMR spectroscopy (methylcyclohexane-*d*₁₄, -10 °C). The η²-silane complex was converted in the dark to give more stable species. One of them was characterized by two equal-intensity proton signals observed as doublets with ²J_{H-H} = 5.2 Hz at δ = -8.25 and -10.39 ppm. The singlet proton resonance at δ = -9.31 flanked by ²⁹Si and ¹⁸³W satellites (¹J_{Si-H} = 43 Hz, ²J_{Si-H} = 34 Hz, ¹J_{W-H} = 40 Hz) was assigned to the agostic proton of the W(η²-H-SiEt₂) group in the most stable compound isolated from the photochemical reaction products in crystalline form. The molecular structure of the bis{(μ-η²-hydridodiethylsilyl)tetracarbonyltungsten(I)} complex [W(μ-η²-H-SiEt₂)(CO)₄]₂ was established by single-crystal X-ray diffraction studies. The tungsten hydride observed in the ¹H NMR spectrum at δ = -9.31 was located in the structure at a chemically reasonable position between the W and Si atoms of the W–Si bond of the bridging silyl ligand. The reactivity of photochemically generated W–Si compounds towards norbornene, cyclopentene, diphenylacetylene, acetone, and water was studied. As was observed by IR and NMR spectroscopy, the η²-silane ligand in the complex [W(CO)₅(η²-H-SiHEt₂)] is very easily replaced by an η²-olefin or η²-alkyne ligand.

Słowa kluczowe

Tungsten, Silicon, Si ligands, Agostic interaction, Hydride ligands

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