Ligand Exchange at a Gold(I) Carbene Complex

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Gold complex [AuCl(NHC)] (NHC = *N*,*N*′-dipropylbenzimidazolin-2-ylidene) **1** undergoes facile substitution reactions at the gold(I) center. Treatment of **1** with anionic phenylacetylide or thiophenolate led to the neutral gold complexes **2** and **3**, respectively. The cationic gold complexes [Au(NHC)(pyridine)](BF_4) [**4**]BF_4 and [Au_2($NHC)_2$(4,4′-bipyridine)]($BF_4)_2$ [**5**]($BF_4)_2$ were obtained *via* abstraction of the chloro ligand from **1** and reaction with the appropriate amine. Reaction of **1** with $AgBF_4$ in the presence of PPh_3 instead of an amine led to an inseparable product mixture of the mixed NHC/PPh_3 complex [**6**]BF_4, the dicarbene complex [Au($NHC)_2$]BF_4, [**7**]BF_4, and [Au($PPh_3)_2$]BF_4, [**8**]BF_4. Crystals of **2** and [**6**]BF_4 were obtained, and X-ray diffraction structure analyses revealed that the gold(I) atoms are coordinated in a linear fashion by the NHC and the co-ligand.

Key words: *N*-Heterocyclic Carbene, Phosphine, Acetylide Ligand, Gold Complexes

Introduction

N-heterocyclic carbenes (NHCs) have been in the focus of interest [1 – 4] due to their application as organocatalysts [5, 6] or as ligands in transition metal complexes [1 – 4, 7, 8], many of which are active in various homogeneous catalytic reactions [9, 10]. NHC complexes feature an impressive stability against air, heat and moisture. This stability is based on the superb σ-donor properties of the NHC donor compared to, for example, tertiary phosphine ligands.

Within the class of NHC donors the imidazolin-2-ylidene is the most frequently used carbene ligand, while the benzimidazolin-2-ylidene is less common, although several procedures for the preparation of such complexes have been established. Complexes with benzimidazolin-2-ylidene donors can be obtained from coordinatively unsaturated transition metal complexes and the free benzimidazolin-2-ylidene [11, 12] or by cleavage of dibenzotetraazafulvalenes in the presence of suitable transition metal compounds [13, 14]. The most facile routes to benzimidazolin-2-ylidene complexes, however, is the *in situ* deprotonation of a benzimidazolium salt in the presence of a metal complex bearing basic ligands like [Pd(OAc)$_2$] [15 – 17] or [Ni(OAc)] [18, 19]. Alternatively, the carbene transfer reaction can be based on NHC complexes possessing a labile M–C_{NHC} bond, which allows a transfer of the carbene ligand to another metal center [20]. In most cases silver complexes are used as transfer reagents [21, 22], although NHC transfer has also been reported *via* tungsten and gold complexes [23]. Less convenient, but highly useful, is the template-controlled intramolecular cyclization of metal-coordinated β-functionalized phenyl isocyanides [24 – 28] as well as the oxidative addition of a C2–X bond (X = H, Cl, I) of benzimidazole derivatives to low-valent metal precursors [29 – 34]. The latter two methods lead to complexes bearing NH,NH- or NH,NR-substituted benzimidazolin-2-ylidene ligands, which can either be further functionalized, or in selected cases, can function as molecular recognition units [35].

Gold NHC complexes are currently of special interest due to their application as catalysts for selected homogeneous transformations [36] and as metallodrugs in antitumor therapy [37, 38]. These successful applications are based on the inertness of the Au-C_{NHC} bond in complexes of type [Au(NHC)L]$^{n+}$, which also allows substitution reactions of the co-

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ligand L for halides [39], nitrogen [40] or phosphorus donors [41, 42].

In our search for gold NHC complexes with superior solubility and new electronic properties we focused on the influence of the co-ligand L on the NHC ligand in complexes of type $[Au(NHC)L]^{n+}$. Here we present our studies on the substitution reaction of the chloro ligand in the complex [Au(NHC)Cl] (NHC = *N*,*N*′-dipropylbenzimidazolin-2-ylidene) **1** [43] with anionic or neutral co-ligands. The influence of these co-ligands on the NHC-Au complex fragment is discussed.

Results and Discussion

The halide exchange of the chloro ligand in (*N*,*N*′-dipropylbenzimidazolin-2-ylidene)gold(I) chloride **1** with a bromo ligand proceeds readily [44]. Thus the exchange of the chloro ligand with other ligands was studied. Treatment of **1** with *in situ* prepared sodium phenylacetylide or sodium thiophenolate in methanol also proceeds readily to give the gold(I) complexes **2** and **3** in good yields (Scheme 1).

The ^{13}C NMR spectra of the gold carbene complexes **2** and **3** exhibit resonances at δ = 194.0 and δ = 188.2 ppm, respectively, for the C_{NHC} atoms. These chemical shifts are significantly downfield from the C_{NHC} resonance found for complex **1** (δ = 178.3 ppm) [43] nicely illustrating the dependence of the C_{NHC} resonance on the co-ligand. The C_{NHC} resonance of **2** falls in the range previously reported for a gold(I) NHC/acetylide complex [45, 46]. The C_{NHC} resonance of complex **3** cannot be compared to other Au^I-NHC-SPh complexes due to lack of available ^{13}C NMR data.

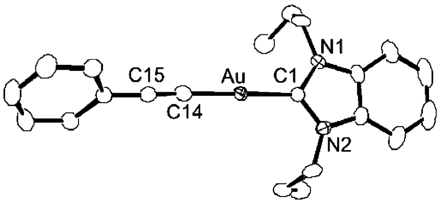
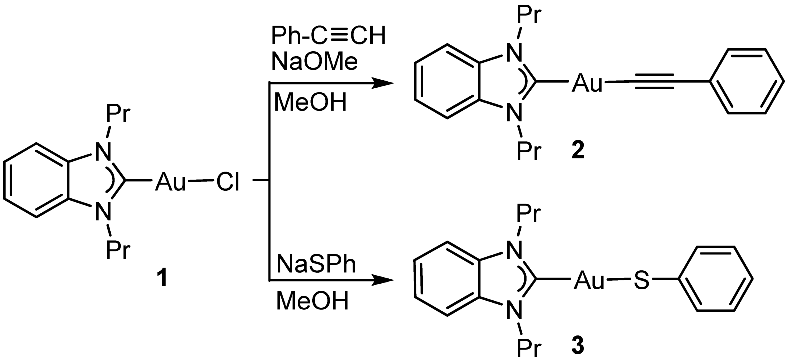


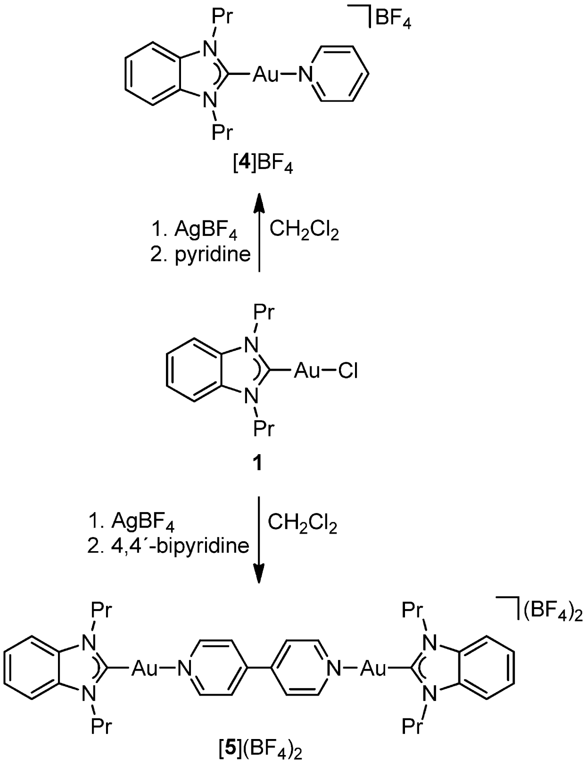
Fig. 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity, displacement ellipsoids are at the 50 % probability level. Selected bond lengths (Å) and angles (deg): Au–C1 2.016(2), Au–C14 1.988(2), C1–N1 1.357(3), C1–N2 1.353(3), C14–C15 1.206(3); C1–Au–C14 177.01(9), Au–C14–C15 177.5(2), N1–C1–N2 106.4(2).

Crystals of **2** suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into saturated chloroform solutions of the complex. The molecular structure is depicted in Fig. 1. The Au–C_{NHC} (2.016(2) Å) as well as the Au–C14 (1.988(2) Å) bond lengths of **1** fall in the range previously reported for similar mixed NHC/acetylide gold(I) complexes featuring a benzimidazolin-2-ylidene ligand [45]. Complex **2** exhibits, as expected, almost linear C1–Au–C14 (177.01(9)°) and Au–C14–C15 (177.5(2)°) units. The N1–C1–N2 bond angle in **2** (106.4(2)°) does not significantly change upon substitution of the chloro ligand in **1** (105.8(5)°, 107.3(5)° [43]) for the acetylide ligand. No aurophilic interactions [47], which have been observed for many other gold carbene complexes [43, 44], are observed for **1**.

Reaction of complex **1** with silver tetrafluoroborate in the presence of pyridine or 4,4′-bipyridine (Scheme 2) led to abstraction of the chloro ligand followed by occupation of the vacant coordination site by the nitrogen atoms from either pyridine or 4,4′-bipyridine, the latter one serving as a bridging unit



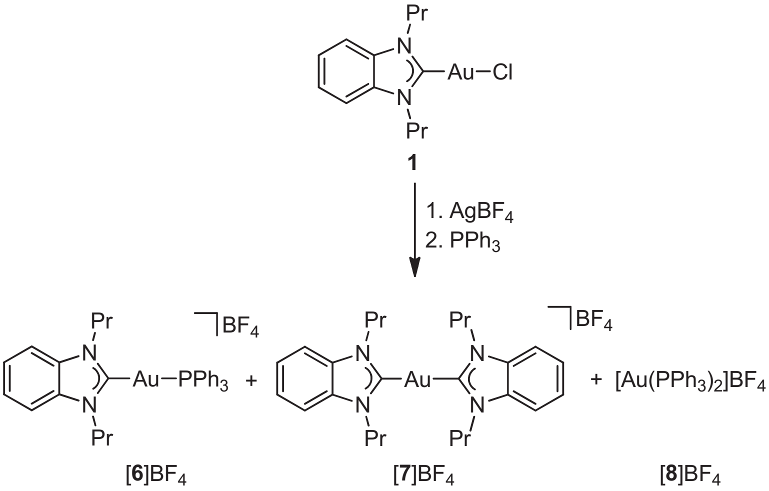
Scheme 1. Synthesis of complexes **2** and **3**.



Scheme 2. Synthesis of complex [**4**]BF_4 and [**5**]$(BF_4)_2$.

between two gold(I)-NHC complex fragments. Formation of the cationic complexes $\mathbf{4}^+$ and $\mathbf{5}^{2+}$ was concluded from NMR data as well as from mass spectra. The ^{13}C NMR spectra of compounds [**4**]BF_4 and [**5**]$(BF_4)_2$ exhibit the resonances for the C_{NHC} atom at $\delta = 171.0$ and $\delta = 170.3$ ppm, respectively. Both resonances fall in the range observed previously for the C_{NHC} atom of benzimidazolin-2-ylidene ligands coordinated to an Au-pyridine complex fragment ($\delta = 174.0 - 170.6$ ppm) [40]. The exchange of the chloro ligand in **1** (C_{NHC} $\delta = 178.3$ ppm) for nitrogen donors leads to a highfield shift of the C_{NHC}resonance ($\Delta\delta \approx 7 - 8$ ppm). This shift is caused by the change of the electronic situation at the metal center upon transition from the neutral complex **1** to the cationic complexes $\mathbf{4}^+$ and $\mathbf{5}^{2+}$. Interestingly, a comparison of the remaining ^{1}H and ^{13}C NMR data of **1** to those of compounds [**4**]BF_4 and [**5**]$(BF_4)_2$ reveals that all other resonances of the benzimidazolin-2-ylidene ligand remain nearly unchanged.

Wang and Lin reported for the reaction of [AuCl(NHC)] (NHC = *N*,*N*′-diethylbenzimidazolin-2-ylidene) and $AgBF_4$ in the presence of PPh_3 the formation of dicarbene and diphosphine complexes, but no mixed NHC/PPh_3 gold complex was obtained [39]. Contrary to this observation, we have found that treatment of complex **1** with $AgBF_4$ in the presence of PPh_3 proceeds with formation of the mixed NHC/PPh_3 complex [**6**]BF_4 together with the dicarbene species [**7**]BF_4 and the diphosphine complex $[Au(PPh_3)_2]BF_4$ [**8**]BF_4 (Scheme 3). The formation of all three compounds was detected by mass spectrometry. Unfortunately, clean separation of the reaction products proved impossible. The complex NMR spectra of the product mixture do not allow a complete assignment of all observed reso-



Scheme 3. Synthesis of complexes [**6**]BF_4, [**7**]BF_4 and [**8**]BF_4.

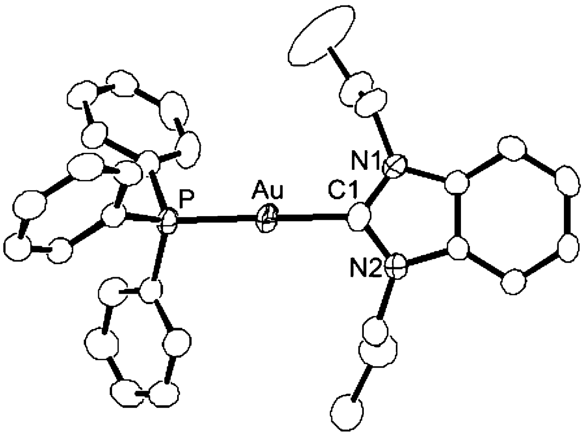


Fig. 2. Molecular structure of $\mathbf{6}^+$ in [**6**]BF_4. Hydrogen atoms are omitted for clarity, displacement ellipsoids are at the 50 % probability level. Selected bond lengths (Å) and angles (deg): Au–C1 2.040(4), Au–P 2.2836(10), C1–N1 1.348(6), C1–N2 1.345(6); C1–Au–P 178.46(15), N1–C1–N2 107.0(4).

nances. However, crystals of [**6**]BF_4 suitable for an X-ray diffraction study have been obtained by slow diffusion of pentane into a chloroform solution of the complex mixture.

The molecular structure of the cation $\mathbf{6}^+$ is depicted in Fig. 2. The Au–C_{NHC} and Au–P bond lengths measure 2.040(4) and 2.2836(10) Å, respectively. These values compare well with equivalent distances in known [Au(NHC)(PR_3)] complexes [41, 42]. Compared to complex **1** (Au–C_{NHC} 1.969(6) and 1.978(6) Å, two independent molecules) the Au–C_{NHC} bond length in $\mathbf{6}^+$ is enlarged. The C_{NHC}–Au–P bond angle in $\mathbf{6}^+$ (178.46(15)°) deviates only slightly from the expected perfectly linear arrangement. In analogy to the observation made for **2**, the N1–C_{NHC}–N2 bond angle in $\mathbf{6}^+$ (107.0(4)°) is not significantly affected by the substitution of the *trans* ligand Cl^- in **1** by PPh_3.

Conclusion

The substitution of the chloro ligand in the benzimidazolin-2-ylidene gold(I) chloride complex **1** for anionic or neutral ligands proceeds readily. The influence of the *trans*-ligand on the electronic situation at the gold(I) atom and consequently on the NHC donor can be detected through changes in the chemical shift of the carbenic carbon atom. An anionic ligand led to a downfield shift of the carbene resonance, while a neutral nitrogen donor ligand led to an upfield shift of the signal compared to that of the parent gold chloride complex. The gold(I) complexes possess a linear geometry, and the bond parameters fall in the expected range.

Experimental Section

(*N*,*N*′-Dipropylbenzimidazolin-2-ylidene)gold(I) chloride (**1**) was prepared according to a described procedure [43]. NMR spectra were recorded using Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen) or Varian MAT 212 spectrometers.

*Synthesis of [(N,N′-dipropylbenzimidazolin-2-ylidene)-gold(I) phenylacetylide] (**2**)*

Phenylacetylene (20 mg, 0.2 mmol) and sodium methanolate (11 mg, 0.2 mmol) were dissolved in methanol (10 mL) and stirred for one hour at ambient temperature. Then complex **1** (87 mg, 0.2 mmol) was added to the solution, and the reaction mixture was stirred for additional 12 h at ambient temperature. The solvent was removed *in vacuo*, the solid residue was dissolved in dichloromethane (20 mL), and the suspension was filtered through Celite. The solvent was removed *in vacuo* giving complex **2** as a colorless powder. Yield: 79 mg (0.16 mmol, 79 %). – ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.53-7.49$ (m, 2 H, Ar-H), 7.46 – 7.41 (m, 2 H, Ar-H), 7.40 – 7.35 (m, 2 H, Ar-H), 7.25 – 7.13 (m, 3 H, Ar-H), 4.47 (t, $^3J = 7.4$ Hz, 4 H, $NCH_2CH_2CH_3$), 2.00 (sext, $^3J = 7.4$ Hz, 4 H, $NCH_2CH_2CH_3$), 1.01 (t, $^3J = 7.4$ Hz, 6 H, $NCH_2CH_2CH_3$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 194.0$ (NCN), 133.4 (Ar-C acetylide), 132.4 (Ar-C NHC), 128.3, 127.8, 126.3 (Ar-C acetylide), 125.5 ($C{\equiv}C$), 124.0, 111.4 (Ar-C NHC), 105.5 ($C{\equiv}C$), 50.0 ($NCH_2CH_2CH_3$), 23.5 ($NCH_2CH_2CH_3$), 11.4 ($NCH_2CH_2CH_3$). – MS (EI): $m/z = 500$ $[M]^+$.

*Synthesis of [(N,N′-dipropylbenzimidazolin-2-ylidene)-gold(I) thiophenylate] (**3**)*

A sample of **1** (185 mg, 0.425 mmol) and a slight excess of sodium thiophenolate (59 mg, 0.45 mmol) were dissolved in a mixture of MeOH (10 mL) and dichloromethane (10 mL). The reaction mixture was stirred at ambient temperature for 12 h. Then the solvents were removed *in vacuo*, the residue was dissolved in dichloromethane (30 mL), and the suspension was filtered through Celite. The solvent was removed *in vacuo* giving **3** as a pale-yellow powder. Yield: 179 mg (0.35 mmol, 83 %). – ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.67-7.62$ (m, 2 H, Ar-H), 7.48 – 7.43 (m, 2 H, Ar-H), 7.42 – 7.37 (m, 2 H, Ar-H), 7.10 – 7.04 (m, 2 H, Ar-H), 6.98 – 6.92 (m, 1 H, Ar-H), 4.43 (t, $^3J = 7.4$ Hz, 4 H, $NCH_2CH_2CH_3$), 1.98

(sext, $^3J = 7.4$ Hz, 4 H, $NCH_2CH_2CH_3$), 0.99 (t, $^3J = 7.4$ Hz, 6 H, $NCH_2CH_2CH_3$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 188.8$ (NCN), 142.2 (Ar-C thiolate), 133.1 (Ar-C NHC), 130.6, 128.9 (Ar-C thiolate), 124.1 (Ar-C NHC), 123.0 (Ar-C thiolate), 111.4 (Ar-C NHC), 50.0 ($NCH_2CH_2CH_3$), 23.4 ($NCH_2CH_2CH_3$), 11.3 ($NCH_2CH_2CH_3$). – MS (EI): $m/z = 508$ $[M]^+$.

*Synthesis of [(N,N′-dipropylbenzimidazolin-2-ylidene)-(pyridine)gold(I) tetrafluoroborate] ([**4**]BF$_4$)*

A sample of complex **1** was dissolved in dichloromethane (20 mL), and a slight excess of silver tetrafluoroborate (42 mg, 0.21 mmol) was added. After five minutes an excess of pyridine (0.25 mL, 3.1 mmol) was added dropwise to the reaction mixture, which was stirred for 12 h at ambient temperature. Then the suspension was filtered through Celite, and the solvent was removed *in vacuo*. The solid residue was dissolved in 3 mL of dichloromethane, and this solution was added to diethyl ether (150 mL) while stirring. The formed colorless precipitate was collected by filtration and dried *in vacuo*. Yield: 102 mg (0.18 mmol, 90 %). – ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 8.08-8.02$ (m, 1 H, pyridine-H), 7.88 – 7.81 (m, 2 H, pyridine-H), 7.74 – 7.68 (m, 2 H, pyridine-H), 7.56 – 7.50 (m, 2 H, Ar-H), 7.46 – 7.40 (m, 2 H, Ar-H), 4.51 (t, $^3J = 7.4$ Hz, 4 H, $NCH_2CH_2CH_3$), 2.05 – 1.94 (m, 4 H, $NCH_2CH_2CH_3$), 0.99 (t, $^3J = 7.4$ Hz, 6 H, $NCH_2CH_2CH_3$). – ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 171.0$ (NCN), 151.9, 142.0 (pyridine-C), 133.6 (Ar-C), 127.5 (pyridine-C), 125.3, 112.3 (Ar-C), 51.1 ($NCH_2CH_2CH_3$), 23.8 ($NCH_2CH_2CH_3$), 11.6 ($NCH_2CH_2CH_3$). – MS (MALDI): $m/z = 478$ $[M]^+$.

*Synthesis of {1,1′-bis[(N,N′-dipropylbenzimidazolin-2-ylidene)gold(I)]-4,4′-bipyridine bistetrafluoroborate} ([**5**](BF$_4$)$_2$)*

A sample of **1** (113 mg, 0.26 mmol) was dissolved in dichloromethane (50 mL). To this was added 4,4′-bipyridine (20 mg, 0.13 mmol) and silver tetrafluoroborate (61 mg, 0.31 mmol). The reaction mixture was stirred for 12 h at ambient temperature. Then the suspension was filtered through Celite, and the solid residue was washed with acetonitrile. Removal of the solvent *in vacuo* gave [**5**]BF$_4$ as a colorless solid. Yield: 133 mg (0.12 mmol, 91 %). – ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): $\delta = 9.13-8.86$ (m, 4 H, bipyrdine-H), 8.35 – 8.06 (m, 4 H, bipyridine-H), 8.00 – 7.86 (m, 4 H, Ar-H), 7.60 – 7.46 (m, 4 H, Ar-H), 4.75 – 4.53 (m, 8 H, $NCH_2CH_2CH_3$), 2.10 – 1.87 (m, 8 H, $NCH_2CH_2CH_3$), 0.97 (t, $^3J = 7.3$ Hz, 12 H, $NCH_2CH_2CH_3$). – ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): $\delta = 170.3$ (NCN), 151.3, 132.4 (bipyridine-C), 132.3, 124.2 (Ar-C), 122.6 (bipyridine-C), 112.0 (Ar-C), 49.3 ($NCH_2CH_2CH_3$), 22.6 ($NCH_2CH_2CH_3$), 10.7 ($NCH_2CH_2CH_3$). – MS (MALDI): $m/z = 954$ $[M-2BF_4]^+$.

*Synthesis of the complex mixture [**6**]BF$_4$, [**7**]BF$_4$ and [**8**]BF$_4$*

A sample of **1** (113 mg, 0.26 mmol) was dissolved in dichloromethane (50 mL). To this was added an excess of silver tetrafluoroborate (61 mg, 0.31 mmol) and triphenylphosphine (75 mg, 0.28 mmol). The reaction mixture was stirred for 12 h at ambient temperature. Then the suspension was filtered through Celite and the solvent removed *in vacuo* to give a colorless solid residue. The three compounds [**6**]BF$_4$, [**7**]BF$_4$ and [**8**]BF$_4$ have been identified in the product mixture *via* NMR spectroscopy. A complete assignment of the NMR resonances was not possible due to the complex spectra and overlapping signals. Separation of the three complexes proved also impossible. – ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 45.1$ ($[Au(PPh_3)_2]BF_4$), 40.9 ([**5**]BF$_4$). – MS (MALDI): $m/z = 601$ $[Au(NHC)_2]^+$, 661 $[Au(NHC)PPh_3]^+$, 721 $[Au(PPh_3)_2]^+$.

X-Ray structure determination

Suitable crystals of **2** and of [**6**]BF$_4$ were mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating anode using MoK_α radiation ($\lambda = 0.71073$ Å). Diffraction data were measured over the full sphere at 153(1) K in the range $3.9 \le 2\theta \le 58.0°$ for **2** and $3.1 \le 2\theta \le 61.0°$ for [**6**]BF$_4$. Structure solution [48] and refinement [49] were achieved with standard Patterson and Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure models on calculated positions.

*Selected crystallographic details for **2***: Formula $C_{21}H_{23}N_2Au$, $M = 500.38$, colorless crystal, $0.21 \times 0.15 \times 0.14$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.4696(3)$, $b = 9.4925(3)$, $c = 11.8074(6)$ Å, $\alpha = 107.6180(10)°$, $\beta = 107.6150(10)°$, $\gamma = 97.516(10)°$, $V = 934.81(6)$ Å^3, $\rho_{calcd} = 1.78$ g cm^{-3}, $\mu = 7.9$ mm^{-1}, empirical absorption correction ($0.289 \le T \le 0.405$), 10313 intensities collected ($\pm h$, $\pm k$, $\pm l$), 4948 independent ($R_{int} = 0.0148$) and 4716 observed intensities [$I > 2\sigma(I)$], 219 refined parameters, residuals for all data $R = 0.0178$, $wR = 0.0397$, largest peak/hole in last Difference Fourier map 0.73/–1.02 e Å^{-3}.

*Selected crystallographic details for [**6**]BF$_4$*: Formula $C_{31}H_{33}N_2AuBF_4P$, $M = 748.34$, colorless crystal, $0.12 \times 0.09 \times 0.07$ mm^3, monoclinic, space group $C2/c$, $Z = 8$, $a = 29.3204(12)$, $b = 11.2663(5)$, $c = 20.4413(9)$ Å, $\beta = 116.5780(10)°$, $V = 6038.9(5)$ Å^3, $\rho_{calcd} = 1.65$ g cm^{-3}, $\mu = 5.0$ mm^{-1}, empirical absorption correction ($0.587 \le T \le 0.722$), 34673 intensities collected ($\pm h$, $\pm k$, $\pm l$), 9196 independent ($R_{\text{int}} = 0.0302$) and 6778 observed intensities [$I > 2\sigma(I)$], 372 refined parameters, residuals for all data $R = 0.0633$, $wR = 0.1040$, largest peak/hole in last Difference Fourier map $4.51/-2.48$ e Å^{-3}. One *n*-propyl group is disordered.

CCDC 926857 (**2**) and CCDC 926858 ([**6**]BF_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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