Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 1674–1682
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Cyclic (alkyl)(amino)carbene gold(I) complexes: A synthetic and structural investigation

Guido D. Frey, Rian D. Dewhurst, Shazia Kousar, Bruno Donnadieu, Guy Bertrand *

UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California, Riverside, CA 92521-0403, USA

Received 16 December 2007; received in revised form 16 January 2008; accepted 16 January 2008
Available online 20 January 2008

Abstract

A series of mono- and dicarbene gold(I) complexes of types Au(CAAC)(Cl) [CAAC = cyclic (alkyl)(amino)carbene] (**1**) and $[Au(CAAC)_2]^+[X]^-$ (X = Cl, $AuCl_2$) (**2**) have been prepared through reaction of $AuCl(SMe_2)$ with free carbenes **a**–**e**, and structurally characterized by single X-ray diffraction studies (**1a**, **1b**, **2d**, **2e**). In addition two new free cyclic (alkyl)(amino)carbenes (**c** and **e**) have been synthesized.

Keywords: Stable carbenes; Carbene complexes; Gold

1. Introduction

Following the discovery of the first stable derivatives [1,2], singlet carbenes have received considerable attention as ligands for transition metals [3,4]. Carbenes feature a strong σ-donating ability, and strongly bind metal centers of high and low oxidation states [5]. Additionally, the possibility to tune their electronic and steric properties by variation of substituents [6], make carbenes versatile ligands for transition metal catalysts [7]. Since the Au(I) catalyzed asymmetric aldol reaction was published in the late 1980s [8], the use of Au(I) complexes in catalysis has received a lot of attention [9,10]. The first NHC substituted neutral and cationic gold(I) complexes were published in 1989 [11], and their application in catalysis stated in 2003 [12].

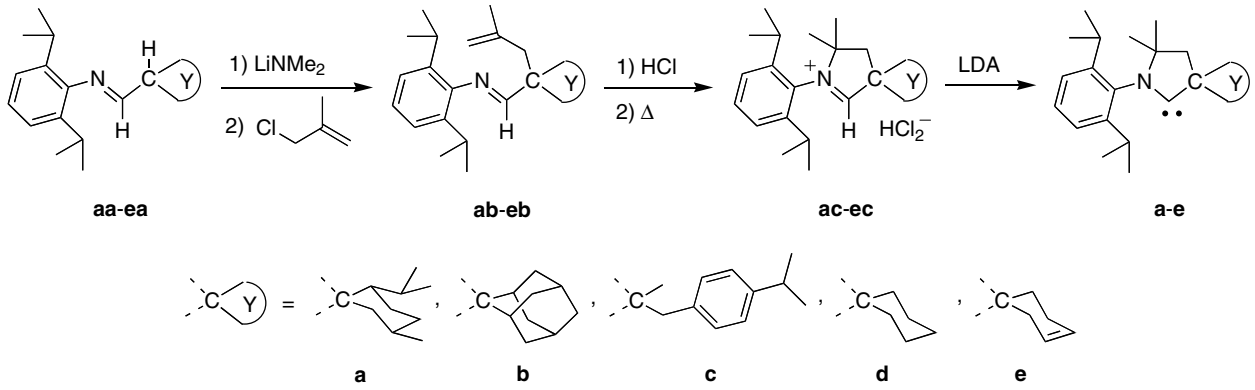
We have already reported the synthesis and isolation of well-defined cyclic (alkyl)(amino)carbenes (CAAC) [13a], their use for the activation of small molecules [13b,13c, 13d], their properties as ligand for transition metals [13e,13f], and recently the preparation of a CAAC gold(I) complex, which allows for the catalytic formation of allenes, starting from enamines and alkynes [14]. This manuscript describes the synthesis and characterization of a series of Au(I) complexes, featuring one or two CAACs, depending on the bulkiness of the carbene ligand.

The free carbenes (**a**–**e**) including the new ones (**c** and **e**) were readily prepared by deprotonation with LDA of the corresponding iminium salts; the latter were synthesized using the hydroiminiumation route [15] as shown in Scheme 1.

The gold complexes **1a**–**d** were then cleanly prepared by stirring the free carbenes **a**–**d** overnight in darkness in THF with $AuCl(SMe_2)$, the same procedure used for the corresponding NHC complexes [16]. After removing the solvent under vacuum and washing with hexanes, the remaining residue was extracted with CH_2Cl_2 or $CHCl_3$. All complexes **1a**–**d** were isolated as colorless analytically pure microcrystalline material in good yields (Scheme 2). They are readily soluble in most common polar solvents (CH_2Cl_2, $CHCl_3$, THF), sparingly in diethyl ether and insoluble in hexanes. Single crystals of complexes **1a** and **1b**, suitable for X-ray diffraction studies (Fig. 1), were obtained by slow evaporation of the solvent (CH_2Cl_2 or $CHCl_3$). Complexes **1a**–**d** are slightly unstable when exposed to incandescent light (giving gold metal) but thermally stable in the solid state at room temperature over several months. The ^{13}C NMR signals for the carbene

* Corresponding author.
E-mail address: gbertran@mail.ucr.edu (G. Bertrand).

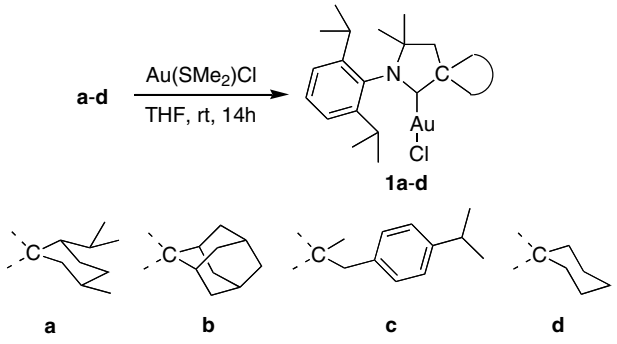
0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.01.026



Scheme 1. Synthesis of carbenes **a**–**e**.

carbon atom of gold complexes **1a**–**d** (**1a**, 237.1; **1b**, 239.9; **1c**, 236.4; **1d**, 235.0 ppm) are shifted toward high field compared to those observed for the corresponding free carbenes **a**–**d** (309–322 ppm).

Under the same reaction conditions, a different behavior was observed for carbene **e**. In this case the reaction of a stoichiometric amount of **e** with $AuCl(SMe_2)$ did not afford



Scheme 2. Synthesis of mono substituted CAAC Au(I) complexes **1a**–**d**.

the expected mono-carbene gold complex (similar to **1a**–**d**), but the cationic dicarbene gold complex **2e** with $AuCl_2^-$ as counteranion (Scheme 3), as demonstrated by a single crystal X-ray diffraction study (Fig. 2). The different nature of **2e**, compared to **1a**–**d**, is also apparent from the ^{13}C NMR spectra, since the carbene carbon gives a signal at 249.7 ppm, some 10–14 ppm downfield compared to those observed for **1a**–**d**. This result suggests that a disproportion reaction occurs, as already observed for related NHC–silver complexes [12,17,18]. Indeed, we found that all attempts to recrystallize complex **1d** from a CD_2Cl_2 solution over several days also led to the homoleptic gold carbene complex **2d**, with chloride as counteranion, as shown by an X-ray single crystal structure (Fig. 2). Here again, the ^{13}C NMR signal for the carbene carbon of **2d** appeared at lower field (251.2 ppm) than that observed for **1d** (235.0 ppm).

All complexes (**1a**, **1b**, **2d**, **2e**) show the expected linear coordination of the two ligands at the gold atom [$C_{carbene}$–Au–X angle (X = Cl, C) between 175.78(6)° [**1b**] and 180° [**2d**, **2e**]] (Table 1), and are in agreement with

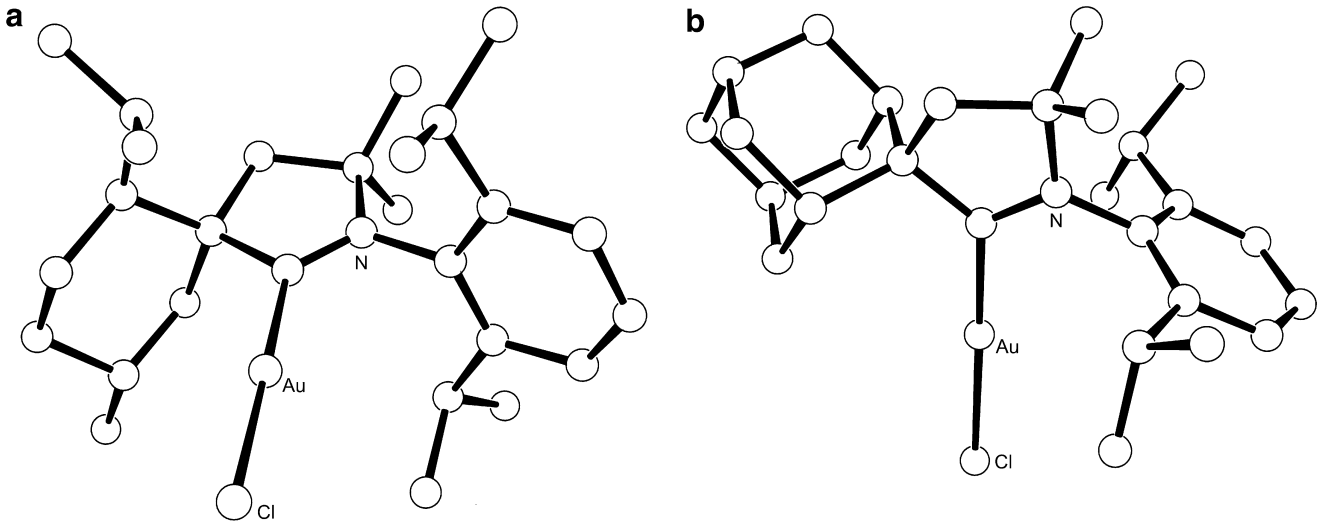
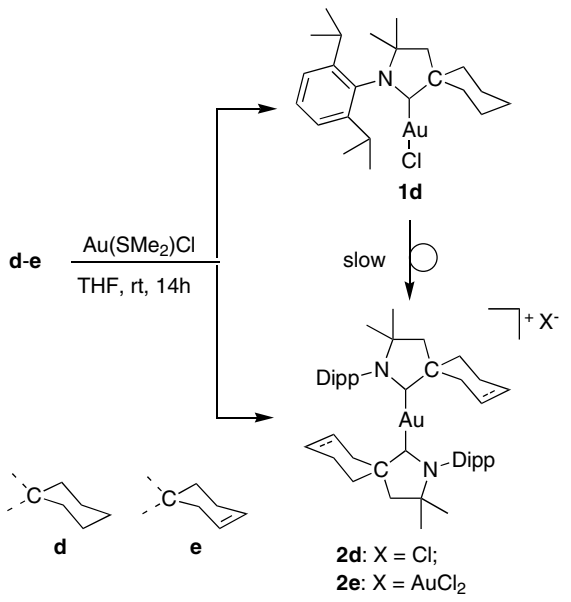


Fig. 1. Ball and Stick plots of complexes **1a** and **1b** in the solid state. Hydrogen atoms are omitted for clarity. Some pertinent metric parameters are given in Table 1.



Scheme 3. Synthesis of homoleptic dicarbene Au(I) complexes **2d** and **2e**.

the literature for gold(I) complexes [12,20–31]. The Au–$C_{carbene}$ bond lengths in **1a** (1.987(9) Å) and **1b** (1.983(2) Å) are comparable with those found in substituted NHC gold(I) chloro complexes [12,18,19], and suggest a single bond character, in good agreement with the strong σ-donor character of CAACs. The cationic complexes **2d** and **2e** have slightly longer Au–$C_{carbene}$ bond lengths [2.0321(11) and 2.033(4) Å, respectively] in the range observed for cationic dicarbene (NHC) gold(I) complexes [24,25]. For all four gold complexes (**1a**, **1b**, **2d** and **2e**), no aurophilic interactions between the Au atoms were observed (>7.4 Å).

The steric hindrance and the flexibility of the carbene carbon substituents have a dramatic effect on the synthetic outcome of the complexation reactions at gold centers. When bulky and rigid substituents are present at carbon, LAuCl complexes **1a**,**b** are isolated, whereas the use of the smaller non-substituted cyclohexyl and cyclohexylene groups (**d**, **e**) give rise to cationic di(carbene) complexes **2d**,**e**. However, despite the presence of relatively small substituents, the non-spiro carbene **c** behaves as **a** and **b**; this is probably due to the higher flexibility of the substitution motive (or to an interaction between the metal and the benzene ring). Given the likelihood that di(carbene) complexes of type **2** are at least partially deactivated in terms of catalysis, these results give a first indication of the range of the substituents, which might allow CAAC gold complexes to find catalytic applications.

2. Experimental

All reactions were performed under an atmosphere of argon and solvents were dried over Na metal or CaH_2. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^1H NMR (300 MHz), and $^{13}C\{^1H\}$NMR (75 MHz) spectra were obtained with a Bruker Avance 300 spectrometer at 298 K. ^1H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to TMS and were referenced to the residual solvent peak. NMR multiplicities are

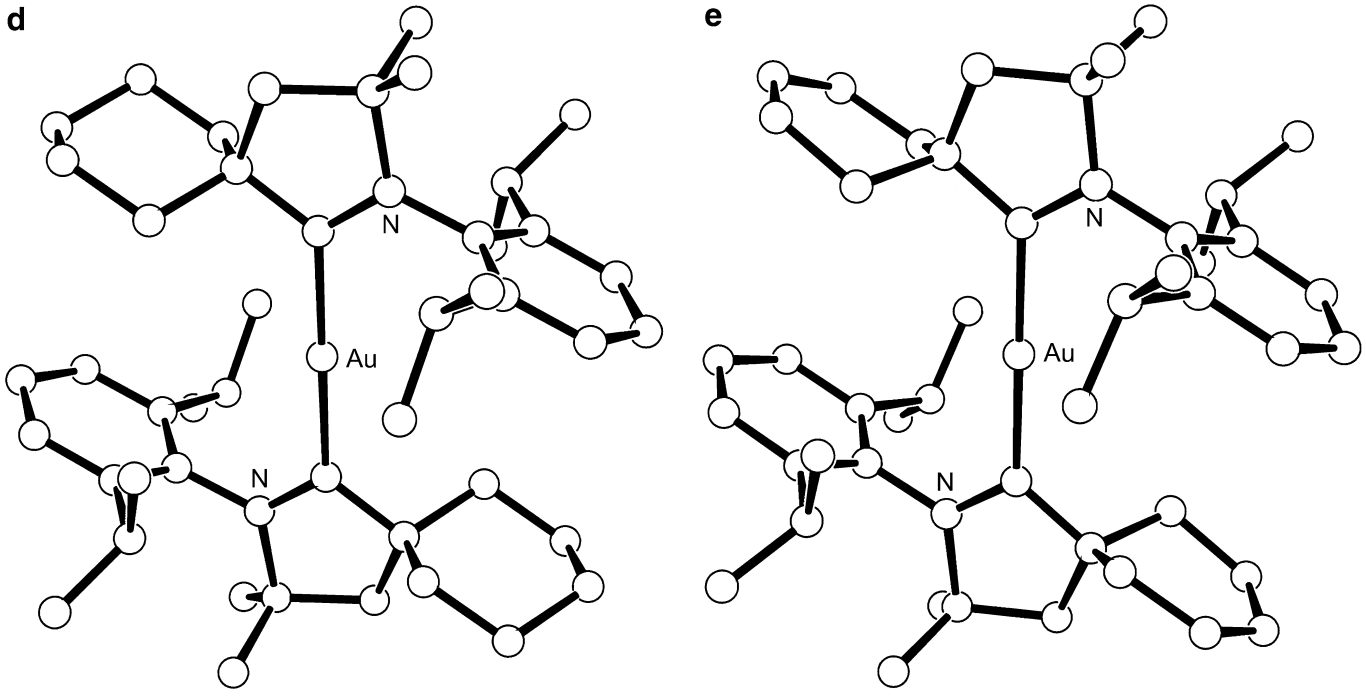


Fig. 2. Ball and Stick plots of complexes **2d** and **2e** in the solid state. Hydrogen atoms are omitted for clarity. Some pertinent metric parameters are given in Table 1.

Table 1
Pertinent bond distances and angles for complexes **1a**, **1b**, **2d**, and **2e**

Compound	**1a**	**1b**	**2d**	**2e**
Au–$C_{carbene}$ [Å]	1.987(9)	1.983(2)	2.0321(11)	2.033(4)
$C_{carbene}$–N [Å]	1.259(11)	1.304(3)	1.304(2)	1.297(5)
$C_{carbene}$–C_{spiro} [Å]	1.572(13)	1.531(3)	1.512(2)	1.506(5)
N–CMe_2 [Å]	1.508(11)	1.525(2)	1.530(2)	1.529(5)
C_{spiro}–CH_2 [Å]	1.534(13)	1.551(3)	1.548(2)	1.566(8)
CMe_2–CH_2 [Å]	1.527(12)	1.531(3)	1.540(2)	1.538(9)
$C_{carbene}$–Au–X (X = C, Cl) [°]	178.6(2)	175.78(6)	180	180
N–$C_{carbene}$–C_q [°]	108.8(8)	109.6(2)	109.99(10)	110.4(3)

abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants (*J*) are reported in hertz (Hz). High-resolution fast atom bombardment (FAB) mass spectra were obtained at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus system (Dr. Tottoli). Free carbenes **a**, **b**, and **d** were prepared according to the literature [15].

2.1. Carbene **c**

2,6-Diisopropylaniline (5.00 mL, 4.70 g, 26.5 mmol) was added at room temperature to a reaction flask containing molecular sieves (15 g) and a hexane solution (50 mL) of 2-methyl-3-(*p*-isopropylphenyl)propionaldehyde (5.84 mL, 5.55 g, 29.2 mmol). The reaction mixture was stirred for 18 h. The molecular sieves were removed by filtration, and the hexane was removed in vacuo. After removal of the excess 2,6-diisopropylaniline by short path distillation at 170 °C under vacuum, imine **ca** was obtained as a light yellow oil. Yield: 6.52 g (70%). ^{1}H NMR ($CDCl_3$) δ 7.57 (d, $^3J = 4.5$ Hz, 1H, NC*H*), 7.22 (br, 4H, H_{ar}), 7.12 (br, 3H, H_{ar}), 3.11–2.74 (m, 6H, C*H*(CH_3)$_2$ + C*H*$_2$ + CHC*H*CH_3), 1.30 (d, $^3J = 6.6$ Hz, 9H, CH(C*H*$_3$)$_2$ + CHCHC*H*$_3$), 1.12 (d, $^3J = 6.8$ Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR ($CDCl_3$) δ 170.1 (N*C*H), 148.7 (C_q), 146.4 (C_q), 137.1 (C_q), 136.7 (C_q), 128.9 (*C*H), 126.3 (*C*H), 123.8 (*C*H), 122.6 (*C*H), 41.7 (NCH*C*H), 39.6 (*C*H$_2$), 33.7 (*C*H), 27.4 (CH(*C*H$_3$)$_2$), 24.1 (*C*H), 23.4 (CH(*C*H$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 17.4 (CH*C*H$_3$). FAB-HRMS calcd for $C_{25}H_{36}N$ $[M+H]^+$: *m*/*z* 350.2848; found, 350.2852. A solution of **ca** (6.52 g, 18.7 mmol) was added slowly to a solution of $LiNMe_2$ (1.00 g, 19.6 mmol) in Et_2O (20 mL). The mixture was allowed to warm to room temperature, and then stirred for 2 h. 3-Chloro-2-methyl-1-propene (2.03 g, 2.19 mL, 22.4 mmol) was added slowly under stirring to this solution. After stirring for 2 h, all volatiles were removed in vacuo. Hexanes (20 mL) were added and the suspension was filtered. The solvent was evaporated to give compound **cb** as an oil. Yield: 6.71 g (89%). ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 1H, NC*H*), 7.27–7.06 (m, 7H, H_{ar}), 4.95 (s, 1H, C*H*), 4.82 (s, 1H, C*H*), 2.95 (s, 2H, C*H*$_2$), 2.86 (sept., $^3J = 6.8$ Hz, 3H, C*H*(CH_3)$_2$), 2.43 (d, $^2J = 13.8$ Hz, 1H, C*H*$_2$), 2.31 (d, $^2J = 13.8$ Hz, 1H, C*H*$_2$), 1.84 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.27 (d, $^3J = 6.8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, $^3J = 6.8$ Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 172.4 (N*C*H), 148.7 (C_q), 146.8 (C_q), 142.4 (C_q), 137.4 (C_q), 135.1 (C_q), 130.9 (*C*H), 126.1 (*C*H), 123.9 (*C*H), 122.9 (*C*H), 115.5 (*C*H$_2$), 46.4 (*C*H$_2$), 44.9 (C_q), 44.5 (*C*H$_2$), 33.8 (*C*H$_3$), 27.5, 25.5, 24.2, 23.6, 22.6. FAB-HRMS calcd for $C_{29}H_{42}N$ $[M+H]^+$: *m*/*z* 404.3317; found, 404.3314. To a solution of **cb** (6.71 g, 16.63 mmol) in acetonitrile (10 mL) was added a solution of HCl in Et_2O (2M, 20.7 mL, 41.6 mmol). The vessel was sealed, and heated to 80 °C for 14 h. The acetonitrile was removed, and the residue was extracted twice with boiling toluene (20 mL). After cooling to room temperature, the suspension was filtered, washed with toluene and dried to obtain **cc** ($X = HCl_2^-$) as a white solid. Yield: 5.74 g (72%). ^{1}H NMR (CD_3CN) δ 9.39 (s, 1H, NC*H*), 7.59 (t, $^3J = 7.7$ Hz, 1H, H_{ar}), 7.44 (t, $^3J = 6.8$ Hz, 2H, H_{ar}), 7.34 (d, $^3J = 7.7$ Hz, 2H, H_{ar}), 7.28 (d, $^3J = 7.7$ Hz, 1H, H_{ar}), 6.13 (br s, 1H, HCl_2), 3.47 (d, $^3J = 14.0$ Hz, 1H, C*H*$_2$), 3.03 (d, $^3J = 14.0$ Hz, 1H, C*H*$_2$), 2.96 (sept., $^3J = 6.9$ Hz, 1H, C*H*(CH_3)$_2$), 2.66 (sept., $^3J = 6.7$ Hz, 1H, C*H*(CH_3)$_2$), 2.64 (d, $^2J = 14.0$ Hz, 1H, C*H*$_2$), 2.35 (d, $^2J = 14.0$ Hz, 1H, C*H*$_2$), 2.15 (sept., $^3J = 6.6$ Hz, 1H, C*H*(CH_3)$_2$), 1.73 (s, 3H, C*H*$_3$), 1.42 (s, 3H, C*H*$_3$), 1.35 (d, $^3J = 6.7$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.26 (d, $^3J = 6.8$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (m, 9H, C*H*$_3$), 0.93 (s, 3H, C*H*$_3$). ^{13}C{^{1}H}NMR (CD_3CN) δ 192.8 (N*C*H), 149.3 (C_q), 145.6 (C_q), 145.0 (C_q), 134.7 (C_q), 132.6 (*C*H), 131.1 (*C*H), 129.7 (C_q), 127.7 (*C*H), 126.5 (*C*H), 125.9 (*C*H), 84.7 (N*C*(CH_3)$_2$), 55.3 (C_q), 44.1 (*C*H$_2$), 43.8 (*C*H$_2$), 34.4, 30.1, 29.8, 28.5, 27.6, 26.3, 24.2, 22.0, 21.8. FAB-HRMS calcd for $C_{29}H_{42}N$ $[M]^+$: *m*/*z* 404.3317; found, 404.3317.

To a Schlenk tube containing the iminium salt **cc** ($X = HCl_2^-$) (4.86 g, 10.20 mmol) and $NaBPh_4$ (3.49 g, 10.20 mmol) was added methylene chloride (40 mL). The mixture was stirred for 1 h at room temperature and filtered afterwards through Celite (3 g). The solvent was removed in vacuo, and the residue was extracted twice with boiling hexanes. The hexanes extract was cooled to −20 °C, and the solution was decanted from the solid. The solid was dried in vacuo to yield **cc** ($X = BPh_4^-$) 5.31 g (72%) as a white powder. A solution of KHMDS (419 mg, 2.10 mmol) in THF (10 mL) was added slowly to a solution of **cc** ($X = BPh_4^-$) (500 mg, 1.05 mmol) in THF (10 mL) at −78 °C. The mixture was allowed to warm to room temperature,

and stirred for 1 h. The THF was removed and the residue was extracted with hexanes (10 + 5 mL), filtered and the hexanes was removed yielding colorless crystals of free carbene **c**. Yield: 236 mg (56%). ^{1}H NMR (C_6D_6) δ 7.75 (m, 1H, H_{ar}), 7.38–7.20 (m, 6H, H_{ar}), 3.93 (sept., $^3J = 6.9$ Hz, 1H, C*H*(CH_3)$_2$), 3.80 (sept., $^3J = 6.8$ Hz, 1H, C*H*(CH_3)$_2$), 3.78 (d, $J = 8.2$ Hz, 1H), 3.60 (sept., $^3J = 6.4$ Hz, 1H, C*H*(CH_3)$_2$), 3.28 (d, $J = 8.3$ Hz, 1H, CH_2), 2.87 (s, 3H, CH_3), 2.15 (d, $^2J = 12.7$ Hz, 1H, CH_2), 1.79 (d, $^2J = 12.7$ Hz, 1H, CH_2), 1.45 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3)$_2$), 1.37 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3)$_2$), 1.36 (s, 3H, CH(CH_3)$_2$), 1.36 (d, $^3J = 6.6$ Hz, 3H, CH(CH_3)$_2$), 1.29–1.25 (9H, CH(CH_3)$_2$), 1.19 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H}NMR (C_6D_6) δ 313.0 ($C_{carbene}$), 152.7 (C_q), 152.5 (C_q), 147.0 (C_q), 139.2 (C_q), 137.7 (C_q), 131.0 (*C*H), 127.6 (*C*H), 126.6 (*C*H), 124.8 (*C*H), 124.7 (*C*H), 80.7 (N*C*(CH_3)$_2$), 61.2 (C_q), 51.5 (CH_2), 46.5 (CH_2), 34.4, 30.1, 29.8, 28.5, 27.6, 26.3, 24.2, 22.0, 21.8.

2.2. Carbene *e*

2,6-Diisopropylaniline (10.00 mL, 9.40 g, 53 mmol) was added at room temperature to a reaction flask containing molecular sieves (15 g) and a hexane solution (50 mL) of 1-cyclohexene-1-carboxaldehyde (90%) (7.23 mL, 7.01 g, 64 mmol). The reaction mixture was stirred for 16 h. The molecular sieves were removed by filtration, and the hexane was removed in vacuo. Excess 2,6-diisopropylaniline was removed by short path distillation at 170 °C under vacuum. The resulting oily residue was recrystallized from ethanol at low temperatures to afford *N*-Dipp-*C*-3-cyclohexene (**ea**) as white crystals. Yield: 11.296 g (79%). ^{1}H NMR ($CDCl_3$) δ 7.63 (d, $^3J = 4.5$ Hz, 1H, NC*H*), 7.16–7.06 (m, 3H, H_{ar}), 5.80 (s, 2H, C*H*), 2.96 (sept., $^3J = 6.9$ Hz, 2H, C*H*(CH_3)$_2$), 2.80–2.74 (m, 1H, NCHC*H*), 2.36–2.30 (m, 2H, CH_2), 2.26–2.21 (m, 2H, CH_2), 2.15–2.06 (m, 1H, CH_2), 1.82–1.72 (m, 1H, CH_2), 1.19 (d, $^3J = 6.9$ Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H}NMR ($CDCl_3$) δ 168.8 (N*C*H), 149.2 ($C_{o,ar}$), 136.6 ($C_{m,ar}$), 126.7 (*C*H), 125.3 (*C*H), 123.6 (*C*H), 122.4 (*C*H), 39.7 (NCH*C*H), 27.5 (*C*H), 27.4 (CH_2), 25.2 (CH_2), 24.2 (CH_2), 23.2 (CH_3). FAB-HRMS calcd for $C_{19}H_{28}N$ $[M+H]^+$: m/z 270.2222; found, 270.2226. A solution of **ea** (8.80 g, 32.7 mmol) was added slowly to a solution of LDA (3.67 g, 34.3 mmol) in Et_2O (20 mL). The mixture was allowed to warm to room temperature, and then stirred for 2 h. 3-Chloro-2-methyl-1-propene (3.55 g, 3.84 mL, 39.2 mmol) was added to this solution slowly under stirring. After stirring for 2 h, all volatile compounds were removed under vacuo. The remaining residue was dried at 50 °C in vacuo to remove all traces of diethyl ether and diisopropylamine. Hexanes (20 mL) was added and the suspension was filtered. The solvent was evaporated to give **eb** as a pale yellow oil. Yield: 7.40 g (70%). ^{1}H NMR ($CDCl_3$) δ 7.62 (s, 1H, NC*H*), 7.15–7.02 (m, 3H, H_{ar}), 5.75 (m, 2H, C*H*), 4.94 (s, 1H, C*H*), 4.80 (s, 1H, C*H*), 2.97 (sept., $^3J = 6.9$ Hz, 2H, C*H*(CH_3)$_2$), 2.52 (d, $^2J = 16.4$ Hz, 1H), 2.39 (s, 2H, CH_2), 2.29–2.20 (m, 3H), 2.03–1.96 (m, 1H, CH_2), 1.88–1.77 (m, 1H, CH_2), 1.85 (s, 3H, CH_3), 1.18 (d, $^3J = 6.9$ Hz, 6H, CH(CH_3)$_2$), 1.17 (d, $^3J = 6.9$ Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H}NMR ($CDCl_3$) δ 171.2 (N*C*H), 149.2 ($C_{o,ar}$), 142.0 (*C*CH_2), 137.0 ($C_{m,ar}$), 126.4 (*C*H), 125.8 (*C*H), 124.1 (*C*H), 122.9 (*C*H), 115.6 (C*C*H_2), 46.2 (*C*H_2), 42.8 (NCH*C*$_q$), 32.7 (*C*H_2), 30.3 (*C*H_2), 27.6 (*C*H), 25.4 (*C*H_3), 23.8 (*C*H_3), 23.3 (*C*H_2). FAB-HRMS calcd for $C_{23}H_{34}N$ $[M+H]^+$: m/z 324.2691; found, 324.2697. To a solution of **eb** (3.04 g, 9.44 mmol) in acetonitrile (10 mL) was added a solution of HCl in Et_2O (2 M, 9.44 mL, 18.82 mmol). The vessel was sealed, and heated to 90 °C for 16 h. The acetonitrile was removed, and the residue was extracted twice with boiling toluene (20 mL). After cooling to −20 °C, the suspension was filtered, washed with toluene and dried. **ec** with HCl_2^- as a counteranion was obtained as a white solid. Yield: 2.95 g (79%). M.p. 164–166 °C (dec.). ^{1}H NMR (CD_3CN) δ 12.88 (s, 1H, *H*Cl_2), 9.17 (s, 1H, NC*H*), 7.62 (t, $^3J = 7.8$ Hz, 1H, $H_{p,ar}$), 7.49 (d, $^3J = 7.8$ Hz, 2H, $H_{m,ar}$), 5.90 (m, 1H, C*H*), 5.78 (m, 1H, C*H*), 2.75 (m, 3H, C*H*(CH_3)$_2$ + CH_2), 2.56–2.39 (m, 3H), 2.28–2.22 (m, 3H), 2.12–2.07 (m, 1H), 1.57 (s, 6H, C(CH_3)$_2$), 1.37 (d, $^3J = 6.7$ Hz, 6H, CH(CH_3)$_2$), 1.12 (d, $^3J = 6.7$ Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H}NMR (CD_3CN) δ 192.5 (N*C*H), 145.4 ($C_{o,ar}$), 132.7 ($C_{m,ar}$), 130.1 ($C_{m,ar}$), 128.1 (*C*H), 126.2 (*C*H), 123.0 (*C*H), 84.6 (N*C*$_q$), 51.5 (NCH*C*$_q$), 45.8 (*C*H_2), 33.9 (*C*H_2), 30.4 (*C*H_2), 30.3 (*C*H_3), 29.0 (*C*H), 28.5 (*C*H), 26.4 (*C*H_3), 22.2 (*C*H_3), 22.1 (*C*H_3), 21.6 (*C*H_2). FAB-HRMS calcd for $C_{23}H_{34}N$ $[M]^+$: m/z 324.2691; found, 324.2699. To a Schlenk tube containing the iminium salt **ec** (2.95 g, 7.45 mmol) and $NaBPh_4$ (2.55 g, 7.45 mmol) was added methylene chloride (40 mL). The mixture was stirred for 1 h at room temperature and filtered afterwards through Celite (3 g). The solvent was removed in vacuo, and the residue was extracted two times with boiling hexanes. The hexanes extract was cooled to −20 °C and the solution was decanted from the solid. The solid was dried in vacuo to yield 4.03 g (84%) of **ec** with BPh_4^- as counteranion as a white powder. A solution of KHMDS (250 mg, 1.26 mmol) in THF (6 mL) was added slowly to a solution of **ec** (BPh_4^-) (810 mg, 1.26 mmol) in THF (5 mL) at −78 °C. The mixture was allowed to warm to room temperature, and stirred for 2 h. The THF was removed and the residue was extracted with toluene (10 + 5 mL), and filtered. After removal of the toluene, carbene **e** was isolated as colorless crystals. Yield: 265 mg (65%). ^{1}H NMR (C_6D_6) δ 7.35–7.18 (m, 3H, H_{ar}), 5.77 (s, 2H, C*H*), 3.84 (sept., $^3J = 6.7$ Hz, 1H, C*H*(CH_3)$_2$), 3.82 (sept., $^3J = 6.7$ Hz, 1H, C*H*(CH_3)$_2$), 3.48 (td, $^3J = 8.5$ Hz, $^3J = 7.0$ Hz, 2H, CH_2), 2.35–2.12 (m, 2H), 1.91 (d, $J = 2.5$ Hz, 2H), 1.79 (t, $^3J = 6.3$ Hz, 2H, CH_2), 1.40 (s, 3H, C(CH_3)$_2$), 1.38 (s, 3H, C(CH_3)$_2$), 1.25 (d, $^3J = 8.6$ Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H}NMR (C_6D_6) δ 311.0, 152.7, 152.6, 139.4, 136.0, 127.5, 127.4, 127.1, 124.6, 85.9, 63.0, 55.3, 40.0, 39.8, 35.0, 29.6, 29.5, 29.1, 29.0, 27.2, 27.1, 24.6, 23.7.

2.3. Complex *1a*

A THF solution (5 mL) of free carbene **a** (666 mg, 1.75 mmol) was added to a THF solution (5 mL) of $AuCl(SMe_2)$ (500 mg, 1.71 mmol). The reaction mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the residue was washed with hexane (10 mL). The residue was extracted with methylene chloride (10 mL), and the solvent was removed under vacuum, affording complex **1a** as a white solid (914 mg, 87% yield). Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a $CHCl_3$ solution. M.p. 124–125 °C. $[\alpha]_D^{20} = 7.5$ ($CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.42 (t, $^3J = 7.1$ Hz, 1H, H_p ar), 7.24 (d, $^3J = 7.1$ Hz, 2H, H_m ar), 3.16–2.89 (m, 2H), 2.83 (sept., $^3J = 6.3$ Hz, 1H, C*H*(CH_3)$_2$), 2.79 (sept., $^3J = 6.3$ Hz, 1H, C*H*(CH_3)$_2$), 2.37 (d, $^3J = 13.6$ Hz, 1H), 2.12–1.99 (m, 2H), 1.95–1.83 (m, 2H), 1.80–1.72 (m, 1H), 1.44 (d, $^3J = 6.7$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.39 (s, 3H, CH_3), 1.37 (d, $^3J = 7.0$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.34 (d, $^3J = 6.5$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.33 (s, 3H, C*H*$_3$), 1.32 (d, $^3J = 7.0$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.30–1.21 (m, 2H), 1.18 (d, $^3J = 6.9$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.75–1.25 (m, 1H), 1.02 (d, $^3J = 6.9$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.89 (d, $^3J = 6.4$ Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR ($CDCl_3$) δ 237.1 ($C_{carbene}$), 145.4 ($C_{o,ar}$), 145.0 ($C_{o,ar}$), 135.2 ($C_{m,ar}$), 129.8 ($C_{p,ar}$), 125.0 ($C_{m,ar}$), 124.9 ($C_{m,ar}$), 76.6 (C), 64.1 (C), 52.6 (*C*H$_2$), 51.4 (*C*H), 49.8 (*C*H$_2$), 35.6 (*C*H$_2$), 30.3, 29.7, 29.7, 29.4, 29.0, 28.1, 27.5, 27.0, 25.2, 24.4 (*C*H$_2$), 23.0, 22.9, 22.8, 20.2. FAB-HRMS (solvent CH_3CN) calcd for $C_{27}H_{43}AuN \cdot CH_3CN$ $[M-Cl+CH_3CN]^+$: *m*/*z* 619.3327; found, 619.3303.

2.4. Complex *1b*

Following the same experimental procedure as for **1a** but free carbene **b** (640 mg, 1.69 mmol) and $AuCl(SMe_2)$ (475 mg, 1.61 mmol), complex **1b** was isolated as a white solid (850 mg, 86% yield). Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a $CHCl_3$ solution. M.p. 194–195 °C (dec.). ^{1}H NMR ($CDCl_3$) δ 7.37 (t, $^3J = 7.7$ Hz, 1H, $H_{p,ar}$), 7.20 (d, $^3J = 7.7$ Hz, 2H, $H_{m,ar}$), 4.00 (d, $^2J = 12.9$ Hz, 2H, C*H*$_2$), 2.71 (sept., $^3J = 6.7$ Hz, 2H, C*H*), 2.32 (s, 2H), 2.12 (s, 1H), 2.02 (s, 1H), 1.98 (s, 1H), 1.92 (s, 3H), 1.78 (m, 6H), 1.39 (d, $^3J = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (s, 6H, C(C*H*$_3$)$_2$), 1.26 (d, $^3J = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (C_6D_6) δ 239.9 ($C_{carbene}$), 144.8 ($C_{o,ar}$), 135.2 ($C_{m,ar}$), 129.7 ($C_{p,ar}$), 125.0 ($C_{m,ar}$), 76.9 (C_q), 63.7 (C_q), 48.5 (*C*H$_2$), 39.0 (*C*H$_2$), 37.0, 35.2, 34.6 (*C*H$_2$), 29.2, 29.1, 27.6, 27.1, 26.9, 23.1. FAB-HRMS (solvent CH_3CN) calcd for $C_{27}H_{39}AuN \cdot CH_3CN$ $[M-Cl+CH_3CN]^+$: *m*/*z* 615.3014; found, 615.2990.

2.5. Complex *1c*

Following the same experimental procedure as for **1a** but free carbene **c** (254 mg, 0.63 mmol) and $AuCl(SMe_2)$ (186 mg, 0.63 mmol), complex **1c** was isolated as a white solid (189 mg, 47% yield). ^{1}H NMR (C_6D_6) δ 7.47 (t, $^3J = 7.5$ Hz, 1H, H_{ar}), 7.39 (d, $^3J = 7.4$ Hz, 2H, H_{ar}), 7.31 (t, $^3J = 7.3$ Hz, 2H, H_{ar}), 7.25 (d, $^3J = 7.5$ Hz, 2H, H_{ar}), 3.52 (d, $J = 13.6$ Hz, 1H, C*H*$_2$), 2.92 (sept., $^3J = 7.0$ Hz, 1H, C*H*(CH_3)$_2$), 2.82 (d, $J = 14.2$ Hz, 1H, C*H*$_2$), 2.79 (m, 1H, C*H*(CH_3)$_2$), 2.39 (d, $J = 13.2$ Hz, 1H, C*H*$_2$), 2.36 (sept., $^3J = 7.0$ Hz, 1H, C*H*(CH_3)$_2$), 2.00 (d, $J = 13.7$ Hz, 1H, C*H*$_2$), 1.57 (s, 3H, CC*H*$_3$), 1.35 (d, $^3J = 6.5$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.30–1.18 (m, 15H, C*H*$_3$), 1.07 (d, $^3J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (C_6D_6) δ 236.4 ($C_{carbene}$), 147.8 (C_q), 145.7 (C_q), 145.3 (C_q), 135.5 (C_q), 131.4 (*C*H), 130.0 (*C*H), 126.4 (*C*H), 125.2 (*C*H), 125.0 (*C*H), 81.3 (N*C*(CH_3)$_2$), 60.2 (C_q), 46.1 (*C*H$_2$), 44.2 (*C*H$_2$), 34.3, 29.7, 29.4, 29.0, 28.6, 27.2, 26.8, 24.1, 23.9, 22.5, 22.3. FAB-HRMS (solvent CH_3CN) calcd for $C_{30}H_{42}AuN_2$ $[MH-(Cl+CH_3)+CH_3CN]^+$: *m*/*z* 627.3014; found, 627.3015.

2.6. Complex *1d*

Following the same experimental procedure as for **1a** but free carbene **d** (331 mg, 1.02 mmol) and $AuCl(SMe_2)$ (294 mg, 1.00 mmol), complex **1d** was isolated as a white powder. Yield: 221 mg (40%). ^{1}H NMR (CD_3CN) δ 7.51 (t, $J = 7.7$ Hz, 1H, $H_{p,ar}$), 7.36 (d, $J = 7.7$ Hz, 2H, $H_{m,ar}$), 2.85 (sept, $^3J = 6.7$ Hz, 2H, C*H*), 2.20 (s, 2H, C*H*$_2$), 2.16–2.10 (m, 2H), 1.85–1.40 (m, 8H), 1.37 (s, 6H, C(C*H*$_3$)$_2$), 1.35 (d, $^3J = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, $^3J = 6.7$ Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (CD_3CN) δ 235.0 ($C_{carbene}$), 145.3 ($C_{o,ar}$), 134.3 ($C_{m,ar}$), 129.9 ($C_{p,ar}$), 125.0 ($C_{m,ar}$), 80.7 (C), 58.6 (C), 44.4 (*C*H$_2$), 36.0 (*C*H$_2$), 28.7, 26.1, 25.0 (*C*H$_2$), 22.0, 21.4 (*C*H$_2$). FAB-HRMS (solvent CH_3CN) calcd for $C_{23}H_{35}AuN \cdot CH_3CN$ $[M-Cl+CH_3CN]^+$: *m*/*z* 563.2701; found, 563.2690.

2.7. Complex *2d*

Complex **1d** slowly rearranges in dichloromethane (48 h) to the dicarbene complex **2d**. The dichloromethane was removed in vacuo to give a white powder. Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated dichloromethane solution. Yield: 1.535 g (85%, relative to carbene **d**). M.p. 248–252 °C. ^{1}H NMR (CD_3CN) δ 7.50 (dd, $^3J = 8.4$ Hz, $^3J = 7.0$ Hz, 2H, $H_{p,ar}$), 7.39 (d, $J = 7.0$ Hz, 4H, $H_{m,ar}$), 2.71 (sept, $^3J = 6.7$ Hz, 4H, C*H*), 2.10 (s, 4H, C*H*$_2$), 1.63–1.52 (m, 8H), 1.37 (s, 12H, C(C*H*$_3$)$_2$), 1.31 (br s, 12 H, C(C*H*$_3$)$_2$), 1.26–1.21 (m, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (CD_3CN) δ 252.2 ($C_{carbene}$), 146.1 ($C_{o,ar}$), 135.8 ($C_{m,ar}$), 131.1 ($C_{p,ar}$), 126.3 ($C_{m,ar}$), 82.7 (C), 60.2 (C), 45.3 (*C*H$_2$), 36.3 (*C*H$_2$), 29.8, 29.6, 27.3, 25.8 (*C*H$_2$), 23.6, 22.2 (*C*H$_2$). ^{13}C NMR (CD_2Cl_2) δ 251.2 ($C_{carbene}$), 145.0 ($C_{o,ar}$), 134.6 ($C_{m,ar}$), 130.3 ($C_{p,ar}$), 125.3 ($C_{m,ar}$), 81.9 (C), 59.6 (C), 45.2 (*C*H$_2$), 35.8 (*C*H$_2$), 29.5, 29.0, 26.8, 25.1 (*C*H$_2$), 23.9, 21.5 (*C*H$_2$). FAB-HRMS calcd for $C_{46}H_{70}AuN_2$ $[M]^+$: *m*/*z* 847.5200; found, 847.5204.

2.8. Complex **2e**

To a hexane solution (5 mL) of free carbene **e** (410 mg, 1.27 mmol) a hexane suspension (5 mL) of $AuCl(SMe_2)$ (372 mg, 1.26 mmol) was added and stirred at room temperature for 14 h. The hexane was removed by filtration and the residue was extracted twice with 5 mL dichloromethane. The dichloromethane was removed in vacuo to give a white powder. Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated dichloromethane solution. Yield: 471 mg (67%). M.p. 148–152 °C (dec.). ^{1}H NMR ($CDCl_3$) δ 7.40 (t, ^3J = 7.7 Hz, 2H, $H_{p,ar}$), 7.22 (d, ^3J = 7.7 Hz, 4H, $H_{m,ar}$), 5.76 (m, 2H, C*H*), 5.63 (m, 2H, C*H*), 2.58 (m, 4H, C*H*(CH_3)$_2$), 2.50–2.38 (m, 2H), 2.18–2.03 (m, 8H), 1.94–1.78 (m, 2H), 1.73–1.57 (m, 4H), 1.39 (s, 6H, C(CH_3)$_2$), 1.34 (s, 6H, C(CH_3)$_2$), 1.26 (d, ^3J = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, ^3J = 6.5 Hz, 6H, CH(CH_3)$_2$), 1.14 (d, ^3J = 6.7 Hz, 4H, CH(CH_3)$_2$), 1.02 (d, ^3J = 6.6 Hz, 4H, CH(CH_3)$_2$), 0.92 (d, ^3J = 6.6 Hz, 4H, CH(CH_3)$_2$). ^{13}C{^{1}H}NMR (CH_2Cl_2) δ 249.7 ($C_{carbene}$), 144.7 ($C_{o,ar}$), 144.5 ($C_{o,ar}$), 133.7 ($C_{i,ar}$), 130.1 ($CH_{p,ar}$), 127.0 (*C*H), 126.9 (*C*H), 125.5 (*C*H), 125.4 (*C*H), 125.1 (*C*H), 125.0 (*C*H), 122.5 (*C*H), 122.4 (*C*H), 81.9 (NC_q), 57.4 (C_q), 45.0 (CH_2), 34.8 (CH_2), 34.7 (CH_2), 32.2 (CH_2), 32.1 (CH_2), 29.5 (CH_3), 29.0 (CH_3), 28.9 (*C*H), 28.8 (*C*H), 26.7 (CH_3), 26.4 (CH_3), 22.9 (CH_3), 22.8 (CH_3), 22.6 (CH_3), 22.5 (CH_3), 20.8 (CH_2), 20.7 (CH_2). FAB-HRMS calcd for $C_{46}H_{66}AuN_2$ $[M]^+$: *m*/*z* 843.4891; found, 843.4891.

2.9. Crystal structure determination of compounds **1a**, **1b**, **2d** and **2e**

The Bruker X8-APEX X-ray diffraction instrument [32] with Mo-radiation was used for data collection. All data frames were collected at low temperature (T = 100 K) using an ω, ϕ-scan mode (0.3°ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package [33]. Intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program [34]. The SIR92 [35] was used for solution. Direct methods of phase determination followed by some subsequent difference Fourier map led to an electron density map from which most of the non-

Table 2
Crystallographic data for **1a**, **1b**, **2d**, and **2e**

	1a	**1b** · ($CHCl_3$)	**2d** · 4($CHCl_3$)	**2e**
Formula	$C_{27}H_{43}AuClN$	$C_{28}H_{40}AuCl_4N$	$C_{50}H_{74}AuCl_{13}N_2$	$C_{46}H_{66}Au_2Cl_2N_2$
Fw	614.04	729.38	1360.92	1111.84
Color/habit	Colorless	Colorless	Colorless	Colorless
Crystal dimensions (mm)	0.46 × 0.40 × 0.13	0.17 × 0.16 × 0.09	0.43 × 0.36 × 0.13	0.32 × 0.25 × 0.17
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space Group	*P*2(1)	*Pbca*	$P\bar{1}$	$P\bar{1}$
a (Å)	12.361(2)	15.6359(13)	10.1388(6)	9.2198(4)
b (Å)	12.268(2)	16.4652(12)	12.1156(7)	11.5608(5)
c (Å)	21.666(4)	22.5014(18)	12.7174(8)	12.1686(5)
α (°)	90.0	90.0	71.544(3)	62.4130(10)
β (°)	103.145(2)	90.0	84.588(3)	75.221(2)
γ (°)	90.0	90.0	75.268(3)	77.4290(10)
V (Å^3)	3199.4(9)	5792.9(8)	1432.95(15)	1104.02(8)
Z	4	8	1	1
T (K)	100	100	100	100
D_{calc} (g cm^{-3})	1.275	1.673	1.577	1.672
μ (mm^{-1})	4.693	5.466	3.208	6.790
F(000)	1232	2896	1376	1096
θ Range[a] (°)	1.92–33.14	6.39–32.57	1.82–51.27	1.92–32.57
Index ranges (*h*, *k*, *l*)	$-18 \leqslant h \leqslant 19$, $-16 \leqslant k \leqslant 18$, $-32 \leqslant l \leqslant 33$	$0 \leqslant h \leqslant 23$, $-19 \leqslant k \leqslant 7$, $-25 \leqslant l \leqslant 5$	$-21 \leqslant h \leqslant 20$, $-23 \leqslant k \leqslant 25$, $-27 \leqslant l \leqslant 27$	$-13 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 10$
Number of reflections collected	39,186	6504	68,429	10,679
Number of independent reflections/R_{int}	19,291/0.0410	4742/0.0250	29,275/0.0258	7327/0.0139
Number of observed reflections [$I > 2\sigma(I)$]	17,952	2828	28,903	6929
Number of data/restraints/parameters	19,291/455/560	4742/15/349	29,275/0/308	7327/0/253
R_1/wR_2 [$I > 2\sigma(I)$][a]	R_1 = 0.0572, wR_2 = 0.1371	R_1 = 0.0291, wR^2 = 0.0406	R_1 = 0.0391, wR_2 = 0.1064	R_1 = 0.0352, wR_2 = 0.0924
R_1/wR_2 (all data)[a]	R_1 = 0.0615, wR_2 = 0.1387	R_1 = 0.0653, wR_2 = 0.0454	R_1 = 0.0402, wR_2 = 0.1075	R_1 = 0.0372, wR_2 = 0.0934
Goodness-of-fit on F^2[a]	1.194	0.787	1.036	1.255
Largest difference in peak and hole (e Å^{-3})[a]	4.518 and −6.799	0.746 and −0.567	3.138 and −3.748	4.705 and −6.688

[a] Because of the very large θ angle, and as often observed for gold complexes, there are large electronic residuals close to gold in complexes **1a**, **2d** and **2e**.

hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. The Bruker SHELXTL software package [36] was used for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawing of molecules was performed using ORTEP3 [37] (Table 2).

3. Supplementary material

CCDC 671264, 671265, 671266, and 671267 contain the supplementary crystallographic data for **1a**, **1b** · ($CHCl_3$), **2d** · 4($CHCl_3$), **2e**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are grateful to Vincent Lavallo for helpful assistance. We thank the NIH (R01 GM 68825) and RHODIA Inc. for financial support, the Alexander von Humboldt Foundation and the Higher Education Commission of Pakistan for a Fellowship to G.D.F. and S.K., respectively.

References

[1] (a) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, J. Am. Chem. Soc. 110 (1988) 6463;
(b) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, Angew. Chem., Int. Ed. Engl. 28 (1989) 621.

[2] (a) A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361;
(b) A.J. Arduengo III, J.R. Goerlich, W.J. Marshall, J. Am. Chem. Soc. 117 (1995) 11027.

[3] (a) F.E. Hahn, Angew. Chem. 118 (2006) 1374;
F.E. Hahn, Angew. Chem., Int. Ed. 45 (2006) 1348;
(b) R.E. Douthwaite, Coord. Chem. Rev. 251 (2007) 702;
(c) J.A. Mata, M. Poyatos, E. Peris, Coord. Chem. Rev. 251 (2007) 841;
(d) R.H. Crabtree, J. Organomet. Chem. 690 (2005) 5451;
(e) C.M. Crudden, D.P. Allen, Coord. Chem. Rev. 248 (2004) 2247;
(f) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290;
(g) W.J. Sommer, M. Weck, Coord. Chem. Rev. 251 (2007) 860.

[4] It is important to note that NHC-complexes were reported long before the discovery of stable carbenes: (a) K. Öfele, J. Organomet. Chem. 72 (1968) P42;
(b) H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem., Int. Ed. Engl. 7 (1968) 141;
(c) D.J. Cardin, B. Cetinkaya, M.F. Lappert, Chem. Rev. 72 (1972) 545.

[5] (a) J.A. Mata, A.R. Chianese, J.R. Miecznikowski, M. Poyatos, E. Peris, J.W. Faller, R.H. Crabtree, Organometallics 23 (2004) 1253;
(b) P.L. Arnold, A.C. Scarisbrick, Organometallics 23 (2004) 2519;
(c) C.D. Abernethy, G.M. Codd, M.D. Spicer, M.K. Taylor, J. Am. Chem. Soc. 125 (2003) 1128;
(d) D. Pugh, A.A. Danopoulos, Coord. Chem. Rev. 251 (2007) 610;
(e) I.J.B. Lin, C.S. Vasam, Coord. Chem. Rev. 251 (2007) 642.

[6] (a) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39;
(b) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, J. Organomet. Chem. 698 (2004) 3857;
(c) W. Kirmse, Angew. Chem., Int. Ed. 43 (2004) 1767.

[7] (a) S.P. Nolan (Ed.), *N*-Heterocyclic Carbenes in Synthesis, Wiley-VCH, Weinheim, Germany, 2006;
(b) F. Glorius (Ed.), Topics in Organometallic Chemistry 21 (*N*-Heterocyclic Carbenes in Transition Metal Catalysis), Springer, Berlin/Heidelberg, Germany, 2007.

[8] Y. Ito, M. Sawamura, T. Hayashi, J. Am. Chem. Soc. 108 (1986) 6405.

[9] (a) J.H. Teles, S. Brode, M. Chabanas, Angew. Chem., Int. Ed. 37 (1998) 1415;
(b) E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, Angew. Chem., Int. Ed. 41 (2002) 4563.

[10] (a) E. Jiménez-Núñez, A.M. Enchavarren, Chem. Commun. (2007) 333;
(b) A.S.K. Hashmi, G.J. Hutchings, Angew. Chem., Int. Ed. 45 (2006) 7896;
(c) D.J. Gorin, F.D. Toste, Nature 446 (2007) 395;
(d) A.S.K. Hashmi, K. Stephen, Chem. Rev. 107 (2007) 3180.

[11] (a) F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 375 (1989) 147;
(b) F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 408 (1991) 271.

[12] S.K. Schneider, W.A. Herrmann, E. Herdtweck, Z. Anorg. Allg. Chem. 629 (2003) 2363.

[13] (a) V. Lavallo, Y. Canac, C. Praesang, B. Donnadieu, G. Bertrand, Angew. Chem., Int. Ed. 44 (2005) 5705;
(b) V. Lavallo, Y. Canac, B. Donnadieu, W.W. Schoeller, G. Bertrand, Angew. Chem., Int. Ed. 45 (2006) 3488;
(c) G.D. Frey, V. Lavallo, B. Donnadieu, W.W. Schoeller, G. Bertrand, Science 316 (2007) 439;
(d) J.D. Masuda, W.W. Schoeller, B. Donnadieu, G. Bertrand, Angew. Chem., Int. Ed. 46 (2007) 7052;
(e) V. Lavallo, Y. Canac, A. DeHope, B. Donnadieu, G. Bertrand, Angew. Chem., Int. Ed. 44 (2005) 7236;
(f) D.R. Anderson, V. Lavallo, D.J. O'leary, G. Bertrand, R.H. Grubbs, Angew. Chem., Int. Ed. 46 (2007) 7262.

[14] V. Lavallo, G.D. Frey, S. Kousar, B. Donnadieu, G. Bertrand, Proc. Natl. Acad. Sci. USA 104 (2007) 13569.

[15] (a) R. Jazzar, R.D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, Angew. Chem., Int. Ed. 46 (2007) 2899;
(b) R. Jazzar, J.-B. Bourg, R.D. Dewhurst, B. Donnadieu, Y. Canac, G. Bertrand, J. Org. Chem. 72 (2007) 3492.

[16] P. de Frémont, N.M. Scott, E.D. Stevens, S.P. Nolan, Organometallics 24 (2005) 2411.

[17] H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972.

[18] A. Corma, E. Gutiérrez-Puebla, M. Iglesias, A. Monge, S. Pérez-Ferreras, F. Sánchez, Adv. Synth. Catal. 348 (2006) 1899.

[19] H.M.J. Wang, C.S. Vasam, T.Y.R. Tsai, S.-H. Chen, A.H.H. Chang, I.J.B. Lin, Organometallics 24 (2005) 486.

[20] S. Singh, S. Shravan Kumar, V. Jancik, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Eur. J. Inorg. Chem. (2005) 3057.

[21] B. Bovio, A. Burini, B.R. Pietroni, J. Organomet. Chem. 452 (1993) 287.

[22] H.M.J. Wang, C.Y.L. Chen, I.J.B. Lin, Organometallics 18 (1999) 1216.

[23] R. Jothibasu, H.V. Huynh, L.L. Koh, J. Organomet. Chem. 693 (2007) 374.

[24] J.F. Britten, C.J.L. Lock, Z. Wang, Acta Crystallogr., Sect. C 48 (1992) 1600.

[25] K.M. Lee, C.K. Lee, I.J.B. Lin, Angew. Chem., Int. Ed. Engl. 36 (1997) 1850.

[26] V.J. Catalano, A.O. Etogo, Inorg. Chem. 46 (2007) 5608.
[27] V.J. Catalano, M.A. Malwitz, A.O. Etogo, Inorg. Chem. 43 (2004) 5714.
[28] M.V. Baker, P.J. Barnard, S.J. Berners-Price, S.K. Brayshaw, J.L. Hickey, B.W. Skelton, A.H. White, Dalton Trans. (2006) 3708.
[29] G.J. Kruger, P.J. Olivier, L. Lindeque, H.G. Raubenheimer, Acta Crystallogr., Sect. C 51 (1995) 1814.
[30] G.J. Kruger, P.J. Olivier, H.G. Raubenheimer, Acta Crystallogr., Sect. C 52 (1996) 624.
[31] H.G. Raubenheimer, F. Scott, G.J. Kruger, J.G. Toerien, R. Otte, W. van Zyl, I. Taljaard, P. Olivier, L. Linford, J. Chem. Soc., Dalton Trans. (1994) 2091.
[32] Bruker, APEX 2 version 2.0-2, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
[33] Bruker, SAINT version V7.21A, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
[34] Bruker, SADABS version 2004/1, Bruker Analytical X-ray System, Inc., Madison, Wisconsin, USA, 2004.
[35] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[36] Bruker, SHELXTL Software Version 6.14, Dec, Bruker Analytical X-ray System, Inc., Madison, Wisconsin, USA, 2003.
[37] ORTEP3 for Windows: L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.