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Article

Reactions of Potassium Bis(phosphinimino)methanide with Group 11 Compounds

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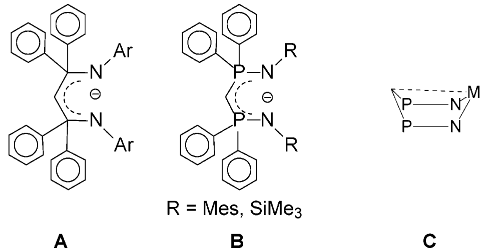
Transmetalation of the potassium methanide complex, K{$CH(PPh_2NSiMe_3)_2$}, with [$(Ph_3P)_2CuI$] afforded the corresponding copper complex [{$CH(PPh_2NSiMe_3)_2$}$CuPPh_3$] (**1**), whereas the reaction of K{$CH(PPh_2NSiMe_3)_2$} with [Ph_3PAuCl] resulted in the dinuclear gold complex [$(Ph_3PAu)_2${$C(PPh_2NSiMe_3)_2$}] (**2**). The solid-state structure of **1** shows the formation of a six-membered metallacycle (N1–P1–C1–P2–N2–Cu) that has a twist boat conformation. In contrast, compound **2** is an α,α-diaurated species, in which the two gold atoms are coordinated in a linear fashion onto the ligand backbone. Photoluminescence measurements show that the latter compound has a strong violet emission.

Introduction

N,N-Bidentate monoanionic ligand systems[1] such as benzamidinates[2] or aminotroponiminates[3] have been used recently in coordination chemistry to stabilize reactive metal centers. Especially, *β*-diiminates (*β*-diketiminatos) (Scheme 1, **A**) became very popular as ligands for a number of metals because they are known to support unusual metal oxidations states[4] and act as spectator ligands in catalysis.[5,6] We and others have recently been attracted by the bis(phosphinimino)methanides ({$CH(PPh_2NR)_2$}$^-$, R = Mes, $SiMe_3$) (Scheme 1, **B**), a P–N ligand system that is topologically related to the *β*-diiminate ligands. The bis(phosphinimino)methanides were used as ligands for a large number of metals ranging from main group[7−10] and transition metals[11−17] to 4f[18,19] and 5f[20] metals. {$CH(PPh_2NSiMe_3)_2$}$^-$ tends to show an uncommon coordination mode. In most of the solid-state structures,

Scheme 1



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the methine carbon atom coordinates via a long interaction onto the metal atom.[7−20] Thus, the six-membered metallacycle (N1−P1−C1−P2−N2−M), which is formed by the chelation of the two trimethylsilylimine groups to the metal center, adopts a pseudo-boat conformation (Scheme 1, **C**). Motivated by these results, we were interested to get some insight into the coordination chemistry of the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand in group 11 chemistry. Although the bis(phosphinimino)methanides have been widely used in transition-metal chemistry, there is, to the best of our knowledge, no report about group 11 compounds. Even with the related and much more common β-diiminate ligands[21] and the inorganic analogues $[CH(EPPh_2)_2]^-$ (E = O, S),[22,23] only a few group 11 complexes have been reported. Herein, we describe the synthesis of the copper compound $[\{CH(PPh_2NSiMe_3)_2\}CuPPh_3]$ (**1**) and the dinuclear gold complex $[(Ph_3PAu)_2\{C(PPh_2NSiMe_3)_2\}]$ (**2**), which does not form a six-membered metallacycle but instead has two gold atoms in the backbone of the ligand. We also investigated the luminescence of the gold complex because of the considerable interest in these properties[24] due to the uncertainty of the assignment of the excited states involved in the transitions.[25]

Experimental Section

General Considerations. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line that was interfaced to a high vacuum (1×10^{-4} Torr) line or in an argon-filled M. Braun glovebox. THF was predried over Na wire and distilled under nitrogen from K and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum-line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥99 atom % D) and were degassed, dried, and stored in vacuo over a Na/K alloy in resealable flasks. NMR spectra were recorded on a JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR). Elemental analyses were carried out with an Elementar Vario. $K\{CH(PPh_2NSiMe_3)_2\}$,[7a] $[(Ph_3P)_2CuI]$,[26] and $[Ph_3PAuCl]$[27] were prepared according to literature procedures.

Photoluminescence measurements at room temperature as well as at 11 K were recorded on a Jobin−Yvon fluorescence spectrometer (Fluorolog 3) equipped with two 0.22 m double monochromators (SPEX, 1680) and a 450 W xenon lamp. The emission spectra were corrected for photomultiplier sensitivity, the excitation spectra for lamp intensity, and both for the transmission of the monochromators. Cooling to 11 K was achieved by the use of a closed-cycle He cryostat (Janis Research Co., CCS-150).

$[\{CH(PPh_2NSiMe_3)_2\}CuPPh_3]$ (1). THF (15 mL) was condensed at −196 °C onto a mixture of 300 mg (0.5 mmol) of $K\{CH(PPh_2NSiMe_3)_2\}$ and 358 mg (0.5 mmol) of $[(Ph_3P)_2CuI]$. The mixture was stirred for 16 h at room temperature. The solvent was then evaporated, and 15 mL of toluene was introduced. The solution was filtered and concentrated. Pentane (10 mL) was layered on the top. Crystals were obtained after 1 day. Yield: 150 mg (34%). ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.21 (s, 18H, $SiMe_3$), 1.97 (t, 1H, CH ^2J(H,P) 4.0 Hz), 6.99−7.04 (m, Ph), 7.4 (br, Ph), 7.6−7.87 (m, Ph). $^{31}P\{H\}$ NMR (C_6D_6, 161.7 MHz 25 °C): δ 21.4 (PCP), 27.5 (PPh_3). Anal. Calcd for $C_{49}H_{54}N_2P_3Si_2Cu$ (883.6): C, 66.60; H, 6.16; N, 3.18. Found: C, 65.71; H, 5.73; N, 2.91.

$[(Ph_3PAu)_2\{C(PPh_2NSiMe_3)_2\}]$ (2). THF (15 mL) was condensed at −196 °C onto a mixture of 300 mg (0.5 mmol) of $K\{CH(PPh_2NSiMe_3)_2\}$ and 248 mg (0.5 mmol) of $[Ph_3PAuCl]$. The reaction vessel was covered with aluminum foil, and the reaction mixture was stirred for 12 h at room temperature. The solvent was then evaporated, and 15 mL of toluene was introduced. The solution was filtered and concentrated. Pentane (10 mL) was layered on the top. Crystals were obtained after 1 day. The crystals are light sensitive. Yield: 200 mg (27%). ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.32 (s, 18H, $SiMe_3$), 6.86−7.03 (m, 30H, Ph), 7.23−7.27 (m, 10H Ph), 8.59−8.65 (m, 10H, Ph). $^{31}P\{H\}$ NMR (C_6D_6, 161.7 MHz 25 °C): δ 12.2 (t, ^3J (P,P) 8.9 Hz), 37.7 (t, ^3J (P,P) 8.9 Hz). IR (KBr, cm^{-1}): 3085(m), 3070(m), 3051(m), 3004(m), 2941(m), 2883(w), 1959(m), 1888(w), 1645(m), 1587(w), 1573(w), 1479(m), 1434(s), 1417(m), 1384(m), 1276(w), 1230(w), 1182(w), 1155(br), 1099(m), 1068(w), 1026(m), 997(br), 972(m), 925(s), 858(m), 823(m), 794(s), 744(s), 709(m), 692(s), 665(m). Anal. Calcd for $C_{67}H_{68}Au_2N_2P_4Si_2$ (1475.2): C, 54.55; H, 4.64; N, 1.90. Found: C, 55.05; H, 4.78; N, 1.93.

X-ray Crystallographic Studies of 1 and 2. Crystals of **1** and **2** were grown from toluene/pentane. Suitable crystals of both compounds were covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystals were transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

All structures were solved by the Patterson method (SHELXS-97[28]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques on *F*, min-

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Table 1. Crystallographic Details of [{CH(PPh$_2$NSiMe$_3$)$_2$}CuPPh$_3$] (**1**) and [(Ph$_3$PAu)$_2${C(PPh$_2$NSiMe$_3$)$_2$}] (**2**)[a]

	1	**2**
formula	$C_{49}H_{54}CuN_2P_3Si_2$	$C_{67}H_{68}Au_2N_2P_4Si_2$
fw	883.57	1475.23
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	40.955(2)	12.6423(5)
b (Å)	9.9826(4)	14.1578(5)
c (Å)	22.7804(11)	19.4929(7)
α (deg)		93.587(3)
β (deg)	96.470(4)	91.235(3)
γ (deg)		115.643(3)
V (Å^3)	9254.0(7)	3134.6(2)
Z	8	2
density (g/cm^3)	1.268	1.562
radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
μ (mm^{-1})	0.663	4.853
absorp corr	integration	integration
no. of reflns collected	43 780	62 112
no. of unique reflns	12 395 [R_{int} = 0.0893]	16 801 [R_{int} = 0.0577]
no. of observed reflns	8830	15 616
GOF on F^2	1.092	1.131
R1[b]; wR2[c]	0.0518; 0.1227	0.0294; 0.0707

[a] All data collected at 200 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

imizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[29] In the final cycles of each refinement, all non-hydrogen atoms except the disordered atoms C35 and C36 in **2** were assigned to anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances, and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-612163 (**1**) and 612164 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: ((44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Transmetalation of the potassium methanide complex, K{CH(PPh$_2$NSiMe$_3$)$_2$}, with [(Ph$_3$P)$_2$CuI] in a 1:1 ratio followed by extraction with toluene and crystallization from toluene/pentane afforded the corresponding copper complex [{CH(PPh$_2$NSiMe$_3$)$_2$}CuPPh$_3$] (**1**) as colorless crystals in good yields (Scheme 2).[30] The new complex has been characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction.

For compound **1**, the ^{1}H NMR spectrum shows a sharp singlet for Me$_3$Si groups of the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand at 0.22 ppm. The methine proton shows a triplet (1.98 ppm), which is in the range of bis(phosphinimino)methanide lanthanide dichloride compounds [{CH(PPh$_2$NSiMe$_3$)$_2$}LnCl$_2$]$_2$ (δ 1.93 (Ln = Y) and 1.97 (Ln = Lu)).[18a] The ^2J(H,P) coupling constant (4.0 Hz) of the methine proton is observed. The signals of the phenyl protons are in the expected range in the ^{1}H NMR spectrum. In the ^{31}P{^{1}H} NMR spectra, two signals are observed at 21.4 and 27.5 ppm that represent two kinds of phosphorus atoms. No coupling between the two signals is observed. The phosphorus atoms of the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand show chemical equivalence in solution, and the chemical shift (21.4 ppm) is in the range of corresponding lanthanide dichloride compounds [{CH(PPh$_2$NSiMe$_3$)$_2$}LnCl$_2$]$_2$ (20.4 (Ln = Y) and 20.5 ppm (Ln = Lu)).[18a] The signal of the triphenylphosphine group is in the expected range of 27.5 ppm.

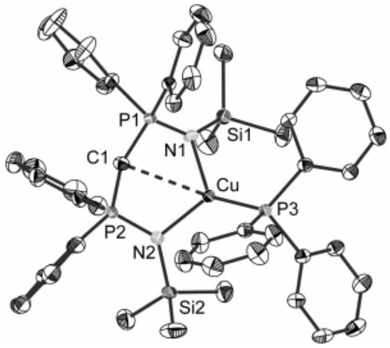

Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to encompass a 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 2

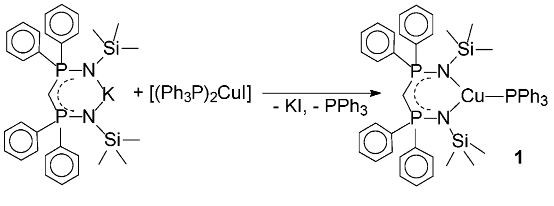

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [{CH(PPh$_2$NSiMe$_3$)$_2$}CuPPh$_3$] (**1**)

bond lengths (Å)		bond angles (deg)	
Cu−N1	2.074(2)	N1−Cu−N2	100.21(9)
Cu−N2	2.058(2)	N1−Cu−C1	64.95(8)
Cu−C1	2.838(3)	N2−Cu−C1	66.45(8)
Cu−P3	2.1756(7)	N1−Cu−P3	129.66(7)
C1−P1	1.719(3)	N2−Cu−P3	130.09(7)
C1−P2	1.724(3)	P3−Cu−C1	128.34(6)
N1−P1	1.587(2)	P1−C1−P2	120.4(2)
N2−P2	1.593(2)		

The solid-state structure of **1** was investigated by single-crystal X-ray diffraction (Figure 1). Compound **1** crystallizes in the monoclinic space group $C2/c$, with eight molecules in the unit cell. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2. If the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand is considered to be a tridentate donor, the copper center is four-coordinated. The {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand is almost symmetrically attached to the center metal. A six-membered metallacycle (N1−P1−C1−P2−N2−Cu) is formed by chelation of the two trimethylsilylimine groups to the copper atom, resulting in a twist

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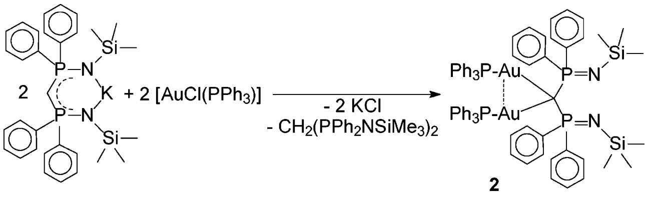
(29) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(30) The bonding situation in the drawings of the ligand system in Schemes 1 and 2 is simplified for clarity.

Scheme 3



boat conformation in which the central carbon atom (C1) and the copper atom are displaced from the N_2P_2 least-squares plane. The Cu−N and Cu−P bond distances are in the expected range of Cu−N1 (2.074(2) Å), Cu−N2 (2.058(2) Å), and Cu−P3 (2.1756(7) Å) (e.g., Cu−N1 = 2.121(6) Å and 2.116(7) Å, and Cu−P = 2.244(2) Å in *cis*-$[Cu_2(\mu\text{-}CN)(Phen)_2(PPh_3)_2]_2[C(CN)_3]\cdot BF_4\cdot 2CH_3CN$ (phen = 1,10 phenanthroline)).[31] The distance between the C1 and the copper atom (2.838(3) Å) is remarkably longer than the usual Cu−C distances (e.g., 1.916(2) Å in $[Cy_3PCuMe]$);[32] however, a tridentate coordination of the ligand is found, as in earlier observations.[7−19] Compared to the starting material, one of the triphenylphosphine groups is detached from the copper atom in the final product. It can be rationalized that Cu(I) mostly favors a coordination number of four. From the bond angles (N2−Cu−C1 = 66.45(8)°, N1−Cu−C1 = 64.95(8)°, N1−Cu−P3 = 129.66(7)°, and N2−Cu−P3 = 130.09(7)°), it is seen that the N2−Cu−C1 and N1−Cu−C1 angles are much shorter than the perfect tetrahedral angle, thus a distorted tetrahedral geometry due to the rigid ligand is observed. The solid-state structure of **1** is consistent with the NMR spectra in solution.

To compare the coordination mode of the copper complex **1** with a corresponding gold compound, we reacted $K\{CH(PPh_2NSiMe_3)_2\}$ with $[Ph_3PAuCl]$ in THF at room temperature to give the corresponding dinuclear gold complex $[(Ph_3PAu)_2\{C(PPh_2NSiMe_3)_2\}]$ (**2**) after extraction with toluene and crystallization from toluene/pentane (Scheme 3). Compound **2** is an air-stable but light-sensitive compound and has been characterized by standard analytical/spectroscopic techniques; the solid-state structure was established by single-crystal X-ray diffraction. The ^1H NMR spectrum of the compound **2** shows a sharp singlet for the Me_3Si groups of the $\{C(PPh_2NSiMe_3)_2\}^{2-}$ at 0.32 ppm. In contrast to compound **1**, the ^1H NMR spectrum of complex **2** does not show any signal corresponding to a methine proton, which means that the proton, originally present at the methine carbon of $K\{CH(PPh_2NSiMe_3)_2\}$, has been deprotonated during the reaction. The signals of the phenyl protons are broadened in the ^1H NMR spectrum and are in the expected range. In the $^{31}P\{^1H\}$ NMR spectra, complex **2** shows two triplets at 12.2 and 37.7 ppm for the $\{C(PPh_2NSiMe_3)_2\}^{2-}$ and Ph_3P phosphorus atoms, respectively; thus both phosphorus atoms of the $\{C(PPh_2NSiMe_3)_2\}^{2-}$ ligand and the two phosphorus atoms of two Ph_3P groups are chemically equivalent in the solution. The chemical shift of methandiide phosphorus is not in the range of compound **1** (21.4 ppm). With respect to the starting material $K\{CH(PPh_2NSiMe_3)_2\}$ (13.0 ppm), there is a highfield shift of only 0.8 ppm for methandiide phosphorus of complex **2**. The other two phosphorus atoms from Ph_3P groups also show a 6.7 ppm downfield shift compared to the starting complex $[Ph_3PAuCl]$ (31.0 ppm). The methandiide phosphorus atoms show a $^3J(P,P)$ coupling of 8.9 Hz with two phosphorus atoms of two Ph_3P groups.

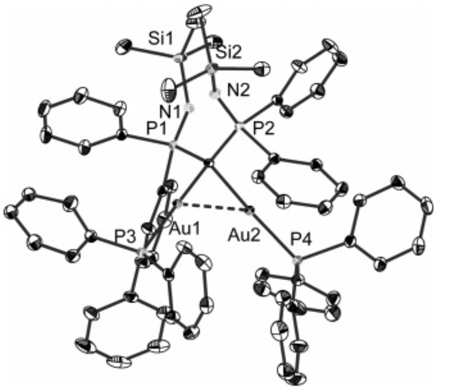


Figure 2. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass a 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $[(Ph_3PAu)_2\{C(PPh_2NSiMe_3)_2\}]$ (**2**)

bond lengths (Å)		bond angles (deg)	
Au1−Au2	3.0224(6)	Au1−C1−Au2	91.93(10)
Au1−C1	2.105(2)	C1−Au1−P3	172.78(8)
Au2−C1	2.099(3)	C1−Au2−P4	173.41(8)
Au1−P3	2.2672(8)	P1−C1−Au1	109.45(13)
Au2−P4	2.2648(12)	P1−C1−Au2	114.02(14)
N1−P1	1.553(3)	P2−C1−Au1	110.61(14)
N2−P2	1.551(3)	P2−C1−Au2	107.76(13)
C1−P2	1.783(3)	P2−C1−P1	119.62(14)
C1−P1	1.789(3)		

The solid-state structure of **2** was investigated by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables1 and 3. The solid-state structure of **2** is consistent with the NMR spectra in solution. Instead of the expected monoaurated species, a "carbenoid" derivative with a double deprotonated bis(phosphinimino)methane is formed. Moreover, the gold atoms are not chelated by the N1−P1−C1−P2−N2 backbone; instead, the expected almost-linear coordination of the gold atoms is observed (C1−Au1−P3 = 172.78(8)° and C1−Au2−P4 = 173.41(8)°). α,α-Diaurated compounds were observed earlier. Geminal diaurated ring systems derived from an aromatic hydrocarbon were first discovered in the 1970s by Nesmeyanov et al. in attempts to introduce gold substituents into ferrocene.[33] It was shown that after conventional monometalation to give $[\{(Ph_3PAu)C_5H_4\}Fe(C_5H_5)]$, the second ligand-backed electrophile Ph_3PAu^+ is attached to the same carbon atom to generate a cationic species of the proposed formula $[\{1,1(Ph_3PAu)_2C_5H_4\}Fe(C_5H_5)]^+$.[34] Recently, Schmidbaur et al. showed that

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thiophen reacts with [Ph$_3$PAu]BF$_4$ to form the cation [2,2-(Ph$_3$PAu)$_2$C$_4$H$_3$S]$^+$.[35] The Au$\cdots$Au distance in compound **2** of 3.0224(6) Å is longer than that in elemental gold (2.88 Å) and in [2,2-(Ph$_3$PAu)$_2$C$_4$H$_3$S]$^+$ (2.8134(4) Å).[35] The Au1−C1−Au2 angle of 91.93(10)° is significantly smaller than the normal tetrahedral angle but larger than in the thiophen complex [2,2-(Ph$_3$PAu)$_2$C$_4$H$_3$S]$^+$ (82.5(2)°),[35] the ferrocenyl complex [{1,1(Ph$_3$PAu)$_2$C$_5$H$_4$}Fe(C$_5$H$_5$)]BF$_4$ (78(1)°),[34] and the trifluorophenyl complex [C$_6$H$_2$F$_3$(AuPPh$_3$)$_2$]BF$_4$ (79.3(3)°).[36] The Au−C bond distances of compound **2** are in the expected range of Au1−C1 (2.105(2) Å) and Au2−C1 (2.099(3) Å).[37] In contrast to the example shown above, which used the salt [Ph$_3$PAu]BF$_4$ as the aurating species, we used [Ph$_3$PAuCl] as the starting material. [Ph$_3$PAuCl] is transformed during the reaction via a salt metathesis into the [Ph$_3$PAu]$^+$ cation. Because [Ph$_3$PAu]$^+$ is isolobal to H$^+$, compound **2** can be considered as being isolobal to CH$_2$(PPh$_2$NSiMe$_3$)$_2$.[38]

As a mechanism for the formation of compound **2**, we propose that in the first step, a monoaurated species of composition [(Ph$_3$PAu){CH(PPh$_2$NSiMe$_3$)$_2$}] is formed that then is deprotonated by an excess of K{CH(PPh$_2$NSiMe$_3$)$_2$} as byproduct CH$_2$(PPh$_2$NSiMe$_3$)$_2$ is isolated. So far, we have not been able to isolate the monoaurated species. In a control experiment, we could show that compound **2** is also formed by reaction of Li$_2${C(PPh$_2$NSiMe$_3$)$_2$} with 2 equiv of [Ph$_3$PAuCl]. The carbenoid type ligand {C(PPh$_2$NSiMe$_3$)$_2$}$^{2-}$ was introduced by Cavell et al. into the coordination chemistry of a series of transition metals.[39] To the best of our knowledge, this type of ligand usually coordinates in a chelating fashion, thus forming either four-membered C1−P2−N2−M or six-membered N1−P1−C1−P2−N2−M metallacycles.

Compound **2** shows a violet emission by irradiation with a UV lamp. After some time, the emission color changes to green, which can be explained by the decomposition of the complex as a result of the UV radiation. Therefore, the photoluminescence measurements were performed as fast as possible and also very carefully using excitation radiation at low intensity.

The thus-obtained excitation and emission spectra are shown in Figure 3. The emission spectrum at room temperature includes three maxima at 431 nm (23 200 cm^{-1}), 502 nm (19 920 cm^{-1}), and a small one at 661 nm (15 130 cm^{-1}). Additionally, a shoulder at about 564 nm (17 730 cm^{-1}) is visible. At 11 K, the shape is almost unchanged. The largest maximum is slightly red-shifted by 1 nm (23 150 cm^{-1}) and the full width at half-maximum (fwhm) is decreased to about 1670 cm^{-1}. The second maximum is shifted to higher energy (484 nm, 20 660 cm^{-1}) and the shoulder is now clearly visible. The excitation spectra show three transitions, at 353 nm (28 300, 28 530 cm^{-1} at 11 K), 287 nm (34 900 cm^{-1}), and 256 nm (39 100 cm^{-1}).

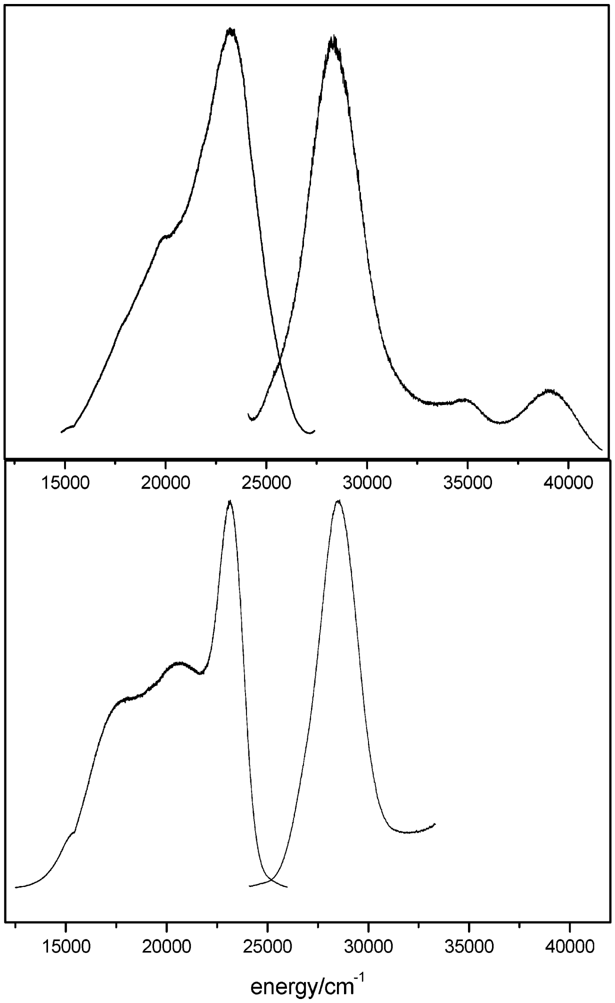

Figure 3. Emission (left, λ_{ex} = 28 600 cm^{-1}) and excitation (right, λ_{em} = 23 000 cm^{-1}) spectra of **2** at room temperature (top) and 11 K (bottom).

For the assignment, we recorded spectra of the starting material CH$_2$(PPh$_2$NSiMe$_3$)$_2$ (not shown). At low temperatures, a broad band with three maxima again at 502, 484, and 661 nm was detected, together with an additional band at 374 nm. Therefore, the respective transitions in the spectra of **2** can be clearly assigned to ligand transitions and the one at 432 nm is due to Au$_2^{2+}$ units. The band at 374 nm was not observed for **2**, so a ligand−Au$_2^{2+}$ energy transfer can be concluded in this case.

The emission energy in the present case is in a comparable range to that of [Au$_2$(dmb)(CN)$_2$] (dmb = 1,8-di-isocyano-p-menthane; λ_{em} = 456 nm, R(Au$\cdots$Au) = 3.536 Å)[40] but remarkably different from that of [Au$_3$(dmmp)$_2$](ClO$_4$)$_3$ (dmmp = bis(dimethylphosphinomethyl)methylphosphine;

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λ_{em} = 580 nm, R(Au···Au) = 2.981(1), 2.962(1) Å)[41] and $[Au_3(dpmp)_2](SCN)_3$ (dpmp = bis(diphenylphosphinomethyl)phenylphosphine; λ_{em} = 600 nm, R(Au···Au) = 3.0137(8), 3.0049(8) Å).[42] Because the distance between the gold ions in **2** is similar to that in the latter compounds, this is obviously not the decisive criterion for the position of the emission bands. Instead, the nature of the donor atoms may have some influence on the emission energy. Whereas the donor atoms are phosphorus atoms in the case of $[Au_3(dmmp)_2](ClO_4)_3$ and $[Au_3(dpmp)_2](SCN)_3$, carbon atoms act as donors in $[Au_2(dmb)(CN)_2]$. In compound **2**, the donor atoms are P as well as C atoms. We suggest that the negative charge of the carbon atoms may be the most important factor for the high-energy emission.

After some irradiation time, the spectra are changed. In the emission spectrum now, a very broad band between 400 and 700 nm, including a maximum at about 520 nm, is visible, in which the shape is comparable to the red part of the emission spectrum. Additionally, a small band at about 375 nm could be observed. Therefore, it can be assumed that the radiation-induced decomposition yielded the ligand and a nonluminescence gold species.

Summary

In summary, we have shown that the reaction of the potassium methanide complex, $K\{CH(PPh_2NSiMe_3)_2\}$, with $[(Ph_3P)_2CuI]$ and $[Ph_3PAuCl]$ leads to two different products. The reaction of the copper compound resulted in $[\{CH(PPh_2NSiMe_3)_2\}CuPPh_3]$, in which the bis(phosphinimino)methanide ligand forms the expected six-membered metallacycle (N1−P1−C1−P2−N2−Cu). The metallacycle has a twist boat conformation, in which the central carbon atom (C1) and the copper atom are displaced from the N_2P_2 least-squares plane. In contrast, the reaction with $[Ph_3PAuCl]$ gave the diaurated gold complex $[(Ph_3PAu)_2\{C(PPh_2NSiMe_3)_2\}]$, in which the two gold atoms are coordinated in a linear fashion onto the ligand backbone. The latter compound shows a strong violet emission, in which the largest band at 432 nm could be assigned to the gold dimer.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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