P−H-Functionalized 2-(Phosphanyl)ethanethiols, Their Titanocene Derivatives $[Cp_2Ti(SCH_2CH_2PHR)_2]$ (R = Ph, 2,4,6-$Me_3C_6H_2$, 2,4,6-$iPr_3C_6H_2$) and Reaction of $[Cp_2Ti(SCH_2CH_2PHPh)_2]$ with $[Cu(CH_3CN)_4]BF_4$

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Dedicated to Prof. M. Herberhold on the occasion of his 65th birthday

Keywords: P−H-Functionalized 2-(phosphanyl)ethanethiols / Titanium / Metallocenes / Bis(phosphanylethanethiolates) / Copper

The P–H-functionalized 2-(phosphanyl)ethanethiols $RHPCH_2CH_2SH$ [R = Ph (**1**), 2,4,6-$Me_3C_6H_2$ (Mes) (**2**), 2,4,6-$iPr_3C_6H_2$ (Tipp) (**3**)] were prepared by ring cleavage of ethylene sulfide with LiPHR, followed by hydrolytic workup and distillation. **1**–**3** react with $[Cp_2TiCl_2]$ in the presence of excess NEt_3 to yield a diastereomeric mixture (ratio ca. 1:1) of *rac*- and *meso*-$[Cp_2Ti(SCH_2CH_2PHR)_2]$ [R = Ph (**4**), Mes (**5**), Tipp (**6**)]. **6** is not obtained in pure form. Compound **4** reacts with $[Cu(CH_3CN)_4]BF_4$ to yield $[Cu\{P,P'\text{-}PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh(B\text{–}P)\}_2]BF_4$ (**7**). **1**–**7** were characterized spectroscopically. **7** exhibits dynamic behavior in solution, as shown by ^{31}P NMR spectroscopy. Crystal structure determinations were carried out on **5** and **7**. In **5**, both diastereomers cocrystallize in the asymmetric unit. Although the cation of **7** has six chiral centers, only the $(R_P,R_P,R_P,R_P,R_B,R_B)/(S_P,S_P,S_P,S_P,S_B,S_B)$ diastereomer is present in the solid state.

Introduction

While tertiary phosphanyl alcohols have been known and employed as ligands in the synthesis of transition metal complexes with catalytic properties for a long time,[1] the synthetic potential of primary[2] and secondary[3] phosphanyl alcohols has only recently been recognized. The corresponding tertiary,[4−9] secondary[4,10,11] and primary[12] phosphanylalkanethiols have received comparatively less attention. The lack of investigations in this area reflects the paucity of commercially available primary phosphanes, the synthesis of which often requires tedious procedures.[13] Catalytic reactions have been reported in which the transition metal center bears a neutral bidentate P,S ligand, such as the chiral phosphanylalkyl thioether $PR_2CH_2CHR'SR''$ (R, R′, R′′ = alkyl or aryl).[8] However, these are rare due to the possibility of metal poisoning by sulfur.

While several transition metal complexes with tertiary phosphanylalkanethiolato ligands[4,6,7,14−28] are known, mainly late "soft" transition metal complexes bearing primary (Ni, Pd, Pt,[12] Co, Rh[29]) or secondary phosphanylalkanethiolato ligands (Ni,[4,30] Pd, Pt,[30] Co,[4,30,31] Cu,[30] Rh[31]) have been described. Here, the phosphanylalkanethiolato ligand acts as a monoanionic bidentate S,P-chelating ligand. In main-group metal chemistry, group-14 metal derivatives $Me_2M(P,S\text{-}SCH_2CH_2PPh)$ (M = Si,[11] Sn,[11,32] Ge[11,33]) and $Sn\{S,P,S\text{-}SCH_2CH_2P(Ph)CH_2CH_2S\}$[34] are known. Only a small number of early transition metal complexes is known.[7,35,36] However, the use of mixed P,S ligands appears attractive for several reasons. Group-4 and other early transition metals have well-established thiolato complexes which can be employed in catalytic processes,[37] while the late transition and coinage metals form stable phosphane complexes which can also be used in catalysis.[38] Thus, the possibility of bridging two different metal centers by using ligands with mixed donor atoms appears feasible and could conceivably result in metal−metal interaction[7] and complexes with new and unique reactivity patterns. To date, only a few heterobimetallic complexes in which a phosphanylalkanethiolato ligand bridges an early and a late transition metal center are known, namely, $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^+$ or $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^0$,[7] $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni]$,[39] $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni(CO)_2]$,[39] $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Pd]^{2+}$,[39] and $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]^+$.[35] Several homodi-[26,40−44] and -trinuclear[16,30,39,45] complexes and heterobimetallic bi-[46,47] and trinuclear[39−41] complexes, in which the P,S ligand bridges two late transition metal centers (Fe, Ni, Co, Pd, Pt, Cu, Ag) have also been reported. Some of these complexes have been structurally characterized.

We now report on the synthesis and spectroscopic studies of the soft-soft P−H-functionalized 2-(phosphanyl)ethanethiols $RHPCH_2CH_2SH$ [R = Ph (**1**), 2,4,6-$Me_3C_6H_2$ (Mes) (**2**), 2,4,6-$iPr_3C_6H_2$ (Tipp) (**3**)]. The synthesis of **1** from NaPHPh and ethylene sulfide in liquid ammonia, followed by hydrolysis with hydrochloric acid was reported by Issleib et al. in 1967.[4] However, characterization of the product was limited to elemental analysis and IR-spectroscopic studies.

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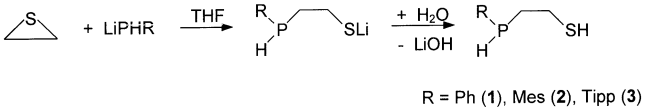
Results and Discussion

Synthesis and Characterization of the 2-(Phosphanyl)ethanethiols $RHPCH_2CH_2SH$ [R = Ph (1), Mes (2), Tipp (3)]

The P−H-functionalized 2-(phosphanyl)ethanethiols $RHPCH_2CH_2SH$ [R = Ph (**1**), Mes (**2**), Tipp (**3**)] were prepared by nucleophilic ring cleavage of ethylene sulfide with the lithium phosphanides LiPHR, prepared in situ from RPH_2 and BuLi, followed by hydrolytic workup and distillation (Scheme 1). A stoichiometric amount of ethylene sulfide had to be employed to prevent further reaction to $RP(CH_2CH_2SH)_2$.[6] **1−3** were obtained in good yields and gave satisfactory elemental analyses. They are readily oxidized by air. At room temperature, the 2-(phosphanyl)ethanethiols are colorless oils that solidify at −30 °C.



Scheme 1

The 2-(phosphanyl)ethanethiols **1−3** were characterized spectroscopically (^{1}H, ^{31}P, ^{13}C NMR spectroscopy; MS; and IR spectroscopy). A comparison of the ^{1}H, ^{31}P and ^{13}C data for **1−3** is given in Table 1. In the proton-coupled ^{31}P NMR spectra, **1−3** give rise to doublets, and the signals of **1** are downfield relative to those of **2** and **3** (**1** < **2** < **3**; Table 1).

In the ^{1}H NMR spectra, the S−H proton gives rise to a triplet (**1** and **2**) or multiplet (**3**) at δ = 1.2−1.3 ($^{3}J_{H-H}$ = 7.8 Hz). The methylene protons of the $HPCH_2CH_2SH$ fragment appear as complex multiplets due to $^{1}H-^{1}H$ and $^{1}H-^{31}P$ coupling. The P−H signal is a doublet of doublets of doublets (**1** and **2**) or a doublet of triplets (**3**) at δ ≈ 4.0−4.3 ($^{1}J_{P-H}$ = 209−217, $^{3}J_{H-H}$ = 7−9 Hz). In the ^{13}C NMR spectra, the $P-CH_2$ and $S-CH_2$ groups give rise to doublets at δ = 24.4−24.8 (P−C, $^{1}J_{C-P}$ = 7.1 and 7.8 Hz for **1** and **2**, 12.6 Hz for **3**) and δ = 27.7 −30.4 (P−C−*C*−S, $^{2}J_{C-P}$ ca. 15.8−17.0 Hz). For all compounds, molecular ion peaks were observed in the mass spectra. In the IR spectra, the S−H stretching band is observed around 2560 cm^{-1}, and ν(P−H) is found in the 2280 to 2340 cm^{-1} region (cf. ref.[4]).

Synthesis and Characterization of *rac*- and *meso*-$[Cp_2Ti(SCH_2CH_2PHR)_2]$ [R = Ph (4), Mes (5), Tipp (6)]

The P−H-functionalized 2-(phosphanyl)ethanethiols **1−3** react with $[Cp_2TiCl_2]$ in the presence of excess triethylamine to give the disubstituted products $[Cp_2Ti(SCH_2CH_2PHR)_2]$ [R = Ph (**4**), Mes (**5**), Tipp (**6**)], and $(NEt_3H)Cl$ (Scheme 2). In the $^{31}P\{^{1}H\}$ NMR spectra (Table 2), two singlets of equal intensity are present, in accordance with the presence of two diastereomers due to the chiral center at the phosphorus atom. Separation of the diastereomers was not achieved, even after repeated recrystallization. The chemical shifts of the 2-(phosphanyl)ethanethiols and of the titanium complexes are similar, the latter exhibiting a downfield shift of only δ ≈ 2.5. This indicates no Ti−P interaction in solution. In complexes in which the phosphanylalkanethiolato ligand acts as bidentate ligand, a downfield shift of δ ≈ 80 is observed in the ^{31}P NMR

Table 1. NMR-spectroscopic data for compounds **1−3**

	$PhPHCH_2CH_2SH$ (**1**)	$MesPHCH_2CH_2SH$ (**2**)	$TippPHCH_2CH_2SH$ (**3**)
^{1}H δ/ppm, *J*/Hz	1.31 (t, 1 H, $^{3}J_{H-H}$ = 7.8, SH) 1.69 (m, 1 H, $P-CH_2$) 1.83 (m, 1 H, $P-CH_2$) 2.27 (m, 2 H, $S-CH_2$) 4.04 (d/d/d, 1 H, $^{1}J_{P-H}$ = 209.6, $^{3}J_{H-H}$ = 8.8, PH) 7.06 (d, 1 H, $^{3}J_{H-H}$ = 4.0, *p*-H in Ph) 7.26 (m, 4 H, *o*- and *m*-H in Ph)	1.21 (t, 1 H, $^{3}J_{H-H}$ = 7.8, SH) 1.59 (m, 1 H, $P-CH_2$) 1.83 (m, 1 H, $P-CH_2$) 2.08 (s, 3 H, *p*-CH_3 in Mes) 2.24 (m, 2 H, $S-CH_2$) 2.31 (s, 6 H, *o*-CH_3 in Mes) 4.24 (d/d/d, 1 H, $^{1}J_{P-H}$ = 216.5, $^{3}J_{H-H}$ = 8.5, PH) 6.71 (s, 2 H, *m*-H in Mes)	1.19 (br, s, 6 H, CH_3 in *o*-*i*Pr) 1.21 (br, s, 6 H, CH_3 in *o*-*i*Pr) 1.28 (br, s, 3 H, CH_3 in *p*-*i*Pr) 1.30 (br, s, 3 H, CH_3 in *p*-*i*Pr) 1.25−1.30 (m, 1 H, SH) 1.72 (m, 1 H, $P-CH_2$) 1.97 (m, 1 H, $P-CH_2$) 2.31 (m, 2 H, $S-CH_2$) 2.75 (sept, 1 H, CH in *p*-*i*Pr, $^{3}J_{H-H}$ = 6.9) 3.71 (sept, 2 H, CH in *o*-*i*Pr, $^{3}J_{H-H}$ = 6.5) 4.13 (d/t, 1 H, $^{1}J_{P-H}$ = 216.5, $^{3}J_{H-H}$ = 7.1, PH) 7.12 (s, 2 H, *m*-H in Tipp)
^{31}P δ/ppm, *J*/Hz	−54.0 (d, $^{1}J_{P-H}$ = 210.2, PH)	−88.8 (d, $^{1}J_{P-H}$ = 216.5, PH)	-97.1 (d, $^{1}J_{P-H}$ = 215.4, PH)
^{13}C[a] δ/ppm, *J*/Hz	24.58 (d, $^{1}J_{C-P}$ = 7.1, $P-CH_2$) 29.30 (d, $^{2}J_{C-P}$ = 15.9, $S-CH_2$ 129.08 (s, *ipso*-C in Ph) 129.43 (d, $^{3}J_{P-C}$ = 5.5, *m*-C in Ph) 134.51 (d, $^{2}J_{P-C}$ = 15.4, *o*-C in Ph) 135.4 (d, $^{4}J_{P-C}$ = 11.9, *p*-C in Ph)	21.67 (s, *p*-CH_3 in Mes) 23.83 (d, $^{3}J_{P-C}$ = 10.9, *o*-CH_3 in Mes) 24.80 (d, $^{1}J_{P-C}$ = 7.8, $P-CH_2$) 27.73 (d, $^{2}J_{P-C}$ = 17.0, $S-CH_2$) 130.07 (d, $^{3}J_{P-C}$ = 2.8, *m*-C in Mes) 138.66 (s, *p*-C in Mes) 142.45 (d, $^{2}J_{P-C}$ = 20.8, *o*-C in Mes)	24.48 (d, $^{1}J_{P-C}$ = 12.6, $P-CH_2$) 24.77 (d, $^{3}J_{P-C}$ = 4.7, CH_3 in *o*-*i*Pr) 25.09 (s, CH_3 in *o*-*i*Pr) 25.72 (s, CH_3 in *p*-*i*Pr) 30.04 (d, $^{2}J_{P-C}$ = 15.8, $S-CH_2$) 33.70 (d, $^{3}J_{P-C}$ = 13.7, CH in *o*-*i*Pr) 35.39 (s, CH in *p*-*i*Pr) 122.42 (d, $^{3}J_{P-C}$ = 3.0, *m*-C in Tipp) 150.68 (s, *p*-C in Tipp) 153.91 (d, $^{2}J_{P-C}$ = 11.1, *o*-C in Tipp)

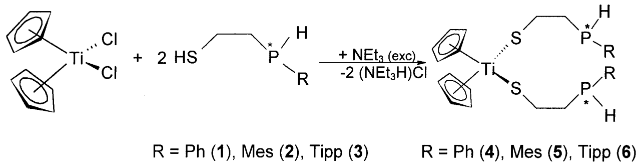
[a] *ipso*-C signal of Ph (for **1**), Mes (for **2**) and Tipp (for **3**) obscured by solvent or not observed.

Table 2. NMR-spectroscopic data for compounds **4−6**

	$[Cp_2Ti(SCH_2CH_2PHPh)_2]$ (**4**)	$[Cp_2Ti(SCH_2CH_2PHMes)_2]$ (**5**)	$[Cp_2Ti(SCH_2CH_2PHTipp)_2]$ (**6**)[a]
^1H δ/ppm, J/Hz	1.98 (m, 2 H, $P-CH_2$) 2.09 (m, 2 H, $P-CH_2$) 3.24 (m, 4 H, $S-CH_2$) 4.32 (d/t, 2 H, $^1J_{P-H} = 208.0$, $^3J_{H-H} = 7.0$, PH) 5.62 (s, 10 H, Cp) 7.09 (m, 6 H, *o*- and *p*-H in Ph) 7.46 (t, 4 H, $^3J_{H-H} = 6.8$, *m*-H in Ph)	1.87 (m, 2 H, $P-CH_2$) 2.10 (s, 2 H + 6 H, $P-CH_2$ and *p*-CH_3 in Mes) 2.52 (m, 12 H, *o*-CH_3 in Mes) 3.23 (m, 4 H, $S-CH_2$) 4.51 (d, br, 2 H, $^1J_{P-H} = 215$, PH) 5.59 (s, 10 H, Cp) 6.80 (s, 4 H, *m*-H in Mes)	[a]
^{31}P δ/ppm, J/Hz	−51.64 (d/t, $^1J_{P-H} = 207$, $^3J_{P-H} = 5$, PH) −51.67 (d/t, $^1J_{P-H} = 207$, $^3J_{P-H} = 5$, PH) (ratio ca. 1:1)	−86.14 (d, $^1J_{P-H} = 215$, PH) −86.30 (d, $^1J_{P-H} = 215$, PH) (ratio 1:1)	−94.8 (d, $^1J_{P-H} = 203$, PH) −94.9 (d, $^1J_{P-H} = 203$, PH) (ratio 4:3)
^{13}C δ/ppm, J/Hz	27.84 (br, t, $P-CH_2$) 44.22 (t, $^1J_{C-H} = 139$, $S-CH_2$) 111.93 (d/t, $^1J_{C-H} = 176$ Hz, $J_{C-H} = 5.8$ Hz, Cp) 126.33 (d, $^1J_{C-H} = 161$, *m*-C in Ph) 129.20 (*o*-C in Ph)[b] 134.71 (d, $^1J_{C-H} = 146$, *p*-C in Ph) 138 (br. s, *ipso*-C in Ph)	21.72 (s, CH_3 in Mes) 23.6 (br, $P-CH_2$) 44.87 ($S-CH_2$) 111.84 (Cp) 130.09 (*m*-C in Mes) 138.43 (*p*-C in Mes) 142.6 (br, *o*-C in Mes) [c]	[a]

[a] Impurity of $TippPHCH_2CH_2SH$ present; therefore the ^1H and ^{13}C NMR spectroscopic data could not be unambiguously assigned. − [b] Obscured by solvent signal. − [c] *ipso*-C signal obscured by solvent signal.

spectrum.[12] In the ^{13}C NMR spectra of **4** and **5**, the signal of the $S-CH_2$ group is shifted downfield by ca. 19 ppm relative to the free ligand.



Scheme 2

For **4** and **6**, separation of the titanium complex and the 2-(phosphanyl)ethanethiol could not be achieved by column chromatography or recrystallization. When the purple oil was heated to ca. 46 °C at 10^{-3} Torr (**4**) or ca. 113 °C at 10^{-3} Torr (**6**), the 2-(phosphanyl)ethanethiol could be distilled off, but decomposition of the titanium complex also occurred.

The related Ti complexes $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2]$[7] and $[Cp_2Ti(SCH_2CH_2PPh_2)_2]$[35] were obtained in a similar way, as a purple solid and a viscous purple oil that could not be crystallized, respectively. The difference in chemical shifts [$\Delta\delta^{31}P$(complex − ligand) = 1.3 or 0.9 ppm] is comparable to that observed for **4−6** relative to **1−3**.

Molecular Structure of $[Cp_2Ti(SCH_2CH_2PHMes)_2]$ (5)

Dark purple crystals of **5** were obtained from a saturated hexane solution at room temperature. **5** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with four molecules in the unit cell. Both diastereomers, *rac*- and *meso*-$[Cp_2Ti(SCH_2CH_2PHMes)_2]$, are present in the asymmetric unit (Figure 1, Table 3). Cocrystallization of the two diastereomers would appear to be the major reason for the failure to separate them by fractional crystallization. Both diastereomers have similar bond lengths and bond angles.

The titanium atom is coordinated in a pseudotetrahedral fashion by two Cp rings and the S atoms of 2-(phosphanyl)ethanethiolato ligands. The Ti−S bond lengths of 2.3699(7) to 2.4155(7) Å [average 2.3925(7) Å] and the S−Ti−S bond angles of 96.04(2) and 96.09(3)° are slightly larger than those of the related complex $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2]$ [Ti−S 2.378(6), 2.384(6) Å, S−Ti−S 93.3(2)°].[7] One of the C−S−Ti bond angles in **5** is large [C(11)−S(1)−Ti(1) 114.6(1); C(43)−S(3)−Ti(2) 114.70(9)°], and the other is smaller, by ca. 5 to 7° [C(22)−S(2)−Ti(1) 109.08(8); C(54)−S(4)−Ti(2) 107.63(8)°]. This suggests some degree of backbonding from S(1) and S(3) to Ti, which are also involved in the shorter Ti−S bonds [Ti(1)−S(1) 2.3899(6); Ti(2)−S(3) 2.3699(7) Å]. In $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2]$, the C−S−Ti bond angles are similar, 109.7(6) and 110.0(6)°.[7] In the titanocene dithiolato complexes, $[Cp^R_2Ti(SR')_2]$[48] (Cp^R = Cp, R′ = Me,[49] Et,[50] *t*Bu,[51] Ph;[52] Cp^R = $C_5H_4SiMe_3$, R′ = C_6F_5 [53]) and $[Cp^*{}_2Ti(SH)_2]$ (Cp* = C_5Me_5),[54] the Ti−S bond lengths range from 2.387(3) (R′ = Et) to 2.438(2) Å (R′ = C_6F_5), and the S−Ti−S angles from 93.6(1) (R′ = Me) to 100.6(1)° (R′ = C_6F_5). The values observed for **5** fall inside this range. In titanocene complexes with chelating S,S ligands, the S−Ti−S angles are smaller (ca. 83°) due to the geometric requirements.[48,51,55,56]

The related heterobimetallic complexes $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^+$ [Ti−S 2.409(3), 2.438(3) Å],[7] $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni]$ [Ti−S 2.484(5), 2.483(5) Å],[39] $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni(CO)_2]$ [Ti−S 2.398(2), 2.398(4) Å],[39] and $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]^+$ [Ti−S 2.465(2), 2.484(3) Å][35] have been structurally characterized. Here, the Ti−S bonds are longer when the S atom is also bonded to a second transition metal.

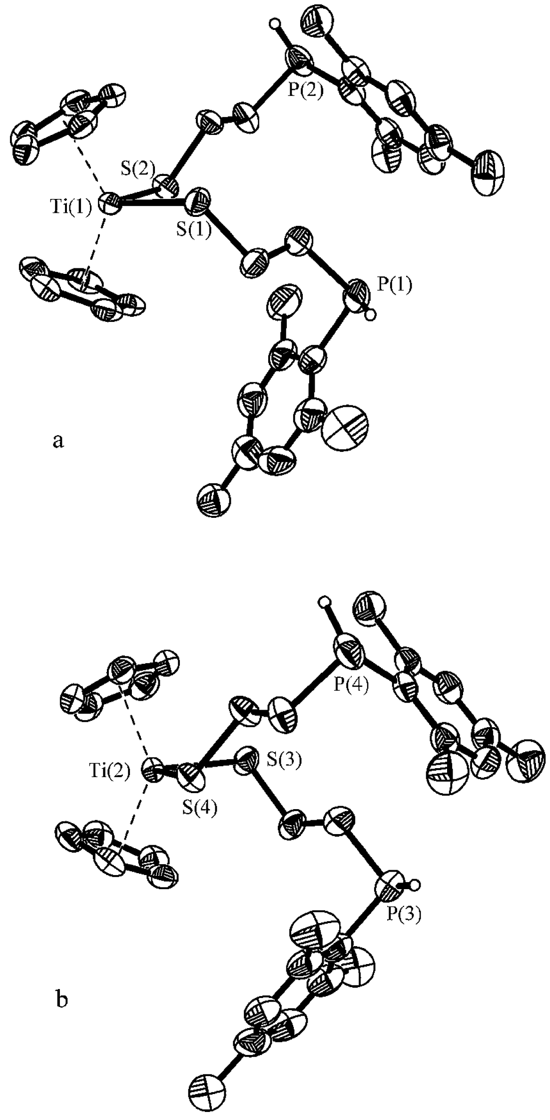


Figure 1. Molecular structure of $[Cp_2Ti(SCH_2CH_2PHMes)_2]$ (**5**) showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP);[70] a) *rac* isomer; b) *meso* isomer; hydrogen atoms (other than P−H) are omitted for clarity

Other related mononuclear transition metal complexes with S,P chelating phosphanylalkanethiolato ligands which have been structurally characterized include $[MoX(\mathit{S,P}\text{-}SCH_2CH_2PPh_2)_2]^{n+}$ ($n = 0$, X = O;[18] $n = 1$, X = Cp[36]), $[Re(SCH_2Ph)(\mathit{S,P}\text{-}SCH_2CH_2PPh_2)_2]$,[22] $[Tc(\mathit{S,P}\text{-}SC_6H_4\text{-}PPh_2)_3]$,[14] $[Tc(\mathit{S,P}\text{-}SCH_2CH_2PPh_2)_2(\mathit{S}\text{-}SCH_2CH_2POPh_2)]$,[15] $[FeCl(CO)(PPh_3)(\mathit{S,P}\text{-}SC\{(\mathit{t}Bu)(SCOMe)\}CH_2PPh_2)]$,[21] $[Fe\{\eta^2\text{-}C(OMe)S\}P(OMe)_3(\mathit{S,P}\text{-}SC(\mathit{t}Bu){=}CHPPh_2)]$,[24] $[Ir(H)(\mathit{S,P}\text{-}SCH_2CH_2PPh_2)(\mathit{S,P}\text{-}HSCH_2CH_2PPh_2)(CO)]^+$,[17] $[Ni(\mathit{S,P}\text{-}SCH_2CH_2PR_2)_2]$ (R = Me,[23] Ph[25]). Complexes with tri-, tetra- or hexadentate phosphanylalkanethiolato ligands which also have been studied are $[Mo\{\mathit{S,P,S}\text{-}(SCH_2CH_2)_2PPh\}_2]$,[6] $[Ni\{\mathit{S,S,P,P}\text{-}SCH_2CH_2P(Ph)CH_2CH_2CH_2P(Ph)CH_2CH_2S\}]$,[20] and $[Os\{\mathit{P,P,S,S,S,S}\text{-}P(CH_2CH_2S)(CH_2CH_2SSCH_2CH_2)_2P(CH_2CH_2S)\}]$.[9]

P,S ligands without a carbon spacer between P and S are present in thiophosphoryltitanocene complexes such as $[Cp'_2Ti\{\eta^2\text{-}\mathit{S,S}\text{-}SP(S)(R)P(S)(R)S\}]$ and $[Cp'_2Ti\{\eta^2\text{-}\mathit{S,S}\text{-}S_2P(S)R\}]$ (Cp′ = C_5H_4Me, R = p-$OMeC_6H_4$),[57] in the (phosphane sulfide)titanocene compounds $[Cp_2Ti(SPCy_2)_2]$ and $[Cp_2Ti\{\eta^2\text{-}\mathit{S,S}\text{-}S_2PCy_2\}]$[58] and in the inorganic titanium(IV) complexes $[TiCl_2\{\eta^2\text{-}\mathit{S,S}\text{-}S_2PEt_2\}_2]$.[59] In $[Cp'_2Ti\{\eta^2\text{-}\mathit{S,S}\text{-}S_2P(S)R\}]$ [2.4898(8), 2.4639(8) Å],[57] $[Cp_2Ti\{\eta^2\text{-}\mathit{S,S}\text{-}S_2PCy_2\}]$ [2.586(4) and 2.611(5) Å],[58] and $[TiCl_2\{\eta^2\text{-}\mathit{S,S}\text{-}S_2PEt_2\}_2]$ [2.503(3) and 2.442(3) Å],[59] which contain chelating P,S ligands, the Ti−S bond lengths are in the range of dinuclear complexes in which the S atom of the thiolato substituent is bonded to two metal atoms. In the complex $[Cp_2Ti(SPCy_2)_2]$, with a nonchelating S,P ligand, the Ti−S bond lengths [2.420(3), 2.427(3) Å][58] are in the range observed for **5**.

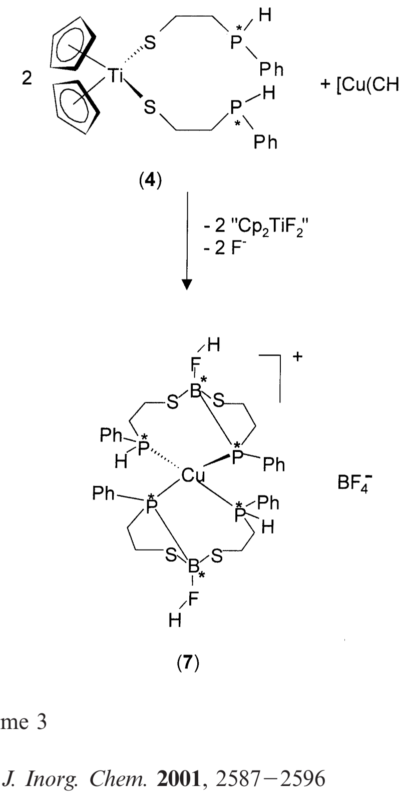
Reaction of $[Cu(CH_3CN)_4]BF_4$ with $[Cp_2Ti(SCH_2CH_2PHPh)_2]$ (4) − Molecular Structure of $[Cu\{\mathit{P,P'}\text{-}PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh(\mathit{B{-}P})\}_2]BF_4$ (7)

When **4** was treated with $[Cu(CH_3CN)_4]BF_4$ we expected the formation of the heterodinuclear complex $[Cp_2Ti(SCH_2CH_2PHPh)_2Cu]BF_4$, analogous to the formation of the green-black complex $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]BF_4$ (obtained in 55% yield).[35] However, although the experiment was carried out in exactly the same way as that leading to the heterodinuclear Ti−Cu complex, we were unable to isolate a heterodinuclear complex. Instead, we observed the formation of a Cu^I complex, $[Cu\{\mathit{P,P'}\text{-}PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh(\mathit{B{-}P})\}_2]BF_4$ (**7**), in a low yield. Apparently this was formed in a complex reaction in which ligand exchange between the BF_4^- anion and the titanium complex occurred with the formation of $[PHPhCH_2CH_2SB(F_2)SCH_2CH_2PHPh]^-$, followed by the substitution of one fluoride atom by the phosphanyl group with the transfer of the P−H proton to the remaining fluoride, to give the cyclized ligand $PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh(\mathit{B{-}P})$. Coordination of this bis(phosphane) ligand to Cu^I gives the cation $[Cu\{\mathit{P,P'}\text{-}PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh(\mathit{B{-}P})\}_2]^+$ (**7**) (Scheme 3). Elimination of HX from the adducts $R_2BX{-}PHR'_2$, with the formation of B−P single bonds, has been observed before.[60]

The participation of the BF_4^- anion in the reaction was rather unexpected and, to the best of our knowledge, is unprecedented. The only reaction reported involving BF_4^- is that with difluorophosphoric acid (HPO_2F_2) in $P_2O_3F_4$ to give $HB(PO_2F_2)_4$.[61] In addition, Stephan et al. were able to synthesize the heterodinuclear complexes $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^+$ [7] and $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]^+$ [35] in ca. 60% yield starting from the corresponding BF_4^- salts of $[Rh(NBD)_2]^+$ (NBD = norbornadiene) and $[Cu(CH_3CN)_4]^+$. However, when $[Ni(CH_3CN)_4](BF_4)_2$ was treated with $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2]$, the trinuclear Ni complex $[Ni\{(SCH_2CH_2PPh_2)_2Ni\}_2]^{2+}$ was obtained in a 75% yield due to ligand exchange.[39] Other heterodinuclear complexes with phosphanylalkanethiolato bridges are $[Ni(\mu\text{-}SCH_2CH_2PPh_2)_2Mo(CO)_4]$,[47] accessible from $[Ni(\mathit{S,P}\text{-}SCH_2CH_2PPh_2)_2]$ and $[Mo(CO)_4(NBD)]$, and [Pt{μ-

Table 3. Selected bond lengths [Å] and angles [°] in **5** (CEN = center of the corresponding cyclopentadienyl ring)

Molecule 1		Molecule 2	
Ti(1)−S(1)	2.3899(6)	Ti(2)−S(3)	2.3699(7)
Ti(1)−S(2)	2.3945(7)	Ti(2)−S(4)	2.4155(7)
S(1)−C(11)	1.827(3)	S(3)−C(43)	1.825(3)
S(2)−C(22)	1.821(2)	S(4)−C(54)	1.819(2)
P(1)−C(13)	1.832(3)	P(3)−C(45)	1.830(3)
P(1)−C(12)	1.855(3)	P(3)−C(44)	1.859(3)
P(1)−H(1P)	1.33(5)	P(3)−H(3P)	1.25(4)
P(2)−C(24)	1.838(2)	P(4)−C(56)	1.842(2)
P(2)−C(23)	1.858(3)	P(4)−C(55)	1.850(3)
P(2)−H(2P)	1.22(4)	P(4)−H(4P)	1.34(5)
C(11)−C(12)	1.490(4)	C(43)−C(44)	1.492(4)
C(22)−C(23)	1.515(3)	C(54)−C(55)	1.513(3)
Ti(1)−C(Cp)	2.356(2) to 2.413(3)	Ti(2)−C(Cp)	2.372(3) to 2.417(2)
C(Cp)−C(Cp)	1.380(4) to 1.407(4)	C(Cp)−C(Cp)	1.380(4) to 1.407(4)
S(1)−Ti(1)−S(2)	96.04(2)	S(3)−Ti(2)−S(4)	96.09(3)
CEN(1)−Ti(1)−CEN(2)	132.6(1)	CEN(3)−Ti(2)−CEN(4)	132.6(1)
C(11)−S(1)−Ti(1)	114.6(1)	C(43)−S(3)−Ti(2)	114.70(9)
C(22)−S(2)−Ti(1)	109.08(8)	C(54)−S(4)−Ti(2)	107.63(8)
C(13)−P(1)−C(12)	102.9(1)	C(45)−P(3)−C(44)	101.0(1)
C(13)−P(1)−H(1P)	98(2)	C(45)−P(3)−H(3P)	102(2)
C(12)−P(1)−H(1P)	94(2)	C(44)−P(3)−H(3P)	103(2)
C(24)−P(2)−C(23)	100.7(1)	C(56)−P(4)−C(55)	100.7(1)
C(24)−P(2)−H(2P)	107(2)	C(56)−P(4)−H(4P)	102(2)
C(23)−P(2)−H(2P)	103(2)	C(55)−P(4)−H(4P)	106(2)
C(12)−C(11)−S(1)	111.7(2)	C(44)−C(43)−S(3)	112.0(2)
C(11)−C(12)−P(1)	115.8(2)	C(43)−C(44)−P(3)	113.9(2)
C(18)−C(13)−P(1)	122.0(2)	C(50)−C(45)−P(3)	120.8(2)
C(14)−C(13)−P(1)	119.2(2)	C(46)−C(45)−P(3)	121.1(2)
C(23)−C(22)−S(2)	110.0(2)	C(55)−C(54)−S(4)	111.6(2)
C(22)−C(23)−P(2)	112.9(2)	C(54)−C(55)−P(4)	112.9(2)
C(25)−C(24)−P(2)	119.4(2)	C(61)−C(56)−P(4)	119.7(2)
C(29)−C(24)−P(2)	121.5(2)	C(57)−C(56)−P(4)	121.3(2)



Scheme 3

$SCH_2CH_2PEt_2)_2Ag\}]_\infty(NO_3)_\infty$,[46] which is obtained from $[Pt(S,P\text{-}SCH_2CH_2PEt_2)_2]$ and $AgNO_3$.

At room temperature, two broad sets of signals are observed at δ ≈ −32 and δ ≈ −43 in the ^{31}P NMR spectrum of **7.** The absence of a signal in the EPR spectrum indicates the presence of Cu^I. The signals at δ ≈ −43 show further proton coupling and are thus assigned to the PHPh groups. In **7**, there are six chiral centers present (two boron and four phosphorus atoms), and hence numerous diastereomers (2^6 enantiomers) can be formed resulting in the observation of a large number of signals in the appropriate region of the NMR spectrum. Additionally, (phosphane)Cu^I complexes exhibit dynamic behavior in solution, and Cu has a quadrupole moment, hence broad signals are usually observed in the ^{31}P NMR spectra.

Only one singlet at δ = −0.97 is observed in the ^{11}B NMR spectrum of **7** in $CDCl_3$. This is assigned to the BF_4^- anion by comparison with the starting material, $[Cu(CH_3CN)_4]BF_4$.[62] Apparently, the signal for the boron atom of the bis(phosphane) ligand is too broad to be observed, and this is probably due to the quadrupole moment of boron, the observed dynamic behavior, and the presence of several possible diastereomers in solution.

7 crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. One molecule of CH_2Cl_2

is present in the asymmetric unit. The BF_4^- anion is highly disordered. Although the cation of **7** has six chiral centers (two boron and four phosphorus atoms) and numerous diastereomers are observed in solution, there is only one diastereomer present in the solid state. In this diastereomer, all six chiral centers have either (*R*) or (*S*) configuration (Figure 2, Table 4). The two enantiomers are related by a crystallographic center of inversion in the centrosymmetric space group $P2_1/n$. To the best of our knowledge, this is the first structurally characterized chiral bis(diphosphane)copper(I) complex.

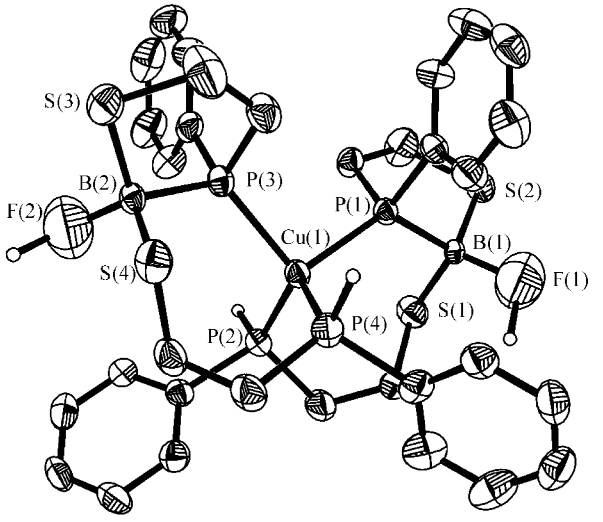


Figure 2. Molecular structure of $(R_P,R_P,R_P,R_P,R_B,R_B)$/$(S_P,S_P,S_P,S_P,S_B,S_B)$-[Cu{*P*,*P'*-$PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh$(*B*−*P*)}$_2$]$BF_4$ (**7**) showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP);[70] only the cation is shown; hydrogen atoms (other than P−H or F−H) are omitted for clarity

Table 4. Selected bond lengths [Å] and bond angles [°] of **7**

Cu(1)−P(1)	2.287(1)	Cu(1)−P(2)	2.268(1)
Cu(1)−P(3)	2.295(1)	Cu(1)−P(4)	2.276(1)
P(1)−B(1)	1.872(4)	P(3)−B(2)	1.877(5)
P(1)−C(1)	1.823(5)	P(1)−C(7)	1.826(5)
P(2)−C(9)	1.824(4)	P(2)−C(15)	1.843(5)
P(2)−H(2P)	1.31(5)	P(4)−H(4P)	1.48(5)
P(3)−C(17)	1.830(5)	P(3)−C(23)	1.839(5)
P(4)−C(25)	1.830(5)	P(4)−C(31)	1.850(5)
S(1)−C(16)	1.820(5)	S(2)−C(8)	1.804(6)
S(1)−B(1)	1.844(5)	S(2)−B(1)	1.817(4)
S(3)−C(24)	1.823(7)	S(4)−C(32)	1.830(6)
S(3)−B(2)	1.821(5)	S(4)−B(2)	1.840(5)
B(1)−F(1)	1.538(7)	B(2)−F(2)	1.546(7)
F(1)−H(1F)	1.43(6)	F(2)−H(2F)	1.30(6)
C(7)−C(8)	1.526(7)	C(15)−C(16)	1.507(7)
C(23)−C(24)	1.518(8)	C(31)−C(32)	1.514(7)
P(2)−Cu(1)−P(4)	117.44(5)	P(2)−Cu(1)−P(1)	104.00(4)
P(4)−Cu(1)−P(1)	115.26(5)	P(2)−Cu(1)−P(3)	116.90(5)
P(4)−Cu(1)−P(3)	101.36(5)	P(1)−Cu(1)−P(3)	101.15(4)
C(1)−P(1)−C(7)	106.8(2)	C(1)−P(1)−B(1)	104.0(2)
C(7)−P(1)−B(1)	95.1(2)	C(1)−P(1)−Cu(1)	112.90(1)
C(7)−P(1)−Cu(1)	111.0(2)	B(1)−P(1)−Cu(1)	124.6(2)
C(9)−P(2)−C(15)	102.2(2)	C(9)−P(2)−Cu(1)	122.4(2)
C(15)−P(2)−Cu(1)	114.6(2)	C(9)−P(2)−H(2P)	93(2)
C(15)−P(2)−H(2P)	104(2)	Cu(1)−P(2)−H(2P)	117(2)
C(17)−P(3)−C(23)	104.8(3)	C(17)−P(3)−B(2)	103.6(2)
C(23)−P(3)−B(2)	95.7(2)	C(17)−P(3)−Cu(1)	116.3(2)
C(23)−P(3)−Cu(1)	112.6(2)	B(2)−P(3)−Cu(1)	121.0(2)
C(25)−P(4)−C(31)	105.8(2)	C(25)−P(4)−Cu(1)	121.5(2)
C(31)−P(4)−Cu(1)	113.9(2)	C(25)−P(4)−H(4P)	94(2)
C(31)−P(4)−H(4P)	103(2)	Cu(1)−P(4)−H(4P)	116(2)
C(16)−S(1)−B(1)	104.2(2)	C(8)−S(2)−B(1)	98.4(2)
B(2)−S(3)−C(24)	97.2(3)	C(32)−S(4)−B(2)	105.4(2)
F(1)−B(1)−S(2)	108.4(3)	F(1)−B(1)−S(1)	113.2(3)
S(2)−B(1)−S(1)	105.0(2)	F(1)−B(1)−P(1)	117.0(3)
S(2)−B(1)−P(1)	105.2(2)	S(1)−B(1)−P(1)	107.2(2)
F(2)−B(2)−S(3)	109.5(3)	F(2)−B(2)−S(4)	113.5(3)
S(3)−B(2)−S(4)	104.6(2)	F(2)−B(2)−P(3)	114.5(3)
S(3)−B(2)−P(3)	104.9(2)	S(4)−B(2)−P(3)	109.1(2)
B(1)−F(1)−H(1F)	115(2)	B(2)−F(2)−H(2F)	111(3)
C(2)−C(1)−P(1)	118.7(4)	C(6)−C(1)−P(1)	123.5(4)
C(8)−C(7)−P(1)	113.4(4)	C(7)−C(8)−S(2)	112.0(4)
C(10)−C(9)−P(2)	121.8(4)	C(14)−C(9)−P(2)	120.5(4)
C(16)−C(15)−P(2)	114.0(4)	C(15)−C(16)−S(1)	112.4(4)
C(22)−C(17)−P(3)	118.1(4)	C(18)−C(17)−P(3)	124.1(4)
C(24)−C(23)−P(3)	112.9(4)	C(23)−C(24)−S(3)	112.5(4)
C(26)−C(25)−P(4)	121.2(4)	C(30)−C(25)−P(4)	119.3(4)
C(32)−C(31)−P(4)	110.6(4)	C(31)−C(32)−S(4)	111.6(4)

In **7**, the copper(I) center is coordinated in a distorted tetrahedral fashion to four P atoms of two neutral chelating bis(phosphane) ligands, $PHPhCH_2CH_2SB(FH)SCH_2CH_2PPh$(*B*−*P*). The Cu−P bond lengths of the secondary phosphane groups [Cu(1)−P(2) 2.268(1), Cu(1)−P(4) 2.276(1) Å] in **7** are slightly smaller than those of the other two phosphane ligands [Cu(1)−P(1) 2.287(1), Cu(1)−P(3) 2.295(1) Å]. The P−Cu−P bond angles of the chelating phosphanes are large [P(4)−Cu(1)−P(1) 115.26(5), P(2)−Cu(1)−P(3) 116.90(5)°], as is the P(2)−Cu(1)−P(4) bond angle [117.44(5)°]. The other P−Cu−P angles range from 101.15(4) to 104.00(4)°.

Several (tetraphosphane)copper(I) [63] and bis(diphosphane) complexes[64] have been structurally characterized (Table 5). The Cu−P bond lengths are comparable with those of **7**, while the P−Cu−P bite angle of the chelating phosphanes is dependent on the ring size. Thus, five-membered rings exhibit P−Cu−P bond angles ranging from 88.3(1) to 90.9(1)°, while these angles are larger in [$Cu(PPh_2CH_2CH_2CH_2PPh_2)_2$]X, which has a six-membered ring [X = ClO_4: 94.56(9), 96.94(9)°;[64c] BF_4: 97.66(5), 98.22(5)°[64a]]. In **7**, which has a seven-membered ring [the largest chelate ring reported for structurally characterized bis(diphosphane)Cu^I complexes to date], the bite angles of 115.26(5), 116.90(5)° are the largest observed so far. Dinuclear Cu^I complexes with bridging bis(phosphane) ligands are generally formed when the chain length of the bis(phosphane) increases to six [$PPh_2CH_2(CH_2)_2CH_2PPh_2$] or eight atoms [$PPh_2CH_2(CH_2)_4CH_2PPh_2$].[64c]

The bis(phosphane) ligands in **7** contain P−B bonds, presumably formed by elimination of HF. The P−B bond lengths of 1.872(4) and 1.877(5) Å agree well with those of other phosphanidoboranes of the general formula $R_2B-PR'_2$.[60] In **7**, the B−S bond lengths of 1.817(4) [S(2)−B(1)], 1.844(5) [S(1)−B(1)], 1.821(5) [S(3)−B(2)] and 1.840(5) Å [S(4)−B(2)] are in the range observed for thioboranes.[65]

Table 5. Comparison of Cu−P bond lengths and P−Cu−P bond angles in **7** and related bis(diphosphane)copper(I) complexes

Complex	Cu−P [Å]	P−Cu−P bite angle [°]	Ref.
7	2.287(1), 2.268(1), 2.295(1), 2.276(1)	115.26(5), 116.90(5)	this work
$[Cu(PPh_2CH_2CH_2PPh_2)_2]$ $[Cu(Mes)_2]$	2.320(4), 2.305(4)	88.3(1), 88.6(1)	[64h]
$[Cu(PPh_2CH_2CH_2PPh_2)_2]_2$ $[Cu_6Fe_4(CO)_{16}]$	2.285	89.6	[64g]
$[Cu(PPh_2CH_2CH_2PPh_2)_2]ClO_4$	2.259(2), 2.301(2), 2.300(2), 2.270(2)	90.34(7), 90.58(7)	[64a]
$[Cu(PMe_2CH_2CH_2PMe_2)_2]$ $[Cu\{Co(CO)_4\}_2]$	2.248(3), 2.250(3), 2.254(3), 2.248(3)	90.9(1)	[64f]
$[Cu(PMe_2CH_2CH_2PMe_2)_2][CpTi(SCH_2CH_2S)_2]$	2.286(6), 2.280(7), 2.293(7), 2.277(7)	90.5(2)	[64d]
$[CuL^1_2]PF_6$ [a]	2.305(1), 2.324(1), 2.322(1), 2.320(1)	91.68(4), 91.26(4)	[64b]
$[Cu(PPh_2CH{=}CHPPh_2)_2]PF_6$	2.276(2), 2.288(2), 2.289(2), 2.287(2)	89.69(7), 89.90(7)	[64e]
$[Cu(PPh_2CH_2CH_2CH_2PPh_2)_2]ClO_4$	2.316(3), 2.312(3) 2.311(3), 2.330(2)	94.56(9), 96.94(9)	[64c]
$[Cu(PPh_2CH_2CH_2CH_2PPh_2)_2]BF_4$	2.303(1), 2.298(1) 2.296(1), 2.317(1)	97.66(5), 98.22(5)	[64a]

[a] L^1 = 2,3-bis(diphenylphosphanyl)maleic anhydride

We are presently further investigating the potential of **1**−**3** as thiolato- and/or phosphanido ligands in transition metal chemistry.

Experimental Section

General: All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. − NMR spectra: Avance DRX 400 (Bruker), standards: ^1H NMR (400 MHz): trace amounts of protonated solvent, C_6D_6; ^{13}C NMR (100.6 MHz): internal solvent; ^{31}P NMR (162 MHz): external 85% H_3PO_4. − The IR spectra were recorded as KBr mulls with a Perkin−Elmer FT-IR spectrometer System 2000 in the range 350−4000 cm^{-1}. − The mass spectra were recorded with a Sektorfeldgerät AMD 402 (AMD Intectra GmbH; EI, 70 eV). − The melting points were determined in sealed capillaries under argon and are uncorrected. RPH_2 (R = Ph,[66] Mes,[67] Tipp[13]), and $[Cu(CH_3CN)_4]BF_4$ [68] were prepared according to literature procedures. $[Cp_2TiCl_2]$ and ethylene sulfide are commercially available (Aldrich).

Preparation of 2-(Phenylphosphanyl)ethanethiol (1): $PhPH_2$ (5 mL, 45 mmol) was dissolved in degassed THF (250 mL) and cooled to −70 °C. BuLi (30.7 mL of a 1.48 M solution, 45 mmol) in hexane was added dropwise over 30 min. The color of the solution changed to turbid orange. After stirring for 1 h at room temp., the solution was cooled again to −70 °C, and ethylene sulfide (3 mL, 49.9 mmol) was added slowly. The color of the solution became clear yellow. After stirring for 30 min at room temp., about 2 mL of degassed water was added. The solution turned turbid white due to the formation of LiOH, which was filtered off. The solvent was then evaporated, and the colorless viscous residue distilled to give **1** (5.4 g, 70%, b.p. 46 °C/10^{-3} Torr; ref.[4]: b.p. 135−137 °C/10 Torr). − EI MS: *m*/*z* (%) = 170 (57) [M^+], 142 (14) [$M^+ - 2\ CH_2$], 137 (82) [$M^+ - SH$], 109 (100) [$PHPh^+$], and fragments thereof. − IR [cm^{-1}]: $\tilde{\nu}$ = 2564 m (νSH; ref.[4]: 2560 cm^{-1}), 2285 vs (νPH; ref.[4]: 2290 cm^{-1}). − $C_8H_{11}PS$ (170.2): calcd. C 56.45, H 6.51, S 18.8; found C 55.00, H 6.59, S 17.6.

Preparation of 2-(Mesitylphosphanyl)ethanethiol (2): $MesPH_2$ (4.88 g, 32 mmol) was dissolved in degassed THF (250 mL), and the solution cooled to −70 °C. BuLi (22 mL of a 1.48 M solution, 32.6 mmol) in hexane was added dropwise over 30 min. The color of the solution changed to turbid orange. After stirring for 1 h at room temp., the solution was cooled again to −70 °C, and ethylene sulfide (2 mL, 33.2 mmol) was added slowly. The color of the solution became clear yellow. After stirring for 30 min at room temp., about 0.8 mL of degassed water was added. The solution turned turbid white due to the formation of LiOH, which was filtered off. The solvent was then evaporated, and the colorless viscous residue distilled to give **2** (4.3 g, 63%, b.p. 100 °C/$10^{-2.5}$ Torr). − EI MS: *m*/*z* (%) = 212 (84) [M^+], 208 (8) [$M^+ - 2\ H_2$], 179 (47) [$M^+ - SH$], 151 (73) [$PHMes^+$], and fragments thereof. − IR [cm^{-1}]: $\tilde{\nu}$ = 2560 m (νSH), 2334 vs (νPH). − $C_{11}H_{17}PS$ (212.3): calcd. C 62.23, H 8.67; found C 61.9, H 8.21.

Preparation of 2-(Triisopropylphenylphosphanyl)ethanethiol (3): $TippPH_2$ (5.18 g, 22 mmol) was dissolved in degassed THF (250 mL), and the solution cooled to −70 °C. BuLi (18.7 mL of a 1.17 M solution, 22 mmol) in hexane was added dropwise over a period of 30 min. The color of the solution changed to yellow, and LiPHTipp precipitated from the solution. This was isolated by filtration (3 g, 57.2%, confirmed by ^{31}P NMR[13]). LiPHTipp (2 g, 8.35 mmol) was then dissolved in THF (200 mL), and the solution cooled to −70 °C. Ethylene sulfide (0.5 mL, 8.39 mmol) was added slowly. The color of the solution became light yellow. After stirring for 30 min at room temp., about 0.2 mL of degassed water was added, and the solution turned turbid white due to the formation of LiOH, which was filtered off. The solvent was then evaporated, and the colorless viscous residue distilled to give **3** (2.1 g, 83%, b.p. 113 °C/10^{-3} Torr). − EI MS: *m*/*z* (%) = 296 (19) [M^+], 263 (100) [$M^+ - SH$], 235 (17) [$PHTipp^+$], and fragments thereof. − $C_{17}H_{29}PS$ (296.4): calcd. C 68.88, H 9.86; found C 69.30, H 9.96.

Preparation of [$Cp_2Ti(SCH_2CH_2PHPh)_2$] (4): $PhPHCH_2CH_2SH$ (0.60 g, 3.5 mmol) was added to a solution of [Cp_2TiCl_2] (0.35 g, 1.4 mmol) in THF (25 mL). A solution of triethylamine (0.9 mL, 6.4 mmol) in THF (25 mL) was added dropwise over 30 min. The solution was stirred for 24 h during which its color changed from red to purple. (Et_3NH)Cl was removed by filtration, and the solvent was removed from the filtrate in vacuum. The oily residue was washed three times with 10 mL of hexane, then recrystallized from toluene/hexane to give **4** as a viscous oil. Yield: 0.65 g (90%). NMR spectra showed that there is a minor impurity of **1** present which could not be eliminated by recrystallization or heating to ca. 46 °C at 10^{-3} Torr (decomp. of **4** occurred). − EI MS: *m*/*z* (%) = 347 (9) [$M^+ - SCH_2CH_2PHPh$], 109 (52) [$PHPh^+$], and fragments thereof. − IR [cm^{-1}]: $\tilde{\nu}$ = 2281 vs (νPH).

Preparation of [$Cp_2Ti(SCH_2CH_2PHMes)_2$] (5): $MesPHCH_2CH_2SH$ (1.1 g, 5.1 mmol) was added to a solution of [Cp_2TiCl_2] (0.59 g, 2.3 mmol) in THF (25 mL). A solution of triethylamine (1.0 mL, 7.1 mmol) in THF (25 mL) was added dropwise over 30 min. The solution was stirred for 24 h during which its color changed from red to purple. (Et_3NH)Cl was separated by filtration. The solvent was removed from the filtrate in vacuum. The oily residue was dissolved in 25 mL hexane and filtered. At room temperature, crystals of **5** formed. Yield: 0.45 g (32%), m.p. 105−108 °C. − EI MS: *m*/*z* (%) = 600 (2) [M^+], 389 (17) [$M^+ - SCH_2CH_2PHMes$], 212 (57) [$HSCH_2CH_2PHMes^+$], 178 (32) [Cp_2Ti^+], 152 (58) [PH_2Mes^+], 119 (100) [Mes^+], and fragments thereof. − $C_{32}H_{42}P_2S_2Ti$ (600.62): calcd. C 63.99, H 7.05, S 10.68; found C 63.9, H 6.57, S 10.5.

Preparation of [$Cp_2Ti(SCH_2CH_2PHTipp)_2$] (6). $TippPHCH_2CH_2SH$ (1.03 g, 3.4 mmol) was added to a solution of [Cp_2TiCl_2] (0.39 g, 1.5 mmol) in THF (25 mL). A solution of triethylamine (1.0 mL, 7.1 mmol) in THF (25 mL) was added dropwise over 30 min. The solution was stirred for 24 h during which its color changed from red to purple. (Et_3NH)Cl was separated by filtration. The solvent was removed from the filtrate in vacuum. The oily residue was dissolved in 25 mL hexane and filtered. The resulting oily residue was recrystallized repeatedly from hexane. However, the NMR spectra showed the presence of an impurity of **3**, which could not be eliminated by recrystallization or heating to ca. 113 °C at 10^{-3} Torr (decomp. of **6** occurred).

Reaction of [$Cu(CH_3CN)_4BF_4$] with [$Cp_2Ti(SCH_2CH_2PHPh)_2$] (4): A solution of **4** (0.18 g, 0.35 mmol) in acetonitrile (20 mL) was added dropwise to a solution of [$Cu(CH_3CN)_4$]BF_4 (0.11 g, 0.35 mmol) in acetonitrile (10 mL). The solution was stirred overnight, after which it was concentrated under vacuum, and diethyl ether was added. A brownish solid precipitated. This was isolated, dissolved in CH_2Cl_2, layered with hexane and then connected to another flask containing toluene. Some yellow crystals formed over a black residue. The yellow crystals were isolated.

Data Collection and Structural Refinement of 5 and 7: Crystallographic data are given in Table 6. Data [λ(Mo-K_α) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for the determination of the unit cell parameters. Empirical absorption correction with SADABS.[69] The structures were solved by direct methods (SHELXTL PLUS[70]). Restrictions for **5**: Zr, S, P, and C atoms anisotropic; restrictions for **7**: Cu, P, B, F, S, and C atoms anisotropic; H atoms located by difference maps and refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (**5**: CCDC-159594; **7**: CCDC-159593). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Crystal data and structure refinement for **5** and **7**

	5	**7**
Empirical formula	$C_{32}H_{42}P_2S_2Ti$	$C_{32}H_{40}B_3CuF_6P_4S_4 \cdot CH_2Cl_2$
M_r	600.62	971.66
Temperature [K]	220(2)	220(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	12.9752(2)	10.7405(2)
b [Å]	15.5545(2)	20.1003(5)
c [Å]	17.2252(1)	20.3827(6)
α [°]	65.836(1)	90
β [°]	89.180(1)	97.289(1)
γ [°]	84.942(1)	90
V [$Å^3$]	3158.57(7)	4364.8(2)
Z	4[a]	4
$\rho_{calcd.}$ [$Mg\ m^{-3}$]	1.263	1.479
F(000)	1272	1984
Crystal size [mm]	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.30
Abs. coeff. [mm^{-1}]	0.524	1.012
$2\Theta_{max}$ [°]	56.0	55.1
Refl. collected	18002	23877
Independent reflections	12971	9090
R_{int}	0.0354	0.0412
Parameters	955	683
R [$I > 2\sigma(I)$]	0.0398	0.0566
$wR2$ (all data)	0.0951	0.1740
$(\Delta/\rho)_{min.}$ [$e \cdot Å^{-3}$]	0.373	0.993
$(\Delta/\rho)_{max.}$ [$e \cdot Å^{-3}$]	−0.359	−0.833

[a] Both diastereomers are present in the asymmetric unit.

Acknowledgments

S. C. thanks the Department of Science and Technology (DST) Delhi, India, for financial support (BOYSCAST).

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[1] [1a] W. Keim, *Angew. Chem.* **1990**, *102*, 251. – [1b] C. A. Willoughby, R. R. Duff, W. M. Davis, S. L. Buchwald, *Organometallics* **1996**, *15*, 472.

[2] J. Heinicke, *Trends Organomet. Chem.* **1994**, *1*, 307; J. Heinicke, I. Kovacs, L. Nyulaszi, *Chem. Ber.* **1991**, *124*, 493.

[3] [3a] J. Heinicke, U. Jux, R. Kadyrov, M. He, *Heteroatom Chem.* **1997**, *8*, 383. – [3b] J. Heinicke, M. He, R. Kadyrov, P. G. Jones, *Heteroatom Chem.* **1998**, *9*, 183.

[4] G. Schwarzenbach, *Chem. Zvesti* **1965**, *19*, 200.

[5] K. Issleib, F. Ungváry, *Z. Naturforsch., Teil B* **1967**, *22*, 1238.

[6] P. J. Blower, J. R. Dilworth, G. J. Leigh, B. D. Neaves, F. B. Normanton, J. Hutchinson, J. A. Zubieta, *J. Chem. Soc., Dalton Trans.* **1985**, 2647.

[7] G. S. White, D. W. Stephan, *Organometallics* **1987**, *6*, 2169.

[8] E. Hauptman, P. J. Fagan, W. Marshall, *Organometallics* **1999**, *18*, 2061 and ref. cited therein.

[9] J. R. Dilworth, Y. Zheng, J. R. Miller, *J. Chem. Soc., Dalton Trans.* **1992**, 1757.

[10] K. Issleib, K.-D. Franze, *J. Prakt. Chem.* **1973**, *315*, 471.

[11] J. D. Andriamizaka, J. Escudié, C. Couret, J. Satgé, *Phosphorus Sulfur* **1982**, *12*, 279.

[12] K. Issleib, W. Gans, *Z. Anorg. Allg. Chem.* **1981**, *475*, 116.

[13] S. Kurz, PhD thesis, University of Leipzig, **1995**.

[14] C. Bolzati, F. Refosco, F. Tisato, G. Bandoli, A. Dolmella, *Inorg. Chim. Acta* **1992**, *201*, 7.

[15] F. Tisato, F. Refosco, G. Bandoli, C. Bolzati, A. Moresco, *J. Chem. Soc., Dalton Trans.* **1994**, 1453.

[16] E. Pfeiffer, M. L. Pasquier, W. Marty, *Helv. Chim. Acta* **1984**, *67*, 654.

[17] D. W. Stephan, *Inorg. Chem.* **1984**, *23*, 2207.

[18] J. Chatt, J. R. Dilworth, J. A. Schmutz, J. A. Zubieta, *J. Chem. Soc., Dalton Trans.* **1979**, 1595.

[19] G. Doyle, *J. Organomet. Chem.* **1975**, *101*, 85.

[20] R. Schmelcer, D. Schwarzenbach, *Cryst. Struct. Commun.* **1981**, *10*, 1317.

[21] A. Samb, B. Demerseman, P. H. Dixneuf, C. Mealli, *Organometallics* **1988**, *7*, 26.

[22] T. Maina, A. Pecorale, A. Dolmella, G. Bandali, U. Mazzi, *J. Chem. Soc., Dalton Trans.* **1994**, 2437.

[23] M. Kita, T. Yamamoto, K. Kashiwabara, J. Fujita, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2272.

[24] [24a] A. J. Carty, F. Hartstock, N. J. Taylor, H. Le Bozec, P. Robert, P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.* **1980**, 361. – [24b] P. Robert, H. Le Bozec, P. H. Dixneuf, F. Hartstock, N. J. Taylor, A. J. Carty, *Organometallics* **1982**, *1*, 1148.

[25] Y.-M. Hsiao, S. S. Chojnacki, P. Hinton, J. H. Reibenspies. M. Y. Darensbourg, *Organometallics* **1993**, *12*, 870.

[26] W. Marty, G. Schwarzenbach, *Chimia* **1970**, *24*, 431.

[27] M. Savignac, P. Cadiot, F. Mathey, *Inorg. Chim. Acta* **1980**, *45*, L43.

[28] V. Korner, G. Huttner, L. Zsolnai, M. Buchner, A. Jacobi, D. Gunauer, *Chem. Ber.* **1996**, *129*, 1587.

[29] K. Issleib, W. Gans, *Z. Anorg. Allg. Chem.* **1982**, *491*, 163.

[30] K. Issleib, D. Wienbeck, *Z. Anorg. Allg. Chem.* **1978**, *440*, 5.

[31] K. Issleib, D. Wienbeck, *Z. Anorg. Allg. Chem.* **1978**, *440*, 237.

[32] C. Couret, J. D. Andriamizaka, J. Escudié, J. Satgé, *J. Organomet. Chem.* **1981**, *208*, C3.

[33] C. Couret, J. Satgé, J. D. Andriamizaka, J. Escudié, *J. Organomet. Chem.* **1978**, *157*, C35.

[34] U. Baumeister, H. Hartung, K. Jurgschat, A. Tzschach, *J. Organomet. Chem.* **1986**, *304*, 107.

[35] G. S. White, D. W. Stephan, *Inorg. Chem.* **1985**, *24*, 1499.

[36] D. Morales, R. Poli, P. Richard, J. Andrieu, E. Collange, *J. Chem. Soc., Dalton Trans.* **1999**, 867.

[37] Review on transition metal complexes with thiolato ligands: P. J. Blower, J. R. Dilworth, *Coord. Chem. Rev.* **1987**, *76*, 121. Review on transition metal complexes with thioether ligands: S. G. Murray, F. R. Hartley, *Chem. Rev.* **1981**, *81*, 365.

[38] [38a] B. R. James, *Adv. Organomet. Chem.* **1979**, *17*, 319. – [38b] J. L. Speier, *Adv. Organomet. Chem.* **1979**, *17*, 407.

[39] G. S. White, D. W. Stephan, *Organometallics* **1988**, *7*, 903.

[40] K. Aurivillius, G.-I. Bertinsson, *Acta Crystallogr., Sect. B* **1982**, *38*, 1295.

[41] W. S. Crane, H. Beall, *Inorg. Chim. Acta* **1978**, *31*, L469.

[42] P.-H. Leung, S.-Y. Siah, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **1998**, 893.

[43] F. Mathey, M.-B. Comarmond, D. Moras, *Chem. Commun.* **1979**, 417.

[44] G. Reinhard, R. Solteck, G. Huttner, A. Barth, O. Walter, L. Zsolnai, *Chem. Ber.* **1996**, *129*, 97.

[45] A. Togni, G. Rihs, R. E. Blumer, *Organometallics* **1992**, *11*, 613.

[46] P. Strickler, *Helv. Chim. Acta* **1969**, *52*, 270.

[47] S. S. Chojnacki, Y.-M. Hsiao, M. Y. Darensbourg, J. H. Reibenspies, *Inorg. Chem.* **1993**, *32*, 3573.

[48] For a recent review see: D. W. Stephan, T. T. Nadasdi, *Coord. Chem. Rev.* **1996**, *147*, 147.

[49] [49a] M. A. A. F. de C. T. Carrondo, G. A. Jeffrey, *Acta Crystallogr., Sect. C* **1983**, *39*, 42. – [49b] T. A. Wark, D. W. Stephan, *Organometallics* **1989**, *8*, 2836.

[50] M. J. Calhorda, M. A. A. F. de C. T. Carrondo, A. R. Dias, C. F. Frazão, M. B. Hursthouse, J. A. M. Simões, C. Teixeira, *Inorg. Chem.* **1988**, *27*, 2513.

[51] F. Senocq, N. Viguier, A. Gleizes, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 1185.

[52] E. G. Muller, S. F. Watkins, L. F. Dahl, *J. Organomet. Chem.* **1976**, *111*, 73.

[53] E. Delgado, E. Hernández, A. Hedayat, J. Tornero, R. Torres, *J. Organomet. Chem.* **1994**, *466*, 119.

[54] F. Bottomley, D. F. Drummond, G. O. Egharevba, P. S. White, *Organometallics* **1986**, *5*, 1620.

[55] A. Kutoglu, *Acta Crystallogr., Sect. B* **1973**, *29*, 2891.

[56] P. R. Stafford, T. B. Rauchfuss, A. K. Verma, S. R. Wilson, *J. Organomet. Chem.* **1996**, *526*, 203.

[57] G. A. Zank, T. B. Rauchfuss, *Organometallics* **1984**, *3*, 1191.

[58] L. Gelmini, D. W. Stephan, *Organometallics* **1987**, *6*, 1515.

[59] W. Kuchen, A. Mamsch, D. Mootz, M. Steffen, *Z. Anorg. Allg. Chem.* **1981**, *472*, 133.

[60] Review: P. P. Power, *Angew. Chem.* **1990**, *102*, 527; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 481.

[61] M. F. A. Dove, R. C. Hibbert, N. Logan, *J. Chem. Soc., Dalton Trans.* **1984**, 2719.

[62] For comparison: NMR-spectroscopic data of [Cu(CH$_3$CN)$_4$]BF$_4$ in CDCl$_3$: ^{1}H: $\delta = 2.11$ (s). – ^{11}B: $\delta = -1.07$ (s, not broad, no B−F coupling is observed). – ^{19}F: $\delta = 54.82, 54.87$ (s, ratio ca. 3:1).

[63] [63a] Kai-Ming Chi, J. Farkas, M. J. Hampden-Smith, T. T. Kodas, E. N. Duesler, *J. Chem. Soc., Dalton Trans.* **1992**, 3111. – [63b] R. Fuchs, P. Klüfers, *Z. Naturforsch., Teil B* **1991**, *46*, 507. – [63c] G. A. Bowmaker, P. C. Healy, L. M. Engelhardt, J. D. Kildea, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1990**, *43*, 1697. – [63d] D. F. Dempsey, G. S. Girolami, *Organometallics* **1988**, *7*, 1208. – [63e] L. M. Engelhardt, C. Pakawatchai, A. H. White, P. C. Healy, *J. Chem. Soc., Dalton Trans.* **1985**, 125. – [63f] I. V. Kourkine, S. V. Maslennikov, R. Ditchfield, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *Inorg. Chem.* **1996**, *35*, 6708.

[64] [64a] P. Comba, C. Katsichtis, B. Nuber, H. Pritzkow, *Eur. J. Inorg. Chem.* **1999**, 777. – [64b] J. S. Lewis, S. L. Heath, A. K. Powell, J. Zweit, P. J. Blower, *J. Chem. Soc., Dalton Trans.* **1997**, 855. – [64c] S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, M. Munakata, *Inorg. Chem.* **1995**, *34*, 1455. – [64d] T. T. Nadasdi, D. W. Stephan, *Inorg. Chem.* **1994**, *33*, 1532. – [64e] S. J. Berners-Price, L. A. Colquhoun, P. C. Healy, K. A. Byriel, J. V. Hanna, *J. Chem. Soc., Dalton Trans.* **1992**, 3357. – [64f] D. J. Darensbourg, Chi-Shan Chao, J. H. Reibenspies,

C. J. Bischoff, *Inorg. Chem.* **1990**, *29*, 2153. – [64g] G. Doyle, K. A. Eriksen, D. Van Engen, *J. Am. Chem. Soc.* **1985**, *107*, 7914. – [64h] P. Leoni, M. Pasquali, C. A. Ghilardi, *Chem. Commun.* **1983**, 240. – [64i] A. Camus, N. Marsich, G. Nardin, L. Randaccio, *Transition Met. Chem.* **1976**, *1*, 205.

[65] [65a] W. Clegg, M. R. J. Elsegood, F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, A. J. Scott, P. Nguyen, N. J. Taylor, T. B. Marder, *Inorg. Chem.* **1998**, *37*, 5289. – [65b] W. Clegg, C. Dai, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, N. L. Pickett, W. P. Power, A. J. Scott, *J. Chem. Soc., Dalton Trans.* **1997**, 839. – [65c] M. Ito, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 4314. – [65d] R. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, M. A. Petrie, P. P. Power, *J. Chem. Soc., Dalton Trans.* **1994**, 2113. – [65e] H. Nöth, H. Pommerening, R. Staudigl, *Z. Naturforsch., Teil B* **1988**, *43*, 501. – [65f] M. Noltemeyer, G. M. Sheldrick, C. Habben, A. Meller, *Z. Naturforsch., Teil B* **1983**, *38*, 1182. – [65g] H. Nöth, K. Niedenzu, *Chem. Ber.* **1983**, *116*, 1132. – [65h] H. Nöth, R. Staudigl, W. Storch, *Chem. Ber.* **1981**, *114*, 3024.

[66] W. Kuchen, H. Buchwald, *Chem. Ber.* **1958**, *91*, 2296.

[67] S. Kurz, PhD thesis, University of Leipzig, **1995**. Synthesis according to the procedure given for (2,4,6-$t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$)$\mathrm{PH}_2$ in: A. H. Cowley, N. C. Norman, M. Pakulski, *Inorg. Synth.* **1990**, *27*, 235.

[68] G. J. Kubas, *Inorg. Synth.* **1979**, *19*, 90.

[69] G. M. Sheldrick, *SADABS – a Program for Empirical Absorption Correction*, Göttingen, **1998**.

[70] *SHELXTL PLUS*, Siemens Analyt. X-ray Inst. Inc., **1990**: XS: *Program for Crystal Structure Solution*; XL: *Program for Crystal Structure Determination*; XP: *Interactiv Molecular Graphics.*

Received March 2, 2001
[I01079]