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Reaction of a cyclopentadienylcobalt(I) phosphane chelate with trimethylsilyl chloride and some pseudohalides: unanticipated formation of new cyclopentadienylcobalt(II) and (III) chelates

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Dedicated to the memory of Wilfred Kratzert

Abstract

Some reactions of the (phosphanylethyl)cyclopentadienylcobalt(I) chelate complex **1** with trimethylsilyl chloride and some pseudohalides were investigated. Reaction of **1** with trimethylsilyl chloride, azide, isocyanate, and isothiocyanate gave cobalt(II) chelates **2**, **3**, **4**, and **5**, some of which were structurally characterized. In contrast to these reactions, treatment of **1** with trimethylsilyl cyanide resulted in the formation of dicyano cobalt(III) chelate **7**, which was also structurally characterized. Reaction of **7** followed by oxidation gave a small yield of the tetrametallic complex **8**, in which the two cobalt parts of the structure are bridged by an $(LiO)_2$ rhombus.

Keywords: Cobalt complexes; Silyl compounds; X-ray structures; Oxidative addition; (Phosphanylalkyl)cyclopentadienyl chelate complexes; Cyclopentadienylcobalt complexes

Reactions between transition metal complexes and silyl compounds play key roles in a number of catalytic as well as stoichiometric silylation reactions [1–5]. In many cases, an oxidative addition of the silyl compound is the first step in these reactions. Depending on the specific silyl compound and the nature of the transition metal, it is not always possible to isolate the intermediate formed by the oxidative addition. Remarkably, commercially available functionalized silanes such as trimethylsilyl halides and pseudohalides have only rarely been successfully used in oxidative addition reactions. In the case of trimethylsilyl chloride, this may be due to the strength of Si–Cl bond [6–8]. However, Stille and Lau [9] reported the oxidative addition of trimethylsilyl chloride to $Pd(PPh_3)_4$ or to $Pd(CO)(PPh_3)_3$ resulting in the formation of $Pd(PPh_3)_2Cl_2$ and hexamethyldisilane at 25 °C over 72 h using 3.55 equivalents of the silyl reagent. The authors propose a radical mechanism for Pd–Si cleavage.

Complexes with metal–silicon bonds are discussed as intermediates in the silyl migration observed in the rearrangement of bis(trimethylsilyl)ethyne complexes to the corresponding bis(trimethylsilyl)vinylidene complexes [10–16]. We have investigated cyclopentadienylcobalt complexes with di-*tert*-butylphosphanylethyl substituent at the cyclopentadienyl ring ($Cp^{\#}Co$) for some time. It was shown that due to the chelation possible in these complexes, the isolation of some interesting cyclopentadienylcobalt(I) complexes bearing, e.g. alkyne, cyclopropene, bicyclopropylidene, vinylcarbene or vinylidene ligands becomes possible [10,17–26]. As the ethene complex **1** easily decoordinates the ethene ligand with creation of a vacant coordination site facilitating the coordination of sensitive ligands presumably because of the stabilizing chelate effect, we decided to investigate the oxidative addition chemistry of **1** with trimethylsilyl chloride and some trimethylsilyl

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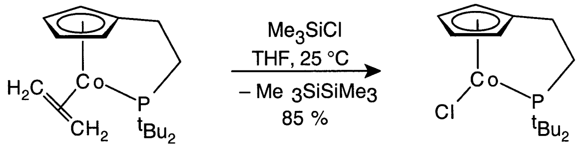
pseudohalides expecting the respective cobalt(III) complexes to be formed. In contrast to this anticipation paramagnetic cobalt(II) complexes, which were structurally characterized, were obtained in most cases. Only in one case, cobalt(III) chelate was obtained; however, the reaction obviously is not explained by a simple oxidative addition.

When **1** was treated with chlorotrimethylsilane at 25 °C in THF, a 85% yield of the paramagnetic 17-electron chlorocobalt(II) chelate **2** was obtained [23]. In addition to **2**, hexamethyldisilane was detected as a reaction product by GC–MS. After crystallization from diethyl ether, a crystal structure analysis of **2** was performed (Fig. 1).



1 **2**

2 crystallizes in the orthorhombic space group *Pbca*. The analysis confirms the constitution of **2** and shows a slight ring slippage of the cyclopentadienyl ring resulting in shortened bond lengths between the cobalt atom and C1 and C2. While the phosphane region is sterically highly shielded, the area around the chloro ligand is well accessible.

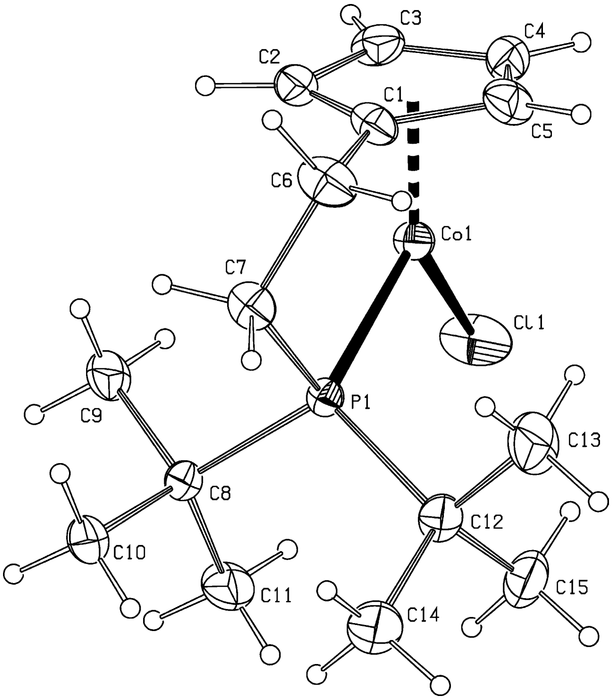
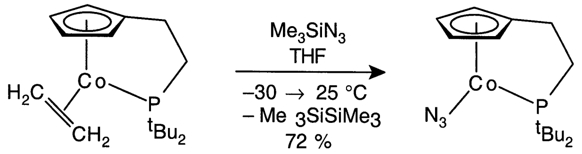


Fig. 1. Structure of **2** in the crystal. Selected bond lengths (Å): Co1–C1, 2.020(6); Co1–C2, 2.072(6); Co1–C3, 2.109(5); Co1–C4, 2.103(6); Co1–C5, 2.097(6); Co1–Cl1, 2.195(2); Co1–P1, 2.204(2). Selected bond angle (°): Cl1–Co1–P1, 103.5(1).

In the next experiment, **1** was treated with trimethylsilyl azide in THF at −30 °C. Upon warming to 25 °C a change in color from red-brown to red-purple was observed indicating the formation of a cobalt(II) complex. The chloro complex **2** dissolves in polar solvents with a similar red-purple color [23]. After work up the moderately air stable, paramagnetic azide cobalt(II) complex **3** was obtained in 72% yield. After solvent removal, hexamethyldisilane was detected in the cold trap by GC–MS.

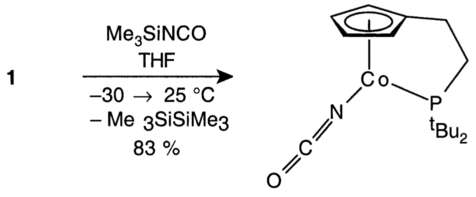


1 **2**

The mass spectrum of **3** shows the molecular ion peak at $m/z = 338$. Loss of N_2 is followed by fragmentation of N to give the $Cp^{\#}Co$ fragment ($m/z = 296$). The IR spectrum shows a characteristic absorption at 2041 cm^{-1}, which is assigned to the asymmetric azide vibration. This value is in accord with those of other azido complexes [27] and indicates a significant degree of back-bonding, which is not found in trimethylsilyl azide (2145 cm^{-1}). Some **3** was crystallized from diethyl ether–pentane (2:1) at −28 °C. The assigned constitution is confirmed by an X-ray structure analysis (Fig. 2) indicating the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit.

Bond lengths and angles are in the typical ranges [17,28]. The angle Co–N1–N2 is 123.1(4)°, which is somewhat smaller than in a rhodium complex prepared by Laubender and Werner [143.7(5)°] [29]. The azido ligand has almost a linear structure.

When **1** was treated with trimethylsilyl isocyanate, a similar change in color was observed and isocyanato chelate **4** was obtained in 83% yield as a red-purple solid. As with **2** and **3**, after solvent removal, hexamethyldisilane was detected in the cold trap by GC–MS. In the mass spectrum, the molecular ion peak is observed at $m/z = 338$ (52%), and IR absorptions for the isocyanate ligand appear at $\tilde{\nu} = 2219$ (sym) and 1330 cm^{-1} (asym). The value for trimethylsilyl isocyanate (2271 cm^{-1}) indicates some back-bonding in the cobalt complex.



4

Recrystallization of **4** from diethyl ether–pentane at

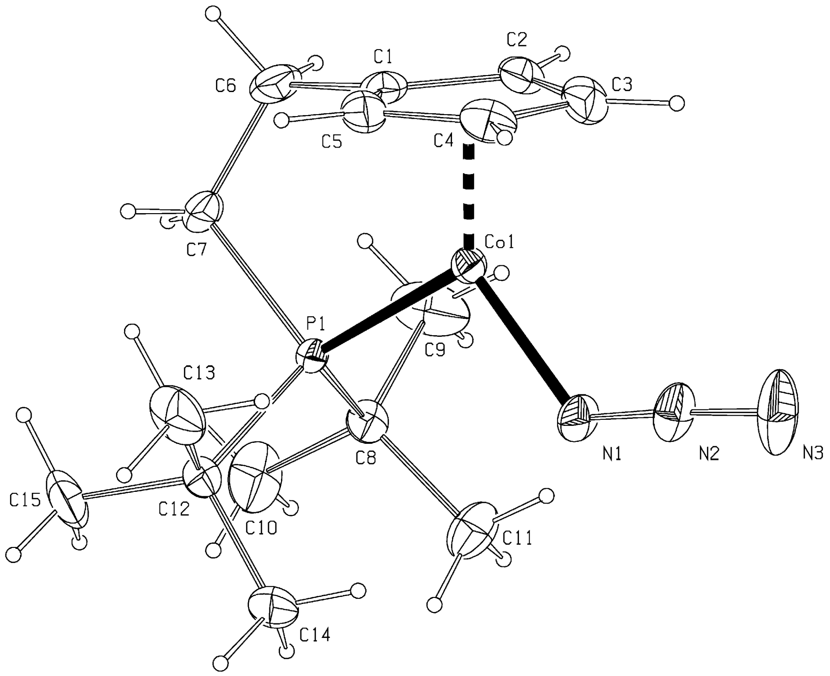


Fig. 2. Structure of **3** in the crystal. Selected bond lengths (Å): Co–C1, 2.022(4); Co–C2, 2.084(5); Co–C3, 2.085(4); Co–C4, 2.102(4); Co–C5, 2.071(4); Co–N1, 1.918(4); N1–N2, 1.111(5); N2–N3, 1.193(5); Co–P, 2.192(1). Selected bond angles (°): Co–N1–N2, 123.1(4); N1–N2–N3, 177.0(7); P–Co–N1, 100.6(1).

−28 °C gave crystals suitable for an X-ray structure analysis (Fig. 3), which is in accord with the assigned constitution. However, on the basis of the crystal structure analysis the alternative cyanate could not be excluded, because the quality of the analysis was slightly better for the cyanate than for the isocyanate. The differentiation of cyanates and isocyanates is not easy and has been discussed in the literature [30–33]. In the case of **4**, we decided to use independent spectroscopic methods in order to assign the correct constitution. For a cyanate (Co–O–C≡N), one has to expect an IR absorption band for the C–O single bond, which one would not expect for an isocyanate (Co–N=C=O) [30,33]. IR spectrum of **4** does definitely not shows an absorption, which could be assigned to C–O single bond. The mass spectrum of **4** shows the molecular ion peak at $m/z = 338$ (83%). A fragment signal at $m/z = 311$ (3%) corresponds to $[M^+ - CO + H]$ (Co–NH) in the case of an isocyanate or to $[M^+ - CN - H]$ (Co–O minus a H) in the case of a cyanate. In spite of the low intensity of this signal, we succeeded in obtaining a high-resolution mass spectrum of this peak at $m/z = 311.1171$ which corresponds to $C_{15}H_{27}CoNP$ (calc. 311.1213) and clearly not to $C_{15}H_{25}CoOP$ ($m/z = 311.0975$). On the basis of these independent measurements, we assign the isocyanate constitution to the isolated compound.

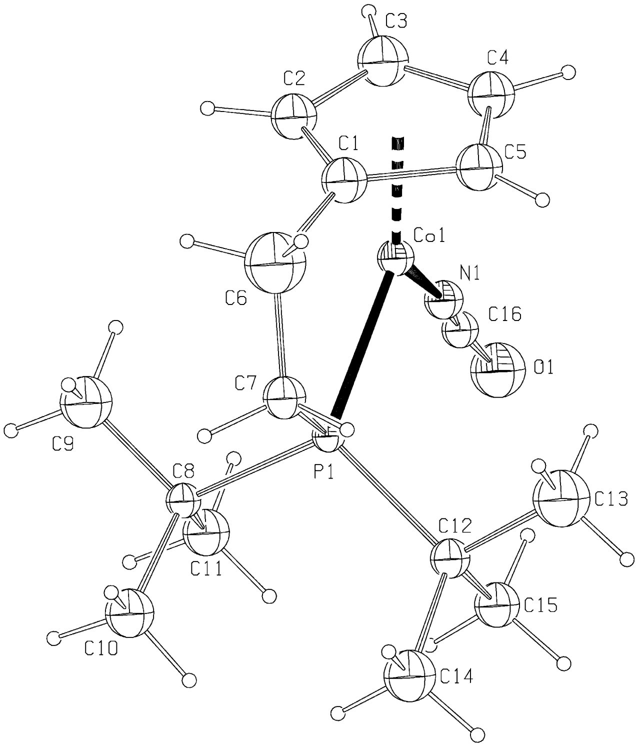
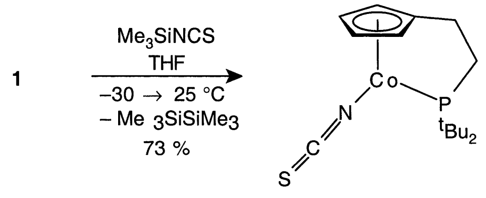


Fig. 3. Structure of **4** in the crystal. Selected bond lengths (Å): Co1–C1, 2.017(9); Co1–C2, 2.042(7); Co1–C3, 2.085(6); Co1–C4, 2.107(7); Co1–C5, 2.041(7); Co1–N1, 1.894(5); N1–C16, 0.949(6); C16–O1, 1.284(6); Co–P1, 2.189(2). Selected bond angles (°): Co1–N1–C16, 173.4(7); N1–C16–O1, 174.7(11); P1–Co1–N1, 103.5(2).

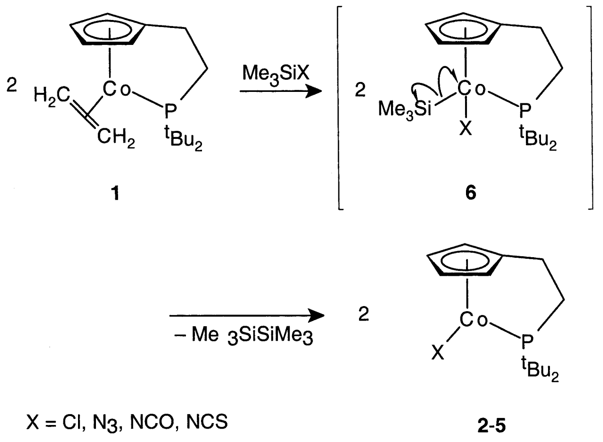
4 crystallizes in the space group *Pbca* with one molecule in the asymmetric unit. A local non-crystallographic mirror plane exists approximately in the molecule running through the atoms Co1, P1, C1, C6, C7, N1, C16, and O1. The anisotropic refinement yielded strong anisotropic displacement ellipsoids for some of these atoms indicating a static or dynamic disorder. We therefore assume that the mirror symmetry is only fulfilled in the average structure of the molecule. The figure was derived from the isotropic refinement for clarity and represents the average structure. The disorder or liberation of the isocyanate group probably causes the too short N–C16 distance of 0.95 Å. This value is slightly increased if OCN is assumed instead of NCO; however, the interatomic distances in the three atomic group are unsatisfying in both cases. A refinement of a split position model was successful for the cyclopentadienylethyl group, but failed for NCO group. Therefore, the result with strong anisotropic displacement ellipsoids was preferred for the deposition in CIF. There are a few rather special examples having longer Co–N bond lengths. **2** and **4** can be regarded as quasi-isotypic (cf. the crystal data in Section 1) [34–36].

In a manner similar to the syntheses of **2**, **3**, and **4**, the ethene complex **1** was treated with trimethylsilyl isothiocyanate. The paramagnetic isothiocyanato cobalt(II) chelate **5** was obtained in 73% yield as a blue-purple, microcrystalline material. Again, after solvent removal hexamethyldisilane was detected in the cold trap by GC–MS. In polar solvents **5** dissolves with deep red color, a solvatochromy not observed with **2**, **3**, and **4** [37]. The reason for this difference might be seen in the differences in the electronegativities of O (3.50) and S (2.44) as compared with N (3.07) resulting in a different polarity in **2** and **4** [38]. **5** was characterized by inspection of its IR and mass spectra ($m/z = 354$, M^+). After loss of the sulfur atom, fragmentation of the Co–NC bond gives the basic chelate system with $m/z = 296$. In IR spectrum the asymmetric isothiocyanate vibration band is observed at 2069 cm^{-1}, whereas the symmetric vibration band gives rise to an absorption at 1366 cm^{-1}. These values are in accordance with literature precedence [39].



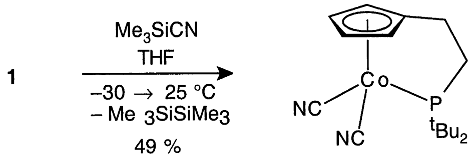
5

To our knowledge, the reactions reported so far are the first cases that a cyclopentadienylcobalt(I) complex is oxidized to cobalt(II) by reaction with trimethylsilyl chloride or pseudohalides. A plausible mechanism involves a decoordination of ethene from **1** followed by an oxidative addition of Me_3SiX (X = Cl, N_3, OCN, SCN) leading to a Co(III) intermediate **6** [40]. As it was not possible to isolate such an intermediate, we believe that a homolytic fission of Co–Si bond readily occurs leading to 17-electron cobalt(II) chelates **2**–**5**. That in **6**, Co–Si bond is cleaved instead of Co–Cl bond is in accordance with the respective bond strengths (D°_{298}(Co–Si) = 276 ± 17 kJ mol^{-1}, D°_{298}(Co–Cl) = 389 kJ mol^{-1}) [41]. Formation of hexamethyldisilane (D°_{298}(Si–Si) = 336.8 kJ mol^{-1}) is thermodynamically clearly favored. In view of the fact that in most other cases [6–8], a corresponding reaction with trimethylsilyl chloride was not observed presumably due to the strength of the Si–Cl bond (D°_{298}380–410 kJ mol^{-1}) [42], it is remarkable that the respective reaction takes place with cobalt(I) chelate **1**.



1 **6** **2-5**

Next, **1** was treated with trimethylsilyl cyanide. In contrast to the preceding experiments no cobalt(II) complex was obtained. Instead dicyano cobalt(III) chelate **7** was isolated in 49% yield. After solvent removal, hexamethyldisilane was detected in the cold trap (NMR). **7**, which forms yellowish-orange air stable crystals, was identified spectroscopically.



7

In contrast to the paramagnetic Co(II) complexes **7** allowed recording NMR spectra. In ^{1}H-NMR spectrum, the signal assigned to the *tert*-butyl groups is found at $\delta = 1.51$ ppm, which is at significantly lower field than all known complexes of Cp$^\#$Co system. The cyclopentadienyl protons give rise to two broad singlets thereby confirming the symmetric nature of the complex. In ^{13}C-NMR spectrum, the cyano resonances are observed as one doublet at $\delta = 125.7$ ($^2J_{P-C} = 10.8$ Hz). ^{31}P-NMR signal at $\delta = 118.6$ ppm indicates a coordinated phosphane tether [17]. In ^{59}Co-NMR spectrum, a signal is observed at $\delta = -171$ ppm ($\nu_{1/2} = 14$ Hz), which is quite different as compared with that of 3,3-diphenylvinylcarbene Cp$^\#$Co(I) complex (δ = ca. 1000 ppm, $\nu_{1/2}$ = ca.

100 000 Hz) [21,43]. ^{59}Co-NMR investigations of a number of cyclopentadienylcobalt complexes have been used by Bönnemann [44] for correlations between their ^{59}Co chemical shift and their catalytic activity in a Cp$^{\#}$Co catalyzed cocyclization of alkynes with nitriles giving pyridines. Recrystallization of **7** (acetone–dichloromethane, 1:1) gave crystals suitable for an X-ray structure analysis (Fig. 4).

The analysis confirms the constitution assigned on the basis of the spectroscopic data and the symmetry of the complex. **7** crystallizes in the monoclinic space group $P2_1/c$ with three complex molecules and one H_2O molecule in the asymmetric unit, which differ mainly in their orientations. The Co–C16 and Co–C17 bond lengths are close to those in hexacyanocobaltates (average Co–C distance is 1.898 Å). The values for C16–N1 and C17–N2 are also in the range of hexacyanocobaltates (average 1.114 Å). Co–C16–N1 and Co–C17–N2 deviate more from linearity than in a hexacyanocobaltate [45]. Both cyano ligands are coplanar (N1–N2–C17–C16, 0.65°).

To explain the result, we envisage an oxidative addition of the trimethylsilyl reagent after decomplexation of the ethene ligand giving an intermediate azido, isocyanato, isothiocyanato or cyano trimethylsilyl Cp$^{\#}$Co(III) complex. In the cases of azide, isocyanate and isothiocyanate then presumably a homolytic fission of Si–Co bond occurs giving Co(II) complex **2**, **3**, **4** or **5**, and a trimethylsilyl radical, which undergoes a dimerization with formation of hexamethyldisilane.

Remarkably, the reaction leads to a different result in the case of trimethylsilyl cyanide. In contrast to other cases here no cobalt(II) complex was observed. Instead, cobalt(III) complex **6** was obtained along with hexamethyldisilane. In contrast to other cases, apparently two trimethylsilyl cyanide molecules are involved. As an explanation one might envisage different pathways. One could be some type of metathesis of trimethylsilyl cyanide giving hexamethyldisilane and cyanogen. The latter might undergo an oxidative addition at **1** resulting in **6**. However, no evidence for the formation of cyanogen from trimethylsilyl cyanide under comparable conditions was found in the literature. The only reference found describes such a transformation in the presence of phosphorus(V) compounds such as PCl_5 [46]. Therefore, this possibility is considered to be less likely. Alternatively, a sequence of two oxidative additions of trimethylsilyl cyanide at cobalt followed by a reductive elimination of hexamethyldisilane might be regarded. This pathway would imply the intermediacy of a cobalt(V) complex, requiring a decomplexation of the phosphane tether. Such a temporary decomplexation in a reaction sequence was recently taken to explain a cycloreversion reaction of a related cobaltcyclobutenone [18]. Cobalt(V) complexes are very rare. Tetra(1-norbornyl)cobalt(V) cation was characterized by Theopold

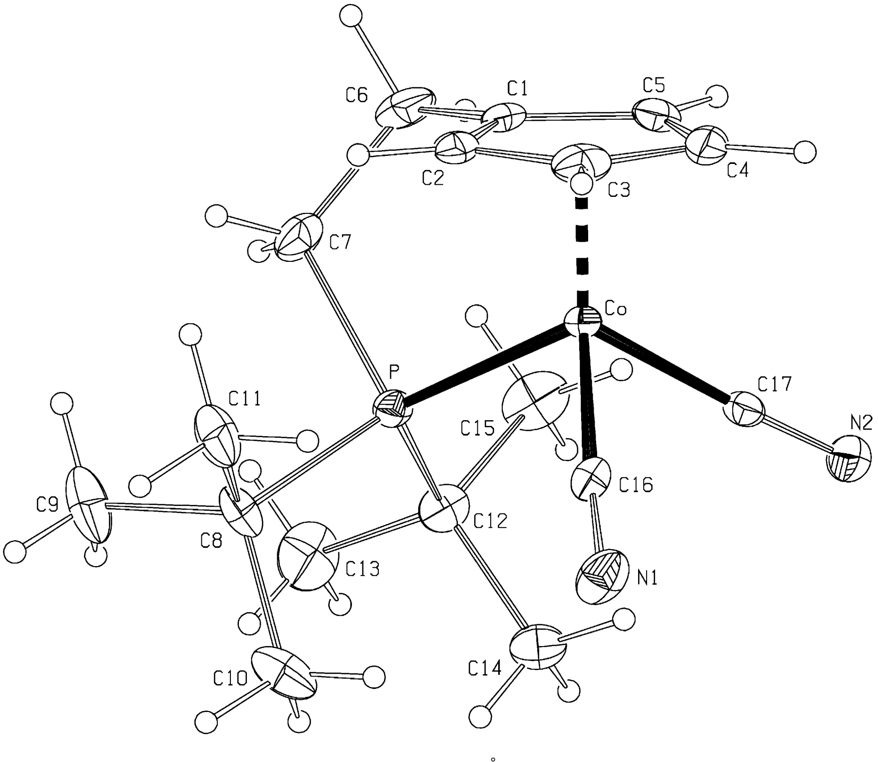


Fig. 4. Structure of one molecule of **7** in the crystal. Selected bond lengths (Å): Co–C1, 2.065(3); Co–C2, 2.079(3); Co–C3, 2.095(3); Co–C4, 2.074(3); Co–C5, 2.064(3); Co–C16, 1.874(4); Co–C17, 1.879(4); Co–P, 2.2582(9); C16–N1, 1.153(4); C17–N2, 1.155(4). Selected bond angles (°): N1–C16–Co, 176.8(3); N2–C17–Co, 175.6(3); C16–Co–P, 97.12(10); C17–Co–P, 100.35(9); C16–Co–C17, 87.86(13).

and coworkers in 1987 [47,48], and only recently Brookhart et al. [49] reported the synthesis and structural characterization of a dihydrodisilyl pentamethylcyclopentadienylcobalt(V) complex. Finally, formation of a Co(II) intermediate corresponding to **2**–**5** might be envisaged. Following decomplexation of the phosphane tether and oxidative addition of Me_3SiCN would give a presumably unstable Co(IV) intermediate which would homolytically dissociate a trimethylsilyl radical finally resulting in the formation of hexamethyldisilane and **7** after recomplexation of the phosphane tether.

There seems to be a significant propensity for a formation of **7** from trimethylsilyl cyanide. In some test experiments, cobalt(II) chloro complex **3** was treated with trimethylsilyl azide, isocyanate, isothiocyanate, and cyanide. While **3** was recovered almost quantitatively in the first three cases, reaction with trimethylsilyl cyanide afforded a 32% yield of **7**. Treatment of **3** with KCN or with AgCN led to no reaction.

In some experiments, nucleophilic attacks at the cyano ligands were tried. Although in most cases no good results were obtained, the reaction of **6** with lithium diisopropylphosphide resulted in an interesting product. In the course of the reaction, which was carried out in THF at low temperature (-30 °C → 25 °C) most of the material decomposed. After the addition of methanol and column chromatography, however, oxidized complex **8** was obtained in 6% yield as a yellowish-orange solid. Presumably during the chromatography some oxygen was introduced.

In IR spectrum, the cyano absorption is observed at 2108 cm^{-1}. The mass spectrum shows the half molecular ion peak at $m/z = 611$. Three ^{31}P-NMR signals are found not showing any P–P coupling. ^{1}H-NMR data also reflect the assigned constitution. **8** was crystallized from diethyl ether at -30 °C, and an X-ray crystal structure analysis was obtained (Fig. 5).

8 crystallizes in the monoclinic space group $P2_1/c$ with one molecule $C_{28}H_{54}CoLiNO_{2.38}P_3$ in the asymmetric unit. The occupation factor of O1 (bonded to P1) is < 1. Two molecules are connected to one another by a $(LiO)_2$ rhombus, which is centered by a crystallographic center of symmetry. The resulting dimer is shown in Fig. 5. A similar structure element has earlier been observed by Snaith and coworkers [50] in dimers and trimers of dibenzylamidolithium. The $(LiO)_2$ rhombus is planar. The lithium atoms have a tetrahedral environment with bonds to the oxygen atoms of the $(LiO)_2$ rhombus, to O3 and to N1. Phosphito complexes with their oxygen atoms being chelated by cobalt have been investigated by Kläui et al. [51]. In their published structure of such a complex, in which two cobalt complex units are connected by $(NaO)_2$ rhombus, Co–P bond lengths are shorter than in **8**.

In summary, we presented new reactions of a (phosphanoethyl)cyclopentadienyl cobalt(I) chelate with Me_3SiX (X = chloride, azide, isocyanate, isothiocyanate, cyanide), which lead to cobalt(II) complexes in the first four cases, whereas trimethylsilyl cyanide causes oxidation to a dicyanocobalt(III) complex. In all cases, hexamethyldisilane was formed along with the cobalt complexes. Presumably the reactions involve oxidative additions of the trimethylsilyl reagents followed by a homolytic Co–Si bond cleavage.

1. Experimental

1.1. General

All operations involving air-sensitive materials were performed under argon using standard Schlenk techniques. Diethyl ether, THF, benzene, and toluene were dried over Na–K–benzophenone. Silica gel was heated at reduced pressure and then put under normal pressure with argon. This was repeated five times. Starting materials were either purchased or prepared according to literature procedures. IR: Bruker ISS 25, Perkin–Elmer FT 580, FT 1710. ^{1}H-NMR: Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz). ^{13}C-NMR: Bruker AVS 200 (50.3 MHz), AVS 400 (100.6 MHz). Spectra were obtained with DEPT and with APT techniques. + and − indicate positive (C, CH_2) and negative phases (CH, CH_3), respectively. ^{31}P-NMR: H decoupled, Bruker AVS 400 (161.9 MHz), 85% aqu. H_3PO_4 as external standard. MS, FAB-MS, HRMS: Finnigan AM 400, Fisons VG Autospec. Elemental analyses: Haeraeus CHN-Rapid. Melting points: Büchi apparatus according to Dr. Tottoli, uncorrected.

1.2. General procedure (GP)

The silyl compound is added to a solution of **1** [23] in THF and is stirred for the given time. After solvent removal into a cold trap at reduced pressure, the residue is dissolved in a small volume of pentane or diethyl ether and is filtered through a frit covered with a 3-cm thick layer of Celite. The solvent is removed into a cold trap, and the residue is either cooled for crystallization or purified by column chromatography.

1.3. [2-(Di-*tert*-butylphosphanyl-κ*P*)ethyl]{η^5-cyclopentadienyl}chlorocobalt(*II*) (**2**) [23]

GP, 162 mg (0.5 mmol) of **1** [23] and 54 mg (0.5 mmol) of trimethylsilyl chloride in 20 ml of THF at 25 °C. After 1 h work up in diethyl ether, 141 mg (0.4 mmol, 85%) of **3** [23] as a black-violet solid, which was crystallized from diethyl ether at -20 °C (m.p. 192 °C, dec.).

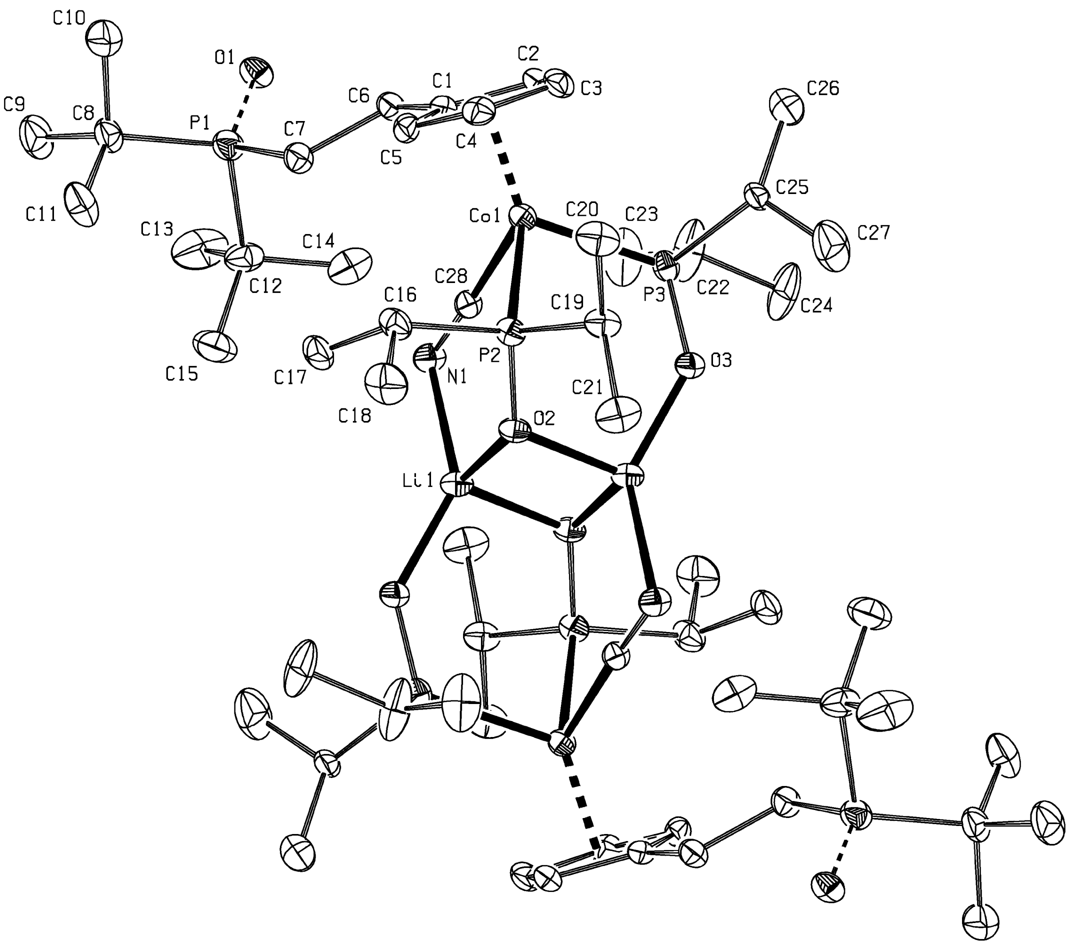


Fig. 5. Structure of **8** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths (Å): Co–C1, 2.155(5); Co–C2, 2.113(5); Co–C3, 2.081(5); Co–C4, 2.095(5); Co–C5, 2.127(4); Co–P2, 2.252(2); Co–P3, 2.247(2); Co–C28, 1.852(5); C28–N, 1.160(5); Li–N, 2.145(9); Li–O2, 1.958(9); Li–O3, 1.844(9); Li–Li, 2.57(2). Selected bond angles (°): P2–Co–P3, 90.6(1); P2–Co–C28, 83.4(2); Co–C28–N, 176.0(5); C28–N–Li, 100.8(4); Li–O3–P3, 137.5(3); N–Li–O2, 99.4(4); N–Li–O3, 135.4(5); Li–O2–Li, 81.0(4); O2–Li–O2, 99.0(4).

*1.4. Crystal structure analysis of **2***

$C_{15}H_{26}ClCoP$, molecular weight 331.71, crystal system orthorhombic, space group *Pbca*, $a = 14.832(12)$ Å, $b = 12.723(6)$ Å, $c = 17.43(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3288(5)$ Å^3, $Z = 8$, $d_{calc} = 1.340$ g cm^{-3}, $F(0\,0\,0) = 1400$ elections, $\mu = 12.9$ cm^{-1}, crystal color red-purple, crystal size 0.5 mm × 0.2 mm × 0.02 mm, Stoe IPDS (Area Detector) diffractometer, $T = 300$ K, Mo–$K_\alpha = 0.71073$ Å, $\theta_{min} = 2.34°$, $\theta_{max} = 26.13°$, three crystals were measured and their data sets combined, details are reported in the deposited CIF, no absorption correction, no extinction correction, refinement program: SHELXL-93, refinement by least-square method (F^2), $R(F) = 0.0500$, $R_w(F^2) = 0.0582$, 163 parameters, min./max. residual electron density −0.393/0.351 e Å^{-3}.

*1.5. (Azido)[2-(di-tert-butylphosphanyl-κP)ethyl]{η^5-cyclopentadienyl}cobalt(II) (**3**)*

GP, 162 mg (0.50 mmol) of trimethylsilyl azide in 30 ml of THF at −50 °C, 3 h, work up with diethyl ether–pentane (2:1). 162 mg (0.47 mmol, 72%) of **3** as a red-purple solid, which was crystallized from pentane at −28 °C (m.p. 127 °C, dec.).

IR (KBr): $\tilde{\nu} = 3440$ cm^{-1}, 3092 (w), 2960 (m, CH_3, $-CH_2-$), 2904 (m), 2868 (m), 2036 [s, $N_{3(asym)}$], 1472 (m), 1392 (w), 1368 [w, $N_{3(sym)}$], 1280 (w), 1176 (m), 1144 (w), 1020 (w), 816 (w), 680 (w), 656 (w), 616 (w), 580 (w), 496 (w), 468 (w), 428 (w). MS (70 eV, 110 °C): *m/z* (%) 338 (14) [M^+], 310 (88) [$M^+ - N_2$], 296 (11) [$M^+ - N_3$], 254 (14), 253 (10), 198 (88) [$M^+ - N_3 - C_4H_9 - C_3H_5$], 197 (100) [$M^+ - N_3 - C_4H_9 - C_3H_6$], 196 (23), 195 (29), 181 (45), 169 (35), 125 (26), 104 (16), 91 (11). HRMS ($C_{15}H_{26}CoN_3P$): calc. 338.118, Found: 338.120.

*1.6. Crystal structure analysis of **3***

$C_{15}H_{26}CoN_3P$, molecular weight 338.29, crystal system orthorhombic, space group $P2_12_12_1$, $a = 10.110(1)$ Å, $b = 12.360(2)$ Å, $c = 13.889(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1735.6(4)$ Å^3, $Z = 4$, $d_{ber} = 1.295$ g cm^{-3}, $F(0\,0\,0) = 716$ electrons, $\mu = 10.76$ cm^{-1}, crystal color red-purple, crystal size 0.41 mm × 0.18 mm × 0.16 mm, Stoe IPDS (Area Detector) diffractometer, $T = 300$ K, Mo–$K_\alpha = 0.71073$ Å, $\theta_{min} = 2.21°$, $\theta_{max} = 24.20°$, 13 715 measured reflections (±11; ±13; ±15), 2719 independent, 1848 observed reflections [$I > 2\sigma$], completeness of data: 99.2%, $R(I) = 0.0618$, no absorption correction, no extinction correction, refinement program: SHELXL-93, refinement by least-square method (F^2), $R(F) = 0.0317$, $R_w(F^2) = 0.0523$, 181 parameters, min./max. residual electron density −0.138/0.223 e Å^{-3}, Flack x parameter 0.00(2).

1.7. [2-(Di-*tert*-butylphosphanyl-κ*P*)ethyl]{η^5-cyclopentadienyl}(iso-cyanato)cobalt(II) (4)

GP, 150 mg (0.46 mmol) of **1** [23] and 53 mg (0.46 mmol) of trimethylsilyl isocyanate in 30 ml of THF at −50 °C, work up in diethyl ether. 130 mg (0.38 mmol) of **4** as a red-purple solid, which was crystallized from diethyl ether–pentane (1:1) at −28 °C (m.p. 146 °C, dec.).

IR ($CHCl_3$): $\tilde{\nu} = 3535$ cm^{-1} (w), 3084 (w), 2961 (m, CH_3, $-CH_2-$), 2219 [s, $NCO_{(asym)}$], 1473 (m), 1409 (w), 1390 (w), 1363 (m), 1330 [m, $NCO_{(sym)}$], 1182 (m), 1165 (m), 1098 (w), 1023 (m), 930 (w), 809 (s), 788 (m). MS (70 eV, 80 °C): *m*/*z* (%) 339 (9) [$M^+ + 1$], 338 (83) [M^+], 311 (3), 282 (19), 239 (62), 237 (72) [$M^+ - CO-N-C_4H_9$], 183 (100) [$Cp^{\#}Co-C_4H_9$], 137 (26). HRMS ($C_{16}H_{26}CoNOP$): Calc. 338.108. Found: 338.108. $C_{16}H_{26}CoNOP$: Calc. C, 56.81; H, 7.75; N, 4.14. Found: C, 56.51; H, 7.64; N, 3.98%.

1.8. Crystal structure analysis of 4

$C_{16}H_{26}CoNOP$, molecular weight 338.28, crystal system orthorhombic, space group *Pbca*, $a = 13.528(2)$ Å, $b = 14.062(2)$ Å, $c = 17.984(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3421.1(8)$ Å^3, $Z = 8$, $d_{ber} = 1.314$ g cm^{-3}, $F(0\,0\,0) = 1432$ e, $\mu = 10.93$ cm^{-1}, crystal color red-purple, crystal size 1.70 mm × 0.07 mm × 0.05 mm, Stoe IPDS (Area Detector) diffractometer, $T = 300$ K, Mo–$K_\alpha = 0.71073$ Å, $\theta_{min} = 2.38°$, $\theta_{max} = 24.19°$, 6961 measured reflections (−15:12; −12:16; −17:20), 2647 independent, 863 observed reflections [$I > 2\sigma$], completeness of data: 97.6%, $R(I) = 0.0861$, no absorption correction, no extinction correction, refinement program: SHELXL-93, refinement by least-square method (F^2), $R(F) = 0.0412$, $R_w(F^2) = 0.0582$, 181 parameters, min./max. residual electron density −0.239/0.254 e Å^{-3}.

1.9. [2-(Di-*tert*-butylphosphanyl-κ*P*)ethyl]{η^5-cyclopentadienyl}(isothio-cyanato)cobalt(II) (5)

GP, 400 mg (1.23 mmol) of **1** [23] and 162 mg (1.23 mmol) of trimethylsilyl isothiocyanate in 50 ml of THF at −50 °C. After 12 h work up in diethyl ether. 320 mg (0.90 mmol, 73%) of **5**, blue-purple solid (m.p. 138 °C, dec.).

IR ($CHCl_3$): $\tilde{\nu} = 3421$ cm^{-1} (m), 2950 (m, CH_3, $-CH_2-$), 2868 (m), 2069 [s, $NCS_{(asym)}$], 1636 (w), 1472 (m), 1391 (w), 1366 [w, $NCS_{(sym)}$], 1175 (w), 1142 (m), 1082 (w), 1019 (w), 935 (w), 580 (w). MS (70 eV, 160 °C): *m*/*z* (%) 356 (3) [$M^+ + 2$], 355 (9) [$M^+ + 1$], 354 (50) [M^+], 322 (2) [$M^+ - S$], 296 [$M^+ - S-NC$], 270 (14), 239 (40) [$M^+ - S-NC-C_4H_9$], 214 (6), 183 (65), 127 (14), 92 (100), 71 (5). HRMS ($C_{16}H_{26}CoNPS$): Calc. 354.085, Found: 354.086.

1.10. [2-(Di-*tert*-butylphosphanyl-κ*P*)ethyl]{η^5-cyclopentadienyl}(dicyano)-cobalt(III) (7)

GP, 430 mg (1.33 mmol) of **1** [23] and 131 mg (1.33 mmol) of trimethylsilyl cyanide in 50 ml of THF at −30 °C. After 6 h work up and purification by column chromatography (1.20 cm, ∅3 cm, SiO_2, acetone–TBME 1:3 → 1:0). 227 mg (0.65 mmol, 49%) of **7**, which was crystallized from dichloromethane–acetone (1:1) at 20 °C; orange-red crystals (m.p. 239 °C, dec.).

IR (KBr): $\tilde{\nu} = 3440$ cm^{-1} (m), 3112 (w), 2964 (m, $-CH_3$, $-CH_2-$), 2908 (m), 2872 (m), 2116 (s, CN), 1636 (m), 1476 (m), 1392 (m), 1372 (m), 1176 (m), 936 (m), 848 (m), 832 (m), 808 (w), 680 (w), 660 (w), 624 (w), 500 (w), 456 (m), 448 (w). ^{1}H-NMR (400.1 MHz, [D_6]-acetone): $\delta = 1.51$ (d, $^3J_{P-H} = 13.8$ Hz, 18H, 9-H, 13-H), 2.50 (m, 2H, 6-H or 7-H), 3.09 (m, 2H, 6-H or 7-H), 5.43 [s, 2H, 2(5)-H or 3(4)H], 5.49 [s, 2H, 2(5)-H or 3(4)H]. ^{13}C-NMR (100.6 MHz, D_3CCN, APT): δ 25.6 (+, d, $^2J_{P-C} = 0.8$ Hz, C-6), 29.7 (−, s, C-9), 38.6 (+, d, $^2J_{P-C} = 22.9$ Hz, C-8, C-12), 38.7 (+, d, $^1J_{P-C} = 13.3$ Hz, C-7), 84.7 [−, d, $^2J_{P-C} = 2.0$ Hz, C-2(5) or C-3(4)], 91.3 [−, d, $^2J_{P-C}$ = C-2(5) or C-3(4)], 112.7 (+, $^2J_{P-C} = 8.8$ Hz, C-1), 125.7 (+, d, $^2J_{P-C} = 10.8$ Hz, C-10). ^{31}P{^{1}H}-NMR (161.9 MHz, D_3CCN): δ 118.6 (s). ^{59}Co-NMR (118.6 MHz, D_3CCN): δ −171.0, $\nu_{1/2} \approx 14\,000$ Hz. MS (70 eV, 240 °C): *m*/*z* (%) 348 (3) [M^+], 322 (10) [$M^+ - CN$], 296 (100) [$M^+ - CN-CN$], 239 (55) [$M^+ - CN-CN-C_4H_9$], 183 (90), 137 (35), 124 (7), 91 (13), 78 (9). $C_{17}H_{26}N_2PCo$: Calc.: C, 58.62; H, 7.52; N, 8.04. Found: C, 58.32; H, 7.52; N, 7.91%.

1.11. Detection of hexamethyldisilane in the reaction mixture by NMR

GP, 100 mg (0.31 mmol) of **1** [23] and 31 mg (0.31 mmol) of trimethylsilyl cyanide in 7 ml of THF at −30 °C. After 4 h all volatiles are condensed into a cold trap. The condensed liquid is subjected to ^{1}H-NMR and MS.

^{1}H-NMR (200.1 MHz, $CDCl_3$): δ 0.043 (s, $(CH_3)_3Si-Si(CH_3)_3$). MS (70 eV, 25 °C): *m*/*z* (%) 145 (4) [$M^+ - H$].

Authentic sample of hexamethyldisilane under identical measurement conditions: ^{1}H-NMR (200.1 MHz, [CDCl$_3$]): δ 0.042 (s).

1.12. Crystal structure analysis of 7

$C_{17}H_{26}CoN_2P \cdot \frac{1}{3}H_2O$, molecular weight 354.30, crystal system monoclinic, space group $P2_1/c$, $a = 13.374(2)$ Å, $b = 22.455(2)$ Å, $c = 17.446(2)$ Å, $\alpha = 90°$, $\beta = 93.28(2)°$, $\gamma = 90°$, $V = 5230.7(11)$ Å^3, $Z = 12$, $d_{\mathrm{ber}} = 1.350$ g cm^{-3}, $F(0\,0\,0) = 2248$ electrons, $\mu = 10.74$ cm^{-1}, crystal color red-orange, crystal size 0.89 mm × 0.22 mm × 0.11 mm, Stoe IPDS (Area Detector) diffractometer, $T = 300(2)$ K, Mo–K$_\alpha$ = 0.71073 Å, $\theta_{\min} = 1.48°$, $\theta_{\max} = 20.89°$, 19 998 measured reflections (±13; −22:20; −17:16), 5458 independent, 4216 observed reflections [$I > 2\sigma$], completeness of data: 99.1%, $R(I) = 0.0296$, no absorption correction, no extinction correction, refinement program: SHELXL-93, refinement by least-square method (F^2), $R(F) = 0.0256$, $R_w(F^2) = 0.0510$, min./max. residual electron density −0.176/0.287 e Å^{-3}.

1.13. *Bis[2-(di-tert-butylphosphanyl-κP)ethyl]{η^5-cyclopentadienyl}bis[di(isopropyloxophosphanyl)-(cyano)lithio]cobaltate(III) (8)*

228 mg (1.84 mmol) of lithium di-*tert*-butylphosphide is added to a −30 °C cold solution of 160 mg (0.46 mmol) of **6** in 30 ml of THF. After 4 h, the mixture is warmed to 25 °C and 1 ml of methanol is added. After solvent removal into a cold trap at reduced pressure the residue is extracted twice with 5 ml of diethyl ether each. After solvent removal into a cold trap 4 mg (0.03 mmol, 6%) of **8** is obtained as a yellow solid, which was crystallized from diethyl ether at −30 °C.

IR (KBr): $\tilde{\nu} = 2957$ cm^{-1} (m, $-CH_3$, $-CH_2-$), 2871 (m), 2108 (s, CN), 1636 (m), 1469 (m), 1378 (w), 1366 (m), 1247 (m), 1145 (m), 1057 (m), 1012 (m), 989 (w), 931 (w), 889 (w), 788 (w), 710 (w), 453 (w). ^{1}H-NMR (400.1 MHz, CDCl$_3$): δ 1.20 (d, $^3J_{\mathrm{P-C}} = 14.3$ Hz, 36H, 9-H, 13-H), 1.31 (m, 48H, 15-H, 17-H), 2.07 (m, 4H, 6-H or 7-H), 2.42 (m, 4H, 6-H or 7-H), 2.86–3.02 (m, 4H, 14-H u. 16-H), 4.78 [s, 4H, 2(5)-H or 3(4)-H], 5.32 [m, 4H, 2(5)-H, 3(4)-H]. ^{31}P{^{1}H}-NMR (161.9 MHz, CDCl$_3$): δ 61.0 (s, $P\bar{1}$ or $P\bar{2}$), 64.7 (s, $P\bar{1}$ or $P\bar{2}$), 136.2 (s, $P\bar{3}$). MS (70 eV, 280 °C): m/z (%) 611 (2) [M$^+$/2], 610, 295 [Cp$^\#$Co–H], 237 (20), 183 (18), 134 (54), 92 (100) [C_7H_8], 74 (44).

1.14. Crystal structure analysis of **8**

$C_{28}H_{54}CoLiNO_{2.38}P_3$, molecular weight 601.50 [Calculated on the basis of the sum formula of the asymmetric unit of **8**. The difference of the molecular weight to that measured by MS is caused by a disorder of the oxygen atom O1 (bonded to P1) in the crystal.], crystal system monoclinic, space group $P2_1/c$, $a = 14.478(1)$ Å, $b = 12.263(1)$ Å, $c = 19.008(2)$ Å, $\alpha = 90°$, $\beta = 94.72(1)°$, $\gamma = 90°$, $V = 3363.3(5)$ Å^3, $Z = 4$, $d_{\mathrm{ber}} = 1.188$ g cm^{-3}, $F(0\,0\,0) = 1292$ electrons, $\mu = 6.77$ cm^{-1}, crystal color yellow, crystal size 0.19 mm × 0.17 mm × 0.16 mm, Stoe IPDS (Area Detector) diffractometer, $T = 300$ K, Mo–K$_\alpha$ = 0.71073 Å, $\theta_{\min} = 1.98°$, $\theta_{\max} = 20.94°$, 13 840 measured reflections (±14; ±12; −18:19), 3530 independent, 1317 observed reflections [$I > 2\sigma$], completeness of data: 99.5%, $R(I) = 0.0845$, no absorption correction, no extinction correction, refinement program: SHELXL-93, refinement by the least-square method (F^2), 335 parameters, $R(F) = 0.0304$, $R_w(F^2) = 0.0483$, min./max. residual electron density −0.171/0.151 e Å^{-3}.

2. Supplementary material

The crystallographic data (without structure factors) of the structures described in this publication were deposited as supplementary publication Nos. CCDC 194382 (**2**), 184686 (**3**), 184687 (**4**), 184688 (**7**), and 184689 (**8**) at the Cambridge Crystallography Data Centre. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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