Published in final edited form as:

J Organomet Chem. 2008 April ; 693(8-9): 1674–1682.

Cyclic (Alkyl)(amino)carbene Gold(I) complexes:

A Synthetic and Structural Investigation

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

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

Abstract

A series of mono- and dicarbene gold(I) complexes of types $\text{Au}(\text{CAAC})(\text{Cl})$ [CAAC = cyclic (alkyl)(amino)carbene] (**1**) and $[\text{Au}(\text{CAAC})_2]^+[\text{X}]^-$ ($\text{X} = \text{Cl}, \text{AuCl}_2$) (**2**) have been prepared through reaction of $\text{AuCl}(\text{SMe}_2)$ 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

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-d], their properties as ligand for transition metals [13e,f], 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 hydroiminium 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 $\text{AuCl}(\text{SMe}_2)$, the same procedure used for the corresponding NHC complexes [16]. After removing the solvent under vacuum and washing with hexanes, the

*To whom correspondence should be addressed. E-mail: gbertran@mail.ucr.edu

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

remaining residue was extracted with CH₂Cl₂ or CHCl₃. 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 (CH₂Cl₂, CHCl₃, 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 (CH₂Cl₂ or CHCl₃). 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 ¹³C NMR signals for the carbene 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(SMe₂) did not afford the expected mono-carbene gold complex (similar to **1a-d**), but the cationic dicarbene gold complex **2e** with AuCl₂⁺ 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 ¹³C 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 CD₂Cl₂ 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 ¹³C 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**] degrees] (Table 1), and are in agreement with 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 [12,18-23], 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 [24-31]. 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.

Experimental Section

All reactions were performed under an atmosphere of argon and solvents were dried over Na metal or CaH₂. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ¹H NMR (300 MHz), and ¹³C{¹H}NMR (75 MHz) spectra were obtained with a Bruker Avance 300 spectrometer at 298 K. ¹H and ¹³C chemical shifts (δ) are reported in parts per million (ppm) relative to TMS and were referenced to the residual

solvent peak. NMR multiplicities are 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].

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%). ¹H NMR (CDCl₃) δ 7.57 (d, ³ J = 4.5 Hz, 1H, NCH), 7.22 (br, 4H, H_{ar}), 7.12 (br, 3H, H_{ar}), 3.11-2.74 (m, 6H, CH(CH₃)₂ + CH₂ + CHCHCH₃), 1.30 (d, ³ J = 6.6 Hz, 9H, CH(CH₃)₂ + CHCHCH₃), 1.12 (d, ³ J = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C{¹H}NMR (CDCl₃) δ 170.1 (NCH), 148.7 (C_q), 146.4 (C_q), 137.1 (C_q), 136.7 (C_q), 128.9 (CH), 126.3 (CH), 123.8 (CH), 122.6 (CH), 41.7 (NCHCH), 39.6 (CH₂), 33.7 (CH), 27.4 (CH(CH₃)₂), 24.1 (CH), 23.4 (CH(CH₃)₂), 23.3 (CH(CH₃)₂), 17.4 (CHCH₃). FAB-HRMS calcd for C₂₅H₃₆N [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 LiNMe₂ (1.00 g, 19.6 mmol) in Et₂O (20 mL). The mixture was allowed to warm to room temperature, and then stirred for two hours. 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 2h, 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%). ¹H NMR (CDCl₃) δ 7.72 (s, 1H, NCH), 7.27-7.06 (m, 7H, H_{ar}), 4.95 (s, 1H, CH), 4.82 (s, 1H, CH), 2.95 (s, 2H, CH₂), 2.86 (sept., ³ J = 6.8 Hz, 3H, CH(CH₃)₂), 2.43 (d, ² J = 13.8 Hz, 1H, CH₂), 2.31 (d, ² J = 13.8 Hz, 1H, CH₂), 1.84 (s, 3H, CH₃), 1.31 (s, 3H, CH₃), 1.27 (d, ³ J = 6.8 Hz, 6H, CH(CH₃)₂), 1.12 (d, ³ J = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃) δ 172.4 (NCH), 148.7 (C_q), 146.8 (C_q), 142.4 (C_q), 137.4 (C_q), 135.1 (C_q), 130.9 (CH), 126.1 (CH), 123.9 (CH), 122.9 (CH), 115.5 (CH₂), 46.4 (CH₂), 44.9 (C_q), 44.5 (CH₂), 33.8 (CH₃), 27.5, 25.5, 24.2, 23.6, 22.6. FAB-HRMS calcd for C₂₉H₄₂N [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 Et₂O (2M, 20.7 mL, 41.6 mmol). The vessel was sealed, and heated to 80 °C for 14h. 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 = HCl₂⁻) as a white solid. Yield: 5.74 g (72%). ¹H NMR (CD₃CN) δ 9.39 (s, 1H, NCH), 7.59 (t, ³ J = 7.7 Hz, 1H, H_{ar}), 7.44 (t, ³ J = 6.8 Hz, 2H, H_{ar}), 7.34 (d, ³ J = 7.7 Hz, 2H, H_{ar}), 7.28 (d, ³ J = 7.7 Hz, 1H, H_{ar}), 6.13 (br s, 1H, HCl₂), 3.47 (d, ³ J = 14.0 Hz, 1H, CH₂), 3.03 (d, ³ J = 14.0 Hz, 1H, CH₂), 2.96 (sept., ³ J = 6.9 Hz, 1H, CH(CH₃)₂), 2.66 (sept., ³ J = 6.7 Hz, 1H, CH(CH₃)₂), 2.64 (d, ² J = 14.0 Hz, 1H, CH₂), 2.35 (d, ² J = 14.0 Hz, 1H, CH₂), 2.15 (sept., ³ J = 6.6 Hz, 1H, CH(CH₃)₂), 1.73 (s, 3H, CH₃), 1.42 (s, 3H, CH₃), 1.35 (d, ³ J = 6.7 Hz, 3H, CH(CH₃)₂), 1.26 (d, ³ J = 6.8 Hz, 6H, CH(CH₃)₂), 1.13 (m, 9H, CH₃), 0.93 (s, 3H, CH₃). ¹³C{¹H}NMR (CD₃CN) δ 192.8 (NCH), 149.3 (C_q), 145.6 (C_q), 145.0 (C_q), 134.7 (C_q), 132.6 (CH), 131.1 (CH), 129.7 (C_q), 127.7 (CH), 126.5 (CH), 125.9 (CH), 84.7 (NC(CH₃)₂), 55.3 (C_q), 44.1 (CH₂), 43.8 (CH₂), 34.4, 30.1, 29.8, 28.5, 27.6, 26.3, 24.2, 22.0, 21.8. FAB-HRMS calcd for C₂₉H₄₂N [M]⁺: m/z 404.3317; found 404.3317. To a Schlenk tube containing the iminium salt **cc** (X = HCl₂⁻) (4.86 g, 10.20 mmol) and NaBPh₄ (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** ($X = \text{BPh}_4^-$) 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** ($X = \text{BPh}_4^-$) (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%). ^1H 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, $\text{CH}(\text{CH}_3)_2$), 3.80 (sept., $J = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.78 (d, $J = 8.2$ Hz, 1H), 3.60 (sept., $^3J = 6.4$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 3.28 (d, $J = 8.3$ Hz, 1H, CH_2), 2.87 (s, 3H, CH), 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, $\text{CH}(\text{CH}_3)_2$), 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 313.0 ($\text{C}_{\text{carbene}}$), 152.7 (C_q), 152.5 (C_q), 147.0 (C_q), 139.2 (C_q), 137.7 (C_q), 131.0 (CH), 127.6 (CH), 126.6 (CH), 124.8 (CH), 124.7 (CH), 80.7 ($\text{NC}(\text{CH}_3)_2$), 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.

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%). ^1H NMR (CDCl_3) δ 7.63 (d, $^3J = 4.5$ Hz, 1H, NCH), 7.16-7.06 (m, 3H, H_{ar}), 5.80 (s, 2H, CH), 2.96 (sept., $^3J = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.80-2.74 (m, 1H, NCHCH), 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, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 168.8 (N CH), 149.2 ($\text{C}_{\text{o,ar}}$), 136.6 ($\text{C}_{\text{i,ar}}$), 126.7 (CH), 125.3 (CH), 123.6 (CH), 122.4 (CH), 39.7 (NCHCH), 27.5 (CH), 27.4 (CH_2), 25.2 (CH_2), 24.2 (CH_2), 23.2 (CH_3). FAB-HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{N}$ [$\text{M}+\text{H}$] $^+$: 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 two hours. 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%). ^1H NMR (CDCl_3) δ 7.62 (s, 1H, NCH 7.15-7.02 (m, 3H, H_{ar}), 5.75 (m, 2H, CH), 4.94 (s, 1H, CH), 4.80 (s, 1H, CH), 2.97 (sept., $^3J = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 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, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, $^3J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 171.2 (CH), 149.2 ($\text{C}_{\text{o,ar}}$), 142.0 (CCH_2), 137.0 ($\text{C}_{\text{i,ar}}$), 126.4 (CH), 125.8 (CH), 124.1 (CH), 122.9 (CH), 115.6 (CCH_2), 46.2 (CH_2), 42.8 (NCHC_q), 32.7 (CH_2), 30.3 (CH_2), 27.6 (CH), 25.4 (CH_3), 23.8 (CH_3), 23.3 (CH_2). FAB-HRMS calcd for $\text{C}_{23}\text{H}_{34}\text{N}$ [$\text{M}+\text{H}$] $^+$: 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 (2M, 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. $164\text{--}166^\circ\text{C}$ (dec.). ^1H NMR (CD_3CN) δ 12.88 (s, 1H, HCl_2), 9.17 (s, 1H, NCH), 7.62 (t, $^3J = 7.8$ Hz, 1H, $\text{H}_{\text{p,ar}}$), 7.49 (d, $^3J = 7.8$ Hz, 2H, $\text{H}_{\text{m,ar}}$), 5.90 (m, 1H, CH), 5.78 (m, 1H, CH), 2.75 (m, 3H, $\text{CH}(\text{CH}_3)_2 + \text{CH}_2$), 2.56-2.39 (m, 3H),

2.28-2.22 (m, 3H), 2.12-2.07 (m, 1H), 1.57 (s, 6H, C(CH₃)₂), 1.37 (d, ³J = 6.7 Hz, 6H, CH(CH₃)₂), 1.12 (d, ³J = 6.7 Hz, 6H, CH(CH₃)₂). ¹³C{¹H}NMR (CD₃CN) δ 192.5 (NCH), 145.4 (C_{o,ar}), 132.7 (C_{m,ar}), 130.1 (C_{i,ar}), 128.1 (CH), 126.2 (CH), 123.0 (CH), 84.6 (NC_q), 51.5 (NCHC_q), 45.8 (CH₂), 33.9 (CH₂), 30.4 (CH₂), 30.3 (CH₃), 29.0 (CH), 28.5 (CH), 26.4 (CH₃), 22.2 (CH₃), 22.1 (CH₃), 21.6 (CH₂). FAB-HRMS calcd for C₂₃H₃₄N [M]⁺: *m/z* 324.2691; found 324.2699. To a Schlenk tube containing the iminium salt **ec** (2.95 g, 7.45 mmol) and NaBPh₄ (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 BPh₄⁻ 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**(BPh₄⁻) (810 mg, 1.26 mmol) in THF (5 mL) at -78 °C. The mixture was allowed to warm to room temperature, and stirred for 2h. 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 colourless crystals. Yield: 265 mg (65%). ¹H NMR (C₆D₆) δ 7.35-7.18 (m, 3H, H_{ar}), 5.77 (s, 2H, CH), 3.84 (sept., ³J = 6.7 Hz, 1H, CH(CH₃)₂), 3.82 (sept., ³J = 6.7 Hz, 1H, CH(CH₃)₂), 3.48 (td, ³J = 8.5 Hz, ³J = 7.0 Hz, 2H, CH₂), 2.35-2.12 (m, 2H), 1.91 (d, ³J = 2.5 Hz, 2H), 1.79 (t, ³J = 6.3 Hz, 2H, CH₂), 1.40 (s, 3H, C(CH₃)₂), 1.38 (s, 3H, C(CH₃)₂), 1.25 (d, ³J = 8.6 Hz, 12H, CH(CH₃)₂). ¹³C{¹H}NMR (C₆D₆) 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.

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(SMe₂) (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 CHCl₃ solution. m.p. 124-125 °C. [α]_D²⁰ = 7.5° (CHCl₃). ¹H NMR (CDCl₃) 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, CH(CH₃)₂), 2.79 (sept., ³J = 6.3 Hz, 1H, CH(CH₃)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(CH₃)₂), 1.39 (s, 3H, CH), 1.37 (d, ³J = 7.0 Hz, 3H, CH(CH₃)₂), 1.34 (d, ³J = 6.5 Hz, 3H, CH(CH₃)₂), 1.33 (s, 3H, CH₃), 1.32 (d, ³J = 7.0 Hz, 3H, CH(CH₃)₂), 1.30-1.21 (m, 2H), 1.18 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 1.75-1.25 (m, 1H), 1.02 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 0.89 (d, ³J = 6.4 Hz, 3H, CH(CH₃)₂). ¹³C{¹H}NMR (CDCl₃) δ 237.1 (C_{carbene}), 145.4 (C_{o,ar}), 145.0 (C_{o,ar}), 135.2 (C_{i,ar}), 129.8 (C_{p,ar}), 125.0 (C_{m,ar}), 124.9 (C_{m,ar}), 76.6 (C), 64.1 (C), 52.6 (CH₂), 51.4 (CH), 49.8 (CH₂), 35.6 (CH₂), 30.3, 29.7, 29.7, 29.4, 29.0, 28.1, 27.5, 27.0, 25.2, 24.4 (CH₂), 23.0, 22.9, 22.8, 20.2. FAB-HRMS (solvent CH₃CN) calcd for C₂₇H₄₃AuN·CH₃CN [M-Cl+CH₃CN]⁺: *m/z* 619.3327; found 619.3303.

Complex 1b

Following the same experimental procedure as for **1a** but free carbene **b** (640 mg, 1.69 mmol) and AuCl(SMe₂) (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 CHCl₃ solution. m.p. 194-195 °C (dec.). ¹H NMR (CDCl₃) 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, CH₂), 2.71 (sept., ³J = 6.7 Hz, 2H, CH), 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(CH₃)₂), 1.31 (s, 6H, C(CH₃)₂), 1.26 (d, ³J = 6.7 Hz, 6H, CH(CH₃)₂). ¹³C{¹H}NMR (C₆D₆) δ 239.9 (C_{carbene}), 144.8 (C_{o,ar}), 135.2 (C_{i,ar}), 129.7 (C_{p,ar}), 125.0 (C_{m,ar}), 76.9 (C_q), 63.7 (C_q), 48.5 (CH₂), 39.0 (CH₂), 37.0, 35.2, 34.6 (CH₂), 29.2, 29.1,

27.6, 27.1, 26.9, 23.1. FAB-HRMS (solvent CH₃CN) calcd for C₂₇H₃₉AuN·CH₃CN [M·Cl + CH₃CN]⁺: *m/z* 615.3014; found 615.2990.

Complex 1c

Following the same experimental procedure as for **1a** but free carbene **c** (254 mg, 0.63 mmol) and AuCl(SMe₂) (186 mg, 0.63 mmol), complex **1c** was isolated as a white solid (189 mg, 47% yield). ¹H NMR (C₆D₆) δ 7.47 (t, ³*J* = 7.5 Hz, 1H, H_{ar}), 7.39 (d, ³*J* = 7.4 Hz, 2H, H_{ar}), 7.31 (t, ³*J* = 7.3 Hz, 2H, H_{ar}), 7.25 (d, ³*J* = 7.5 Hz, 2H, H_{ar}), 3.52 (d, *J* = 13.6 Hz, 1H, CH₂), 2.92 (sept., ³*J* = 7.0 Hz, 1H, CH(CH₃)₂), 2.82 (d, *J* = 14.2 Hz, 1H, CH₂), 2.79 (m, 1H, CH(CH₃)₂), 2.39 (d, *J* = 13.2 Hz, 1H, CH₂), 2.36 (sept., ³*J* = 7.0 Hz, 1H, CH(CH₃)₂), 2.00 (d, *J* = 13.7 Hz, 1H, CH₂), 1.57 (s, 3H, CCH₃), 1.35 (d, ³*J* = 6.5 Hz, 6H, CH(CH₃)₂), 1.30-1.18 (m, 15H, CH₃), 1.07 (d, ³*J* = 6.8 Hz, 3H, CH(CH₃)₂). ¹³C{¹H}NMR (C₆D₆) δ 236.4 (C_{carbene}), 147.8 (C_q), 145.7 (C_q), 145.3 (C_q), 135.5 (C_q), 131.4 (CH), 130.0 (CH), 126.4 (CH), 125.2 (CH), 125.0 (CH), 81.3 (NC(CH₃)₂), 60.2 (C_q), 46.1 (CH₂), 44.2 (CH₂), 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 CH₃CN) calcd for C₃₀H₄₂AuN₂ [MH·(Cl+CH₃)+CH₃CN]⁺: *m/z* 627.3014; found 627.3015.

Complex 1d

Following the same experimental procedure as for **1a** but free carbene **d** (331 mg, 1.02 mmol) and AuCl(SMe₂) (294 mg, 1.00 mmol), complex **1d** was isolated as a white powder. Yield: 221 mg (40%). ¹H NMR (CD₃CN) 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., ³*J* = 6.7 Hz, 2H, CH), 2.20 (s, 2H, CH₂), 2.16-2.10 (m, 2H), 1.85-1.40 (m, 8H), 1.37 (s, 6H, C(CH₃)₂), 1.35 (d, ³*J* = 6.7 Hz, 6H, CH(CH₃)₂), 1.32 (d, ³*J* = 6.7 Hz, 6H, CH(CH₃)₂). ¹³C{¹H}NMR (CD₃CN) δ 235.0 (C_{carbene}), 145.3 (C_{o,ar}), 134.3 (C_{i,ar}), 129.9 (C_{p,ar}), 125.0 (C_{m,ar}), 80.7 (C), 58.6 (C), 44.4 (CH₂), 36.0 (CH₂), 28.7, 26.1, 25.0 (CH₂), 22.0, 21.4 (CH₂). FAB-HRMS (solvent CH₃CN) calcd for C₂₃H₃₅AuN·CH₃CN [M·Cl+CH₃CN]⁺: *m/z* 563.2701; found 563.2690.

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. ¹H NMR (CD₃CN) δ 7.50 (dd, ³*J* = 8.4 Hz, ³*J* = 7.0 Hz, 2H, H_{p,ar}), 7.39 (d, *J* = 7.0 Hz, 4H, H_{m,ar}), 2.71 (sept., ³*J* = 6.7 Hz, 4H, CH), 2.10 (s, 4H, CH₂), 1.63-1.52 (m, 8H), 1.37 (s, 12H, C(CH₃)₂), 1.31 (br. s, 12H, C(CH₃)₂), 1.26-1.21 (m, 24H, CH(CH₃)₂). ¹³C{¹H}NMR (CD₃CN) δ 252.2 (C_{carbene}), 146.1 (C_{o,ar}), 135.8 (C_{i,ar}), 131.1 (C_{p,ar}), 126.3 (C_{m,ar}), 82.7 (C), 60.2 (C), 45.3 (CH₂), 36.3 (CH₂), 29.8, 29.6, 27.3, 25.8 (CH₂), 23.6, 22.2 (CH₂). ¹³C NMR (CD₂Cl₂) δ 251.2 (C_{carbene}), 145.0 (C_{o,ar}), 134.6 (C_{i,ar}), 130.3 (C_{p,ar}), 125.3 (C_{m,ar}), 81.9 (C), 59.6 (C), 45.2 (CH₂), 35.8 (CH₂), 29.5, 29.0, 26.8, 25.1 (CH₂), 23.9, 21.5 (CH). FAB-HRMS calcd for C₄₆H₇₀AuN₂ [M]⁺: *m/z* 847.5200; found 847.5204.

Complex 2e

To a hexane solution (5 mL) of free carbene **e** (410 mg, 1.27 mmol) a hexane solution (5 mL) of AuCl(SMe₂) (372 mg, 1.26 mmol) was added and stirred at room temperature for 14h. 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.). ¹H NMR (CDCl₃) δ 7.40 (t, ³*J* = 7.7 Hz, 2H, H_{p,ar}), 7.22 (d, ³*J* = 7.7 Hz, 4H, H_{m,ar}), 5.76 (m, 2H, CH), 5.63 (m, 2H, CH), 2.58 (m, 4H, CH(CH₃)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(CH₃)₂), 1.34 (s, 6H, C(CH₃)₂), 1.26 (d, ³J = 6.6 Hz, 6H, CH(CH₃)₂), 1.25 (d, ³J = 6.5 Hz, 6H, CH(CH₃)₂), 1.14 (d, ³J = 6.7 Hz, 4H, CH(CH₃)₂), 1.02 (d, ³J = 6.6 Hz, 4H, CH(CH₃)₂), 0.92 (d, ³J = 6.6 Hz, 4H, CH(CH₃)₂). ¹³C{¹H}NMR (CH₂Cl₂) δ 249.7 (CH), 144.7 (C_{o,ar}), 144.5 (C_{o,ar}), 133.7 (C_{i,ar}), 130.1 (CH_{p,ar}), 127.0 (CH), 126.9 (CH), 125.5 (CH), 125.4 (CH), 125.1 (CH), 125.0 (CH), 122.5 (CH), 122.4 (CH), 81.9 (NC_q), 57.4 (NCHC_q), 45.0 (CH₂), 34.8 (CH₂), 34.7 (CH₂), 32.2 (CH₂), 32.1 (CH₂), 29.5 (CH₃), 29.0 (CH₃), 28.9 (CH), 28.8 (CH), 26.7 (CH₃), 26.4 (CH₃), 22.9 (CH₃), 22.8 (CH₃), 22.6 (CH₃), 22.5 (CH₃), 20.8 (CH₂), 20.7 (CH₂). FAB-HRMS calcd for CH₄₆₆₆AuN₂ [M]⁺: *m/z* 843.4891; found 843.4891.

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-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 F². All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawing of molecules was performed using Ortep3 [37]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-671264 [1a], CCDC-671265 [1b·(CHCl₃)], CCDC-671266 [2d·4(CHCl₃)], and CCDC-671267 [2e]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

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). Igau A, Grützmacher H, Baceiredo A, Bertrand G. *J. Am. Chem. Soc.* 1988;110:6463. (b) Igau A, Baceiredo A, Trinquier G, Bertrand G. *Angew. Chem., Int. Ed. Engl.* 1989;28:621.
- [2](a). Arduengo AJ III, Harlow RL, Kline M. *J. Am. Chem. Soc.* 1991;113:361. (b) Arduengo AJ III, Goerlich JR, Marshall WJ. *J. Am. Chem. Soc.* 1995;117:11027.
- [3](a). Hahn FE. *Angew. Chem.* 2006;118:1374. Hahn FE. *Angew. Chem., Int. Ed.* 2006;45:1348. (b) Douthwaite RE. *Coord. Chem. Rev.* 2007;251:702. (c) Mata JA, Poyatos M, Peris E. *Coord. Chem. Rev.* 2007;251:841. (d) Crabtree RH. *J. Organomet. Chem.* 2005;690:5451. (e) Crudden CM, Allen DP. *Coord. Chem. Rev.* 2004;248:2247. (f) Herrmann WA. *Angew. Chem., Int. Ed.* 2002;41:1290. (g) Sommer WJ, Weck M. *Coord. Chem. Rev.* 2007;251:860.
- [4](a). Öfele K. *J. Organometal. Chem.* 1968;72:P42. It is important to note that NHC-complexes were reported long before the discovery of stable carbenes (b) Wanzlick H-W, Schönherr H-J. *Angew. Chem., Int. Ed. Engl.* 1968;7:141. (c) Cardin DJ, Cetinkaya B, Lappert MF. *Chem. Rev.* 1972;72:545.
- [5](a). Mata JA, Chianese AR, Miecznikowski JR, Poyatos M, Peris E, Faller JW, Crabtree RH. *Organometallics* 2004;23:1253. (b) Arnold PL, Scarisbrick AC. *Organometallics* 2004;23:2519. (c) Abernethy CD, Codd GM, Spicer MD, Taylor MK. *J. Am. Chem. Soc.* 2003;125:1128. [PubMed:

- 12553789] (d) Pugh D, Danopoulos AA. *Coord. Chem. Rev* 2007;251:610. (e) Lin IJB, Vasam CS. *Coord. Chem. Rev* 2007;251:642.
- [6](a). Bourissou D, Guerret O, Gabbai FP, Bertrand G. *Chem. Rev* 2000;100:39. [PubMed: 11749234] (b) Canac Y, Soleilhavoup M, Conejero S, Bertrand G. *J. Organomet. Chem* 2004;698:3857. (c) Kirmse W. *Angew. Chem., Int. Ed* 2004;43:1767.
- [7](a). Nolan, SP., editor. *N-heterocyclic Carbenes in Synthesis*. Wiley-VCH; Weinheim, Germany: 2006. Glorius, F., editor. *Topics in Organometallic Chemistry 21 (N-heterocyclic Carbenes in Transition Metal Catalysis)*. Springer; Berlin/Heidelberg, Germany: 2007.
- [8]. Ito Y, Sawamura M, Hayashi T. *J. Am. Chem. Soc* 1986;108:6405.
- [9](a). Teles JH, Brode S, Chabanas M. *Angew. Chem., Int. Ed* 1998;37:1415. (b) Mizushima E, Sato K, Hayashi T, Tanaka M. *Angew. Chem., Int. Ed* 2002;41:4563.
- [10](a). Jiménez-Núñez E, Enchavarren AM. *Chem. Commun* 2007:333. (b) Hashmi ASK, Hutchings GJ. *Angew. Chem., Int. Ed* 2006;45:7896. (c) Gorin DJ, Toste FD. *Nature* 2007;446:395. [PubMed: 17377576] (d) Hashmi ASK, Stephen K. *Chem. Rev* 2007;107:3180. [PubMed: 17580975]
- [11](a). Bonati F, Burini A, Pietroni BR, Bovio B. *J. Organomet. Chem* 1989;375:147. (b) Bonati F, Burini A, Pietroni BR, Bovio B. *J. Organomet. Chem* 1991;408:271.
- [12]. Schneider SK, Herrmann WA, Herdtweck E. *Z. Anorg. Allg. Chem* 2003;629:2363.
- [13](a). Lavallo V, Canac Y, Praesang C, Donnadieu B, Bertrand G. *Angew. Chem., Int. Ed* 2005;44:5705. (b) Lavallo V, Canac Y, Donnadieu B, Schoeller WW, Bertrand G. *Angew. Chem., Int. Ed* 2006;45:3488. (c) Frey GD, Lavallo V, Donnadieu B, Schoeller WW, Bertrand G. *Science* 2007;316:439. [PubMed: 17446400] (d) Masuda JD, Schoeller WW, Donnadieu B, Bertrand G. *Angew. Chem., Int. Ed* 2007;46:7052. (e) Lavallo V, Canac Y, DeHope A, Donnadieu B, Bertrand G. *Angew. Chem., Int. Ed* 2005;44:7236. (f) Anderson DR, Lavallo V, O'leary DJ, Bertrand G, Grubbs RH. *Angew. Chem. Int. Ed* 2007;46:7262.
- [14]. Lavallo V, Frey GD, Kousar S, Donnadieu B, Bertrand G. *Proc. Natl. Acad. Sci. USA* 2007;104:13569. [PubMed: 17698808]
- [15](a). Jazzar R, Dewhurst RD, Bourg J-B, Donnadieu B, Canac Y, Bertrand G. *Angew. Chem., Int. Ed* 2007;46:2899. (b) Jazzar R, Bourg J-B, Dewhurst RD, Donnadieu B, Canac Y, Bertrand G. *J. Org. Chem* 2007;72:3492. [PubMed: 17408289]
- [16]. de Frémont P, Scott NM, Stevens ED, Nolan SP. *Organometallics* 2005;24:2411.
- [17]. Wang HMJ, Lin IJB. *Organometallics* 1998;17:972.
- [18]. Corma A, Gutiérrez-Puebla E, Iglesias M, Monge A, Pérez-Ferreras S, Sánchez F. *Adv. Synth. Catal* 2006;348:1899.
- [19]. Wang HMJ, Vasam CS, Tsai TYR, Chen S-H, Chang AHH, Lin IJB. *Organometallics* 2005;24:486.
- [20]. Singh S, Kumar S. Shravan, Jancik V, Roesky HW, Schmidt H-G, Noltemeyer M. *Eur. J. Inorg. Chem* 2005:3057.
- [21]. Bovio B, Burini A, Pietroni BR. *J. Organomet. Chem* 1993;452:287.
- [22]. Wang HMJ, Chen CYL, Lin IJB. *Organometallics* 1999;18:1216.
- [23]. Jothibasu R, Huynh HV, Koh LL. *J. Organomet. Chem.* 2007doi: 10.1016/j.jorganchem.2007.11.003
- [24]. Britten JF, Lock CJL, Z. Wang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun* 1992;48:1600.
- [25]. Lee KM, Lee CK, Lin IJB. *Angew. Chem., Int. Ed. Engl* 1997;36:1850.
- [26]. Catalano VJ, Etogo AO. *Inorg. Chem* 2007;46:5608. [PubMed: 17547393]
- [27]. Catalano VJ, Malwitz MA, Etogo AO. *Inorg. Chem* 2004;43:5714. [PubMed: 15332824]
- [28]. Baker MV, Barnard PJ, Berners-Price SJ, Brayshaw SK, Hickey JL, Skelton BW, White AH. *Dalton Trans* 2006:3708. [PubMed: 16865184]
- [29]. Kruger GJ, Olivier PJ, Lindeque L, Raubenheimer HG. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun* 1995;51:1814.
- [30]. Kruger GJ, Olivier PJ, Raubenheimer HG. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun* 1996;52:624.
- [31]. Raubenheimer HG, Scott F, Kruger GJ, Toerien JG, Otte R, van Zyl W, Taljaard I, Olivier P, Linford L. *J. Chem. Soc., Dalton Trans* 1994:2091.

- [32]. Bruker. APEX 2 version 2.0-2. Bruker AXS Inc.; Madison, Wisconsin, U.S.A.: 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]. Altomare A, Burla MC, Camalli M, Cascarano GL, Giacovazzo C, Guagliardi A, Moliterni AGG, Polidori G, Spagna R. SIR 97. J. Appl. Crystallogr 1999;32:115.
- [36]. Bruker. SHELXTL Software Version 6.14, Dec. Bruker Analytical X-Ray System, Inc.; Madison, Wisconsin, USA.: 2003.
- [37]. Farrugia LJ. ORTEP3 for Windows. J. Appl. Crystallogr 1997;30:565.

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.

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.

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.

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.

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

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

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

Table 1Pertinent 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 ₃ [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 ₃ -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} -Cq [°]	108.8(8)	109.6(2)	109.99(10)	110.4(3)

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 ₄ N	C ₅₀ H ₇₄ AuCl ₁₃ N ₂	C ₄₆ H ₆₆ Au ₂ Cl ₂ N ₂
Fw	614.04	729.38	1360.92	1111.84
Color / habit	colorless	colorless	colorless	colorless
Crystal dimensions (mm ³)	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	P2(1)	Pbca	P-1	P-1
<i>a</i> (Å)	12.361(2)	15.6359(13)	10.1388(6)	9.2198(4)
<i>b</i> (Å)	12.268(2)	16.4652(12)	12.1156(7)	11.5608(5)
<i>c</i> (Å)	21.666(4)	22.5014(18)	12.7174(8)	12.1686(5)
<i>α</i> (°)	90.0	90.0	71.544(3)	62.4130(10)
<i>β</i> (°)	103.145(2)	90.0	84.588(3)	75.221(2)
<i>γ</i> (°)	90.0	90.0	75.268(3)	77.4290(10)
<i>V</i> (Å ³)	3199.4(9)	5792.9(8)	1432.95(15)	1104.02(8)
<i>Z</i>	4	8	1	1
<i>T</i> (K)	100	100	100	100
<i>D</i> _{calcd} (g cm ⁻³)	1.275	1.673	1.577	1.672
<i>μ</i> (mm ⁻¹)	4.693	5.466	3.208	6.790
<i>F</i> (000)	1232	2896	1376	1096
<i>θ</i> Range (°) ^{a)} Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	1.92 - 33.14 -18<= <i>h</i> <=19, -16<= <i>k</i> <=18, -32<= <i>l</i> <=33	6.39 - 32.57 0<= <i>h</i> <=23, -19<= <i>k</i> <=7, -25<= <i>l</i> <=5	1.82 - 51.27 -21<= <i>h</i> <=20, -23<= <i>k</i> <=25, -27<= <i>l</i> <=27	1.92 - 32.57 -13<= <i>h</i> <=13, -17<= <i>k</i> <=16, -18<= <i>l</i> <=10
No. of rflns. collected	39186	6504	68429	10679
No. of indep. rflns. / <i>R</i> _{int}	19291 / 0.0410	4742 / 0.0250	29275 / 0.0258	7327 / 0.0139
No. of obsd. rflns. [<i>I</i> >2σ(<i>I</i>)]	17952	2828	28903	6929
No. of data / restraints / params	19291 / 455 / 560	4742 / 15 / 349	29275 / 0 / 308	7327 / 0 / 253
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)] ^{a)}	<i>R</i> ₁ = 0.0572, <i>wR</i> ₂ = 0.1371	<i>R</i> ₁ = 0.0291, <i>wR</i> ₂ = 0.0406	<i>R</i> ₁ = 0.0391, <i>wR</i> ₂ = 0.1064	<i>R</i> ₁ = 0.0352, <i>wR</i> ₂ = 0.0924
<i>R</i> ₁ / <i>wR</i> ₂ (all data) ^{a)}	<i>R</i> ₁ = 0.0615, <i>wR</i> ₂ = 0.1387	<i>R</i> ₁ = 0.0653, <i>wR</i> ₂ = 0.0454	<i>R</i> ₁ = 0.0402, <i>wR</i> ₂ = 0.1075	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.0934
GOF (on <i>F</i> ²) ^{a)}	1.194	0.787	1.036	1.255
Largest diff. 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**.