Direct Hydride/Silyl Exchange — Synthesis and X-ray Study of the Bis(silyl) Complex [Cp₂NbH(SiCl₃)₂]

Konstantin Yu. Dorogov,^[a] Andrei V. Churakov,^[b] Lyudmila G. Kuzmina,^[b] Judith A. K. Howard,^[c] and Georgii I. Nikonov^{*[a]}

Keywords: Hydride ligands / Niobium / Si ligands / X-ray diffraction

Niobocene trihydride reacts directly with the chlorosilanes $SiCl_2R'R''$ (R', R'' = Me, Ph) and $SiCl_3Me$ to give the dihydridomonosilyl derivatives $[Cp_2Nb(H)_2(SiCl_nR_{3-n})]$ (n = 1, 2), whereas the analogous reaction with $SiCl_4$ affords $[Cp_2Nb-$

Introduction

Silvl transition metal complexes are of great current interest as intermediates in silane dehydrogenative coupling reactions^[1-3] and various hydrosilylation reactions.^[4-6] It is therefore not surprising that a large number of silvl complexes have been prepared by oxidative addition of the H-Si bond.^[7,8] We have been developing an alternative approach to main-group element substituted transition metal complexes L_nM-ER_m based on *direct interaction* of a basic transition metal hydride with the main-group element halides.^[9-18] The niobocene trihydride Cp₂NbH₃ was a substrate of choice to test such reactivity because it possesses basic metal-hydride bonds but lacks any lone pair or a vacant coordination site, thus eliminating competing reaction pathways.^[17] This approach works very well for the bond construction between metal atoms and group-5 (P, As, Sb, Bi)^[9-15] and heavy group-4 (Ge, Sn, Pb)^[16-18] atoms, but no such study has been done for silicon so far. In the literature there are only two reports dealing with the reactions of metal hydrides with halosilanes; both consider the reactivity of electron-rich metal centers bearing metal-centered lone pairs. Lemke et al. have recently reported that the reaction between the basic d⁶ ruthenium complex [CpRuH(PMe₃)₂] and chlorosilanes gives silvl derivatives by an anticipated *chloridelmetal exchange* (Scheme 1).^[19,20] Jutzi et al. have reported a similar reaction with the d² molybdenum complex [Cp₂MoH₂], resulting in the silyl hydride derivatives [Cp₂MoH(SiR₃)], although no mechanism was proposed.^[21] There is also a practical aspect that motivated us to study the reactivity of metal-hydride bonds towards chlorosilanes: Chlorosilanes are precursors for industrially important silicones, but only a few are available by direct synthesis.^[22] Metal-catalyzed hydrosilylation of unsaturated hydrocarbons,^[4] which circumvents this problem, is believed to proceed by H–Si bond oxidative addition to metal atoms to generate metal hydride intermediates.^[23,24] Therefore one can expect that any interaction of the resultant M–H bond with an excess of chlorosilane should have a significant impact on the overall process of hydrosilylation, for example by giving rise to side-products or deactivation of the catalyst.

 $(H)_2(SiCl_3)$] and the bis(silvl) complex $[Cp_2NbH(SiCl_3)_2]_1$

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim,

whose X-ray structure was determined.

Germany, 2004)



Scheme 1

Here we report our investigation of the reactions of niobocene trihydride $[Cp_2NbH_3]$ (1) with a series of chlorosilanes and present evidence for both a single and double silyl/hydride exchange. This synthetic approach has a potential for the preparation of silyl complexes not accessible by the silane oxidative addition route.

Results and Discussion

Synthesis of Mono- and Bis(silyl) Derivatives

The addition of dichlorosilanes $SiCl_2R'R''$ (R', R'' = Me, Ph) to 1 in the presence of NEt₃ as an HCl sponge

 [[]a] Chemistry Department, Moscow State University, Vorob'evy Gory, 119992 Moscow, Russia Fax: (internat.) + 7-095-932-8846 E-mail: nikonov@org.chem.msu.su

Institute of General and Inorganic Chemistry RAS Leninskii Prosp. 31, 119991 Moscow, Russia E-mail: kuzmina@igic.ras.ru

[[]c] Chemistry Department, University of Durham South Road, Durham DH1 3LE, UK E-mail: j.a.k.howard@durham.ac.uk

gives the mono(silyl) complexes 2-4 in moderate to high yields. Compounds 2-4 are produced as an almost equimolar mixture of the central (a) and lateral (b) isomers, the latter being stabilized by nonclassical interligand hypervalent interactions (IHI) between the hydrido and silvl ligands.^[25] The analogous reaction of 1 with the trichlorosilane SiCl₃Me affords a mixture, the main component of which is the lateral isomer [Cp₂Nb(H)₂(SiMeCl₂)] (5b) together with a small amount of 5a and the monochloride [Cp₂NbCl]₂.^[26] In contrast, the reaction of HSiCl₂Me with 1 does not give the expected complex [Cp₂Nb(H)₂-(HSiClMe)]. Instead, **5b** is formed in high yield as an Si-H addition product (this reaction apparently proceeds by conventional H₂ elimination to give the transient Cp₂NbH, amenable to oxidative addition^[27,28]). Treatment of pure **5b** with SiCl₃Me results in a partial isomerization to 5a, but 5b remains the main component of the mixture (65%). Complexes 2-4 were prepared independently by oxidative addition of silanes to 1 according to established procedures.^[25] Reaction of 1 with bulkier (SiCl₂Et₂, SiCl₂iPr₂) or less acidic [SiCl(OMe)Me2, SiClMe3] silanes does not give any significant amount of [Cp₂Nb(H)₂(SiR₃)]. In this case, the reaction is accompanied by dihydrogen evolution and formation of a mixture of unidentified products, the main component of which is insoluble in non-polar solvents. One of the target complexes, $[Cp_2Nb(H)_2(SiCliPr_2)]$ (6a), was obtained by the reaction of Cp_2NbBH_4 with HSiCliPr₂ in the presence of NEt₃. Only the central isomer was obtained, the structure of which was determined by an X-ray diffraction study (vide infra).



Reaction of 1 with an excess of SiCl₄ is remarkable in that, in addition to the central and lateral mono(silyl) compounds $[Cp_2Nb(H)_2(SiCl_3)]$ (7a,b), the major product (60%) is the bis(silyl) complex $[Cp_2NbH(SiCl_3)_2]$ (8), which is formed by an unprecedented double hydride/silyl exchange. This compound was isolated from the more soluble 7a and 7b by washing the mixture with diethyl ether. The ¹H NMR spectrum of 8 shows the hydride resonance at $\delta = -3.29$ ppm, about 2 ppm downfield from the bis(silyl)-niobocene complexes with interligand hypervalent interactions (IHI),^[25] suggesting a significantly reduced IHI. An X-ray diffraction study further confirmed this conclusion (vide infra). Compounds 7a and 7b were obtained independently by heating 1 with HSiCl₃ at 60 °C.

An important conclusion of this work is that the reactions of halosilanes with basic transition metal hydrides do not necessarily involve halogen/metal substitution/deprotonation steps because niobocene trihydride does not possess any metal-based lone-pair. Moreover, this molecule does not possess a vacant coordination site either, and the reaction occurs readily at temperatures below 25 °C, where dihydrogen elimination from pure [Cp₂NbH₃] does not occur at any significant rate in the absence of silanes. Another thinkable pathway to 2-4 and 7 based on deprotonation of [Cp₂NbH₃] by an amine, followed by nucleophilic substitution of the chloride of the silane can also be reliably ruled out, since it has previously been shown that amines cannot deprotonate [Cp₂NbH₃].^[17] The only reasonable option we are left with is that the reaction occurs by precoordination of the σ^* -Lewis acid Cl-SiR₃ to the basic hydride center, forming a hypervalent M−H→SiR₃−Cl structure 9 (Scheme 2). Bridge formation is known to acidify the M-H-M' bond drastically,^[29] so that the hydride ion can now be abstracted from the complex 10 by a base as weak as an amine, affording eventually the silvlated product. Several observations support this view. First, the hydrido ligands in 1 are Lewis bases of moderate strength (basicity factor $E_i = 0.93$.^[30] Second, it is now recognized that even in the presence of metal-centered lone-pairs, the hydrido ligands are the kinetic sites for protonation,^[31,32] and thus they are expected to be amenable for the interaction with other Lewis acids, too. It should be noted that Lewis acidity of silanes has precedents, for example, in the formation of hypervalent structures like [H₂SiPh₃]^{-.[33]} Third, the coordination of transition metal centers to M-H bonds is well established.^[34] It is therefore reasonable to assume that this direct silyl/hydride exchange mechanism is general even for d^n (n > 0) systems, like the Ru and Mo complexes cited above. Complications can arise from the substitution of the silane in 10 by the chloride anion, leading (possibly) to the transient [Cp₂Nb(H)₂Cl] and eventually to [Cp₂NbCl]₂ (as in the reaction with SiCl₃Me), and, in the case of bulkier or less acidic silanes [such as SiCl₂Et₂, SiCl₂iPr₂, SiCl-(OMe)Me2 and SiClMe3], when Lewis acid induced dihydrogen elimination^[35] occurs faster than deprotonation.



Scheme 2

772 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FULL PAPER

X-ray Studies

The molecular structure of 8 is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The Nb-Si bonds for the two chemically equivalent silvl groups are very short [2.5597(5) and 2.5776(5) Å] due to the presence of three electron-withdrawing chlorine substituents at the silicon atom. The Si-Cl bond lengths fall within a narrow range [2.0835-2.0989(7) Å] without any significant difference between the chlorine atoms in and out of the niobocene bisectral plane. This fact, and the large Si-Nb-Si bond angle of 109.61(2)°, close to the values in classical bis(silyl) systems^[25,27,28,36] and about 5° larger than in complexes with IHI, suggests the absence of any significant interligand Si-H interactions. This open Si-Nb-Si bond angle results in long Si-H contacts of 2.14(3) and 2.11(3) Å, about 0.1 Å longer than in complexes with IHI. This unexpected lack of Si-H interactions is either due to the low basicity of the Nb-H bond stemming from the



Figure 1. Molecular structure of $[Cp_2NbH(SiCl_3)_2]$ (8); displacement ellipsoids are shown at the 50% probability level; cyclopentadienyl hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for 8

Nb-Si(1)	2.5776(5)	Nb-Si(2)	2.5597(5)
Si(1) - Cl(1)	2.0984(7)	Si(1)-Cl(2)	2.0835(7)
Si(1) - Cl(3)	2.0836(7)	Si(2)-Cl(4)	2.0841(7)
Si(2) - Cl(5)	2.0926(6)	Si(2)-Cl(6)	2.0988(7)
Nb-H	1.79(3)	Si(1)-H	2.14(3)
Si(2)-H	2.11(3)		
Si(2) - Nb - Si(1)	109.61(2)	H-Si(1)-Nb	43.4(8)
Cl(2) - Si(1) - Cl(1)	101.73(3)	H-Si(2)-Nb	43.8(8)
Cl(3) - Si(1) - Cl(1)	101.69(3)	Cl(2) - Si(1) - Cl(3)	101.69(3)
Cl(1)-Si(1)-Nb	116.57(3)	Cl(2)-Si(1)-Nb	116.55(3)
Cl(4) - Si(2) - Nb	116.67(2)	Cl(3)-Si(1)-Nb	116.17(3)
Cl(5)-Si(2)-Nb	116.50(3)	Cl(4) - Si(2) - Cl(5)	101.92(3)
Cl(5) - Si(2) - Cl(6)	100.74(3)	Cl(4) - Si(2) - Cl(6)	101.77(3)
Cl(6)-Si(2)-Nb	116.67(2)		

presence of a large number of electron-withdrawing chlorine substituents on both the silyl centers, or due to hyperconjugation between the in-plane $(Si-Cl)^*$ antibonding orbital with the out-of-plane chlorine lone pairs of electrons. It should be emphasised that high basicity of the hydride ligand is a prerequisite for this type of interligand interaction tooccur because IHI stems from the interaction of an M–H bonding orbital with the $(Si-X)^*$ antibonding orbital.^[25]



Figure 2. Molecular structure of $[Cp_2Nb(H)_2(SiCliPr_2)]$ (6); displacement ellipsoids are shown at the 50% probability level; all hydrogens apart from hydrides are omitted for clarity

The molecular structure of **6** is shown in Figure 2, and selected bond lengths and angles are given in Table 2. The silyl group is located in the central position in the niobocene bisectral plane, and two hydrides were found in the lateral positions with Nb–H distances of 1.65(3) Å. In spite of the presence of a chlorine substituent at silicon, the Nb–Si distance of 2.6496(7) Å is similar to the Nb–Si bond length in related alkyl- and aryl-substituted silyls.^[25,27,28,36] Electron-withdrawing substituents X are known to diminish the M–Si bond lengths^[37] due to the operation of Bent's rule.^[38] Another exceptional feature in **6** is the long Si–Cl bond length of 2.1694(9) Å, which can be compared with the range 2.094–2.149 Å found in classical L_nMSiR₂Cl complexes (R = alkyl, aryl).^[39–43] Apparently, these struc-

Table 2. Selected bond lengths [Å] and angles [°] for 6

tural abnormalities are caused by the steric bulkiness of the two isopropyl groups at the silicon atom. Indeed, in the bulky silyl complex *fac*-[Ir(H)₂(Si*t*Bu₂Cl)(PMe₃)₃] both the Si–Cl bond of 2.187(4) Å and the Ir–Si bond of 2.392(3) Å are unusually long.^[44] In the related complex [Ir(H)₂{Si(H)Cl(C₆H₃-Mes₂-2,6)}(PEt₃)₃], with one very bulky substituent at the silicon atom, the Si–Cl bond length is 2.148(3) Å.^[45]

Conclusion

This work has shown that halosilanes can interact with basic metal hydrides in the absence of metal-centered lone pairs, leading (depending on the silane) either to silyl derivatives or decomposition products. This reaction suggests new opportunities for the synthesis of silyl transition metal complexes and must be taken into account as a feasible (undesired) route during transition metal catalyzed hydrosilylation reactions of halosilanes.

Experimental Section

General Remarks: All manipulations were carried out using conventional Schlenk high vacuum and argon techniques. Solvents were dried with sodium or sodium benzophenone ketyl and distilled into the reaction vessel by high-vacuum gas-phase transfer. NMR spectra were recorded with a Varian VXR-400 spectrometer (¹H, 400 MHz; ¹³C, 100.4 MHz). IR spectra were obtained in Nujol with an FTIR Perkin–Elmer 1600 series spectrometer. Silanes were purchased from Aldrich.

General Procedure for the Preparation of [Cp₂Nb(H)₂(SiClR₂)]: NEt₃ (2 mL, 6-7 equiv.) and 0.5 mL (ca. 2 equiv.) of the dichlorosilane were added to a solution of 1 (2-3 mmol) in diethyl ether (20 mL). A white voluminous precipitate formed immediately. The mixture was stirred for 3 h during which time a light-brown color developed. The solution was filtered and the residue washed with diethyl ether (10 mL). Volatiles were removed from the combined fractions in vacuo to give a brown solid. The material was recrystallized from a saturated diethyl ether solution at -26 °C to give the product as a mixture of two isomers. Yields: 29% (2a,b), 83% (3a,b), 35% (4a,b). 2a,b: Characterization data as reported previously.^[25] **3a:** ¹H NMR ([D₆]benzene): $\delta = -4.06$ (s, 2 H, Nb-H), 4.53 (s, 10 H, Cp), 7.21–7.01 (Ph of **3a** and **3b**), 8.14 (d, $J_{\rm H,H}$ = 7.1 Hz, 4 H, Ph) ppm. ¹³C NMR ([D₆]benzene): $\delta = 148.39, 134.72$ (Ph), 89.62 (s, Cp) ppm. **3b:** ¹H NMR ([D₆]benzene): $\delta = -3.93$ (s, 1 H, Nb-H), -3.48 (s, 1 H, Nb-H), 4.62 (s, 10 H, Cp), 7.21-7.01 (Ph of **3a** and **3b**), 8.26 (d, $J_{H,H} = 7.4$ Hz, 4 H, Ph) ppm. ¹³C NMR ([D₆]benzene): $\delta = 145.78, 134.60$ (Ph), 90.28 (s, Cp) ppm. C₂₂H₂₂ClNbSi (442.9): calcd. C 59.67, H 5.01; found C 59.34; H 5.14. 4a,b: IR: v(Nb-H) = 1725, 1694 cm⁻¹. 4a: ¹H NMR ($[D_6]$ benzene): $\delta = -4.15$ (s, 2 H, Nb-H), 0.57 (s, 3 H, Me), 4.53 (s, 10 H, Cp), 7.20–7.02 (Ph of **4a** and **4b**), 8.26 (d, $J_{H,H}$ = 7.7 Hz, 4 H, Ph) ppm. ¹³C NMR ([D₆]benzene): $\delta = 89.15$ (s, Cp) ppm. **4b:** ¹H NMR ([D₆]benzene): $\delta = -4.50$ (s, 1 H, Nb-H), -4.24 (s, 1 H, Nb-H), 0.91 (s, 3 H, Me), 4.50 (s, 5 H, Cp), 4.73 (s, 5 H, Cp), 7.20–7.02 (Ph of 4a and 4b), 8.15 (d, $J_{H,H} = 7.2$ Hz, 4 H, Ph) ppm. ¹³C NMR ([D₆]benzene): $\delta = 90.17$ (s, Cp), 89.23 (s, Cp) ppm. C₁₇H₂₀ClNbSi (380.8): calcd. C 53.68, H 5.29; found C 53.47; H 4.90.

Preparation of [Cp₂Nb(H)₂(Si*i***Pr₂Cl)] (6): NEt₃ (2 mL) followed by HSi***i***Pr₂Cl (0.32 mL, 1.89 mmol) was added to a solution of Cp₂NbBH₄ (0.45 g, 1.89 mmol) in 40 mL of toluene. The mixture was stirred overnight. All volatiles were removed in vacuo and the residue was extracted with diethyl ether, filtered and concentrated under reduced vacuum until a yellow compound started to form. Keeping the mixture at -20 °C afforded 6** in the form of yellow crystals. The cold solution was further concentrated and decanted. Yield: 0.511 g (1.36 mmol, 72%). IR: v(Nb-H) = 1736 cm⁻¹. ¹H NMR ([D₆]benzene): $\delta = -4.64$ (s, 2 H, Nb-H), 1.35 (d, $J_{H,H} =$ 4.5 Hz, 6 H, Me), 1.32 (m, 2, CH), 1.19 (d, $J_{H,H} = 6.0$ Hz, 6 H, Me), 4.66 (s, 10 H, Cp) ppm. ¹³C NMR ([D₆]benzene): $\delta = 88.5$ (s, Cp), 23.2 (CH), 18.9 (Me), 18.8 (Me) ppm. C₁₆H₂₆ClNbSi (374.8): calcd. C 51.27, H 6.99; found C 51.03; H 7.08.

Reactions of 1 with SiCl₄. Reaction a: NEt₃ (1.2 mL, 8.6 mmol, 2.5 equiv.) and SiCl₄ (0.42 mL, 3.66 mmol) were added to a solution of 1 (0.773 g, 3.42 mmol) in toluene (20 mL). A white precipitate formed immediately and the solution became amber, accompanied by gas evolution. The mixture was stirred overnight. The mixture was filtered and the residue washed with toluene (2×20 mL). Volatiles were removed from the combined fractions in vacuo to give a red crystalline substance. This was washed with diethyl ether (3 \times 15 mL) and the volatiles were removed from the combined fractions affording a light amber crystalline solid, which according to the ¹H NMR spectrum was a mixture of 8, 7a and 7b, along with some minor by-products. Yield: 0.361 g. The pink residue (0.100 g, 0.203 mmol, 6%) from the toluene-soluble fraction left after washing with diethyl ether was pure 8. Reaction b: Compound 1 (0.77 g, 3.41 mmol) was added to a solution of NEt₃ (1.1 mL, 7.9 mmol, 1.1 equiv.) and SiCl₄ (0.8 mL, 7.0 mmol) in toluene (20 mL). Within 5 min, the solution became red-brown, accompanied by evolution of a gas that was not condensable by liquid nitrogen (apparently dihydrogen). After 0.5 h of stirring, a precipitate had formed. The mixture was then stirred overnight. The mixture was filtered and the residue washed with toluene (20 mL). The volatiles were removed from the combined fractions in vacuo to give an amber crystalline substance which, according to its ¹H NMR spectrum, was 8 along with a small amount of 7a and 7b. This material was recrystallized from diethyl ether. Yield: 0.21 g (0.43 mmol, 12%). 8: IR: $v(Nb-H) = 1694 \text{ cm}^{-1}$. ¹H NMR ([D₆]benzene): $\delta =$ -3.29 (br. s, 1 H, Nb-H). 4.77 (s, 10 H, Cp) ppm. ¹³C NMR $([D_6]benzene): \delta = 96.6$ (s, Cp) ppm. $C_{10}H_{11}Cl_6NbSi_2$ (492.98): calcd. C 24.36, H 2.25; found C 24.20, H 2.60. 7a: IR: v(Nb-H) = 1716 cm⁻¹. ¹H NMR ([D₆]benzene): $\delta = -3.86$ (s, 2 H, Nb-H), 4.65 (s, 10 H, Cp) ppm. ¹³C NMR ([D₆]benzene): $\delta = 90.4$ ppm. 7b: IR: $v(Nb-H) = 1766 \text{ cm}^{-1}$. ¹H NMR ([D₆]benzene): $\delta = -3.81$ (s, 1 H, Nb-H), -3.69 (s, 1 H, Nb-H), 4.68 (s, 10 H, Cp) ppm. ¹³C NMR ([D₆]benzene): $\delta = 92.2$ ppm. C₁₀H₁₂Cl₃NbSi (359.58): calcd. C 33.41, H 3.36; found C 32.95, H 3.21.

X-ray Crystallographic Study. Crystal Data for 6: $C_{16}H_{26}$ ClSiNb, $M_r = 374.82$, a = 9.32040(10), b = 11.8553(2), c = 15.60840(10)Å, $\beta = 99.54^{\circ}$, V = 1700.82(4) Å³, Z = 4, d = 1.464 g cm⁻³, monoclinic, $P2_1/n$. Data collection: Bruker Smart three-circle diffractometer with CCD area detector with Mo- K_a radiation and graphite monochromator, μ (Mo- K_a) = 0.921 mm⁻¹, T = 120(2)°C, data-collection mode, $2.17^{\circ} < \Theta < 26.99^{\circ}$, 3706 reflections measured, 3041 symmetry-independent reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by fullmatrix least-squares procedures with anisotropic approximation for all non-hydrogen atoms, using the SHELXTL software.^[46] The hydrogen atoms were found from difference maps and refined isotropically, reflection/parameter ratio in the final refinement was 13.4, $R_1 = 0.0290$, $wR_2 = 0.0578$ and GOF = 1.100. Crystal Data for 8: $C_{10}H_{11}Cl_6Si_2Nb$, $M_r = 492.98$, a = 9.1658(2), b = 14.3502(4), c = 13.3894(4) Å, $\beta = 99.620(1)^{\circ}$, V = 1736.36(8) Å³, Z = 4, d =1.886 g cm⁻³, monoclinic, $P2_1/n$. Data collection: Bruker Smart three-circle diffractometer with CCD area detector with Mo- K_{α} radiation and graphite monochromator, μ (Mo- K_{α}) = 1.737 mm⁻¹, crystal size $0.30 \times 0.30 \times 0.08$ mm, T = 120(2) °C, data-collection mode, $2.66^{\circ} < \Theta < 30.15^{\circ}$, 3984 reflections measured, 3678 symmetry-independent reflections with $I > 2\sigma(I)$, multi-scan absorption correction with maximum and minimum transmission equal to 0.8735 and 0.6238, respectively. The structure was solved by direct methods and refined by full-matrix least-squares procedures with anisotropic approximation for all non-hydrogen atoms, using SHELXTL software.^[46] The hydrogen atoms were found from difference maps and refined isotropically, reflection/parameter ratio in the final refinement was 18.4, $R_1 = 0.0226$, $wR_2 = 0.0575$ and GOF = 1.041. CCDC-219856 (6) and -190915 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Support from the Russian Foundation for Basic Research for GIN (grant no. 00-03-32850) and LGK (grant no. 01-03-32474) is gratefully acknowledged. A. V. C. thanks the Royal Society of Chemistry for an RSC Journal Grant for International Authors.

- [1] J. Y. Corey, in Advances in Silicon Chemistry (Ed.: G. Larson), JAI Press, Greenwich, CT, 1991, vol. 1, p.327.
- ^[2] T. D. Tilley, Acc. Chem. Res. **1993**, 26, 22.
- [3] F. Gauvin, J. F. Harrod, H. G. Woo, J. Organomet. Chem. 1998, 42, 363.
- [4] I. Ogima, in *The Chemistry of Organic Compounds* (Eds.: S. Patai, Z. Rapport), Wiley, New York, **1989**, chapter 25.
- [5] P.-F. Fu, L. Brard, Y. Li, T. J. Marks, J. Am. Chem. Soc. 1995, 117, 7157.
- [6] M. B. Carter, B. Schiott, A. Butierrez, S. L. Buchwald, J. Am. Chem. Soc. 1994, 116, 11667.
- [7] J. Y. Corey, J. Braddock-Wilking, Chem. Rev. 1999, 99, 175.
- ^[8] T. D. Tilley, in *The Chemistry of Organosilicon Compounds* (Eds.: S. Patai, Z. Rapport), Wiley, New York, **1989**, chapter 24.
- [9] G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, Organometallics 1994, 13, 3127.
- [10] G. I. Nikonov, L. G. Kuzmina, P. Mountford, D. A. Lemenovskii, Organometallics 1995, 14, 3588.
- [11] G. I. Nikonov, K. Harms, J. Lorberth, D. A. Lemenovskii, *Inorg. Chem.* **1995**, 34, 2461.
- [12] G. I. Nikonov, D. A. Lemenovskii, J. Lorberth, *Polyhedron* 1996, 15, 1565.
- ^[13] G. I. Nikonov, A. J. Blake, J. Lorberth, D. A. Lemenovskii, S. Wocadlo, J. Organomet. Chem. 1997, 547, 235.
- ^[14] G. I. Nikonov, L. G. Kuzmina, Yu. K. Grishin, D. A. Lemenovskii, N. B. Kazennova, J. Organomet. Chem. 1997, 547, 183.
- ^[15] G. I. Nikonov, L. G. Kuzmina, J. A. K. Howard, *Organometallics* **1997**, *16*, 3723.

- ^[16] G. I. Nikonov, E. V. Avtomonov, W. Massa, *Chem. Ber./Recueil* 1997, 130, 1629.
- [^{17]} G. I. Nikonov, L. G. Kuzmina, J. Lorberth, *Eur. J. Inorg. Chem.* 1999, 825.
- [18] G. I. Nikonov, A. V. Churakov, M. Y. Antipin, *Organometallics* 2003, 22, 2178.
- ^[19] F. R. Lemke, J. Am. Chem. Soc. 1994, 116, 11183.
- ^[20] F. R. Lemke, K. J. Galat, W. J. Youngs, *Organometallics* 1999, 18, 1419.
- [21] P. Jutzi, S. H. A. Petri, in Organosilicon Chemistry III: From Molecules to Materials (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, 1998, p.275.
- [22] G. H. Wagner, in Abstracts of the 34th Organosilicon Symposium, White Plains, NY, May 3-5, 2002, HR4-1.
- ^[23] A. J. Chalk, J. F. Harrod, J. Am. Chem. Soc. 1965, 87, 16.
- ^[24] A. K. Roy, R. B. Taylor, J. Am. Chem. Soc. 2002, 124, 9510 and references cited therein.
- ^[25] G. I. Nikonov, L. G. Kuzmina, S. F. Vyboishchikov, D. A. Lemenovskii, J. A. K. Howard, *Chem. Eur. J.* **1999**, *5*, 2497.
- ^[26] D. A. Lemenovskii, T. V. Baukova, V. P. Fedin, J. Organomet. Chem. **1977**, 132, C14.
- [27] M. D. Curtis, L. G. Bell, N. M. Buter, Organometallics 1985, 4, 701.
- ^[28] A. Antiñolo, F. Carrillo, M. Fajardo, A. Otero, M. Lanfranchi, M. A. Pellingheli, *Organometallics* **1995**, *14*, 1518.
- ^[29] K. W. Kramarz, J. R. Norton, Prog. Inorg. Chem. 1994, 42, 14.
- ^[30] J. T. Amella, V. V. Bakhmutov, E. V. Bakhmutova, N. V. Belkova, L. M. Epstein, A. Lledos, G. I. Nikonov, E. S. Shubina, *Chem. Eur. J.*, accepted for publication.
- [31] G. Parkin, J. E. Bercaw, J. Chem. Soc., Chem. Commun. 1990, 255.
- ^[32] E. T. Papish, F. C. Rix, N. Spetseris, J. R. Norton, R. D. Williams, J. Am. Chem. Soc. 2000, 122, 12235.
- ^[33] M. J. Bearpark, G. S. McGrady, P. D. Prince, J. W. Steed, J. Am. Chem. Soc. 2001, 123, 7735 and references cited therein.
- [^{34]} See, for example: A. Antinolo, F. Carrillo-Hermosilla, B. Chaudret, M. Fajardo, J. Fernandez Baeza, M. Lanfranchi, H. H. Limbach, M. Maurer, A. Otero, M. A. Pellinghelli, *Inorg. Chem.* **1996**, *35*, 7873.
- ^[35] S. Camanyes, F. Masera, M. Moreno, A. Lledós, J. M. Lluch, J. Bertrán, Angew. Chem. Int. Ed. Engl. 1997, 36, 265.
- ^[36] I. Tanaka, T. Ohhara, N. Niimura, Y. Ohashi, Q. Jiang, D. H. Berry, R. Bau, J. Chem. Res. **1999**, 14.
- ^[37] K. Hübler, P. A. Hunt, S. M. Maddock, C. E. F. Rickard, W. R. Roper, D. M. Salter, P. Schwerdtfeger, L. J. Wright, *Or-ganometallics* **1997**, *16*, 5076.
- ^[38] H. A. Bent, Chem. Rev. 1961, 61, 275.
- ^[39] K. E. Lee, A. M. Arif, J. A. Gladysz, Chem. Ber. 1991, 124, 309.
- ^[40] B. R. Jagirdar, R. Palmer, K. J. Klabunde, L. Radonovich, *Inorg. Chem.* **1995**, *34*, 278.
- ^[41] M. K. Hays, R. Eisenberg, *Inorg. Chem.* **1991**, *30*, 2623.
- [42] T. S. Koloski, D. C. Pestana, P. J. Carroll, D. H. Berry, Organometallics 1994, 13, 489.
- [43] G. I. Nikonov, P. Mountford, S. R. Dubberley, *Inorg. Chem.* 2003, 42, 258.
- ^[44] E. A. Zarate, V. O. Kennedy, J. A. McCune, R. S. Simons, C. A. Tessier, *Organometallics* 1995, 14, 1802.
- [^{45]} R. S. Simons, J. C. Gallicci, C. A. Tessier, W. J. Youngs, J. Organomet. Chem. 2002, 654, 224.
- [46] G. M. Sheldrick, SHELXTL 5.04/VMS, An integrated system for solving, refining and displaying crystal structures from diffraction data, Siemens Analytical X-ray Instrument Inc., Madison, WI, 1995.

Received March 10, 2003 Early View Article Published Online December 12, 2003