

Alternativ-Liganden XXXVIII. [1]

Neue Versuche zur Synthese von Pd(0)- und Pt(0)-Komplexen des Tripod-Phosphanliganden $\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$

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Further Attempts to Synthesize Pd(0) and Pt(0) Complexes with the Tripod Phosphane Ligand $\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$

Joseph Grobe^a, Kai Lütke-Brochtrup^a, Bernt Krebs^a, Mechtild Läge^a,
Hans-Hermann Niemeyer^a und Ernst-Ulrich Würthwein^b

^a Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität
Münster, Corrensstraße 36, D-48149 Münster, Deutschland

^b Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Corrensstraße 40,
D-48149 Münster, Deutschland

Sonderdruckanforderungen an Prof. Dr. J. Grobe. E-mail: grobe@uni-muenster.de

Z. Naturforsch. **2007**, 62b, 55 – 65; eingegangen am 17. August 2006

Professor Karl Otto Christe zum 70. Geburtstag gewidmet

The tripod phosphane ligand $\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (**1**) has been prepared again and attempts to generate $\text{F}_3\text{CSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (**2**) were undertaken for the preparation of transition metal cage compounds of the type $\text{A}(\text{CCP})_3\text{M}$ or $\text{A}(\text{CCP})_3\text{M-L}$ ($\text{A} = \text{FSi}, \text{F}_3\text{CSi}$). The photochemical addition of dimethylphosphane to trifluoromethyl-trivinylsilane, however, gave **1** instead of the expected CF_3Si -tripod ligand **2**, obviously due to difluorocarbene elimination. **1** was used to prepare the chromium carbonyl derivative $(\text{CO})_3\text{Cr}[(\text{Me}_2\text{PCH}_2\text{CH}_2)_3\text{SiF}]$ (**3**) from $\text{Cr}(\text{CO})_3\text{CHT}$, and **3** was characterized by NMR and IR spectroscopy. The novel complex $\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3\text{Pd}$ (**4**) and its PPh_3 derivative $[\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3\text{Pd}]\text{PPh}_3$ (**5**) have been obtained by reacting **1** with $\text{Pd}(\text{PPh}_3)_4$ and were characterized by NMR (**4**) and X-ray diffraction (**5**). The data prove the expected $\text{Pd} \rightarrow \text{Si}$ interaction by characteristic coordination shifts and a Pd-Si distance of 3.875 Å which is smaller than the Ni-Si distance in the corresponding nickel compound (3.92 Å). The preparation of the analogous platinum complex from the precursors $\text{Pt}(\text{PPh}_3)_4$, $\text{Pt}(\text{C}_7\text{H}_{10})_3$, or $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ failed, whereas the reaction of **1** with $\text{Pt}(\text{PET}_3)_4$ was successful, but surprisingly led to the trinuclear complex $[\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3\text{Pt}]_3(\text{PMe}_2\text{CH}_2\text{CH}_2)_3\text{SiF}$ (**6**) with three cages of type **4** and an additional ligand **1** as a bridging unit. Complex **6** was isolated and characterized spectroscopically. Quantum chemical calculations have been used to elucidate the coordination geometry expected for **4**, **5** and the corresponding platinum cage **4'** in **6**. The calculations support the structure of **5** within the expected limitations of the experimental and theoretical methods and – in spite of the extremely soft coordination sphere of the studied cages – are in accord with the spectroscopic results.

Key words: Phosphane Ligands, Silicon Acceptor Centres, Chromium(0), Palladium(0),
Platinum(0) Complexes, Through-Cage-Bonding