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Three-Coordinated Aminotroponiminate and Aminotroponate Complexes of Gold(I)

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Potassium *N*-isopropyl-2-(isopropylamino)troponiminate, K{(*i*Pr)$_2$ATI}, and potassium *N*-cyclohexyl-2-(cyclohexylamino)troponiminate, K{(Cy)$_2$ATI}, were synthesized by treatment of the neutral ligands with an excess of KH in THF. Reaction of the potassium reagents with [AuClPPh$_3$] resulted in the gold complexes [Au{(*i*Pr)$_2$ATI}PPh$_3$] and [Au{(Cy)$_2$ATI}PPh$_3$]. The solid-state structures of both compounds, in which the ligands are arranged in plane, show distorted trigonal planar coordinated gold atoms. Potassium 2-(isopropylamino)troponate (K(*i*PrAT)) and the cyclohexyl analogue (K(CyAT)) were obtained by deprotonation of corresponding aminotropones with KH. In an analogous fashion the gold complexes of composition [Au(*i*PrAT)PPh$_3$] and [Au(CyAT)PPh$_3$] were prepared by reaction of K(*i*PrAT) and K(CyAT) with [AuClPPh$_3$], respectively.

Introduction

Beside the challenges in synthetic chemistry gold(I) compounds[1] are also of interest for photophysical,[2−4] catalytic,[5] and pharmaceutical[6] applications. Although the coordination chemistry of gold phosphine compounds has been investigated intensively, the factors influencing the coordination number of gold are not so well understood.[7] As a result of the strong tendency of gold(I) toward a 2-fold coordination, the number of complexes with higher coordination numbers is still low.[8,9] Most of the three-coordinated complexes have phosphine ligands in the coordination sphere. The maybe most prominent examples in this series are the trisphosphine cations [Au(PR$_3$)$_3$]$^+$.[10] Three-coordinated monophosphine complexes were obtained by using bidentate ligands although the strong tendency of gold(I) to form linear complexes may force the bidentate ligand into an asymmetric coordination mode as it is observed for the cation [Au(PPh$_3$)(bipy)]$^+$ (bipy = 2,2′-bipyridine),[11] [Au(PPh$_3$)(Me$_2$NCH$_2$CH$_2$NMe$_2$)]BF$_4$,[12] and the 2,9-dimethyl-1,10-phenanthroline (dmphen) gold(I) complex [Au(C$_6$H$_2$(NO$_2$)-2,4,6)(dmphen)] ((C$_6$H$_2$(NO$_2$)-2,4,6) = 2,4,6-trinitrophenyl).[13] Even though a four-coordinated tris(pyrazolylborato)(triphenylphosphine)-gold(I) complex is known,[14] there are to the best of our

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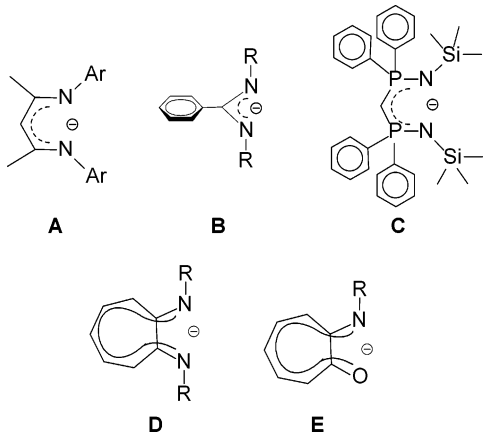
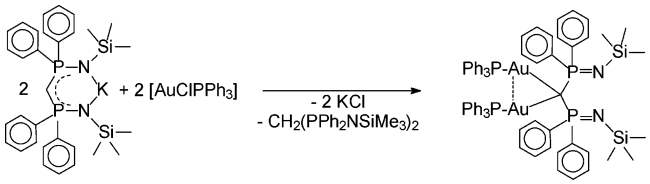
Scheme 1



knowledge no three-coordinated gold(I) complexes bearing N,N′-bidentate anionic ligand systems in the coordination sphere.

Whereas N,N′-bidentate monoanionic ligand systems[15] such as β-diiminate (β-diketiminato) (**A**)[16−19] or benzamidinates (**B**)[20] have been used recently in coordination chemistry to stabilize reactive metal centers (Scheme 1), gold(I) complexes of these ligands are not known. We recently wanted to introduce bis(phosphinimino)methanide ($\{CH(PPh_2NSiMe_3)_2\}^-$) (**C**), a P−N ligand system, which is topologically related to the β-diiminate ligands, in gold(I) chemistry. In most of the solid-state structures a six-membered metallacycle (N1−P1−C1−P2−N2−M) is formed by chelation of the two trimethylsilylimine groups to the metal center. Moreover, the methine carbon atom of the bis(phosphinimino)methanide ligand coordinates via a long-range interaction onto the metal atom;[21−33] thus, the metallacycle adopts a pseudoboat conformation. To our surprise we did not isolate a complex, in which the nitrogen atoms coordinate to the metal atom, but instead the reaction of

Scheme 2



$K\{CH(PPh_2NSiMe_3)_2\}$ with $[AuClPPh_3]$ 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.[34] Moreover, Au(I)−Au(I) contacts are observed (Scheme 2).

Therefore, we intended to introduce a more rigid N,N-bidentate monoanionic ligand system into gold(I) chemistry. Herein we report on the coordination of aminotroponiminate ligands (**D**) (Scheme 1) onto gold(I) leading to trigonal planar complexes. Moreover we also coordinated aminotroponate ligands (**E**) related N,O-bidentate monoanionic ligands onto gold(I). In this context the N,O-chelating donor quinolin-8-olate was used earlier for the synthesis of a dinuclear gold(I) complex.[35] Whereas aminotroponiminate[36] and aminotroponate complexes[37−39] of some main group and transition metals are known, to the best of our knowledge no gold complexes were reported so far.

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Experimental Section

General Methods. 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, interfaced to a high-vacuum (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 or Euriso-Top GmbH (all ≥99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR), respectively. Elemental analyses were carried out with an Elementar vario EL or EL III. (CyAT)H,[40] {(Cy)$_2$ATI}H,[40] K(*i*PrAT),[41] K{(*i*Pr)$_2$ATI},[42] and [AuClPPh$_3$][43] were prepared according to literature procedures.

K{(Cy)$_2$ATI}. A 90 mL volume of THF was slowly added to a mixture of 3.71 g (13.0 mmol) of H(Cy$_2$ATI) and 0.980 g (24.4 mmol) of KH at room temperature, and the mixture was stirred for 18 h at room temperature. The solution was then filtered, and the remaining residue was extracted with 25 mL of THF. The solvent was removed in vacuo, and the muddy-yellowish solid was washed with pentane (2 × 50 mL) to obtain a light yellow, fine powder. Yield: 3.25 g (78%). ^{1}H NMR [THF-d_8, 400 MHz, RT (room temperature)]: δ = 1.06−1.24 (m, 6 H), 1.35−1.48 (m, 4 H), 1.64−1.79 (m, 6 H), 1.81−1.90 (m, 4 H), 3.31 (tt, 2 H, 2 NC*H*Cy, $^3J_{H,H}$ = 10.8 Hz, 3.2 Hz), 5.05 (t, 1 H, $^3J_{H,H}$ = 8.7 Hz), 5.50 (d, 2 H, $^3J_{H,H}$ = 11.3 Hz), 6.17 (dd, 2 H, $^3J_{H,H}$ = 11.3 Hz, 8.7 Hz). ^{13}C{^{1}H} NMR (THF-d_8, 110.4 MHz, RT): δ = 25.9, 26.9, 35.5, 59.8, 103.7, 103.8, 131.7, 163.0 ($C_{1,2}$).

[Au{(*i*Pr)$_2$ATI}PPh$_3$] (1). Under exclusion of light and under stirring, 50 mL of THF was dropped into a mixture of 925 mg (1.87 mmol) of [AuClPPh$_3$] and 472 mg (1.89 mmol) of K{(*i*Pr)$_2$ATI} at −40 °C. The solution was slowly warmed to room temperature, and the mixture was stirred for 18 h. The solvent was removed in vacuo, and the remaining orange solid was extracted with toluene (2 × 50 mL). The reddish extract was reduced to dryness. The remaining solid was washed several times with pentane (100 mL) and dried in vacuo. A light-sensitive yellow powder was obtained. Yield: 1.16 g (94%). Mp: 124 °C (dec). ^{1}H NMR (THF-d_8, 400 MHz, RT): δ = 1.16 (d, 12 H, 2 NCH(C*H*$_3$)$_2$, $^3J_{H,H}$ = 6.1 Hz), 4.17 (sept, 2 H, 2 NC*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.1 Hz), 5.81 (t, 1 H, $^3J_{H,H}$ = 8.9 Hz), 6.23 (d, 2 H, $^3J_{H,H}$ = 11.2 Hz), 6.77 (dd, 2 H, $^3J_{H,H}$ = 11.2 Hz, 8.9 Hz), 7.39−7.49 (m, 9 H, 9 C*H*$_{Ph}$ *o/p*), 7.58−7.67 (m, 6 H, 6 C*H*$_{Ph}$ *m*). ^{13}C{^{1}H} NMR (THF-d_8, 110.4 MHz, RT): δ = 25.4 (2 NCH(*C*H$_3$)$_2$), 49.7 (2 N*C*H(CH$_3$)$_2$), 109.1 (C_5), 113.7 ($C_{3,7}$), 129.4 (d, *C*H$_{Ph}$ *m*, $^3J_{C,P}$ = 10.3 Hz), 131.4 (d, *C*H$_{Ph}$ *p*, $^4J_{C,P}$ = 4.1 Hz), 133.1, 134.8 (d, *C*H$_{Ph}$ *o*, $^2J_{C,P}$ = 13.2 Hz), 161.9 ($C_{1,2}$). The *ipso* C of the PPh$_3$ group could not clearly be located. ^{31}P{^{1}H} NMR (THF-d_8, 161.7 MHz, RT): δ = 34.8. MS (80 eV, EI, 30 °C): *m*/*z* (%) = 662.1 (0.4) [M]$^+$, 618.7 (2.1) [M − *i*Pr], 459.4 (0.1) [M − *i*Pr$_2$AT]$^+$, 262.1 (100) [PPh$_3$]$^+$. Anal. Calcd for $C_{31}H_{34}AuN_2P$ (M_r = 662.56): C, 56.20; H, 5.17; N, 4.23. Found: C, 55.81; H, 4.94; N, 3.78.

[Au{(Cy)$_2$ATI}PPh$_3$] (2). Under exclusion of light and under stirring, 25 mL of THF was dropped into a mixture of 0.508 g (1.03 mmol) of [AuClPPh$_3$] and 0.340 g (1.06 mmol) of K(Cy$_2$-ATI) at 0 °C. The solution was slowly warmed to room temperature, and the mixture was stirred for 18 h. The solvent was removed in vacuo, and the remaining orange solid was extracted with 75 mL of toluene. The extract was reduced to dryness. The remaining dark beige solid was washed with 50 mL of pentane and dried in vacuo resulting in a light-sensitive light yellow powder. Yield: 471 mg (62%). Mp: 130 °C (dec). ^{1}H NMR (THF-d_8, 400 MHz, RT): δ = 0.76−0.90 (m, 2 H), 1.27−1.40 (m, 4 H), 1.44−1.62 (m, 10 H), 1.70−1.80 (m, 4 H), 3.72−3.84 (m, 2 H, 2 NC*H*Cy), 5.81 (t, 1 H, $^3J_{H,H}$ = 8.9 Hz), 6.25 (d, 2 H, $^3J_{H,H}$ = 11.8 Hz), 6.75 (dd, 2 H, $^3J_{H,H}$ = 11.8 Hz. 8.9 Hz), 7.41−7.48 (m, 9 H, 9 C*H*$_{Ph}$ *o/p*), 7.59−7.67 (m, 6 H, 6 C*H*$_{Ph}$ *m*). ^{13}C{^{1}H} NMR (THF-d_8, 110.4 MHz, RT): δ = 26.5, 26.6, 36.5, 59.2, 109.2, 113.8, 129.4 (d, *C*H$_{Ph}$ *m*, $^3J_{C,P}$ = 11.2 Hz), 131.4 (d, *C*H$_{Ph}$ *p*, $^4J_{C,P}$ = 2.1 Hz), 132.9 ($C_{4,6}$), 134.8 (d, *C*H$_{Ph}$ *o*, $^4J_{C,P}$ = 13.6 Hz), 134.8 (d, *C*H$_{Ph}$ *i*, $^1J_{C,P}$ = 54.6 Hz), 161.9 ($C_{1,2}$). ^{31}P{^{1}H} NMR (THF-d_8, 161.7 MHz, RT): δ = 34.2. MS (80 eV, EI, 30 °C): *m*/*z* (%) = 742.3 (2.7) [M]$^+$, 262.1 (52) [PPh$_3$]$^+$, 182.8 (100) [PPh$_2$]$^+$. Anal. Calcd for $C_{31}H_{34}AuN_2P$ (M_r = 742.68): C, 59.84; H, 5.70; N, 3.77. Found: C, 59.14; H, 5.32; N, 3.50.

K(CyAT). A 0.354 g (1.74 mmol) amount of (CyAT)H dissolved in 8 mL of THF was added to 0.120 g (2.99 mmol) of KH at room temperature, and the mixture was stirred for 18 h at room temperature. The solution was then filtered, and the remaining residue was extracted with THF (3 × 3 mL). The solvent of the combined extracts was removed in vacuo to obtain a fine light yellow powder. Yield: 282 mg (67%). ^{1}H NMR (THF-d_8, 400 MHz, RT): δ = 1.05−1.45 (m, 5 H), 1.50−1.81 (m, 5H), 3.26 (m, 1 H, NC*H*Cy), 5.69 (dd, 1 H, $^3J_{H,H}$ = 8.5 Hz, 8.2 Hz), 6.13 (d, 1 H, $^3J_{H,H}$ = 10.6 Hz), 6.27 (d, 1 H, $^3J_{H,H}$ = 11.6 Hz), 6.39−6.56 (m, 2 H). ^{13}C{^{1}H} NMR (THF-d_8, 110.4 MHz, RT): δ = 26.5, 26.9, 34.7 (NCH*C*H$_{2(Cy)}$), 58.7 (N*C*HCy), 112.9, 114.4, 115.0, 132.6, 134.2, 164.7 (C_2), 180.2 (C_1).

[Au(*i*PrAT)PPh$_3$] (3). Under exclusion of light and under stirring, 30 mL of THF was dropped into a mixture of 0.727 g (1.47 mmol) of [AuClPPh$_3$] and 0.310 g (1.54 mmol) of K(*i*PrAT) at room temperature. The solution was stirred for 32 h, the solvent was removed in vacuo, and the remaining residue was extracted with 50 mL of toluene. The extract was reduced to dryness, and a yellow light-sensitive powder was obtained. Yield: 799 mg (88%). Mp: 135−136 °C (dec). ^{1}H NMR (THF-d_8, 400 MHz, RT): δ = 1.41 (d, 6 H, NCH(C*H*$_3$)$_2$, $^3J_{H,H}$ = 6.2 Hz), 4.23 (sept, 1 H, NC*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.2 Hz), 6.16 (dd, 1 H, $^3J_{H,H}$ = 9.3 Hz, 9.3 Hz), 6.54 (d, 1 H, $^3J_{H,H}$ = 11.2 Hz), 6.78 (d, 1 H, $^3J_{H,H}$ = 11.2 Hz), 6.91 (ddd, 1 H, $^3J_{H,H}$ = 11.2 Hz, 9.3 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.00 (ddd, 1 H, $^3J_{H,H}$ = 11.2 Hz, 9.3 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.42−7.52 (m, 9 H, 9 C*H*$_{Ph}$ *o/p*), 7.63−7.74 (m, 6 H, 6 C*H*$_{Ph}$ *m*). ^{13}C{^{1}H} NMR (THF-d_8, 110.4 MHz, RT): δ = 26.1 (NCH(*C*H$_3$)$_2$), 50.6 (N*C*H(CH$_3$)$_2$), 112.6, 117.8, 124.3, 129.7 (d, *C*H$_{Ph}$ *m*, $^3J_{C,P}$ = 11.6 Hz), 131.9 (d, *C*H$_{Ph}$ *p*, $^4J_{C,P}$ = 2.1 Hz), 132.6 (d, *C*H$_{Ph}$ *i*, $^1J_{C,P}$ = 58.7 Hz), 134.6, 134.7, 135.1 (d, *C*H$_{Ph}$ *o*, $^2J_{C,P}$ = 14.0 Hz), 165.3 (C_2), 179.7 (C_1). ^{31}P{^{1}H} NMR (THF-d_8, 161.7 MHz, RT): δ = 33.2. MS (80 eV, EI, 30 °C): *m*/*z* (%) = 621.1 (50) [M]$^+$, 459.4 (71) [M − *i*PrAT]$^+$, 262.3 (100) [PPh$_3$]$^+$. Anal. Calcd for $C_{28}H_{27}AuNOP$ (M_r = 621.46): C, 54.11; H, 4.38; N, 2.25. Found: C, 54.00; H, 4.29; N, 1.98.

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Table 1. Crystallographic Details of [Au{(*i*Pr)$_2$ATI}PPh$_3$] (**1**) and [Au{(Cy)$_2$ATI}PPh$_3$] (**2**)[a]

param	**1**	**2**
formula	$C_{31}H_{34}AuN_2P$	$C_{37}H_{42}AuN_2P$
fw	662.54	742.66
space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a, Å	14.3624(7)	11.1572(8)
b, Å	10.3495(4)	13.0802(10)
c, Å	19.4897(9)	13.3000(10)
α, deg		109.540(6)
β, deg	106.771(4)	110.119(6)
γ, deg		101.708(6)
V, Å^3	2773.8(2)	1602.9(3)
Z	4	2
density, g/cm^3	1.587	1.539
radiatn (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	5.383	4.667
abs corr	integration	integration
reflcns collcd	35 534	11 137
unique reflcns	7466 (R_{int} = 0.0652)	5600 (R_{int} = 0.0597)
obsd reflcns	5872	4570
GOF on F^2	1.023	1.032
R1,[b] wR2[c]	0.0329, 0.0780	0.0422, 0.0831

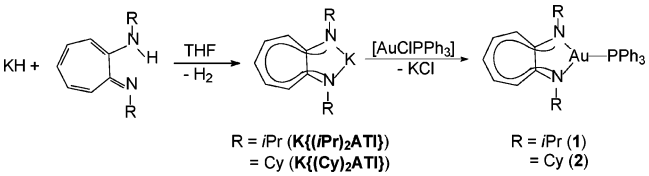
[a] All data collected at 200 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

[Au(CyAT)PPh$_3$] (4). Under exclusion of light and under stirring, 20 mL of THF was dropped into a mixture of 0.412 g (0.833 mmol) of [AuClPPh$_3$] and 0.250 g (1.04 mmol) of K(CyAT) at room temperature. The mixture was stirred for 18 h, the solvent was removed in vacuo, and the remaining residue was extracted with 10 mL of toluene after stirring for 1 h. The extract was reduced to dryness, and a yellow light-sensitive powder was obtained. Yield: 0.510 g (93%). Mp: 125 °C (dec). ^{1}H NMR (THF-d_8, 400 MHz, RT): δ = 1.08−1.20 (m, 1 H), 1.39−1.52 (m, 2 H), 1.62−1.81 (m, 3 H), 1.81−1.93 (m, 2 H), 1.94−2.04 (m, 2 H), 3.85 (tt, 1 H, NC*H*Cy, $^3J_{H,H}$ = 10.7 Hz, 3.9 Hz), 6.17 (dd, 1 H, $^3J_{H,H}$ = 8.9 Hz, 8.9 Hz), 6.55 (d, 1 H, $^3J_{H,H}$ = 11.5 Hz), 6.76 (d, 1 H, $^3J_{H,H}$ = 11.2 Hz), 6.90 (dd, 1 H, C$_6$*H*, $^3J_{H,H}$ = 11.2 Hz, 8.9 Hz), 6.98 (dd, 1 H, $^3J_{H,H}$ = 11.5 Hz, 8.9 Hz), 7.43−7.53 (m, 9 H, 9 C*H*$_{Ph}$ *o/p*), 7.66−7.77 (m, 6 H, 6 C*H*$_{Ph}$ *m*). ^{13}C{^{1}H} NMR (THF-d_8, 110.4 MHz, RT): δ = 26.7, 27.1, 37.7 (NCH*C*H$_{2(Cy)}$), 59.8 (N*C*HCy), 112.6, 117.8, 124.2, 129.7 (d, *C*H$_{Ph}$ *m*, $^3J_{C,P}$ = 11.6 Hz), 131.9 (d, *C*H$_{Ph}$ *p*, $^4J_{C,P}$ = 2.1 Hz), 132.7 (d, *C*H$_{Ph}$ *i*, $^1J_{C,P}$ = 59.5 Hz), 134.5, 134.6, 135.1 (d, *C*H$_{Ph}$ *o*, $^4J_{C,P}$ = 14.1 Hz), 165.2, 179.7. ^{31}P{^{1}H} NMR (THF-d_8, 161.7 MHz, RT): δ = 33.9. MS (80 eV, EI, 30 °C): *m/z* (%) = 661.3 (0.9) [M]$^+$, 459.1 (3.8) [M − CyAT]$^+$, 262.2 (49.6) [PPh$_3$]$^+$. Anal. Calcd for $C_{31}H_{31}AuNOP$ (M_r = 661.52): C, 56.28; H, 4.72; N, 2.12. Found: C, 56.02; H, 4.71; N, 2.00.

X-ray Crystallographic Studies of 1 and 2. Crystals of **1** were grown by slow evaporation of toluene, and crystals of **2** were obtained 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 4 PC.

All structures were solved by the Patterson method (SHELXS-97[44]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[45] In the final cycles of each refinement, all non-hydrogen atoms except the disordered atoms C12 and C13 in **1** were assigned 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, and 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 a supplementary publication Nos. CCDC 641196 (**1**) and 641197 (**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; email, deposit@ccdc.cam.ac.uk).

Scheme 3



Results and Discussion

Potassium *N*-isopropyl-2-(isopropylamino)troponiminate, K{(*i*Pr)$_2$ATI}, and *N*-cyclohexyl-2-(cyclohexylamino)troponimine, K{(Cy)$_2$ATI}, were synthesized by treatment of the neutral ligand with an excess of KH in THF (Scheme 3). Whereas K{(*i*Pr)$_2$ATI} was described earlier by us,[42] K{(Cy)$_2$ATI} is a new compound, which was characterized by ^{1}H and ^{13}C NMR spectroscopy. The spectra indicate that the alkali metal cation of K{(Cy)$_2$ATI} is not coordinated by THF. As it has been observed previously for K{(*i*Pr)$_2$ATI}, the room-temperature NMR spectrum is indicative of a very symmetrical structure. Transmetalation of K{(*i*Pr)$_2$ATI} and K{(Cy)$_2$ATI} with [AuClPPh$_3$] in a 1:1 ratio followed by extraction with toluene afforded the corresponding gold complexes [Au{(*i*Pr)$_2$ATI}PPh$_3$] (**1**) and [Au{(Cy)$_2$ATI}PPh$_3$] (**2**), respectively, as yellow powders in good yields (Scheme 3). Both compounds can be shortly handled in air, but they are light sensitive. The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures were established by single-crystal X-ray diffraction.

The room-temperature ^{1}H and ^{13}C NMR spectra of compounds **1** and **2** point to a symmetric coordination of the aminotroponiminate ligand in solution, which is in contrast to the asymmetric coordination observed in the solid state (see below). Thus, the ligand may show fluctional behavior in solution. The signal of the isopropyl C*H* of **1** is well-resolved into a septet but shows a marked downfield shift (δ = 4.17 ppm) compared to the potassium salt (δ =

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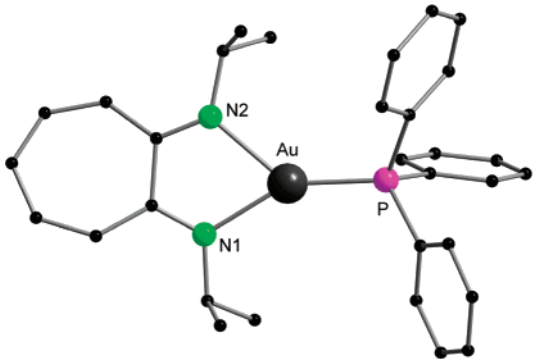


Figure 1. Solid-state structure of **1** showing the atom-labeling scheme, omitting hydrogen atoms. Hydrogen atoms are omitted for clarity.

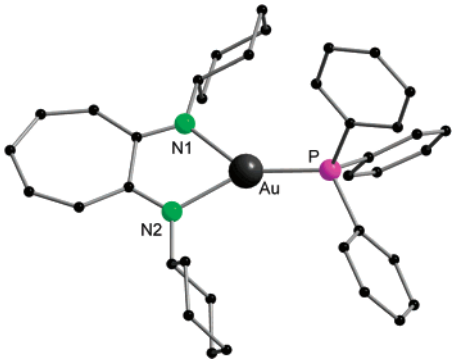


Figure 2. Solid-state structure of **2** showing the atom-labeling scheme, omitting hydrogen atoms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [Au{(*i*Pr)$_2$ATI}PPh$_3$] (**1**) and [Au{(Cy)$_2$ATI}PPh$_3$] (**2**)

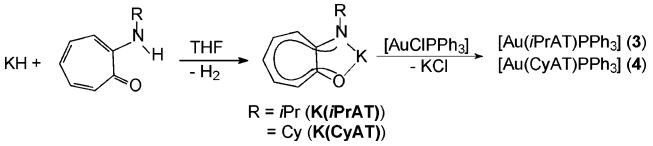
param	**1**	**2**
	Bond Lengths (Å)	
Au−N1	2.178(3)	2.188(6)
Au−N2	2.262(3)	2.237(5)
Au−P	2.2036(10)	2.204(2)
	Bond Angles (deg)	
N1−Au−N2	71.79(13)	72.2(2)
N1−Au−P	151.10(9)	147.9(2)
N2−Au−P	137.11(10)	139.90(15)

3.67 ppm). As expected, the alkyl resonances of the cyclohexyl ring of compound **2** are not well resolved. In contrast the signals of the seven-membered rings of compounds **1** and **2** show the typical well-resolved pattern expected for aminotroponiminate ligands. In the $^{31}P\{^1H\}$ NMR spectra, both complexes show the expected signal for the Ph_3P phosphorus atoms at $\delta = 34.8$ ppm (**1**) and 34.2 (**2**) ppm, respectively, which are in the range of the starting material [AuClPPh$_3$].

The solid-state structures of compounds **1** and **2** were investigated by single-crystal X-ray diffraction. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ having four molecules in the unit cell (Figure 1). The gold atom in compound **1** is distorted trigonal planar coordinated by the PPh_3 group and the two nitrogen atoms (N1 and N2) of the aminotroponiminate ligand. The tendency of Au(I) to form a linear setup results in an asymmetric attachment of the {(*i*Pr)$_2$ATI}$^-$ ligand to the metal center. Thus, the Au−N1 bond length of 2.178(3) Å is significantly shorter than the Au−N2 bond distance of 2.262(3) Å. As a result of this distortion the N−Au−P angle differs by about 14° (N1−Au−P 151.10(9)° and N2−Au−P 137.11(10)°). The ligand atoms N1, N2, and P as well as the gold atom are in plane. No intermolecular Au(I)−Au(I) contacts within 5.0 Å are observed in the solid state.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ having two molecules in the unit cell (Figure 2). As already observed for compound **1** the gold atom in compound **2** is a distorted trigonal planar coordinated by the ligands. In contrast to compound **1**, the difference of the Au−N bond distances of the {(Cy)$_2$ATI}Au subunit is smaller (Au−N1 2.188(6) Å and Au−N2 2.237(5) Å), and thus, the distortion of the trigonal planar setup is less significant, resulting in N−Au−P bond angles of 147.9(2) and 139.90(15)°. Again, the ligand atoms N1, N2, and P as well as the gold atom are in plane. As described above, no intermolecular Au(I)−Au(I) contacts are observed in the solid state.

Scheme 4



To compare the reactivity and the coordination mode of the aminotroponiminate ligand (**D**, Scheme 1) with a similar bidentate ligand system, we also introduced aminotroponates (**E**, Scheme 1) into Au(I) chemistry. In comparison to aminotroponiminates, the imine group is formally replaced by an oxo group in aminotroponates. Thus, both ligand systems **D** and **E** are closely related. As transfer reagents we again used potassium derivatives of the ligands. Whereas potassium 2-(isopropylamino)troponate (K(*i*PrAT))[41] was described earlier, the corresponding cyclohexyl analogue (K(CyAT)) was unknown. The latter compound was obtained by deprotonation of (CyAT)H with KH in THF at room temperature (Scheme 4). K(CyAT) is a air-sensitive yellow powder, which was characterized by ^1H and ^{13}C NMR spectroscopy. The spectra show the expected set of signals.

Reaction of K(*i*PrAT) and K(CyAT) with [AuClPPh$_3$] in THF resulted after extraction with toluene in the corresponding gold complexes of composition [Au(*i*PrAT)PPh$_3$] (**3**) and [Au(CyAT)PPh$_3$] (**4**) (Scheme 4). Complexes **3** and **4** were characterized by MS, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and elemental analysis. The ^1H and $^{13}C\{^1H\}$ NMR spectra show the expected set signals for the (*i*PrAT)$^-$ ligand. The signals of the isopropyl C*H* of **3** appear as a well-resolved septet at $\delta = 4.23$ ppm, which is a significant downfield shift compared to the starting material K(*i*PrAT) ($\delta = 3.61$)[41] As observed for compound **2** in complex **4**, the alkyl resonances of the cyclohexyl ring are not well resolved but the signals of the seven membered rings of compounds **3** and **4** show the typical well-resolved pattern expected for aminotroponate ligands. In the $^{31}P\{^1H\}$ NMR the signal for

the PPh_3 group is seen at $\delta = 33.2$ ppm (**3**) and 33.9 (**2**) ppm, which is in the range of compounds **1** and **2**. All the analytical data obtained for complexes **3** and **4** point toward monomeric gold complexes although we cannot absolutely exclude Au(I)−Au(I) contacts in the solid state. Single crystals of compounds **3** and **4** could not be obtained. So far we can only speculate about the coordination number of the gold atoms. In analogy to compounds **1** and **2**, we suggest that as a result of the rigid nature of the aminotroponate ligand also the gold atoms in compounds **3** and **4** could be three-coordinated. Compounds **1**−**4** do not show any emission by irradiation with an UV lamp. Photoluminescence measurements of compounds **2** and **4** were performed at room temperature. These measurements show only a broad photoluminescence with a low intensity.[46]

Summary

In summary, we have synthesized the potassium compounds K{(*i*Pr)$_2$ATI} and K{(Cy)$_2$ATI} of the isopropyl- and cyclohexyl-substituted aminotroponimines by deprotonation reaction. In a similar way the potassium derivatives K(*i*PrAT) and K(CyAT) were obtained from the isopropyl- and cyclohexyl-substituted aminotropones. Both aminotroponates and aminotroponiminates are rigid bidentate monoanionic ligand systems. Transmetalation of the potassium compounds with [AuClPPh$_3$] resulted in the gold complexes [Au{(*i*Pr)$_2$ATI}PPh$_3$], [Au{(Cy)$_2$ATI}PPh$_3$], [Au(*i*PrAT)PPh$_3$], and [Au(CyAT)PPh$_3$]. The solid-state structures of the aminotroponiminate complexes were investigated by single-crystal X-ray diffraction. The gold atoms in both compound are distorted trigonal planar coordinated by the PPh_3 group and the two nitrogen atoms of the aminotroponiminate ligand. The ligand atoms N1, N2, and P as well as the gold atom are in plane. Thus, a new class of three-coordinated gold(I) complexes was established, which to the best of our knowledge are the first gold(I) complexes having an N,N'-bidentate monoanionic ligand in the coordination sphere.

Acknowledgment. Umicore AG & Co. KG is acknowledged for the donation of $HAuCl_4$.

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.

IC0701662

(46) **2**: UV−vis−emission ($\lambda_{ex} = 465$ nm, OD465 = 0.785) (nm): $\lambda_{em} =$ 570−830 (broad band, with the maximum of intensity at 620 nm). **4**: UV−vis−emission ($\lambda_{ex} = 445$ nm, OD445 = 0.520) (nm): $\lambda_{em} =$ 455−695 (broad band, with the maximum of intensity at 535 nm).