ACES Asian Chemical Editorial Society
doi.org/10.1002/asia.202301084
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Bi- and tridentate coordination behaviour of a novel bis(phosphinimino)methanide ligand

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Herein, we report the synthesis of a novel ferrocenyl-functionalized bis(phosphinimino)methane ligand ($CH_2(PPh_2NFc)_2$). Deprotonation of $CH_2(PPh_2NFc)_2$ with $KN(SiMe_3)_2$ gave the dimeric species $[K\{CH(PPh_2NFc)_2\}]_2$, which was further reacted with ECl_2 (E=Ge, Sn) to yield the tetrylene compounds $[\{CH(PPh_2NFc)_2\}ECl]$. The ligand and the resulting tetrylenes were examined for their electrochemical properties with the aid of cyclic voltammetry. Furthermore, the reaction of the tetrylenes $[\{CH(PPh_2NFc)_2\}ECl]$ with $[AuC_6F_5(tht)]$ resulted in the bimetallic complexes $[\{(AuC_6F_5)CH(PPh_2NFc)_2\}ECl]$ with an unusual Au coordination on the ligand backbone.

Introduction

Bis(phosphinimino)methane $CH_2(PPh_2NR)_2$ is a bidentate ligand, which can be deprotonated once to monoanionic bis(phosphinimino)methanide ($\{CH(PPh_2NR)_2\}^-$) and twice to dianionic bis(phosphinimino)methandiide ($\{C(PPh_2NR)_2\}^{2-}$).[1] Both anions are suitable ligands for metal complexes.[1b] The complexes, which were reported over the last decades, show a great variety in terms of coordinated metals. Complexes with alkali metals,[2] alkaline-earth metals,[3] p-block elements[4] as well as d-block[5] and f-block metals[6] have been reported. However, there is only a limited number of heterobimetallic complexes known.[5a,7]

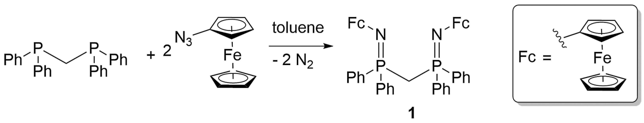
While the reported bis(diphenylphosphinimino)methane-based complexes show a great diversity in terms of the metals, the number of functional groups bound to the N atoms is quite limited. One of the commonly used ligands contain two $SiMe_3$ moieties on the N atoms, which can be attributed to the affordability of the starting materials and the efficient and high-yield synthesis. Besides that, only a few other ligand systems with other groups are known[2d,e,6d,8] and redox-active entities have not been used as as substituents on the N atoms so far. This is an attractive goal considering the coordination chemistry with redox-active ligand systems, which has become more popular since these ligands can actively affect the reaction behaviour of the coordinated metal centre and are capable of stabilizing multielectron reactions.[9] A cornerstone for such kind of ligands is ferrocene with its well-known redox properties.[10] Up to now, a great variety of mono- and multidentate ligands incorporated with ferrocene units have been developed, where the ferrocenyl moiety potentially can act as a redox-switchable unit.[9a,11]

Herein, we introduce ferrocenyl-functionalities within the bis(diphenylphosphinimino)methane ligand framework. Using this novel ligand as starting material, deprotonation with a potassium base led to the respective monoanion, which was subsequently introduced in the coordination sphere of Ge(II) and Sn(II) halides *via* salt elimination reaction. The reactivity of these tetrylenes was further investigated with an Au precursor, which led to unexpected coordination modes of the ligand. The coordination chemistry of the Me_3Si-functionalized bis(phosphinimino)methanide $\{CH(PPh_2NSiMe_3)_2\}^-$ for Ge(II) and Sn(II) was investigated by Mak *et al.*[4c,d,12] However, the heterobimetallic compounds were not described.

Results and Discussion

The new ferrocenyl-functionalized bis(phosphinimino)methane $CH_2(PPh_2NFc)_2$ (**1**) was obtained by Staudinger reaction. Treatment of ferroceneylazide[13] with bis(diphenylphosphino)methane (DPPM) in toluene lead to the formation of compound **1** under N_2 evolution (Scheme 1).

Compound **1** was isolated in analytically pure form in a good yield (91 %). Single crystals of **1**, which were suitable for single crystal X-ray diffraction (SCXRD) analysis, were obtained from a concentrated THF solution. Compound **1** crystallizes solvent-free in the orthorhombic space group $P2_12_12_1$ as yellow



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Scheme 1. Staudinger reaction of bis(phosphinimino)methane with ferrocenylazide.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/asia.202301084 plates, and the molecular structure in the solid-state is depicted in Figure 1. The bond lengths within the NPCPN framework of **1** are in good agreement with those reported for the Ph and $SiMe_3$ analogues, namely $CH_2(PPh_2NPh)_2$ and $CH_2(PPh_2NSiMe_3)_2$.[2d,14] Notably, a difference appears for the bonding angle of the P–C–P unit, where compound **1** exhibits a significantly smaller angle (116.4(2)°) compared to $CH_2(PPh_2NSiMe_3)_2$ (124.94(15)°). However, this angle is more consistent with the phenyl analogue $CH_2(PPh_2NPh)_2$ (115.97(7)°). In the ^1H NMR spectrum of **1**, the distinct signals for the phenyl and ferrocene groups are observed. While the signals of the protons of the functionalized ferrocene cyclopentadienyl (Cp) ring appear as two singlets at $\delta = 3.90$ and 3.85 ppm, the unfunctionalized Cp ring displays a singlet at $\delta = 4.10$ ppm. A triplet at $\delta = 3.59$ ppm ($^2J_{HP} = 13.7$ Hz) was assigned to the methylene protons of the NPCPN scaffold. Compared to the ^1H NMR spectrum of the starting material ferrocenylazide the proton signals of compound **1** are slightly shifted to lower frequencies.[13]

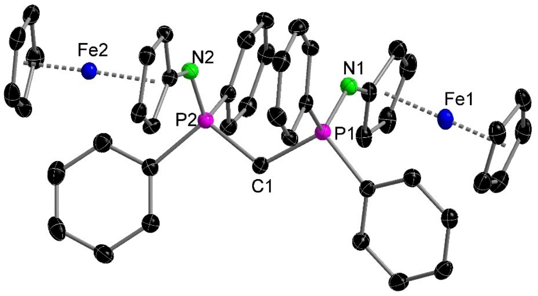
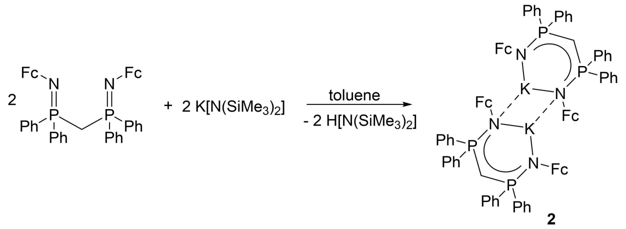


Figure 1. Molecular structure of the compound **1** in the solid-state. Thermal ellipsoids are set at 30% probability level. Selected bond distances [Å] and angles [°]: C1–P1 1.835(3), C1–P2 1.831(3), P1–N1 1.565(3), P2–N2 1.571(2); N1–P1–C1 118.55(14), N2–P2–C1 117.44(13), P1–C1–P2 116.4(2).



Scheme 2. Deprotonation of **1** by equimolar amounts of potassium bis(trimethylsilyl)amide.

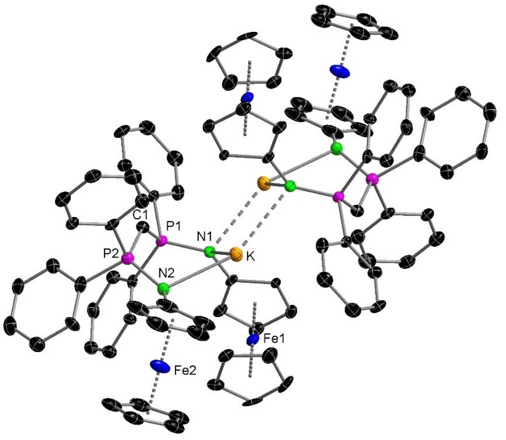


Figure 2. Molecular structure of the complex **2** in the solid-state. Thermal ellipsoids are set at 30% probability level. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°]: C1–P1 1.703(7), C1–P2 1.706(7), P1–N1 1.597(5), P2–N2 1.599(5), N1–K 2.645(5), N1–K' 2.930(5), N2–K 2.731(5); N1–P1–C1 113.8(3), N2–P2–C1 112.0(3), P1–C1–P2 128.8(4), N1–K–N2 90.4(2).

The $^{31}P\{^1H\}$ NMR spectrum shows one singlet at $\delta = 0.3$ ppm, which indicates the chemical equality of both phosphorus atoms in solution, as expected. Compared to $CH_2(PPh_2NSiMe_3)_2$ ($^{31}P\{^1H\}$ $\delta = -4.7$ ppm), the ferrocene groups in **1** leads to a slight shift of this signal to higher frequencies.[15]

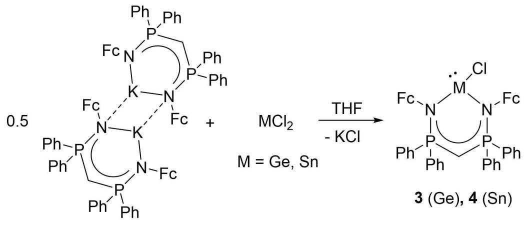
$CH_2(PPh_2NFc)_2$ (**1**) could be readily deprotonated by using equimolar amounts of potassium bis(trimethylsilyl)amide to afford the potassium complex $[K\{CH(PPh_2NFc)_2\}]_2$ (**2**) (Scheme 2).

Complex **2** crystallizes as a dimer in the monoclinic space group $P2_1/n$ as orange prisms from the separated toluene reaction solvent overnight (Figure 2). Group 1 bis(phosphinimino)methanides are known to exhibit in dependence of the solvent used for crystallization different coordination polyhedra.[2b,c,16] Compound **2** adopts a dimeric structure in the solid-state. The molecular structure of **2** resembles that of $[K\{CH(PPh_2NSiMe_3)_2\}]_2$ when crystallized from toluene[2b] and the respective bond lengths and angles are in good agreement. As previously seen for $[K\{CH(PPh_2NSiMe_3)_2\}]_2$ compound **2** forms a loose dimer, in which the inter- and intramolecular K–N distances differ by around 0.3 Å (N1–K 2.647(5) Å and N1–K' 2.923(6) Å). The six-membered metallacycle (N1–P1–C1–P2–N2–K) is formed, which adopts a twist boat conformation.

In the $^{31}P\{^1H\}$ NMR spectrum of complex **2** in THF-d_8, a singlet at $\delta = 15.6$ ppm was observed, which is shifted to higher frequencies compared to compound **1** ($\delta = 0.3$ ppm). Both phosphorous nuclei are equivalent in solution. In the $^{13}C\{^1H\}$ NMR spectrum of complex **2**, the methine carbon signal appears as a triplet at $\delta = 15.2$ ppm. This signal is about 14.5 ppm upfield-shifted compared to the methylene signal of **1** ($\delta = 29.7$ ppm). A significant change was observed in the solubility for compound **2**. While compound **1** is soluble in toluene and THF, complex **2** is only soluble in THF.

Since we were interested in studying the new ferrocene-functionalized ligand as redox-active ligand, we aimed to combine this compound with redox-active main group compounds. Therefore, complex **2** was reacted with the low valent tetrylene precursors $GeCl_2\bullet$(dioxane) or $SnCl_2$ in THF for 24 h at room temperature (Scheme 3). This resulted in the formation of the chlorogermylene $[\{CH(PPh_2NFc)_2\}GeCl]$ (**3**) or chlorostannylene $[\{CH(PPh_2NFc)_2\}SnCl]$ (**4**). Similar reactions were performed by Mak *et al.* using the $SiMe_3$-functionalized bis(phosphinimino)methanide ligand.[4d,12]

Single crystals of both compounds suitable for SCXRD measurement were obtained by layering their THF solution with *n*-pentane. Both compounds crystallize as monomers. While compound **3** crystallizes as yellow plates in the triclinic space group $P\bar{1}$, **4** forms colourless prisms and crystallizes in the monoclinic space group $P2_1/c$ (Figure 3).



Scheme 3. Synthesis of the chlorotetrylenes **3** and **4**.

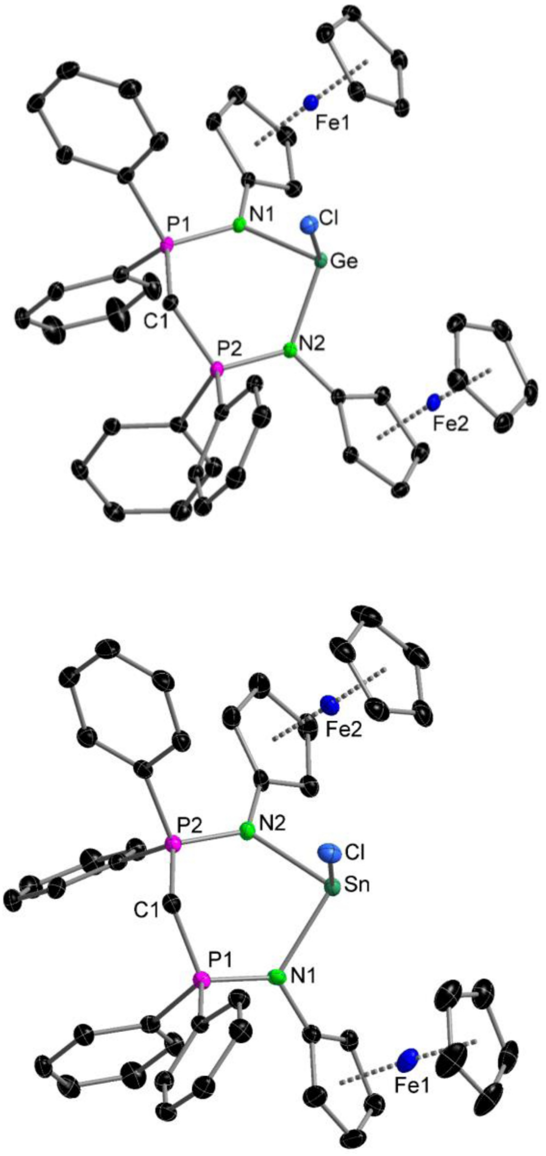


Figure 3. Molecular structures of the complexes **3** (top) and **4** (bottom) in the solid-state. Thermal ellipsoids are set at 30 % probability level. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°] for **3:** C1–P1 1.711(2), C1–P2 1.710(2), P1–N1 1.642(2), P2–N2 1.647(2), Ge–Cl 2.3660(5), Ge–N1 1.981(2), Ge–N2 1.980(2), Ge–C1 3.3901(2); N1–P1–C1 111.04(9), N2–P2–C1 111.11(9), P1–C1–P2 119.39(12), N1–Ge–N2. for **4:** C1–P1 1.704(4), C1–P2 1.706(4), P1–N1 1.640(3), P2–N2 1.640(3), Sn–Cl 2.5188(9) Sn–N1 2.183(3), Sn–N2 2.177(3), Sn–C1 3.4814(1); N1–P1–C1 111.13(16), N2–P2–C1 112.2(2), P1–C1–P2 122.3(2), N1–Sn–N2 93.57(10).

In the chlorotetrylenes **3** and **4**, the bis(phosphinimino)methanide ligand is coordinated to the central metal atom in N,N′-chelate fashion. Due to the stereo-active lone pair of electrons at the metal centre, the Ge and Sn atoms exhibit distorted trigonal-pyramidal geometries. The Ge–C1 and Sn–C1 distances are 3.3901(2) Å and 3.4814(1) Å, respectively, which are longer than the sum of the van-der-Waals radii, therefore, excluding the existence of a direct bond interaction between the metal and the methanide carbon atom. In both complexes, the respective bond lengths within the N–P–C–P–N unit lie between the values known from the literature for CP and NP single and double bonds.[17]

The difference in size between tin and germanium atoms leads to significant different bond lengths between the metal and the coordinating nitrogen atoms (M–N: 1.981(2) Å and 1.980(2) Å (**3**) and 2.183(3) Å and 2.177(3) Å (**4**)), as well between the metal and the coordinated chlorine atom (Ge–Cl 2.3660(5) Å and Sn–Cl 2.5188(9) Å). The bond lengths and bonding angles within the ligand framework are in good agreement with those of the related $SiMe_3$-functionalized bis(phosphinimino)methanide ligand,[4d,12] showcasing that the substitution of the two $SiMe_3$ groups on the N atoms by two ferrocenyl groups only marginally effect the bonding metrics.

The ^1H NMR spectra of **3** and **4** display triplets at $\delta = 1.77$ ppm ($^2J_{HP} = 1.0$ Hz) (**3**) and $\delta = 1.92$ ppm ($^2J_{HP} = 1.0$ Hz) (**4**) which can be assigned to the methanide protons of the P–C–P backbone. The ^{119}Sn NMR spectrum of **4** displays only one signal at $\delta = -185.7$ ppm which is shifted to lower frequencies compared to compound $[HC(PPh_2NSiMe_3)_2SnCl]$ ($\delta = -139.2$ ppm).[4d]

The redox behaviour of the bis(phosphinimino)methanide-based ferrocene ligand **1** and its metal complexes **3** (Ge) and **4** (Sn) was investigated by cyclic voltammetry. It has to be noted that the electrochemical response of the title compounds is surprisingly poor. The measured half-wave potentials, peak potential differences and corresponding i_{pc}/i_{pa} values are summarized in Table 1. The redox potential of the free ligand **1** ($E^0_{1/2} = -0.23$ V) is cathodically shifted with respect to free ferrocene, which can be explained by the donating character of the bis(phosphinimino)methane moiety of the ligand. Since the CV measurement of **1** shows only one redox wave, although two redox-active centres are present, the intramolecular electronic communication is poor.[18] For the germanium compound **3**, two quasi-reversible redox processes were observed at $E^0_{1/2} = -0.45$ V and $E^0_{1/2} = -0.75$ V, which are even

Table 1. Half wave potentials, peak potential differences and corresponding i_{pc}/i_{pa} values of the synthesized ligand **1** and the metal complexes **3** (Ge) and **4** (Sn) in THF vs. Fc/Fc^+ (internal standard Fc^*/Fc^{*+}, Fc* = decamethyl ferrocene; conditions: $Pt/[NBu_4][PF_6]/Ag$, v = 100 mV/s).

Compound	$E^0_{1/2}$ [V]	ΔE_p [V]	i_{pc}/i_{pa}	ΔE [V] vs. **1**
1	−0.23	0.08	1.56	0
3 (Ge)	−0.45	0.1	0.60	−0.22
	−0.75	0.02	0.94	−0.52
4 (Sn)	−0.68	0.07	0.83	−0.45

more cathodically shifted compared to free ligand **1**. Compared to literature-known germanium compounds, the redox potentials of **3** are significant cathodically shifted.[11d,19] For the tin compound **4**, however only one quasi-reversible redox process centered at $E^0_{1/2} = -0.68$ V was obsereved, while a second one appeared with much smaller intensity. Overall, it can be concluded that the incorporation of the group 14 elements provides more electron-rich bis(phosphinimino)methane entities featuring cathodically shifted, Fc-based redox processes.

In earlier studies, the reactivity of the $\mathrm{SiMe_3}$-functionalized bis(phosphinimino)methanide chlorotetrylenes (Ge, Sn) was investigated. Within the corresponding complexes, the tetrylene atoms may either undergo oxidative addition and nucleophilic substitution or act as Lewis bases.[4d,20] Therefore, we reacted compounds **3** and **4** with the soft Lewis acid $[\mathrm{AuC_6F_5(tht)}]$ (tht = tetrahydrothiophene) in THF at room temperature in order to generate bimetallic complexes $\{(\mathrm{AuC_6F_5})\mathrm{CH(PPh_2NFc)_2}\}\mathrm{GeCl}]$ (**5**) and of $[\{(\mathrm{AuC_6F_5})\mathrm{CH(PPh_2NFc)_2}\}\mathrm{SnCl}]$ (**6**) as orange (**5**) or yellow crystals (**6**) (Scheme 4).

Interestingly, within **5** and **6**, the gold moiety is not coordinated to the precursors **3** and **4** *via* the tetrylene lone pairs. Instead, the reaction of **3** and **4** with $\mathrm{AuC_6F_5}$ takes place at the backbone methanide carbon of the ligand system. Although some bimetallic bis(phosphinimino)methanide complexes are known, the observed step-wise metalation is unprecedented. In the only comparable report, the reaction of $[\mathrm{AuCl(PPh_3)}]$ with the potassium compound $[\mathrm{K\{CH(PPh_2NSiMe_3)_2\}}]_2$ led to ligand deprotonation and formation of the germinal diaurated dinuclear bis(phosphinimino)methandiide complex $[(\mathrm{Ph_3PAu})_2\{\mathrm{C(PPh_2NSiMe_3)_2}\}]$.[5c] In contrast, no further deprotonation of the $\{\mathrm{CH(PPh_2NFc)_2}\}$ scaffold is seen in compounds **5** and **6**. Thus, the methanide carbon atom acts here as Lewis base, which coordinates to the Lewis acidic $\mathrm{AuC_6F_5}$. There are other heterobimetallic complexes based in the bis(phosphinimino)methane scaffold reported, e.g., $[\mathrm{Ir(cod)}\text{-}\{(\mathrm{C_6H_4})(\mathrm{Ph})\mathrm{P}(=\mathrm{NSiMe_3})\mathrm{CHP(Ph)_2}=\mathrm{NSiMe_3}\}\mathrm{Li(THF)}]$ and $\mathrm{AlCl_2[C\text{-}(Ph_2P{=}NSiMe_3)_2AlCl_3]}$.[4a,5a] However, both compounds are derivatives of the double-deprotonated bis(phosphinimino)methandiide ligand. Heterobimetallic complexes based on mono-deprotonated bis(phosphinimino)methanide are, to the best of our knowledge, unknown.

The molecular structures of the bimetallic Au/Ge and Au/Sn complexes **5** and **6** in the solid-state are depicted in Figure 4. The expected linear geometry with an C1–Au–C2 angle of 176.34(4)° for **5** and 178.04(2)° for **6** was observed for the Au atoms. In both complexes, the C1–Au bond lengths are almost identical with 2.1004(1) Å for **5** and 2.0992(1) Å for **6**. The coordination of the Au atom in the ligand backbone do not affect the geometry around the central Ge or Sn atoms. The atoms remain coordinated by the ligand in N,N'-chelating fashion and therefore feature trigonal-pyramidal geometries. Upon coordination of $\mathrm{AuC_6F_5}$ in **5** and **6**, the distance between the Ge and Sn atoms and the methanide carbon atom is slightly elongated compared to **3** and **4**. A similar trend is observed for the P–C bonds which indicates the decreased interaction between C and P by delocalization of electron density to the Au. In contrast, the P–N bond distances are shorter in **5** and **6** as in **3** and **4** and the P1–C1–P2 angles get more acute (~4°). In the respective ^{1}H NMR spectrum, the methine proton signals were detected at $\delta = 4.64$ ppm (**5**) and $\delta = 4.69$ ppm (**6**), which

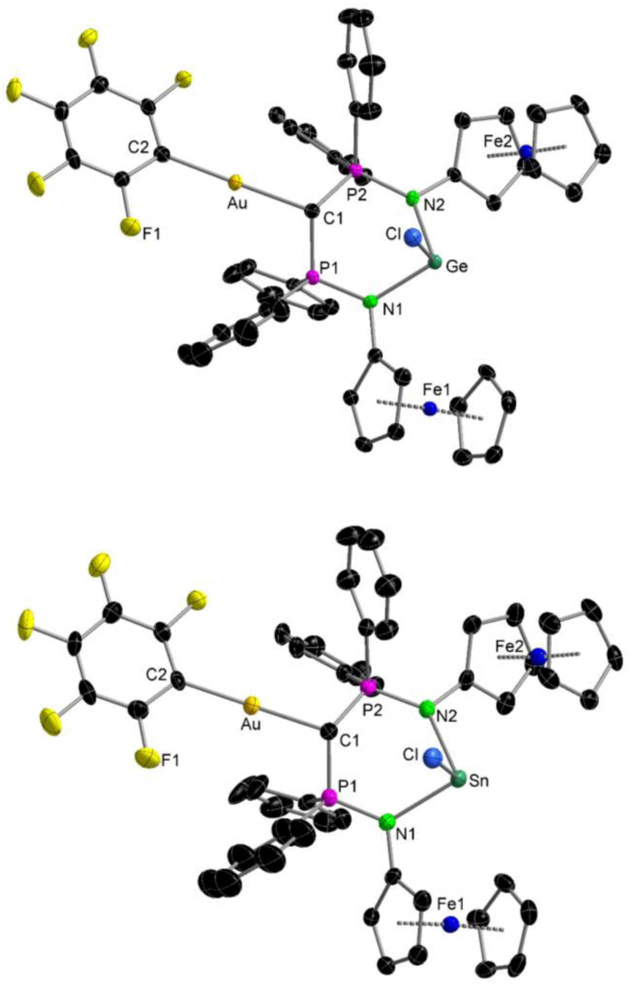
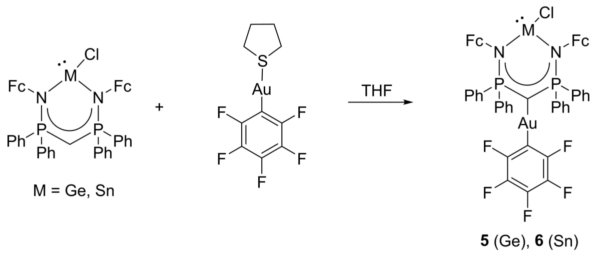


Figure 4. Molecular structure of **5** (top) and **6** (bottom) in the solid-state. Thermal ellipsoids are set at 30% probability level. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°] for **5**: C1–P1 1.771(3), C1–P2 1.762(3), P1–N1 1.633(3), P2–N2 1.633(3), Ge–Cl 2.3690(9), Ge–N1 1.973(3), Ge–N2 1.993(3), Ge–C1 3.4221(2), Au–C1 2.100(3), Au–C2 2.022(4); N1–P1–C1 109.6(2), N2–P2–C1 107.9(2), P1–C1–P2 115.8(2), N1–Ge–N2 95.97(11), C1–Au–C2 176.34(13). for **6**: C1–P1 1.789(6), C1–P2 1.772(6), P1–N1 1.628(5), P2–N2 1.619(5), Sn–Cl 2.5523(15), Sn–N1 2.183(5), Sn–N2 2.199(5), Sn–C1 3.5599(1), Au–C1 2.099(5), Au–C2 2.008(5); N1–P1–C1 110.4(3), N2–P2–C1 109.5(2), P1–C1–P2 117.5(3), C1–Au–C2 178.0(2).



Scheme 4. Reaction of **3** and **4** with $[\mathrm{AuC_6F_5(tht)}]$.

are shifted to higher frequencies as compared to the germylene **3** ($\delta = 1.77$ ppm) and stannylene **4** ($\delta = 1.92$ ppm). A similar trend can be seen for the phosphorus nuclei in the respective $^{31}P\{^1H\}$ NMR spectrum of **5** ($\delta = 34.0$ ppm) and **6** ($\delta = 33.3$ ppm), as the signals are shifted to higher frequencies by about 7 ppm compared to those of **3** and **4**. In the ^{119}Sn NMR spectrum of complex **6**, the signal was detected at $\delta = -253.0$ ppm, which shows a significant shift to lower frequencies compared to **4** ($\delta = -185.7$ ppm).

Conclusions

In summary, the synthesis of a new ferrocenyl-substituted bis(diphenylphosphinimino)methane ligand $[CH_2(PPh_2NFc)_2]$ (**1**) and its deprotonation by a potassium base to $[K\{CH(PPh_2NFc)_2\}]_2$ are shown. The chlorogermylene $[\{CH(PPh_2NFc)_2\}GeCl]$ (**3**) and the chlorostannylene $[\{CH(PPh_2NFc)_2\}SnCl]$ (**4**) were synthesized from the reaction of **2** with $GeCl_2{\bullet}$(dioxane) and $SnCl_2$. In complexes **2**, **3** and **4**, the ligand coordinates to the central metal atoms in N,N′-bidentate chelating fashion. Cyclic voltammetry studies of **1**, **3** and **4** show cathodically shifted Fc-based redox processes. Further reaction of **3** and **4** with $[AuC_6F_5(tht)]$ gave the first heterobimetallic bis(phosphinimino)methanide complexes $[\{(AuC_6F_5)CH(PPh_2NFc)_2\}GeCl]$ (**5**) and $[\{(AuC_6F_5)CH(PPh_2NFc)_2\}SnCl]$ (**6**), in which the methanide carbon atom acts, without further deprotonation, as a Lewis base. With this work, we hope to encourage further study of ferrocene-based redox-active ligand systems with different ligand scaffolds. Exploiting various oxidation states of the ferrocenyl unit may allow for even greater variety in coordination chemistry and interesting properties in the future.

Supporting Information

The authors have cited additional references within the Supporting Information.[13,21]

Acknowledgements

Financial support by the DFG-funded transregional collaborative research center SFB/TRR 88 "Cooperative Effects in Homo and Heterometallic Complexes (3MET)" is gratefully acknowledged. Support by the Federal Ministry of Education and Research (BMBF Project No. 02NUK059F) is also gratefully acknowledged. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: bis(phosphinimino)methane · ferrocene · gold · redox-active · tetrylene

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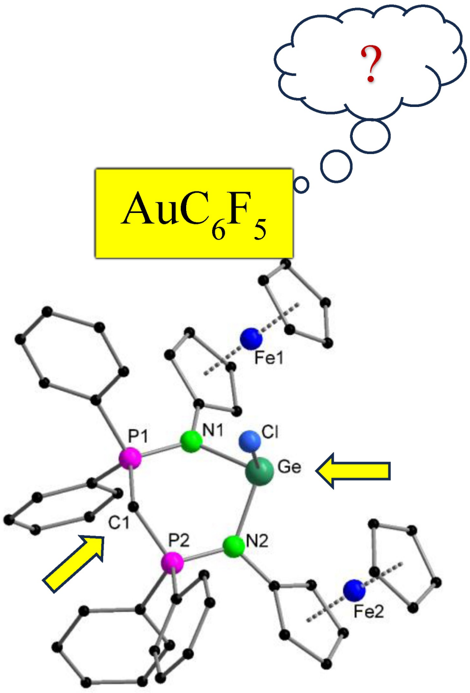
Manuscript received: December 1, 2023
Revised manuscript received: January 9, 2024
Accepted manuscript online: January 10, 2024
Version of record online: ■■, ■■



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Bi- and tridentate coordination behaviour of a novel bis(phosphinimino)methanide ligand

Time for new functional groups: A new ferrocenyl-functionalized bis(phosphinimino)methane ligand with redox-active properties was synthesized and introduced into tetrylene chemistry, leading to unprecedented coordination behaviour.