Synthesis and Properties of Donor/Acceptor-Substituted Metal-Capped Twofold-Sila-Bridged Cyclobutadieno Superphanes

Rolf Jens Schaller,[a] Gebhard Haberhauer,[a] Rolf Gleiter,*[a] and Frank Rominger[a]

Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

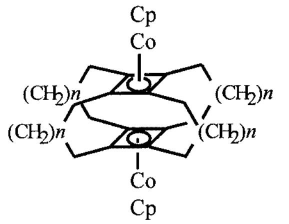
Keywords: Donor-acceptor systems / Phanes / Cyclic voltammetry / Electron transfer / Cobalt

The synthesis of the tetrasilasuperphanes **10**–**18** can be achieved from 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**), 1,1,2,2-tetramethyl-1,2-disilacyclonona-3,8-diyne (**8**) or 1,1,4,4-tetramethyl-1,4-disilacyclodeca-5,9-diyne (**9**) by heating with [RCpCoL$_2$] [R = H, Si(CH$_3$)$_3$, (CH$_3$)$_5$, CO$_2$CH$_3$; L$_2$ = COD, (CO)$_2$, (C$_2$H$_4$)$_2$]. The reaction of **7** with [RCpCo(CO)$_2$] [R = H, CH$_3$, Si(CH$_3$)$_3$, (CH$_3$)$_5$] produces the tricyclic cobalt-stabilized cyclobutadienediynes **20**–**23**, whereas reaction with [R′CpCo(L$_2$)] [R′ = H, (CH$_3$)$_5$, CO$_2$CH$_3$; L$_2$ = COD, (CO)$_2$] leads to the donor/acceptor superphanes **24**–**31**. X-ray investigations on the superphanes **10**, **13**–**15** and **18** reveal distances between the two cyclobutadiene units in the range of 2.65 Å and 3.79 Å. Investigations by means of cyclic voltammetry of the superphanes **10**–**18** show a dependence of the oxidation potentials on the nature of the bridges. A comparison between the first oxidation potentials of **10/28**, **24/29**, and **26/31** gives evidence for a partial charge delocalization over both CpCoCbd fragments of the superphanes.

Introduction

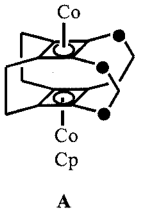
Rigid metallorganic species with two or more metal centers are often used as model systems for generating intervalence compounds. Attractive examples are biferrocene[1–3] and related species as well as metal-capped cyclophanes with benzene[4] or cyclobutadiene rings[5] as π-systems. For such intervalence compounds Robin and Day suggested a classification scheme 35 years ago[6] which is based on the extent of electron transfer between the metal fragments. According to this classification the charge can either be localized (class I), fully delocalized (class III) or partly delocalized (class II). The latter two classes deserve special interest because the delocalization promises new properties of the radical cations as compared to the localized species. Those systems on the interface of class II and class III with a relatively low barrier to intramolecular electron transfer have been called “almost delocalized” and are currently of considerable interest.[7]

Our recent studies of a series of superphanes with two[5] or four[8] cobalt centers revealed that for larger bridges between the metal fragments (**2**, **3**) the mixed valent monocations are valence trapped with very weak interactions between the metal centers.

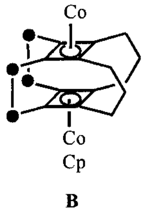


$n = 1, 2, 3$
1 2 3

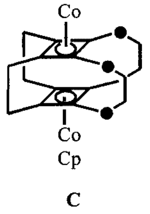
For **1** we found strong interactions between the molecular halves which suggested classifying this system as an “almost delocalized” intervalence compound.[9] This finding encouraged us to synthesize related superphanes with smaller bridges between the metal fragments. In this paper we report on the synthesis, structural and electrochemical properties of CpCo-capped cyclobutadieno superphanes derived from **A**, **B** or **C**.



A



B

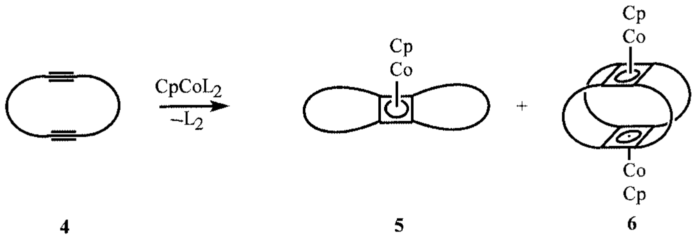


C

● = Si(CH$_3$)$_2$

---

[a] Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (internat.) +49-(0)6221-544205
E-mail: rolf.gleiter@urz.uni-heidelberg.de



Scheme 1

Results and Discussion

Synthesis

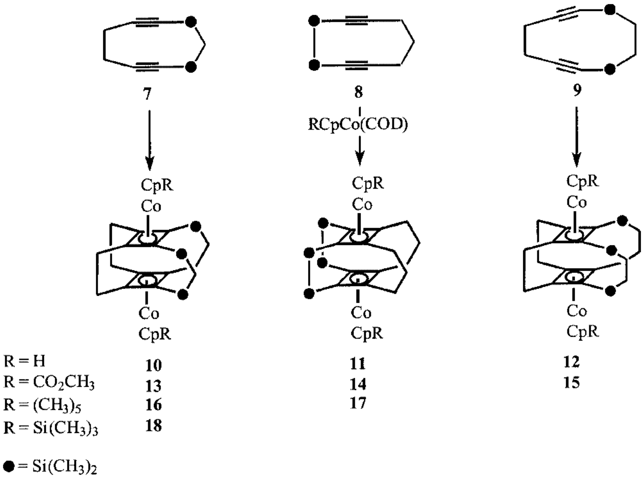
Our studies on the reactivity of cyclic diynes with (η^5-cyclopentadienyl)cobalt complexes at 150 °C revealed two major products:[5] the intramolecular tricyclic system **5** and the intermolecular product **6** (Scheme 1).

If one side of the two alkyne units in **4** is tethered by an ethano or tetramethyldisilano bridge only superphanes **6** are obtained.[10] To prepare the target systems **A**−**C** we used 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**),[11] 1,1,2,2-tetramethyl-1,2-disilacyclonona-3,8-diyne (**8**)[11] and 1,1,4,4-tetramethyl-1,4-disilacyclodeca-5,9-diyne (**9**)[11] as starting materials (Scheme 2).

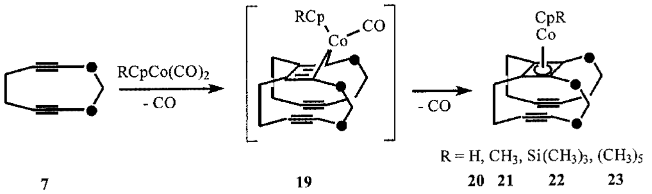
Heating these alkynes with [RCpCo(COD)] [R = H, $Si(CH_3)_3$, $(CH_3)_5$, CO_2CH_3] at 150 °C in cyclooctane afforded the superphanes **10**−**18** in yields between 10% and 68%. Especially noteworthy are the high yields (>60%) of **10**, **12**, **13** and **18**.

Donor/Acceptor Superphanes

In view of the mechanism of the formation of the superphanes[5] shown in Scheme 2 it was of interest to try and isolate some reaction intermediates. When we heated the diyne **7** with various substituted (η^5-cyclopentadienyl)(dicarbonyl)cobalt complexes (Scheme 3) at 100 °C[10] instead of 150 °C we were able to isolate the intermediates **20**−**23**. In all cases the bulky silyl groups are found adjacent to each other.[5,12] We ascribe this observation to the intermediate metallacycle[13] **19** in which the bulky groups are pointing away from each other. The yields of **20**−**23** vary between 20% and 30%.



Scheme 2



Scheme 3

In the case of **23** we were able to isolate single crystals which confirm the assigned stereochemistry (Figure 1). The two triple bonds are nearly parallel to each other with an intermolecular distance of 4.7 Å on the ethano-tethered side and 5.3 Å on the other side.

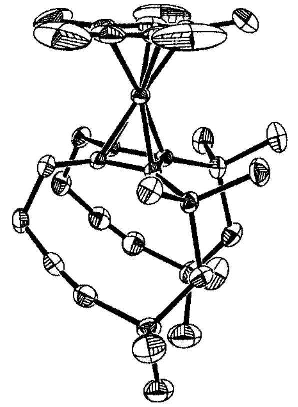
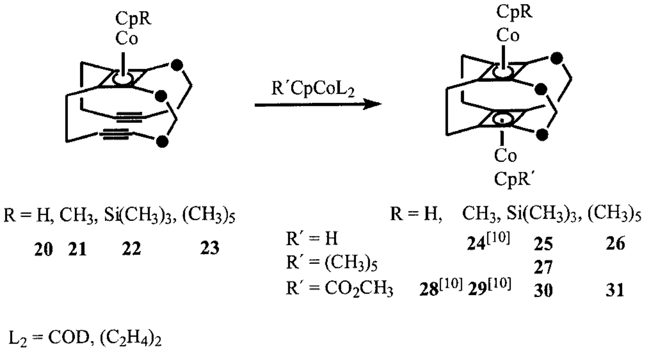


Figure 1. Molecular structure of **23** (ORTEP drawing, 50% probability ellipsoids); the hydrogen atoms have been omitted for clarity

Having in our hands the intermediates **20**−**23** prompted us to synthesize the donor- and acceptor-substituted superphanes **24**−**31** (Scheme 4) in order to compare their electronic properties with those of **10**−**18**.



Scheme 4

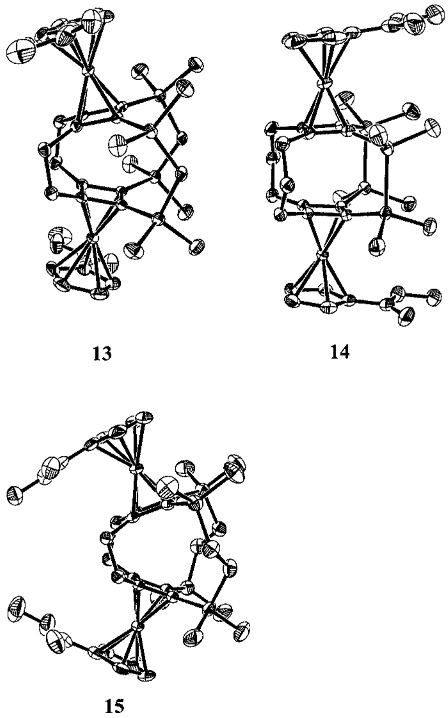


Figure 2. Molecular structures of **13−15** (ORTEP drawing 50% probability ellipsoids); the hydrogen atoms have been omitted for clarity

The species **24−31** were obtained in a straightforward way by heating **20−23** with [R′CpCoL$_2$] [L$_2$ = COD, (C$_2$H$_4$)$_2$] [R′ = H, (CH$_3$)$_5$, CO$_2$CH$_3$] in cyclooctane. The yields of **24−31** vary from 24% up to 97%.

Structural Studies on the Superphanes

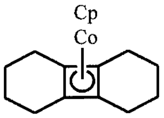
We were able to grow single crystals of **10**, **13−15** and **18** which allowed us to study the molecular structures of these species in the solid state. In Figure 2 we compare the molecular structures of **13−15** as examples.

In this series the tilting of the planes of the cyclobutadiene rings varies considerably. To demonstrate this we have listed the intramolecular distance at the short-bridged (*c*) and the long-bridged side (*d*) of the two cyclobutadiene units as well as the interplanar angle γ in Table 1. The disilano and propano bridges in **14** provide approximately the same intramolecular distance giving rise to a small value for γ (6.2°) and almost equal lengths for *c* and *d* (Table 1). For **10**, **13** and **18** the differences between *c* and *d* amount to ca. 0.7 Å and the interplanar angle γ varies between 24° and 25°. The deviation is largest for **15** with about 1.1 Å difference between *c* and *d* and a γ value of 41°.

The average distances between the ligands and the cobalt atom (*a*, *b*) are close to those found for other (η^5-cyclopentadienyl)(cyclobutadiene)cobalt complexes.[14−19]

Cyclovoltammetric Investigations

To probe the interactions between the [RCpCoCbd] units in **10−18** we carried out cyclic voltammetry studies (CV).[20] As reference we used the oxidation potentials of **1** and **32**.[21] The latter species serves as a model for systems that are not influenced by the interaction of a second CpCo(Cbd) unit.



32

Compound **32** shows only one oxidation potential (Table 2) whereas for **1** two oxidation steps are observed. The one at $E^{1}_{1/2}$ = 656 mV was found to be reversible, whereas the second one at E^{ox}_{2p} = 1101 mV is irreversible.[9,21] The observed half-wave potentials for the reversible redox steps ($E^{1}_{1/2}$ and $E^{2}_{1/2}$) and the oxidation peak potentials for the irreversible steps (E^{ox}_{1p} and E^{ox}_{2p}) of **10−18** are compiled in Table 2.

We found that the differences $\Delta E = E^{2}_{1/2} - E^{1}_{1/2}$ are, with the exception of **12** and **16**, close to that found for **1**. As anticipated the oxidation potentials are highest for **13−15**

Table 1. Average distances [Å] between the metal and the C(Cp) atoms (*a*) and the C(Cbd) atoms (*b*), respectively, the distances between the cyclobutadiene rings on the short-bridged side (*c*) and opposite (*d*) as well as the average angle (γ) [°] between the planes of both cyclobutadiene units of **10**, **13−15** and **18**

Compound	a	b	c	d	γ
10	2.06 ± 0.01	1.98 ± 0.01	2.64 ± 0.02	3.29 ± 0.02	25.3 ± 0.5
13	2.07 ± 0.01	2.00 ± 0.01	2.65 ± 0.02	3.27 ± 0.02	24.5 ± 0.5
14	2.06 ± 0.01	1.99 ± 0.01	3.00 ± 0.02	3.16 ± 0.02	6.2 ± 0.5
15	2.06 ± 0.01	1.99 ± 0.01	2.72 ± 0.02	3.79 ± 0.02	41.4 ± 0.5
18	2.06 ± 0.01	1.99 ± 0.01	2.65 ± 0.02	3.27 ± 0.02	24.0 ± 0.5

Table 2. Half wave potentials ($E^1_{1/2}$ and $E^2_{1/2}$) or oxidation peak potentials (E^{ox}_{1p} and E^{ox}_{2p}) of **1**, **10**−**18** and **32**; the values are given in mV vs. Ag/AgCl[a]

Compound	$E^1_{1/2}$	E^{ox}_{1p}	$E^2_{1/2}$	E^{ox}_{2p}
32	801			
1	656			1101[b]
10	857		1260	
11	742		1278	
12	889		1218	
13	1119			1520[b]
14		1196[b]		1596[b]
15	1176			1567[b]
16		682[b]		1032[b]
17	835		1233	
18	856		1279	

[a] Solvent: CH_2Cl_2, 0.1 M of NBu_4PF_6. [b] Irreversible oxidation.

due to the electron-withdrawing effect of the methoxycarbonyl group. The difference between ΔE correlates approximately with the average distance [$(c + d)/2$] of the cyclobutadiene moieties: it is largest for **11** and smallest for **15**. To probe any transannular interactions between the molecular halves we carried out further cyclovoltammetric studies on the donor/acceptor superphanes **24** and **26**−**31**. The measured half wave potentials ($E^1_{1/2}$ and $E^2_{1/2}$) or the oxidation peak potentials (E^{ox}_{1p} and E^{ox}_{2p}) are compared in Table 3.

Table 3. Half wave potentials ($E^1_{1/2}$ and $E^2_{1/2}$) or oxidation peak potentials (E^{ox}_{1p} and E^{ox}_{2p}) of **24** and **26**−**31**; the values are given in mV vs. Ag/AgCl[a]

Compound	$E^1_{1/2}$	E^{ox}_{1p}	$E^2_{1/2}$	E^{ox}_{2p}
24	851		1270	
26		737[b]		1260[b]
27		733[b]		1316[b]
28	941			1505[b]
29	899			1382[b]
30	916		1430	
31		803[b]		1485[b]

[a] Solvent: CH_2Cl_2, 0.1 M of NBu_4PF_6. [b] Irreversible oxidation.

We noticed that the first oxidation step is reversible with the exception of the superphanes containing the $(CH_3)_5$Cp ligand (**26**, **27** and **31**). The second oxidation step was found to be irreversible in most cases, possibly indicating an electrochemical-chemical-electrochemical (ECE) mechanism.

A comparison between the first oxidation potentials of **10** (857 mV), **24** (851 mV) and **26** (737 mV) as well as **28** (941 mV), **30** (916 mV), **29** (899 mV) and **31** (803 mV) shows a decrease of the first oxidation step in both series. This was anticipated since the donor character of one Cp ring increases in both series.[22] This finding suggests that the first electron is removed from the RCpCo fragment where R is either CH_3, $Si(CH_3)_3$ or $(CH_3)_5$. The assumption that the electrochemical oxidation removes the first electron from the donor-substituted unit allows us to probe the intramolecular interaction in the radical cation. A comparison of the first oxidation potentials of the pairs **10/28**, **24/29** and **26/31** shows in all three cases that the methoxycarbonyl substituent causes a shift of the first oxidation potential to higher values: $E^1_{1/2}(\mathbf{10}) - E^1_{1/2}(\mathbf{28}) = -84$ mV, $E^1_{1/2}(\mathbf{24}) - E^1_{1/2}(\mathbf{29}) = -48$ mV and $E^{ox}_{1p}(\mathbf{26}) - \mathrm{E}^{ox}_{1p}(\mathbf{31}) = -66$ mV. Due to the irreversibility the values obtained for **26** and **31**, their differences have to be taken with a grain of salt. This increase of the oxidation potential is indicative of the delocalization of the positive charge between the two π-fragments of the cyclophanes. These results demonstrate the same tendency as for the carbocyclic systems.

Conclusion

The use of cyclic diynes with a short bridge on one side enabled us to synthesize and characterize the superphanes **10**−**18** and **24**−**31**. Structural investigations reveal that the two planes of the cyclobutadiene rings deviate from being parallel due to the different lengths of the bridges. The CV data indicate that the intramolecular distance of the cyclobutadiene rings affects the potential difference between the first two oxidation potentials. The comparison between the pairs of donor/acceptor superphanes **10/28**, **24/29** and **26/31** shows a clear substituent effect of the distant ester group on the electron-rich part of the molecule. This result corroborates the model of charge delocalization for the superphanes investigated.

Experimental Section

General: All melting points are uncorrected. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^{1}H NMR at 200, 300 or 500 MHz and ^{13}C NMR at 50, 75 or 125 MHz) using the solvent as internal standard (δ). The mass spectra refer to data from a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22 FT-IR-spectrometer. UV/Vis absorption data were recorded using a Hewlett Packard HP 8452A Diode Array-spectrometer. Elemental analysis: Microanalytical laboratory of the University of Heidelberg. All reactions were carried out under an argon atmosphere using dried and oxygen-free solvents.

X-ray Crystallography and Structure Solution: Data were collected on a Siemens CCD-diffractometer at 200 K. Relevant crystal and data collection parameters are given in Table 4. The structures were solved by direct methods and refined against F^2 with a full-matrix least-square algorithm by using SHELXTL-97[23] software. An empirical absorption correction was applied by using SADABS,[24] based on the Laue symmetry of the reciprocal space.

CCDC-179719 (**10**), CCDC-179720 (**13**), CCDC-179721 (**14**), CCDC-179722 (**15**), CCDC-179723 (**18**) and CCDC-179724 (**23**) 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].

Electrochemistry: A traditional three-electrode, three-compartment cell was employed for cyclic voltammetry experiments with a Ag/AgCl reference electrode in CH_2Cl_2 separated from the test solution by a Haber−Luggin capillary. The $E^1_{1/2}$ and $E^2_{1/2}$ values reported for

Table 4. Crystal data and structural refinement for **10**, **13**, **14**, **15**, **18** and **23**

	10	**13**	**14**	**18**	**15**	**23**
Empirical formula	$C_{32}H_{46}Co_2Si_4$	$C_{36}H_{50}Co_2O_4Si_4$	$C_{36}H_{50}Co_2O_4Si_4$	$C_{38}H_{62}Co_2Si_6$	$C_{38.50}H_{54}Cl_{1.50}Co_2O_4Si_4$	$C_{32}H_{51}CoSi_4$
Mol. wt.	660.91	776.98	776.98	805.28	864.21	607.02
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$C2/c$	$P2/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temp [K]	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
Z	4	4	4	2	8	2
a [Å]	23.6960(4)	20.7948(4)	9.3517(1)	9.3254(1)	18.8837(2)	9.1911(2)
b [Å]	8.5413(1)	8.4898(1)	21.6918(2)	14.7928(1)	22.5698(2)	13.3105(3)
c [Å]	18.1854(3)	20.8561(4)	18.4924(2)	17.1732(2)	22.6874(1)	13.9913(3)
α [deg]	90	90	90	67.525(1)	66.6690(10)	97.282(1)
β [deg]	113.010(1)	93.4340(10)	94.3120(10)	78.383(1)	73.0420(10)	90.167(1)
γ [deg]	90	90	90	74.740(1)	89.7280(10)	92.351(1)
V [Å^3]	3387.78(9)	3675.40(11)	3740.66(7)	2098.37(4)	8424.89(12)	1696.38(6)
$D_{calcd.}$ [g/m^3]	1.30	1.40	1.38	1.27	1.36	1.19
Abs coeff μ [mm^{-1}]	1.14	1.07	1.05	0.99	1.03	0.67
Crystal shape	polyhedron	polyhedron	block	polyhedron	polyhedron	polyhedron
Crystal size [mm^3]	0.38 × 0.19 × 0.10	0.50 × 0.10 × 0.06	0.48 × 0.18 × 0.16	0.40 × 0.30 × 0.20	0.48 × 0.30 × 0.16	0.55 × 0.20 × 0.04
θ range for data coll [deg]	1.9 to 25.6	2.0 to 27.5	1.9 to 27.4	1.3 to 27.5	1.9 to 27.5	1.5 to 26.4
Index ranges	$-27 \le h \le 28$ $-10 \le k \le 10$ $-21 \le l \le 20$	$-26 \le h \le 26$ $-10 \le k \le 11$ $-27 \le l \le 26$	$-12 \le h \le 12$ $-28 \le k \le 28$ $-23 \le l \le 23$	$-12 \le h \le 12$ $-19 \le k \le 19$ $-22 \le l \le 22$	$-24 \le h \le 24$ $-29 \le k \le 29$ $-29 \le l \le 29$	$-11 \le h \le 11$ $-16 \le k \le 16$ $-17 \le l \le 17$
Reflns collected	12193	36700	38155	21918	87422	16324
Indep reflns [R(int)]	2943 (0.023)	8382 (0.0859)	8527 (0.0402)	9545 (0.0282)	38545 (0.0522)	6912 (0.0361)
Observed reflns	2545 [$I > 2\sigma(I)$]	5546 [$I > 2\sigma(I)$]	6819 [$I > 2\sigma(I)$]	7936 ($I > 2\sigma(I)$]	22537 ($I > 2\sigma(I)$]	4984 ($I > 2\sigma(I)$]
Max. and min. transm.	0.92 and 0.79	0.95 and 0.77	0.86 and 0.64	0.86 and 0.75	0.87 and 0.76	0.97 and 0.81
Data/restraints/params.	2942/110/222	8382/15/454	8527/0/425	9545/0/42	38545/154/1911	6912/0/347
Goodness-of-fit on F^2	1.08	1.00	1.02	1.04	1.00	1.02
$R(F)$	0.026	0.042	0.034	0.030	0.053	0.040
$R_W(F^2)$	0.067	0.079	0.080	0.076	0.117	0.094
(Δp)max, (Δp)min [e Å^{-3}]	0.39 and −0.21	0.45 and −0.50	0.92 and −0.42	0.60 and −0.36	0.94 and −0.95	0.42 and −0.37

chemically reversible systems are an average of the observed anodic and cathodic peak potentials, whereas the E_{1p}^{ox} and E_{2p}^{ox} values for chemically irreversible systems are the absolute values of the anodic peak potential. A supporting electrolyte concentration of 0.1 M of NBu_4PF_6 was employed unless otherwise noted. The working electrode for cyclic voltammetry was a glassy carbon disk GC disk of 3 mm diameter. The potential of the ferrocene/ferrocenyl system was set with an error of 5 mV at 721 mV vs. SCE at a scan rate of 100 mVs^{-1} and of 200 mVs^{-1}.

1,1,2,2-Tetramethyl-1,2-disilacyclonona-3,8-diyne (8): 1,6-Heptadiyne (0.46 g, 5.0 mmol) was dissolved in 50 mL of THF. At −20 °C a butyllithium solution (1.6 M in hexane; 7.5 mL, 12.0 mmol) was added and the mixture was stirred for 30 minutes at this temperature. After warming the mixture to room temperature it was cooled again (−20 °C) and 1,2-dichloro-1,1,2,2-tetramethyldisilane (0.94 g, 5.0 mmol) dissolved in 25 mL of THF was added over two hours. While stirring for a further hour the reaction mixture reached room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CCl_4) to give 0.10 g (10.0%) of colorless crystals; m.p. 49 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (m, 4 H, CH_2), 1.85 (m, 2 H, CH_2), 0.21 [s, 12 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 114.8 [$Si(CH_3)_2$], 88.1 ($C_{\equiv}$), 28.4 (CH_2), 21.2 (CH_2), −2.4 (CH_2) ppm. HRMS (positive EI) calcd. for $C_{11}H_{18}Si_2$ ([M]$^+$): 206.0947; found 206.0959 (+1.2 mmu). IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2896, 2157, 1428, 1320, 1244. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 226 nm (3.88). $C_{11}H_{18}Si_2$ (206.4): calcd. C 64.00, H 8.79; found C 63.89, H 8.81.

Superphane 10: A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (93 mg, 0.45 mmol) and [CpCo(COD)] (130 mg, 0.55 mmol) in 8 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 8 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CCl_4) to give 104 mg (70.0%) of yellow crystals; m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (s, 10 H, CpH), 2.25−2.00 (m, 8 H, CH_2), 0.09 [s, 24 H, $Si(CH_3)_2$], −0.19 (m, 4 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 90.1 (C_{Cbd}), 77.9 (CH), 64.4 (C_{Cbd}), 24.5 (CH_2), 7.0 ($SiCH_2$), 3.0 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_2$] ppm. HRMS (positive EI) calcd. for $C_{32}H_{46}Co_2Si_4$ ([M]$^+$): 660.1340; found 660.1340 (±0.0 mmu). IR (KBr): $\tilde{\nu}$ = 2949 cm^{-1}, 2848, 1624, 1478, 1407, 1248. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 224 nm (4.62), 294 (4.64), 336 (3.59), 392 (3.08). $C_{32}H_{46}Co_2Si_4$ (660.9): calcd. C 58.15, H 7.02; found C 58.29, H 7.15.

Superphane 11: A solution of 1,1,2,2-tetramethyl-1,2-disilacyclonona-3,8-diyne (**8**) (93 mg, 0.45 mmol) and [CpCo(COD)] (130 mg, 0.55 mmol) in 8 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 8 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (alumina III/petroleum ether) to give 16 mg (11.0%) of yellow crystals; m.p. > 250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.68 (s, 10 H, CpH), 2.13−1.26 (m, 12 H, CH_2), 0.21 (s, 12 H, $SiCH_3$), 0.12 (s, 12 H, $SiCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 93.0 (C_{Cbd}), 78.2 (CH), 65.3 (C_{Cbd}), 28.4 (CH_2), 26.9 (CH_2), −1.5 [$Si(CH_3)_2$], −1.7 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{32}H_{46}Co_2Si_4$ ([M]$^+$): 660.1340; found 660.1306 (−3.6 mmu). IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 2941, 2900, 1631, 1245. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 234 nm (4.53), 300 (4.49), 404 (3.04). $C_{32}H_{46}Co_2Si_4$ (660.9): calcd. C 58.15, H 7.02; found C 58.54, H 7.33.

Superphane 12: A solution of 1,1,4,4-tetramethyl-1,4-disilacyclodeca-5,9-diyne (**9**) (100 mg, 0.45 mmol) and [CpCo(COD)] (130 mg, 0.55 mmol) in 8 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 8 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CCl_4) to give 94 mg (61.0%) of yellow crystals; m.p. > 250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.60 (s, 10 H, CpH), 2.36−1.94 (m, 8 H, CH_2), 0.45 (s, 8 H, $SiCH_2$), 0.00 [s, 12 H, $Si(CH_3)_2$], −0.08 [s, 12 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 90.5 (C_{Cbd}), 79.0 (CH), 64.3 (C_{Cbd}), 26.7 (CH_2), 8.6 ($SiCH_2$), 0.1 [$Si(CH_3)_2$], −0.4 [$Si(CH_3)_2$] ppm. HRMS (positive EI) calcd. for $C_{34}H_{50}Co_2Si_4$ ([M]$^+$): 688.1654; found 688.1659 (+0.5 mmu). IR (KBr): $\tilde{\nu}$ = 2943 cm^{-1}, 2898, 1624, 1473, 1408, 1246. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 224 nm (4.62), 284 (4.66), 322 (3.70), 394 (3.23). $C_{34}H_{50}Co_2Si_4$ (689.0): calcd. C 59.27, H 7.31; found C 59.41, H 7.42.

Superphane 13: A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (93 mg, 0.45 mmol) and [H_3CO_2CCpCo(COD)] (160 mg, 0.55 mmol) in 8 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 12 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2, petroleum ether/diethyl ether 5:1) to give 116 mg (66.0%) of yellow crystals; m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (pseudo t., 4 H, CpH), 4.90 (pseudo t., 4 H, CpH), 3.72 (s, 6 H, OCH_3), 2.10−1.93 (m, 8 H, CH_2), 0.08 [s, 24 H, $Si(CH_3)_2$], −0.20 (m, 4 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0 (CO), 92.0 (C_{Cp}), 83.5 (C_{Cbd}), 81.3 (CH), 80.2 (CH), 67.3 (C_{Cbd}), 50.9 (OCH_3), 23.4 (CH_2), 6.8 ($SiCH_2$), 2.8 [$Si(CH_3)_2$], −0.3 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{36}H_{50}Co_2O_4Si_4$ ([M]$^+$): 776.1450; found 776.1411 (−3.9 mmu). IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1}, 1710, 1464, 1281, 1247. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 222 (4.66), 282 (4.45), 298 (4.62), 344 (3.67), 414 (2.32). $C_{36}H_{50}Co_2O_4Si_4$ (777.0): calcd. C 55.65, H 6.49; found C 55.76, H 6.65.

Superphane 14: A solution of 1,1,2,2-tetramethyl-1,2-disilacyclonona-3,8-diyne (**8**) (54 mg, 0.26 mmol) and [H_3CO_2CCpCo(COD)] (88 mg, 0.30 mmol) in 6 mL of cyclooctane was heated to 130 °C. The reaction progress was checked by TLC and after 5 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/petroleum ether/diethyl ether 10:1) to give 15 mg (14.7%) of orange crystals; m.p. 242 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23 (pseudo t., 4 H, CpH), 4.89 (pseudo t., 4 H, CpH), 3.73 (s, 6 H, OCH_3), 2.00−1.97 (m, 8 H, CH_2), 1.71−1.65 (m, 4 H, CH_2), 0.20 [s, 12 H, $Si(CH_3)_2$], 0.11 [s, 12 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5 (CO), 94.8 (C_{Cp}), 83.5 (C_{Cbd}), 81.5 (CH), 80.4 (CH), 68.3 (C_{Cbd}), 51.2 (OCH_3), 27.9 (CH_2), 26.0 (CH_2), −1.9 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{36}H_{51}Co_2O_4Si_4$ ([M + H]$^+$): 777.1528; found 777.1481 (−4.7 mmu). IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 1710, 1630, 1466, 1361, 1256. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 282 nm (4.35), 300 (4.46).

Superphane 15: A solution of 1,1,4,4-tetramethyl-1,4-disilacyclodeca-5,9-diyne (**9**) (230 mg, 1.04 mmol) and [(H_3CO_2CCp)Co(COD)] (350 mg, 1.20 mmol) in 25 mL of cyclooctane was heated to 130 °C. The reaction progress was checked by TLC and after 7 days the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2, CH_2Cl_2/EtOAc 20:1) to give 38 mg (9.0%) of orange crystals; m.p. 176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.23 (pseudo t., 4 H, CpH), 4.90 (pseudo t., 4 H, CpH), 3.74 (s, 6 H, OCH_3), 2.25−2.23 (m, 4 H, CH_2), 2.01−1.99 (m, 4 H, CH_2), 0.54 (s, 8 H, $SiCH_2$), 0.10 [s, 12 H, $Si(CH_3)_2$], 0.00 [s, 12 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7 (CO), 93.0 (C_{Cp}), 85.0 (C_{Cbd}), 82.8 (CH), 81.9 (CH), 68.0 (C_{Cbd}), 51.9 (OCH_3), 26.0 (CH_2), 9.2 ($SiCH_2$), 0.4 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{38}H_{54}Co_2O_4Si_4$ ([M]$^+$): 804.1763; found 804.1793 (+3.0 mmu). IR (KBr): $\tilde{\nu}$ = 2949 cm^{-1}, 2896, 1712, 1633, 1465, 1325, 1282. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 288 nm (4.39), 318 (3.56), 400 (2.91). $C_{38}H_{54}Co_2O_4Si_4$ (805.1): calcd. C 56.69, H 6.76; found C 56.10, H 7.04.

Superphane 16: A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (81 mg, 0.39 mmol) and [$(CH_3)_5CpCo(C_2H_4)_2$] (113 mg, 0.45 mmol) in 10 mL of cyclooctane was heated to 50 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/petroleum ether/diethyl ether 10:1) to give 17 mg (10.8%) of orange crystals; m.p. 226 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.89 (s, 30 H, $CpCH_3$), 1.85 (m, 8 H, CH_2), 0.26 [s, 12 H, $Si(CH_3)_2$], 0.17 [s, 12 H, $Si(CH_3)_2$], −0.02 (d, 2 H, $SiCH_2$), −0.31 (d, 2 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 88.3 (C_{Cbd}), 88.3 (C_{Cp}), 86.2 (C_{Cbd}), 23.9 (CH_2), 11.4 [$(CH_3)_5$], 11.0 ($SiCH_2$), 3.1 [$Si(CH_3)_2$], 0.7 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{42}H_{66}Co_2Si_4$ ([M]$^+$): 800.2899; found 800.2902 (+0.3 mmu). IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1}, 2903, 1633, 1245. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 242 nm (4.75), 252 (4.77), 308 (4.85). $C_{42}H_{66}Co_2Si_4$ (801.2): calcd. C 62.96, H 8.31; found C 62.96, H 8.21.

Superphane 17: A solution of 1,1,2,2-tetramethyl-1,2-disilacyclonona-3,8-diyne (**8**) (54 mg, 0.26 mmol) and [$(CH_3)_5CpCo(C_2H_4)_2$] (75 mg, 0.30 mmol) in 6 mL of cyclooctane was heated to 55 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (alumina III/petroleum ether) to give 41 mg (39.1%) of orange crystals; m.p. > 250 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.92 [s, 30 H, $Cp(CH_3)_5$], 1.94−1.67 (m, 12 H, CH_2), 0.35 [s, 12 H, $Si(CH_3)_2$], 0.28 (s, 12 H, $Si(CH_3)_2$ ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 88.1 (C_{Cbd}), 88.0 (C_{Cp}), 64.0 (C_{Cbd}), 28.9 (CH_2), 25.3 (CH_2), 11.2 [$(CH_3)_5$], −1.5 [$Si(CH_3)_2$], −2.0 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{42}H_{66}Co_2Si_4$ ([M]$^+$): 800.2938; found 800.2922 (−1.6 mmu). IR (KBr): $\tilde{\nu}$ = 2902 cm^{-1}, 1629, 1244. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 318 nm (4.96), 364 (3.79), 408 (3.13). $C_{42}H_{66}Co_2Si_4$ (801.2): calcd. C 62.97, H 8.30; found C 62.46, H 8.53.

Superphane 18: A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (93 mg, 0.45 mmol) and [$(CH_3)_3Si$ $CpCo(CO)_2$] (107 mg, 0.55 mmol) in 8 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 6 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/petroleum ether) to give 105 mg (68.0%) of yellow crystals; m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.63 (m, 4 H, CpH), 4.56 (m, 4 H, CpH), 2.2−2.0 (m, 8 H, CH_2), 1.9 (s, 6 H, CH_3), 0.1 [s, 24 H, $Si(CH_3)_2$], −0.2 (m, 4 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.7 (C_{Cp}), 89.2 (C_{Cbd}), 79.0 (CH), 76.8 (CH), 64.0 (C_{Cbd}), 24.5 (CH_2), 13.5 (CH_3), 7.3 ($SiCH_2$), 3.1 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{34}H_{50}Co_2Si_4$ ([M]$^+$): 688.1654; found 688.1664 (+1.0 mmu). IR (KBr): $\tilde{\nu}$ = 2947 cm^{-1}, 2923, 2850, 1632, 1473, 1246. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 224 nm (4.68), 296 (4.69), 376 (3.22). $C_{34}H_{50}Co_2Si_4$ (689.0): calcd. C 59.27, H 7.31; found C 59.33, H 7.45.

{(1,2,10,11-η)-3,3,5,5,16,16,18,18-Octamethyl-3,5,16,18-tetrasilatricyclo[9.7.0.0$^{2.10}$]octadeca-1,10-diene-6,14-diyne}(η^5-cyclopentadienyl)cobalt (20): A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (290 mg, 1.40 mmol) and [$CpCo(CO)_2$] (126 mg, 0.70 mmol) in 20 mL of cyclooctane was heated to 100 °C. The reaction progress was checked by TLC and after 7 days the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CCl_4, CCl_4/CH_2Cl_2 10:1) to give 140 mg (37.0%) of orange crystals; m.p. 152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.71 (s, 5 H, CpH), 2.34−2.11 (m, 8 H, CH_2), 0.34 [s, 6 H, $Si(CH_3)_2$], 0.22 [s, 6 H, $Si(CH_3)_2$], 0.10 [s, 12 H, $Si(CH_3)_2$], 0.05 (d, 2 H, $SiCH_2$), −0.16 (d, 2 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.6 ($C_{\equiv}$), 89.7 ($C_{\equiv}$), 88.7 (C_{Cbd}), 79.5 (C_{Cp}), 68.7 (C_{Cbd}), 27.5 (CH_2), 20.9 (CH_2), 5.7 ($SiCH_2$), 5.1 [$Si(CH_3)_2$], 1.2 [$Si(CH_3)_2$], 0.6 [$Si(CH_3)_2$], 0.5 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{27}H_{41}CoSi_4$ ([M]$^+$): 536.1617; found 536.1603 (−1.4 mmu). IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2904, 2176, 1624, 1474, 1432, 1250. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 222 nm (4.32), 276 (4.43), 306 (3.33), 398 (3.16). $C_{27}H_{41}CoSi_4$ (536.9): calcd. C 60.40, H 7.70; found C 60.58, H 7.98.

{(1,2,10,11-η)-3,3,5,5,16,16,18,18-Octamethyl-3,5,16,18-tetrasilatricyclo[9.7.0.0$^{2.10}$]octadeca-1,10-diene-6,14-diyne}(η^5-methylcyclopentadienyl)cobalt (21): A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (206 mg, 1.00 mmol) and [$(CH_3)CpCo(CO)_2$] (97 mg, 0.50 mmol) in 15 mL of cyclooctane was heated to 100 °C. The reaction progress was checked by TLC and after 7 days the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CCl_4, CCl_4/CH_2Cl_2 10:1) to give 82 mg (30.0%) of orange crystals; m.p. 113 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.58 (m, 2 H, CpH), 4.37 (m, 2 H, CpH), 2.34−2.05 (m, 8 H, CH_2), 1.82 (s, 3 H, CH_3), 0.22−0.00 [m, 26 H, $Si(CH_3)_2$, $SiCH_2$], −0.26 (d, 2 H, $SiCH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 109.8 ($C_{\equiv}$), 93.4 ($C_{\equiv}$), 88.9 (C_{Cbd}) 88.6 (C_{Cbd}), 80.6 (CH), 78.5 (CH), 68.2 (C_{Cp}), 27.1 (CH_2), 21.0 (CH_2), 13.3 (CH_3), 6.1 ($SiCH_2$), 5.3 [$Si(CH_3)_2$], 1.4 [$Si(CH_3)_2$], 0.80 [$Si(CH_3)_2$], 0.76 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{28}H_{43}CoSi_4$ ([M]$^+$): 550.1774; found 550.1804 (+3.0 mmu). IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2905, 2173, 1631, 1472, 1431, 1251. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 232 (4.23), 278 (4.42), 308 (3.31), 390 (2.87). $C_{28}H_{43}CoSi_4$ (550.9): calcd. C 61.04, H 7.87; found C 60.78, H 7.93.

{(1,2,10,11-η)-3,3,5,5,16,16,18,18-Octamethyl-3,5,16,18-tetrasilatricyclo[9.7.0.0$^{2.10}$]octadeca-1,10-diene-6,14-diyne}(η^5-trimethylsilylcyclopentadienyl)cobalt (22): A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (206 mg, 1.00 mmol) and [$(CH_3)_3SiCpCo(CO)_2$] (126 mg, 0.50 mmol) in 11 mL of cyclooctane was heated to 100 °C. The reaction progress was checked by TLC and after 7 days the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/petroleum ether/diethyl ether 10:1) to give 78 mg (23.7%) of an orange solid; m.p. 135 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 5.07 (pseudo t., 2 H, CpH), 4.55 (pseudo t., 2 H, CpH), 2.15−1.81 (m, 8 H, CH_2), 0.52 [s, 6 H, $Si(CH_3)_2$], 0.39 [s, 6 H, $Si(CH_3)_2$], 0.29 [s, 6 H, $Si(CH_3)_2$], 0.24 [s, 6 H, $Si(CH_3)_2$], 0.20 [s, 9 H, $Si(CH_3)_3$], 0.20 (d, 2 H, $SiCH_2$), −0.17 (d, 2 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 110.1 ($C_{\equiv}$), 90.2 (C_{Cbd}), 89.2 (C_{Cbd}), 87.1 (C_{Cp}), 84.7 (CH), 82.7 (CH), 70.3 ($C_{\equiv}$), 28.6 (CH_2), 21.3 (CH_2), 8.7 ($SiCH_2$), 5.7 [$Si(CH_3)_2$], 1.8 [$Si(CH_3)_2$], 1.1 [$Si(CH_3)_2$], 0.2 [$Si(CH_3)_3$] ppm. HRMS (FAB+) calcd. for $C_{30}H_{49}CoSi_5$ ([M]$^+$): 608.2012; found 608.1996 (−1.6 mmu). IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2904, 2177, 1477, 1429, 1406, 1247. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 280 nm (4.38), 312 (3.36), 398 (3.12).

{(1,2,10,11-η)-3,3,5,5,16,16,18,18-Octamethyl-3,5,16,18-tetrasilatricyclo[9.7.0.0$^{2.10}$]octadeca-1,10-dien-6,14-diyne}(η^5-pentamethylcyclopentadienyl)cobalt (23): A solution of 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**7**) (206 mg, 1.00 mmol) and [$(CH_3)_5CpCo(CO)_2$] (125 mg, 0.50 mmol) in 11 mL of cyclooctane was heated to 100 °C. The reaction progress was checked by TLC and after 7 days the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/petroleum ether/diethyl ether 10:1) to give 82 mg (27.1%) of yellow crystals; m.p. 231 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 2.07−1.61 (m, 8 H, CH_2), 1.76 (s, 15 H, $CpCH_3$), 0.49 [s, 6 H, $Si(CH_3)_2$], 0.40 [s, 6 H, $Si(CH_3)_2$], 0.32 [s, 6 H, $Si(CH_3)_2$], 0.26 [s, 6 H, $Si(CH_3)_2$], 0.20 (d, 2 H, $SiCH_2$), −0.16 (d, 2 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 110.6 ($C_{\equiv}$), 89.2 (C_{Cbd}), 88.6 (C_{Cp}), 84.5 (C_{Cbd}), 67.1 ($C_{\equiv}$), 26.9 (CH_2), 21.1 (CH_2), 11.1 [$(CH_3)_5$], 8.2 ($SiCH_2$), 4.8 [$Si(CH_3)_2$], 1.9 [$Si(CH_3)_2$], 1.2 [$Si(CH_3)_2$], 1.0 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{32}H_{51}CoSi_4$ ([M]$^+$): 606.2400; found 606.2384 (−1.6 mmu). IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1}, 2904, 2862, 2176, 1248. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 296 nm (4.54), 330 (3.44), 400 (2.92).

Superphane 24: A solution of **20** (30 mg, 0.056 mmol) and [$(CH_3)CpCo(CO)_2$] (28 mg, 0.14 mmol) in 3 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2, petroleum ether) to give 22 mg (58.0%) of yellow crystals; m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.71 (s, 5 H, CpH), 4.62 (m, 2 H, CpH), 4.56 (m, 2 H, CpH), 2.27−2.01 (m, 8 H, CH_2), 1.93 (s, 3 H, CH_3), 0.10 [s, 12 H, $Si(CH_3)_2$], 0.09 [s, 12 H, $Si(CH_3)_2$], −0.21 (m, 4 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.7 (C_{Cbd}), 90.1 (C_{Cbd}), 89.2 (C_{Cbd}), 79.0 (CH), 77.1 (CH), 76.8 (CH), 64.4 (C_{Cp}), 64.0 (C_{Cbd}), 24.5 (CH_2), 24.0 (CH_2), 13.5 (CH_3), 7.2 ($SiCH_2$), 3.0 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{33}H_{48}Co_2Si_4$ ([M]$^+$): 674.1497; found 674.1490 (−0.7 mmu). IR (KBr): $\tilde{\nu}$ = 2949 cm^{-1}, 2848, 2362, 1632, 1479, 1247. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 222 nm (4.60), 278 (4.38), 296 (4.63), 334 (3.82). $C_{33}H_{48}Co_2Si_4$ (675.0): calcd. C 58.72, H 7.17; found C 58.81, H 7.45.

Superphane 25: A solution of **22** (50 mg, 0.08 mmol) and [CpCo(COD)] (48 mg, 0.21 mmol) in 5 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 6 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2/petroleum ether 1:2) to give 27 mg (44.9%) of an orange solid; m.p. 172 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.93 (pseudo t., 2 H, CpH), 4.72 (s, 7 H, CpH), 2.24 (s, 4 H, CH_2), 2.04 (s, 4 H, CH_2), 0.12 [(br, 33 H, $Si(CH_3)_3/Si(CH_3)_2$], 0.18 (s, 4 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 90.6 (C_{Cbd}), 90.5 (C_{Cbd}), 86.0 (C_{Cbd}), 83.1 (CH), 81.1 (CH), 78.4 (CH), 64.6 (C_{Cp}), 64.0 (C_{Cbd}), 25.6 (CH_2), 25.1 (CH_2), 7.7 ($SiCH_2$), 3.5 [$Si(CH_3)_2$], 3.4 [$Si(CH_3)_2$], 0.5 [$Si(CH_3)_2$], 0.4 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_3$] ppm. HRMS (FAB+) calcd. for $C_{35}H_{54}Co_2Si_5$ ($[M]^+$): 732.1736; found 732.1740 (+0.4 mmu). IR (micro pellet): 2951 cm^{-1}, 2851, 1631, 1248. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 280 nm (4.04), 314 (3.89), 460 (3.02). $C_{35}H_{54}Co_2Si_5$ (733.1): calcd. C 57.34, H 7.42; found C 57.61, H 7.67.

Superphane 26: A solution of **23** (16 mg, 0.03 mmol) and [CpCo(COD)] (14 mg, 0.06 mmol) in 2 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 7 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2, petroleum ether) to give 11 mg (57.6%) of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.71 (s, 5 H, CpH), 2.19 (m, 8 H, CH_2), 1.79 (s, 15 H, $CpCH_3$), 1.54 (cyclooctane), 0.39 (s, 4 H, $SiCH_2$), −0.01 [s, 24 H, $Si(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 96.0 (C_{Cbd}), 88.3 (C_{Cbd}), 86.0 (C_{Cbd}), 78.2 (CH), 63.7 (C_{Cp}), 26.7 (cyclooctane), 24.7 (CH_2), 23.7 (CH_2), 11.1 [$(CH_3)_5$], 9.1 ($SiCH_2$), 1.1 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{37}H_{56}Co_2Si_4$ ($[M]^+$): 730.2123; found 730.2142 (+1.9 mmu). IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1}, 2852, 1632, 1445, 1378, 1247. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 282 nm (4.01), 306 (4.22), 352 (3.34), 382 (3.04).

Superphane 27: A solution of **22** (41 mg, 0.07 mmol) and [$(CH_3)_5CpCo(COD)$] (49 mg, 0.17 mmol) in 4 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 7 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2/petroleum ether 1:2) to give 13 mg (24.1%) of an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.96 (pseudo t., 2 H, CpH), 4.71 (s, 2 H, CpH), 2.23 (s, 4 H, CH_2), 1.90 (s, 4 H, CH_2), 1.56 (s, 15 H, $CpCH_3$), 0.11 [br, 33 H, $Si(CH_3)_3/Si(CH_3)_2$], −0.20 (d, 4 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 90.9 (C_{Cbd}), 88.6 (C_{Cbd}), 86.3 (C_{Cbd}), 83.1 (CH), 81.3 (CH), 63.8 (C_{Cp}), 27.1 (CH_2), 25.7 (CH_2), 11.4 [$(CH_3)_5$], 9.6 ($SiCH_2$), 3.8 [$Si(CH_3)_2$], 2.9 [$Si(CH_3)_2$], 1.4 [$Si(CH_3)_3$], 0.6 [$Si(CH_3)_2$], 0.3 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{40}H_{64}Co_2Si_5$ ($[M]^+$): 802.2519; found 802.2507 (−1.2 mmu). IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1}, 2853, 1638, 1261, 1244. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = nm 284 (4.21), 306 (4.41), 348 (3.57), 398 (2.12).

Superphane 28: A solution of **20** (30 mg, 0.056 mmol) and of [$H_3CO_2CCpCo(COD)$] (41 mg, 0.14 mmol) in 3 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2) to give 32 mg (79.0%) of orange crystals; m.p. 225 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (pseudo t., 2 H, CpH), 4.90 (pseudo t., 2 H, CpH), 4.71 (s, 5 H, CpH), 3.72 (s, 3 H, OCH_3), 2.27−1.88 (m, 8 H, CH_2), 0.09 [s, 12 H, $Si(CH_3)_2$], 0.08 [s, 12 H, $Si(CH_3)_2$], −0.19 (m, 4 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4 (CO), 92.6 (C_{Cp}), 90.2 (C_{Cbd}), 83.7 (C_{Cbd}), 81.5 (CH), 80.4 (CH), 78.4 (CH), 67.7 (C_{Cbd}), 64.6 (C_{Cbd}), 51.1 (OCH_3), 24.6 (CH_2), 24.0 (CH_2), 7.2 ($SiCH_2$), 3.4 [$Si(CH_3)_2$], 3.0 [$Si(CH_3)_2$], 0.3 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{34}H_{48}Co_2O_2Si_4$ ($[M]^+$): 718.1395; found 718.1371 (−2.4 mmu). IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2850, 2362, 1715, 1632, 1465, 1281, 1249. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 224 nm (4.67), 282 (4.51), 296 (4.61). $C_{34}H_{48}Co_2O_2Si_4$ (719.0): calcd. C 56.80, H 6.73; found C 56.96, H 7.01.

Superphane 29: A solution of **21** (25 mg, 0.045 mmol) and [$(H_3CO_2CCp)Co(COD)$] (33 mg, 0.11 mmol) in 3 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2) to give 32 mg (97.0%) of yellow crystals; m.p. 198 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (m, 2 H, CpH), 4.90 (m, 2 H, CpH), 4.62 (m, 2 H, CpH), 4.55 (m, 2 H, CpH), 3.72 (s, 3 H, OCH_3), 2.18−2.02 (m, 8 H, CH_2), 1.92 (s, 3 H, CH_3), 0.09 [s, 12 H, $Si(CH_3)_2$], 0.08 [s, 12 H, $Si(CH_3)_2$], −0.19 (m, 4 H, $SiCH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1 (CO), 92.9 (C_{Cp}), 92.3 (C_{Cbd}), 89.1 (C_{Cbd}), 83.4 (C_{Cbd}), 81.2 (CH), 80.1 (CH), 79.1 (CH), 77.0 (CH), 67.4 (C_{Cbd}), 63.9 (C_{Cp}), 50.8 (OCH_3), 23.7 (CH_2), 23.6 (CH_2), 13.5 (CH_3), 7.1 ($SiCH_2$), 3.1 [$Si(CH_3)_2$], 2.7 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_2$], −0.3 [$Si(CH_3)_2$] ppm. HRMS (FAB+) calcd. for $C_{35}H_{50}Co_2O_2Si_4$ ($[M]^+$): 732.1552; found 732.1550 (−0.2 mmu). IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2850, 2362, 1714, 1632, 1466, 1281, 1247. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 222 nm (4.74), 280 (4.55), 296 (4.69). $C_{35}H_{50}Co_2O_2Si_4$ (733.0): calcd. C 57.35, H 6.88; found C 57.42, H 6.92.

Superphane 30: A solution of **22** (33 mg, 0.05 mmol) and [$H_3CO_2CCpCo(COD)$] (40 mg, 0.14 mmol) in 3 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2/petroleum ether 1:2) to give 34 mg (79.1%) of a yellow solid; m.p. 146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.28 (pseudo t., 2 H, CpH), 4.92 (m, 4 H, CpH), 4.68 (pseudo t., 2 H, CpH), 3.74 (s, 3 H, OCH_3), 2.14−1.95 (m, 8 H, CH_2), 0.13 [br, 33 H, $Si(CH_3)_3/Si(CH_3)_2$], −0.18 (s, 4 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.5 (CO), 92.7 (C_{Cp}), 90.4 (C_{Cbd}), 86.2 (C_{Cbd}), 83.2 (CH), 81.7 (CH), 81.2 (CH), 80.0 (CH), 67.6 (C_{Cbd}), 63.9 (C_{Cp}), 51.3 (OCH_3), 25.4 (CH_2), 24.1 (CH_2), 7.6 ($SiCH_2$), 3.6 [$Si(CH_3)_2$], 3.1 [$Si(CH_3)_2$], 0.5 [$Si(CH_3)_2$], 0.1 [$Si(CH_3)_2$], 0.0 [$Si(CH_3)_3$] ppm. HRMS (FAB+) calcd. for $C_{37}H_{56}Co_2O_2Si_5$ ($[M]^+$): 790.1791; found 790.1788 (−0.3 mmu). IR (micro pellet): 2952 cm^{-1}, 2850, 1712, 1637, 1462, 1248. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 252 nm (4.08). $C_{37}H_{56}Co_2O_2Si_5$ (791.1): calcd. C 56.17, H 7.13; found C 56.62, H 7.39.

Superphane 31: A solution of **23** (100 mg, 0.40 mmol) and [$H_3CO_2CCpCo(COD)$] (130 mg, 0.45 mmol) in 3 mL of cyclooctane was heated to 150 °C. The reaction progress was checked by TLC and after 4 hours the reaction mixture was allowed to cool to room temperature. After removal of the solvent the crude product was purified by column chromatography (silica gel/CH_2Cl_2/petroleum ether 1:2) to give 22 mg (55.0%) of an orange solid; m.p. 212 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.28 (pseudo t., 2 H, CpH), 4.91 (pseudo t., 2 H, CpH), 3.74 (s, 3 H, OCH_3), 2.11 (s, 4 H, CH_2), 2.00 (s, 4 H, CH_2), 1.86 (s, 15 H, $CpCH_3$), 0.09 [s, 24 H, $Si(CH_3)_2$], −0.22 (s, 4 H, $SiCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.6 (CO), 92.6 (C_{Cp}), 88.4 (C_{Cbd}), 85.8 (C_{Cbd}), 83.6 (C_{Cbd}), 81.5 (CH), 80.4 (CH), 67.3 (C_{Cbd}), 63.6 (C_{Cp}), 51.2 (OCH_3), 23.7 (CH_2), 23.4 (CH_2), 11.1 [$(CH_3)_5$], 8.8 ($SiCH_2$), 2.6 [$Si(CH_3)_2$], 2.3 [$Si(CH_3)_2$], 0.3 [$Si(CH_3)_2$], −0.1 [$Si(CH_3)_2$] ppm. HRMS

(FAB+) calcd. for $C_{39}H_{58}Co_2O_2Si_4$ ($[M]^+$): 788.2178; found 788.2135 (−4.3 mmu). IR (KBr): $\tilde{\nu}$ = 2948 cm^{-1}, 2902, 2849, 1714, 1628, 1465, 1279, 1248. UV/Vis (CH_2Cl_2) (log ε): λ_{max} = 286 nm (4.50), 306 (4.58), 396 (3.26).

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft, Ludwigshafen, for their continuing support of our studies. The authors are grateful to Dr. J. Classen and A. Flatow for recording the cyclovoltammetric data.

---

[1] D. O. Cowan, F. Kaufman, *J. Am. Chem. Soc.* **1970**, *92*, 219−220.

[2] D. O. Cowan, D. Le Vanda, J. Park, F. Kaufman, *Acc. Chem. Res.* **1973**, *6*, 1−7.

[3] U. T. Mueller-Westerhoff, *Angew. Chem.* **1986**, *98*, 700−716; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 702−718.

[4] R. H. Voegeli, H. C. Kang, R. G. Finke, V. Boekelheide, *J. Am. Chem. Soc.* **1986**, *108*, 7010−7016.

[5] R. Gleiter, M. Merger, *Angew. Chem.* **1997**, *109*, 2532−2546; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2426−2439.

[6] M. Robin, P. Day, *Adv. Inorg. Radiochem.* **1967**, *10*, 247−422.

[7] S. F. Nelson, *Chem. Eur. J.* **2000**, *6*, 581−588 and references therein.

[8] R. Roers, J. Hofmann, J. Classen, R. Gleiter, *Tetrahedron Lett.* **2001**, *42*, 5871−5873.

[9] M. E. Stoll, S. R. Lovelace, W. E. Geiger, H. Schimanke, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* **1999**, *121*, 9343−9351.

[10] G. Haberhauer, R. Gleiter, *Tetrahedron Lett.* **1998**, *39*, 6695−6698.

[11] G. Haberhauer, R. Roers, R. Gleiter, *Tetrahedron Lett.* **1997**, *38*, 8679−8682.

[12] R. Gleiter, H. Stahr, B. Nuber, *Tetrahedron Lett.* **1995**, *36*, 4607−4610.

[13] Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, *J. Am. Chem. Soc.* **1983**, *105*, 1907−1912 and references therein.

[14] R. Gleiter, M. Karcher, M. L. Ziegler, B. Nuber, *Tetrahedron Lett.* **1987**, *28*, 195−198.

[15] P. E. Riley, R. E. Davis, *J. Organomet. Chem.* **1976**, *113*, 157−166.

[16] A. Efraty, *Chem. Rev.* **1977**, *77*, 691−744.

[17] A. C. Villa, L. Coghi, A. G. Manfredotti, C. Guastini, *Acta Crystallogr., Sect. B* **1974**, *30*, 2101−2112.

[18] A. Clearfield, R. Gopal, M. D. Rausch, E. F. Tokas, F. A. Higbie, I. Bernal, *J. Organomet. Chem.* **1977**, *135*, 229−248.

[19] M. D. Rausch, G. F. Westhofer, E. Mintz, G. M. Reisner, I. Bernal, A. Clearfield, J. M. Troup, *Inorg. Chem.* **1979**, *18*, 2605−2615.

[20] J. Heinze, *Angew. Chem.* **1984**, *96*, 823−840; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 831−848.

[21] R. Gleiter, H. Röckel, G. Pflästerer, B. Treptow, D. Kratz, *Tetrahedron Lett.* **1993**, *34*, 8075−8078.

[22] R. Gleiter, R. Roers, J. Classen, A. Jacobi, G. Huttner, T. Oeser, *Organometallics* **2000**, *19*, 147−151.

[23] SHELXTL V5.10 G, M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin **1997**.

[24] G. Sheldrick, **1996**, unpublished work based on the method described in: R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, S1−S33.

Received February 22, 2002
[I02092]