Novel inter- and intra-molecular donor-stabilized 1-metalla-2-sila-1,3-dienes

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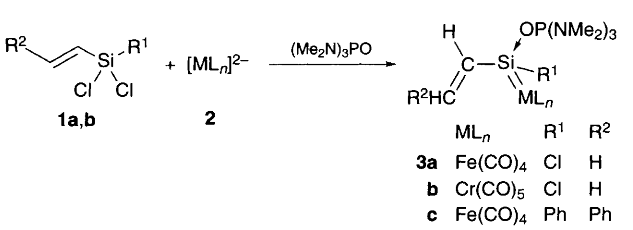
The synthesis of the inter- and intra-molecular donor-stabilized 1-metalla-2-sila-1,3-dienes $Cl(H_2C{=}CH)Si{=}ML_n{\cdot}OP(NMe_2)_3$ [ML_n = $Fe(CO)_4$ 3a, $Cr(CO)_5$ 3b], $Ph(PhHC{=}CH)Si{=}Fe(CO)_4{\cdot}OP(NMe_2)_3$ 3c and $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}ML_n$ [ML_n = $Fe(CO)_4$ 6a, $Cr(CO)_5$ 6b] is described; the X-ray structures of compounds 3c and 6b are reported.

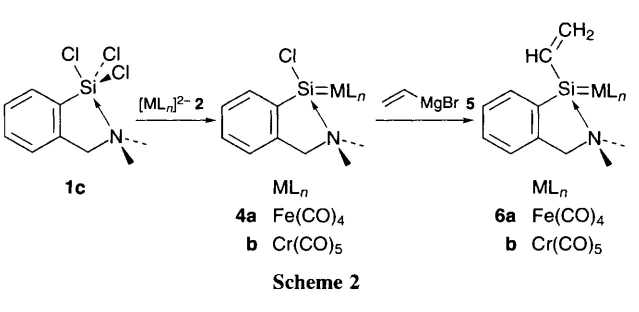
Neutral phosphenium ion compounds $(R)(R')P{=}ML_n$ (ML_n = 15-valence electron fragment, R = singly bonded organic ligand, R′ = HC=CHPh, C≡CPh) show versatile chemistry at both the phosphorus–metal double bond and the carbon–carbon multiple bond.[1–3] These compounds can formally be reduced to yield their componental parts, the cationic phosphenium ion moiety $(R)(R')P^+$ and the anionic 16-valence electron transition-metal fragment ML_n^-. In terms of the concept of isolobal analogy[4] the electron-sextet species $(R)(R')P^+$ are equivalents of H_2C and R_2Si, as well as of organometallic 16-valence electron moieties. In this respect, 1-metalla-2-sila-1,3-dienes can be considered as heterobutadienes. In this context, we report the synthesis of the acyclic 1-metalla-2-sila-1,3-diene compounds $R^1(R^2HC{=}CH)Si{=}ML_n{\cdot}OP(NMe_2)_3$ and $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}ML_n$ (ML_n = 16-valence electron fragment; R^1 = Cl, Ph; R^2 = H, Ph).

The acyclic intermolecular donor-stabilized heterobutadienes $R^1(R^2HC{=}CH)Si{=}ML_n{\cdot}OP(NMe_2)_3$ **3a–c** can be synthesized according to a method previously described by Zybill *et al.*[5] by treatment of **1a** or **1b** with $[ML_n]^{2-}$ **2a, b** in thf at −30 °C in the presence of $(Me_2N)_3PO$ (Scheme 1). **3a–3c** are obtained in 35, 60 and 25% yield respectively.†

A route for the synthesis of intramolecular donor-stabilized 1-metalla-2-sila-1,3-dienes[6] $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}ML_n$ **6a, b**, is the reaction of $[ML_n]^{2-}$ with the pentavalent trichlorosilane **1c**, yielding the chloro functionalized silanediyl compounds $Cl(C_6H_4CH_2NMe_2\text{-}2)Si{=}ML_n$ **4a, b** first, followed by treatment of the latter compounds with $H_2C{=}CHMgBr$ **5** (Scheme 2).



Scheme 1



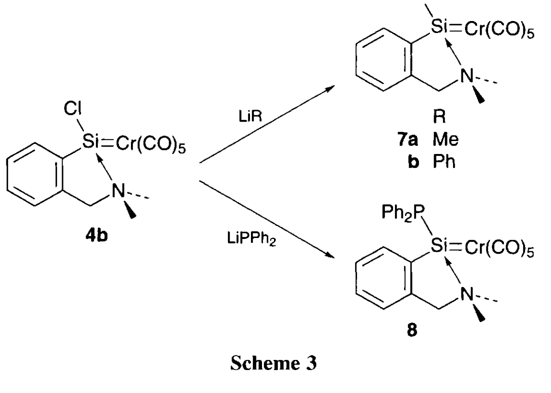
Scheme 2

Moreover, **4a** and **4b** provide the constituents for the preparation of further functionalized silanediyl compounds, since they can smoothly be reacted with lithium organyls. For instance $R(C_6H_4CH_2NMe_2\text{-}2)Si{=}Cr(CO)_5$ **7a, b, 8** could be isolated by treatment of **4b** with LiMe, LiPh or $LiPPh_2$ with precipitation of LiCl (Scheme 3).

The purification of all synthesized compounds **3**, **4** and **6–8** has to be performed by crystallization from thf–*n*-pentane solutions at −30 °C, since the use of chromatographic methods leads to an irreversible fixation of the obtained silanediyl compounds on the surface of most common chromatography materials used.[7] Compounds **3a**, **3c**, **4a** and **6a** are deep red, whereas compounds **3b**, **4b**, **6b**, **7** and **8** are yellow crystalline solids, which are soluble in most common polar organic solvents. These compounds decompose significantly on being exposed to air in solution and in the solid state.

On the basis of spectroscopic data the 1-metalla-2-sila-1,3-diene structures could be unambiguously assigned to compounds **3** and **6**. The most suitable analytical method for the characterization of the heterobutadienes **3** and **6** is ^{29}Si NMR spectroscopy. On changing from the starting materials **1a** (δ −3), **1b** (δ 5.2) and **1c** (δ −62.6) to compounds **3** and **6** a significant low-field shift (**3a** δ 75.8, **3b** δ 83.3, **3c** δ 83.6, **6a** δ 116.8, **6b** δ 114.9) is observed. The deshielding of a silicon atom is typical for low-valent silicon compounds.[5,8,9] The IR data in the ν(CO) region are in agreement with a trigonal-bipyramidal (**3a**, **3c**, **4a**, **6a**) or octahedral (**3b**, **4b**, **6b**, **7**, **8**) coordination sphere around the iron or chromium centres. This conclusion is confirmed by a single-crystal X-ray structure determination of compounds $Ph(PhHC{=}CH)Si{=}Fe(CO)_4{\cdot}OP(NMe_2)_3$ **3c** and $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}Cr(CO)_5$ **6b** (Fig. 1).†

For the intermolecular donor-stabilized molecule **3c** a distorted tetrahedral arrangement around the silicon atom is found in which the Ph(PhHC=CH)Si entity occupies an apical position within the coordination sphere of the Fe atom. The silicon atom is further complexed by the $(Me_2N)_3PO$ donor molecule. The Si–O(5) bond length of 1.725(2) Å, as well as the bond angle of the Si–O(5)–P unit [146.9(1)°] can likewise be explained by the donor character of the oxygen atom of the $(Me_2N)_3PO$ group. The bond angles around the silicon atom [Fe–Si–C(18) 115.8(1), Fe–Si–C(5) 117.4(1), Fe–Si–O(5) 109.7(1) and O(5)–Si–C(18) 103.7(1)°] indicate that two angles



Scheme 3

are close to those expected for a trigonal-planar coordinated silicon atom, one being close to a tetrahedral surrounding and one being almost 100°. This observation is typical for silanediyl transition-metal compounds and results most likely from steric interactions of the ligands present at the silicon atom with the metal-bonded carbonyl groups.[5,7,8] The four atoms Fe, Si, C(5) and C(6), which form the heterobutadiene framework, are bonded in plane (max. deviation 0.04 Å). The Si–Fe and the C–C units are thereby *s-cis* configured and the C–C bond lengths [**3c** 1.320(4), **6b** 1.309(4) Å] observed show the typical behaviour expected for butadienes and heterobutadienes. The Fe–Si bond length at 2.280(1) Å is similar to those found in other compounds of this type.[5a,b]

In the intramolecular donor-stabilized compound **6b** the silanediyl fragment $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si$, wherein the silicon atom shows a pseudo-tetrahedral geometry, is bonded to a $Cr(CO)_5$ fragment with an octahedral environment around the chromium atom. The Cr–Si distance at 2.385(1) Å is indicative of a double bond character in the Cr–Si unit (typical Cr=Si 2.4–2.5 Å).[5c,7] Moreover, the N–Si distance at 1.954(2) Å in **6b** is shorter than those found in pentavalent $C_6H_4CH_2NMe_2$-2 substituted chlorosilanes [*e.g.* $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)SiCl_2$ 2.261(5) Å][10] but still is within the van der Waals distance.[11] A further noticeable feature of compound **6b**, as compared with the intermolecular stabilized heterobutadiene **3c**, is the orientation of the vinyl group in the coordination sphere of the silicon atom. The atoms of the 1-chroma-2-sila-1,3-diene unit are not in-plane bonded [interplanar angle CrSiC(20) and SiC(20)C(21) planes = 125.8°].

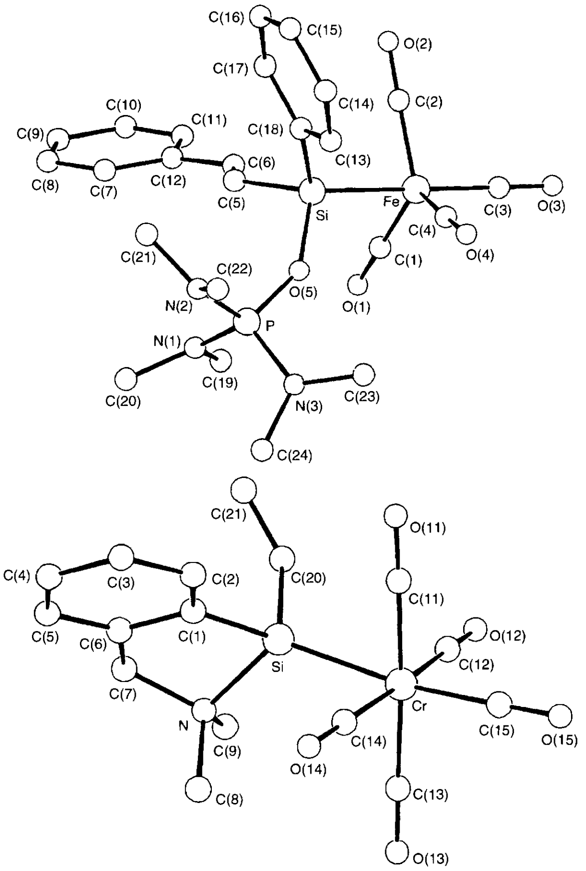


Fig. 1 Molecular geometry and atom labelling scheme for **3c** (top) and **6b** (bottom).† Important bond distances (Å) and angles (°): **3c**: Fe–Si 2.280(1), Si–C(18) 1.904(2), Si–C(5) 1.865(3), Si–O(5) 1.725(2), P–O(5) 1.535(2), C(5)–C(6) 1.320(4); Fe–Si–C(18) 115.8(1), Fe–Si–C(5) 117.4(1), Fe–Si–O(5) 109.7(1), O(5)–Si–C(18) 103.7(1), O(5)–Si–C(5) 102.9(1), C(18)–Si–C(5) 105.7(1), Si–O(5)–P 146.9(1), Si–C(5)–C(6) 126.9(2). **6b**: Si–Cr 2.385(1), Si–N 1.954(2), Si–C(1) 1.878(3), Si–C(20) 1.881(3), C(20)–C(21) 1.309(4); Cr–Si–N 122.64(7), Cr–Si–C(1) 121.60(9), Cr–Si–C(20) 117.37(9), C(1)–Si–C(20) 104.4(1), N–Si–C(1) 86.8(1), N–Si–C(20) 98.1(1).

In conclusion, an efficient method for the synthesis of novel 1-metalla-2-sila-1,3-dienes is described. The potential use of these compounds as heterobutadienes in organic and organometallic synthesis is the subject of further research.

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 247), the Fonds der Chemischen Industrie and Professor Dr G. Huttner for financial support. We thank T. Jannack for carrying out the MS measurements and Dr C. Limberg and S. Ahrens for many discussions.

Footnote

† *Crystal data*: **3c**; $C_{24}H_{30}FeN_3O_5PSi$, M = 555.43, monoclinic, space group $P2_1/n$; a = 11.647(5), b = 14.911(6), c = 16.131(7) Å, β = 100.62(3)°, U = 2753(1) Å^3, Z = 4, D_c = 1.340 g cm^{-3}. R3m/V Siemens diffractometer, using the θ–2θ technique [$2.0 \leqslant 2\theta \leqslant 46.0°$, scan range 0.75°, scan speed $2.3 \leqslant \dot{\omega} \leqslant 29.3°$ min^{-1} (in 2θ)] and Mo-Kα radiation (λ = 0.71069 Å), graphite monochromator. Crystal dimensions: 0.40 × 0.30 × 0.30 mm^3, 4703 observed data [$I \geqslant 2\sigma(I)$] of 5198 data measured (205 K) were refined to R = 0.037, R_w = 0.033 (statistical weights).[12] No. of refined parameters = 302.

For **6b**; $C_{16}H_{15}CrNO_5Si$, M = 381.38, monoclinic, space group $P2_1/n$, a = 9.249(3), b = 17.54(1), c = 10.920(4) Å, β = 82.66(3)°, U = 1757(1) Å^3, Z = 4, D_c = 1.442 g cm^{-3}. $2.2 \leqslant 2\theta \leqslant 23.6°$, scan range 0.6°, scan speed $5.0 \leqslant \dot{\omega} \leqslant 29.3°$ min^{-1} (in 2θ), other parameters as above. Crystal dimensions: 0.20 × 0.30 × 0.30 mm^3, 2599 observed data [$I \geqslant 2\sigma(I)$] of 2777 data measured (200 K) were refined to R = 0.032, R_w = 0.080 (statistical weights, F^2-refinement).[12] No. of refined parameters = 277.

Both structures were solved by direct methods (SHELXL-93).[12] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/67.

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Received, 19th February 1996; Com. 6/01172A