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[7] The formation of bis(silyl)palladium(II) complexes was observed in the reactions of **3** with several palladium complexes ([Pd(PPh$_3$)$_4$], [Pd(dba)$_2$]/2PEt$_3$ (dba = dibenzylideneacetone), [Me$_2$Pd(PPh$_2$Me)$_2$]), while decomposition to black precipitates occurred in the case of [Me$_2$Pd(tmeda)] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) and [Me$_2$Pd(bpy)] (bpy = 2,2′-bipyridyl). The detailed results will be reported separately.

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[11] Crystal data for **5**: $0.30 \times 0.20 \times 0.20$ mm^3, hexagonal, space group $P6_122$ (No.178), $a = 8.583(1)$, $c = 60.373(3)$ Å, $V = 3851(1)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.37$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 87.9$ cm^{-1}, $T = -70$ °C; Rigaku AFC5R diffractometer, ω scans; 1351 measured reflections, of which 862 with $I > 3.0\sigma(I)$ were used in the refinement. The structure was solved by direct methods (SAPI91) and refined by full-matrix least-squares techniques against $|F|^2$ with teXsan crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined; $R = 0.035$, $Rw = 0.049$, residual electron density $+0.34/-0.40$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-55. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

[12] The reaction of **2** and **3** in C$_6$D$_6$ at 50 °C monitored over 5 days by NMR spectroscopy showed that another complex (^{31}P NMR: $\delta = 16.26$) was generated in the transformation as a transient intermediate. This signal appeared before the emergence of the signal assignable to **5** ($\delta = 15.87$). The amount of the transient species reached its maximum (about 15% by ^{31}P NMR integration) after 10 hours and then gradually decreased. Further characterization or isolation of the transient species was not feasible.

[13] Broad NMR signals appear to indicate that **7** is in equilibrium with monomer **4** in solution. **7**: M.p. 133–137 °C (decomp, under vacuum); ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta = 1.25$–1.37 (br. m, 36H), 1.64 (br. d, 12H, $J = 14$ Hz), 4.94 (s, 8H, ^1J(Si-H) = 160 Hz, SiH$_2$), 7.05 (dd, 4H, $J = 3, 5$ Hz), 7.54 (dd, 4H, $J = 3, 5$ Hz); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF): $\delta = 14.28$ (br., PCH$_3$), 29.65 (br. t, $J = 19$ Hz, PCH$_2$CH$_2$P), 126.84 (s), 134.37 (s), 152.42 (s); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF): $\delta = 2.68$ (br.); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_8$]THF): $\delta = -18.5$ (br); IR (KBr): $\tilde{\nu} = 2006$ cm^{-1} (SiH); C,H analysis: calcd for $C_{30}H_{64}P_6Pd_2Si_4$: C 38.50, H 6.89; found: C 38.72, H 6.78. The dimeric structure was confirmed by X-ray analysis. The detailed results will be reported separately.

[14] Note that complex **2** is thermally stable at room temperature and slowly decomposes at 90 °C to form methane and ethane; see ref. [8]. Accordingly, generation of palladium(0) species prior to the oxidative addition of **3** is unlikely.

[15] K. Tamao, T. Hayashi, M. Kumada, *J. Organomet. Chem.* **1976**, *114*, C19–C21; Y. Tanaka, Y. Uchimaru, M. Tanaka, *Chem. Lett.* **1995**, 164.

Metallomesogens with Branched, Dendrimeric Amino Ligands[**]

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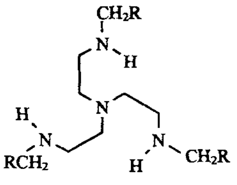
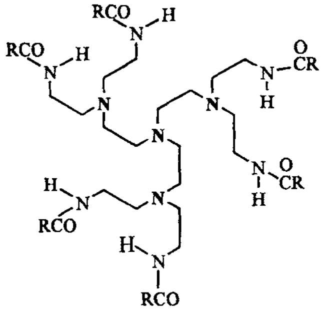
In the search for compounds with novel electric or magnetic behavior, the desire to combine the properties of liquid crystals (LC) with those of metal complexes has led to the synthesis of a large number of metallomesogens, mostly with square-planar or linear coordination geometry.[1] However, high-spin transition metal complexes often unavoidably have different geometries whose higher degree of isometry has been regarded for a long time as unsuitable for mesomorphic behavior.[2] Only recently have, for example, liquid-crystalline nickel(II) complexes with paramagnetic properties based on octahedral[3] and tetrahedral coordination[4] been described. The previously known LC complexes with trigonal-bipyramidal configuration have a distorted shape, as in the case of the dimeric zinc alkoxydithiobenzoates[5] and the iron complexes, which have coordination geometries lying between square-pyramidal and trigonal-bipyramidal.[4b, 6]

The branched amine ligands **L^1** and **L^2**, which are ethyleneimine dendrimers of the first and second generation and are derivatives of tris(2-aminoethyl)amine (tren), allow access to a novel class of liquid-crystalline transition metal complexes with trigonal-bipyramidal or octahedral coordination geometry. The use of dendrimeric ligands in metallomesogens has not been reported before.

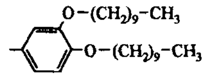


L^1



L^2

R =



$R = -C_6H_3(O(CH_2)_9CH_3)_2$

The transition temperatures (determined by polarization microscopy and differential calorimetry) of the metal complexes **K^1**–**K^8** are listed in Table 1. Up to **K^3** (**L^1**·Ni(NO$_3$)$_2$), all complexes show mesomorphic behavior with relatively low glass transition temperatures. With **K^1**, **K^4**, and **K^7** there is no crystalline phase, for the other compounds a crystalline phase appears only before the first heating. No double refraction is ob-

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Table 1. Transition temperatures [°C] of complexes **K**^{1}–**K**^{8} (in parentheses: ΔH [kJ mol^{-1}]).

Complex	T_g	ΔC_p	K		M		I
K^1, **L**^{1}·$CoCl_2$	56	0.37	–		●	85.5 (0.4)	●
K^2, **L**^{1}·$NiCl_2$	40	0.61	●	47.0 (3.4)[a]	●	64.5 (1.7)	●
K^3, **L**^{1}·$Ni(NO_3)_2$	36	0.64	●	46.5 (11.1)[a]	–		●
K^4, **L**^{1}·$CuCl_2$	41	0.57	–		●	75.0 (0.8)	●
K^5, **L**^{1}·$Cu(SCN)_2$	41	0.39	●	48.5 (4.6)[a]	●	75.0 (1.1)	●
K^6, **L**^{1}·$Cu(NO_3)_2$	36	0.88	●	47.5 (12.4)[a]	●	79.0 (1.4)	●
K^7, **L**^{1}·$ZnCl_2$	60	0.41	–		●	126.0 (1.3)	●
K^8, **L**^{2}·$CuCl_2$	49	0.64	–		●	140.0 (2.8)	●

[a] Only on first heating; T_g: glass transition temperature [°C]; ΔC_p [kJ mol^{-1} K^{-1}]; K: crystalline phase, M: mesophase, I: isotropic phase.

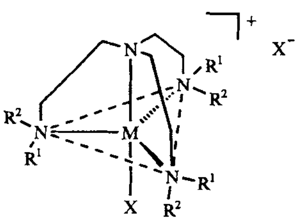
Table 2. X-ray reflections and lattice constants in the mesophase of complexes of **L**^{1} and **L**^{2} and of the ligand **L**^{2}.

Complex	d_{10}	d_{11}	d_{20}	d_{30}	a_{hex}
K^1, **L**^{1}·$CoCl_2$	28.67	–	–	–	–
K^2, **L**^{1}·$NiCl_2$	30.13	–	–	–	–
K^4, **L**^{1}·$CuCl_2$	30.48	–	15.37	–	–
K^5, **L**^{1}·$Cu(SCN)_2$	32.63	–	16.34	–	–
K^7, **L**^{1}·$ZnCl_2$	30.78	17.49	15.07	10.16	35.2
L^2	31.09	18.64	15.93	–	36.4
K^8, **L**^{2}·$CuCl_2$	31.98	18.99	16.09	10.57	36.9

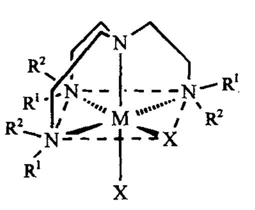
served with the polarization microscope, but **K**^{7} has a fine, needlelike texture.

For the complexes **L**^{1}·$CoCl_2$ (**K**^{1}) and **L**^{1}·$NiCl_2$ (**K**^{2}), X-ray diffraction of the mesophase (Table 2) gave only a first order reflection apart from a halo at 4.4 Å. For **L**^{1}·$CuCl_2$ (**K**^{4}) and **L**^{1}·$Cu(SCN)_2$ (**K**^{5}), a second order reflection was observed as well, which is attributed to a lamellar phase. For **L**^{1}·$ZnCl_2$ (**K**^{7}), the mixed d_{11} reflection is indicative of a hexagonal-columnar phase (Col_h).

The tren skeleton is in principle able to accomodate two coordination geometries: a) trigonal-bipyramidal (**1**) with fivefold coordination ("azatran geometry" with elements of Groups 1, 2, and 12–15[7] and with transition metals of Groups 3–11[8], resulting in ionic complexes), and b) octahedral geometry (**2**) in the case of neutral complexes of transition metals. The azatran geometry **1** is preferred with most divalent metal centers.[9] Only in the case of the Ni^{II} complex with unsubstituted tren ligands does the octahedral geometry **2** also occur;[8d] with hexamethyl-substituted tren, the trigonal-bipyramidal structure is again favored.[10]



1



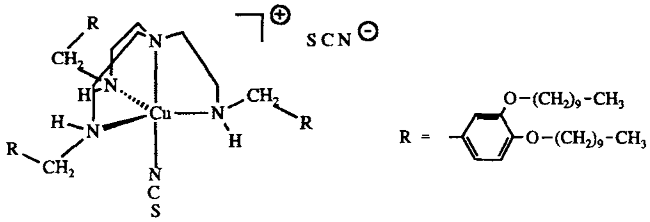
2

As the **L**^{1} complexes do not form stable crystalline phases, it was not possible to carry out X-ray structural analysis. However, the complex geometry can be established by comparison with known non-liquid-crystalline analogs. The trigonal-bipyramidal[11] complex formed from the unsubstituted tren ligands and $Cu(SCN)_2$ shows a special feature in the IR spectrum—two sets of two absorption bands corresponding to an isothiocyanato ligand and an ionic thiocyanate group.[12] Comparison of the IR data for this complex with those for **L**^{1}·$Cu(SCN)_2$ (**K**^{5}) shows that the absorption bands of the coordinated isothiocyanate group and the thiocyanate anion correspond (Table 3). The trigonal-bipyramidal azatran structure may therefore also be assigned to **K**^{5} (Scheme 1).

Table 3. IR and UV absorption bands of the complexes **K**^{1}–**K**^{6} and **K**^{8}.

Complex	ν(C–N) st [cm^{-1}]	ν(C–S) st [cm^{-1}]	λ [nm]	ε_{mol} [L mol^{-1}]
K^1, [**L**^{1}·CoCl]Cl			696, 668, 628	188, 180, 178
			616, 492, 468	–, 111, –
K^2, [**L**^{1}·$NiCl_2$]			960, 624, 396	19, 20, 44
K^3, [**L**^{1}·$Ni(NO_3)_2$]			908, 568, 372	26, 22, –
K^4, [**L**^{1}·CuCl]Cl			924, 752	381, 289
[tren·Cu(NCS)](SCN)	2094[a],	818[a],		
	2060[b]	745[b]		
K^5, [**L**^{1}·Cu(NCS)](SCN)	2087[a],	813[a],	816, 672, 372	285, 258, 1167
	2059[b]	748[b]		
K^6, [**L**^{1}·$Cu(NO_3)$](NO_3)			844, 676	296, –
K^8, [**L**^{2}·CuCl]Cl			926, 752	578, 761

[a] Stretching vibrations of the ligand NCS. [b] Stretching vibrations of the anion SCN^-.



Scheme 1. Structure of [**L**^{1}·Cu(NCS)](SCN).

With the other complexes, the geometry cannot be deduced from the IR data. However, important information is available from the UV/Vis spectra (Table 3).[13] The measured wavelengths and molar extinction coefficients of the Co^{II} complex **K**^{1} (Fig. 1) would not expected from octahedral geometry,[13] but correspond to trigonal-bipyramidal coordination.[10] The two or three very intense bands of the Cu^{II} complexes **K**^{4}–**K**^{6} cannot be due to an octahedral structure (only one band of low intensity),[13] but confirm the trigonal-bipyramidal coordination that was established by IR spectroscopy for **K**^{5}, which can therefore also be assumed for **K**^{4} and **K**^{6}. The absorption bands of the Ni^{II} complexes are of only low intensity. Their number, position, and extinction coefficients agree very well with typical values for

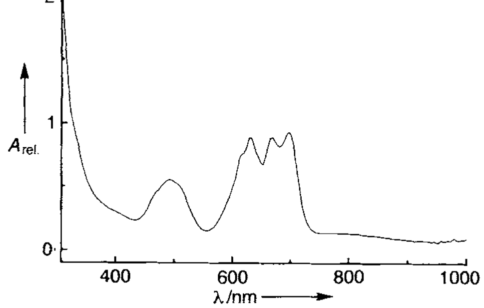


Fig. 1. UV/Vis spectrum of [**L**^{1}·CoCl]Cl (**K**^{1}) (hexane, $c = 5 \times 10^{-3}$ mol L^{-1}).

octahedral nickel complexes.[13] No information on the coordination geometry of the complex $L^1 \cdot ZnCl_2$ (K^7) can be derived from the spectroscopic data.

Owing to the very low coordination tendency of the peripheral amide groups, the situation for L^2 is similar to that for L^1. The copper(II) dichloride complex $[L^2 \cdot CuCl]Cl$ (K^8) does not show any crystalline phase; the enantiotropic mesophase is frozen in the glassy state above room temperature (Table 1), and the texture is broken spherolitic (Fig. 2). X-ray diffraction experiments show the presence of a hexagonal-columnar mesophase (Col_h) with a_{hex} = 36.9 Å (Table 2, Fig. 3). The lattice constant is only 0.4 Å greater than that of the free ligand, which indicates that complexation has only a negligible influence on the space filling of the molecule. The UV/Vis spectrum of K^8 is almost identical to that of K^4 (Table 3), so that trigonal-bipyramidal coordination may also be assumed for K^8.

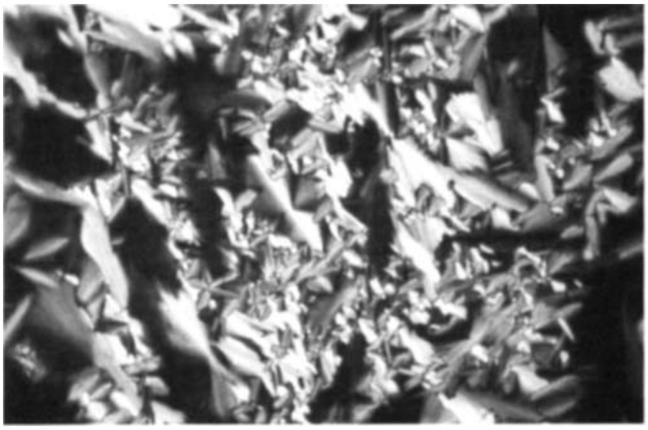


Fig. 2. Texture of the complex $[L^2 \cdot CuCl]Cl$ (K^8) (T = 132 C, 120-fold magnification, crossed polarizers).

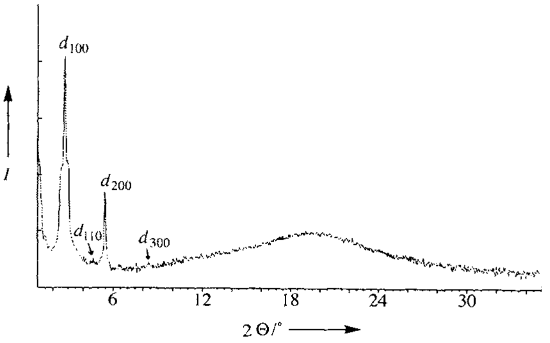


Fig. 3. X-ray diffraction diagram of the complex $[L^2 \cdot CuCl]Cl$ (K^8).

The complexes described here are the first examples of metallomesogens with branched, dendrimeric oligoalkyleneamino ligands. These mesogens are not based on the classical rod or disklike shape. They show a trigonal-bipyramidal coordination geometry; only the nickel complexes studied are octahedral. The transition temperatures of all the complexes—in the absence of a crystalline phase—are relatively low for metallomesogens. The hexagonal-columnar phase appears to be formed when either the larger ligand L^2 or the Zn^{II} ion are present. Initial measurements have shown that the nickel complexes described here are also paramagnetic.

Experimental Procedure

L^1: Tris(2-aminoethyl)amine was allowed to react with 3,4-bis(decyloxy)benzoyl chloride [14], and the product was reduced to the amine [3] (54% yield); IR (KBr): $\tilde{\nu}$ = 3302 cm^{-1}, 2925, 2855, 1606, 1589, 1512, 1467, 1380, 1264, 1231, 1134, 1044, 801, 722; ^1H NMR (250 MHz, $CDCl_3$): δ = 6.85 (s, 1 H, arom.), 6.65–6.80 (m, 2 H, arom.), 3.95 (m, 4 H, OCH_2), 3.65 (s, 2 H, $ArCH_2$), 2.60 (m, 4 H, CH_2N), 1.75 (m, 4 H, OCH_2CH_2), 1.10–1.60 (m, 28 H, alkoxy-CH_2), 0.85 (t, 6 H, CH_3); EI-MS (70 eV): m/z (%): 1352 (11) [M^+], 460 (100); Elemental analysis (%): calcd for $C_{87}H_{150}N_4O_9$ (1354.15 g mol^{-1}): C 77.17, H 11.61, N 4.14, O 7.09; found: C 77.17, H 11.55, N 4.08.

L^2: This ligand was prepared as described elsewhere [15].

K^1–K^8: To L^1 or L^2 in EtOH at 60 C was added dropwise an equimolar amount of the metal salt dissolved in EtOH. The mixture was stirred for 3 h at 60 °C, stored in a refrigerator for 12 h, and then filtered. The residue was recrystallized from EtOH, and the solid dissolved in benzene and freeze-dried. **K^5** was synthesized by adding NaSCN in acetone to an equimolar amount of **K^4** in acetone at 50 °C. After 30 min, this was filtered hot, worked up as described, and recrystallized from benzene (85–92% yield).

Complexes with L^1 (for example: $L^1 \cdot ZnCl_2$): IR (KBr): $\tilde{\nu}$ = 3193 cm^{-1}, 2925, 2855, 1606, 1589, 1515, 1467, 1380, 1265, 1141, 1044, 812, 722; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.05 (br., 1 H, arom.), 6.95 (br., 1 H, arom.), 6.75 (d, 1 H, arom.), 3.8–4.1 (m, 6 H, OCH_2, $ArCH_2N$), 2.5–2.8 (br., 4 H, NCH_2CH_2N), 1.6–1.9 (m, 4 H, OCH_2CH_2), 1.1–1.5 (m, 28 H, alkoxy-CH_2), 0.9 (t, 3 H, CH_3); Elemental analysis (%): $[L^1 \cdot CoCl]Cl$ (K^1): calcd for $C_{87}H_{156}Cl_2CoN_4O_6$ (1483.99 g mol^{-1}): C 70.42, H 10.60, N 3.78, Cl 4.78, Co 3.97, O 6.47; found: C 70.25, H 10.60, N 3.94; $[L^1 \cdot NiCl_2]$ (K^2): calcd for $C_{87}H_{156}Cl_2NiN_4O_6$ (1483.75 g mol^{-1}): C 70.43, H 10.60, N 3.78, Cl 4.78, Ni 3.96, O 6.47; found: C 70.17, H 10.87, N 3.80; $[L^1 \cdot Ni(NO_3)_2]$ (K^3): calcd for $C_{87}H_{156}NiN_6O_{12}$ (1536.85 g mol^{-1}): C 67.99, H 10.23, N 5.47, Ni 3.82, O 12.49; found: C 68.05, H 10.11, N 5.37; $[L^1 \cdot CuCl]Cl$, (K^4): calcd for $C_{87}H_{156}Cl_2CuN_4O_6$ (1488.60 g mol^{-1}): C 70.20, H 10.56, N 3.76, Cl 4.76, Cu 4.27, O 6.45; found: C 69.69, H 10.95, N 4.28; $[L^1 \cdot Cu(NCS)](SCN)$ (K^5): calcd for $C_{89}H_{156}CuN_6O_6S_2$ (1533.93 g mol^{-1}): C 69.68, H 10.25, N 5.48, Cu 4.14, S 4.18, O 6.47; found: C 68.80, H 10.35, N 6.55, Cu 4.30, S 4.10; $[L^1 \cdot Cu(NO_3)](NO_3)$ (K^6): calcd for $C_{87}H_{156}CuN_6O_{12}$ (1541.70 g mol^{-1}): C 67.78, H 10.20, N 5.45, Cu 4.25, O 12.45; found: C 67.64, H 10.05, N 5.45; $L^1 \cdot ZnCl_2$ (K^7): calcd for $C_{87}H_{156}Cl_2ZnN_4O_6$ (1490.45 g mol^{-1}): C 70.11, H 10.55, N 3.76, Cl 4.76, Zn 4.39, O 6.44; found: C 68.95, H 10.38, N 4.07.

Complex with L^2: $[L^2 \cdot CuCl]Cl$ (K^8): IR (KBr): $\tilde{\nu}$ = 3304 cm^{-1}, 2924, 2855, 1635, 1602, 1581, 1508, 1468, 1392, 1270, 1131, 1040, 761, 722; Elemental analysis (%): calcd for $C_{180}H_{312}Cl_2CuN_{10}O_{18}$ (3038.81 g mol^{-1}): C 71.15, H 10.35, N 4.61, Cl 2.33, Cu 2.17, O 9.48; gef.: C 70.42, H 10.47, N 4.35, Cl 2.32, Cu 2.34.

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An Intermolecularly Donor-Stabilized Silanediyl(silyl)nickel Complex: Combined Si–Si Bond Cleavage and Methyl Migration between Silicon Centers**

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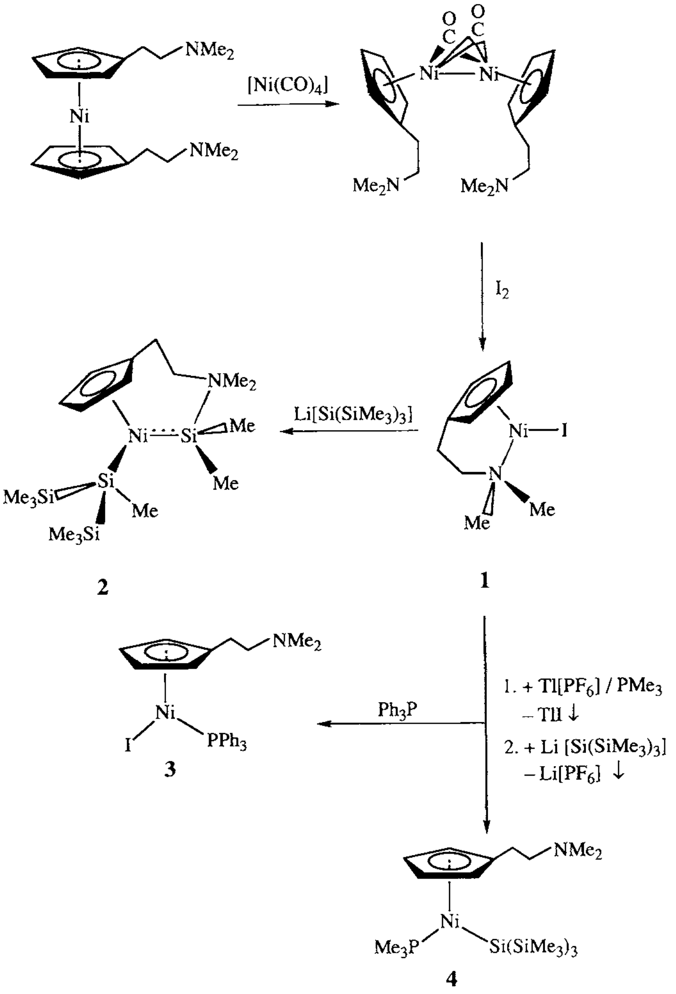
Roland A. Fischer*

Dedicated to Professor Hans Georg von Schnering
on the occasion of his 65th birthday

Cyclopentadienyl derivatives with Lewis bases in the side groups that are capable of binding to hard and soft centers in a hemilabile manner promise a rich coordination chemistry and unusual reactions at the metal center. Prominent ligands include [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl and its tetramethyl-substituted derivative (Cp^N and Cp^{*N}, respectively), and intermolecular adducts of these to various metal centers are known.[1] However, convincing examples in which reactions are specifically controlled by the binding properties of this ligand have not been reported.

The nickel dimer [$Cp^N_2(CO)_2Ni_2$] can be synthesized quantitatively by the "classical" reaction of [Cp^N_2Ni] and tetracarbonylnickel (the corresponding Cp* compound has been described previously[1b]). Oxidative cleavage of the nickel dimer with iodine, followed by decarbonylation gave the key compound **1** (Scheme 1). The quality of the crystallographic data[3a] (Fig. 1) of **1** is affected by dynamic disorder of the aminoethyl substituent (large anisotropic thermal parameters at C6 and C7). To the best of our knowledge there is only one further structurally characterized example of a nickel complex with intramolecular coordination of the substituent at Cp: [η^5:η^2-2,3,4,5-tetramethyl-1-(4-pentenyl)cyclopentadienyl](bromo)nickel(II).[4]



Scheme 1. Syntheses of the compounds discussed in this work.

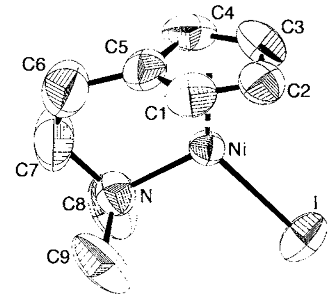


Fig. 1. Crystal structure of **1** (ORTEP, thermal ellipsoids at 50% probability level). Selected bond lengths [pm] and angles [°]: Ni–I 250.0(1), Ni–N 196.0(5), Ni–C1 212.8(6), Ni–C2 213.0(5), Ni–C3 214.2(7), Ni–C4 211.9(7), Ni–C5 199.7(7), N–C7 152(1), N–C8 146.6(8), N–C9 147.0(8), C5–C6 149(1), C6–C7 138(1); I-Ni-N 103.3(2), C1-C5-C6 125.8(7), C4-C5-C6 125.6(7), C5-C6-C7 112.1(8), N-C7-C6 116.2(8).

Reaction of **1** with [$(thf)_3Li\{Si[Si(CH_3)_3]_3\}$] selectively yields bright yellow, air-sensitive crystals of **2** in 80–90% yield (Fig. 2).[3b] This is the first structurally characterized example of a silanediyl(silyl) metal complex. The occurrence of both π(M=Si) and σ(M–Si) bonds in one molecule permits a direct comparison these two types of bonding. Complex **1** is related to some bissilanediyl complexes, for example [(η^5-C_5Me_5)Ru(PPh_3){η^2-[(μ-CH_3O)($SiMe_2$)$_2$]}],[5] which are also stabilized by intramolecular base coordination, but contain identical Si complex fragments. The only other known silanediylnickel complex is [bis(1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene)](dicarbonyl)nickel, which was described as a "donor-free" system. However, in this compound silicon is bound to two nitrogen atoms, and π(Si–N) interactions cannot be neglected.[6] Even when the reduced coordination number of three is taken into consideration, the Ni–Si4 bond length in **2** (213.7(1) pm; Fig. 2) is significantly shorter than the corresponding bonds in the above-mentioned $NiSi_2$ complex (220.7(2) pm and 221.6(2) pm).[6] According to T. D. Tilley et al.

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