Polyhedron 38 (2012) 137–140

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Structural variation in gold(I)-chelate systems: Synthesis of an asymmetrically bridged β-diketiminato complex of gold

Nicky Savjani, Mark Schormann, Manfred Bochmann *

Wolfson Materials and Catalysis Centre, School of Chemistry, University of East Anglia, Norwich NR4 7TJ, United Kingdom

ARTICLE INFO

Article history:
Received 6 February 2012
Accepted 23 February 2012
Available online 8 March 2012

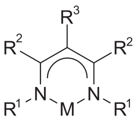
Keywords:
Gold
Chelate complex
Diketiminate
Coordination compound
Phosphine complex

ABSTRACT

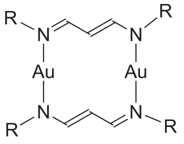
The reaction of the potassium diketiminate K[RN=C(CF_3)CH=(CF_3)CNR)], where R = 3,5-$C_6H_3Me_2$, with PPh_3AuCl afford the complex [RN=C(CF_3)CH=(CF_3)CNR)$AuPPh_3$]. Unlike gold(I) diketiminates without backbone-CF_3 substituents, the complex is thermally stable in the solid state and in solution. The crystal structure confirms that, unlike previous examples of Au(I) ketiminates, this complex possesses a three-coordinate metal centre with a distorted Y-shaped coordination geometry.

1. Introduction

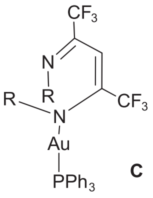
β-Diketiminato ligands are attractive as versatile ligands with easily tuneable steric and electronic properties. They form complexes with most metallic elements across the Periodic table, and in the majority of cases the complexes are of the well-known *N,N*-bonded chelate type (structure **A**) [1]. The exception from this important class is gold(I): complexes with methyl-substituted ligands such as $[HC(MeC{=}NC_6H_3Pr^i{}_2)_2]^-$ are thermally unstable, and 1,5-diazapentadienyls form dimers with W-conformation (structure **B**; R = 2,6-$Pr^i{}_2C_6H_3$ and 2,4,6-$Br_3C_6H_2$), in which Au(I) is linearly coordinated [2]. This lack of chelation of gold(I) towards N^N is also seen with imidato and α-diimine complexes [3].



A

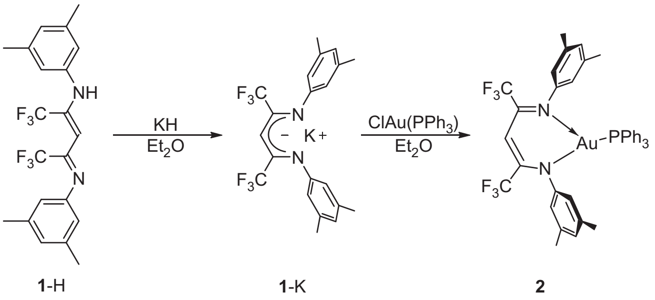


B



C

We have recently reported the synthesis, structure and fluxional behaviour of a bis(trifluoromethyl)phenyl-substituted derivative, [(κ^1-RN=C(CF_3)CH=(CF_3)CNR)$AuPPh_3$], where R = 3,5-$C_6H_3(CF_3)_2$. Here the metal is coordinated to only one N donor, and in the solid state the C_3N_2 backbone is twisted into a U-conformation (**C**) [4]. By contrast, β-diketiminato complexes of gold(III) show the expected *N,N*-chelate structure [5].



Scheme 1. Synthesis of complex **2**.

We report here the synthesis of a closely related complex with non-fluorinated aryl substituents, [RN=C(CF_3)CH=(CF_3)CNR)$AuPPh_3$] where R = 3,5-$C_6H_3(CH_3)_2$. It turns out that the comparatively subtle electronic change of replacing the meta-CF_3 substituents of the aryl ring by methyl groups has unexpected structural consequences.

2. Results and discussion

The potassium salt of the β-diketimide **1** reacted cleanly with AuCl(PPh_3) in diethyl ether at 0–20 °C to give the corresponding diketiminato complex **2** as orange crystals in essentially quantitative yield (Scheme 1). Like complex **C**, this compound is temperature stable in the solid state and in solution.

---

* Corresponding author. Fax: +44 01603592044.
E-mail address: m.bochmann@uea.ac.uk (M. Bochmann).

0277-5387/$ - see front matter
http://dx.doi.org/10.1016/j.poly.2012.02.026

The crystal structure of **2** (Fig. 1) shows that both *N*-atoms of the diketiminato ligand are coordinated to the gold cation, albeit in an asymmetric manner [Au(1)–N(1) 2.137(4), Au(1)–N(2) 2.384(4) Å]. In line with this, the [NCCCN] backbone shows bond alternation, i.e. only partial charge delocalisation. Unlike **C**, the N(1)–Au–P moiety is distorted significantly from linear towards a Y-shaped, three-coordinate geometry of the metal centre [N(1)–Au(1)–P(1) 151.91(12)°]. The backbone of the diketiminato ligand and the gold-phosphine cation exist within a symmetry plane, with only two phenyl groups from the phosphine and two from the *N*-aryl moieties protruding from this plane. The Au–Au distances are in excess of 5 Å, which rules out aurophilic interactions.

Within the backbone, there is evidence for strong intramolecular H–F interactions between the one fluoride of both CF_3 groups and the C–H unit of the β-diketiminate (F(3)–H(2) 2.20(5), F(4)–H(2) 2.20(6) Å) [6]. An investigation of the X-ray data of related Cu and Ru complexes bearing CF_3-substituted diketiminato ligands suggest the existence of similar CH···F bonding patterns, although these reports make no specific comments [7–10]. The fluorine–hydrogen-bonding interactions of these compounds fall within the range of 1.9–2.2 Å, significantly shorter than the sum of the van der Waals radii (*ca.* 2.55 Å).

As was seen with the derivative **C** [4], complex **2** is fluxional. In toluene-d_8 at 22° C, two separate, but broadened ^{19}F signals are observed for the two CF_3 substituents in 2- and 4-positions of the diazapentadienyl ligand, at δ–70.1 and –64.3, respectively (Fig. 2). Heating solutions of **2** up to the boiling point of toluene-d_8 results in broadening of the CF_3 signals into the baseline. The spectra closely resemble those of **C** in the temperature range up to 73° C; however, in the case of **2** coalescence of the two CF_3 groups is not reached below the boiling point of the solvent. The original spectrum was restored on cooling; without apparent decomposition.

In conclusion, the coordination geometry of β-diketiminato gold complexes provides a nice example of the surprising sensitivity of these complexes to minor changes in electronic characteristics of the N-substituents: Replacement of 3,5-$C_6H_3(CF_3)_2$ by 3,5-$C_6H_3(CH_3)_2$ enforces a trend towards *N,N*-chelate formation, without however reaching the symmetric chelate structure of typical transition metal NCCCN chelates [1,3,7,8]. The chelate is stabilised by C–H···F hydrogen bonding interactions between the C(3)–H moiety and the two CF_3 substituents. To our knowledge compound **2** represents the first example of a gold(I) complex coordinating to this class of ligand in chelate fashion. The presence of two CF_3 substituents on the backbone makes the ligand system sufficiently electron accepting to render this Au(I) diketiminate thermally stable in solution to ⩾100 °C.

3. Experimental

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified by distillation under nitrogen was from sodium–potassium alloy (light petroleum, bp 40–60 °C) or sodium-benzophenone (diethyl ether, THF). Deuterated toluene was degassed by several freeze–thaw cycles and dried over activated 4 Å molecular sieves. NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker Avance DPX-300 spectrometer. ^{1}H NMR spectra were referenced to residual solvent protons. The ligand precursor **1**-H was prepared following the method by Sadighi and co-workers [11].

3.1. Synthesis of K[RN=C(CF$_3$)CH=(CF$_3$)CNR)] (R = 3,5-C$_6$H$_3$Me$_2$) (**1**-K)

A suspension of potassium hydride (32 mg, 0.81 mmol) in diethyl ether (15 mL) was added to a solution of **1**-H (315 mg, 0.76 mmol) in diethyl ether (10 mL). The solution turned immediately from yellow to orange. The mixture was stirred for 5 h at room temperature and filtered. The solvent was removed under vacuum to leave **1**-K an orange solid (320 mg, 0.71 mmol, 93%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.80 (2H, s, *p*-Ar), 6.63 (4H, s, *o*-Ar),

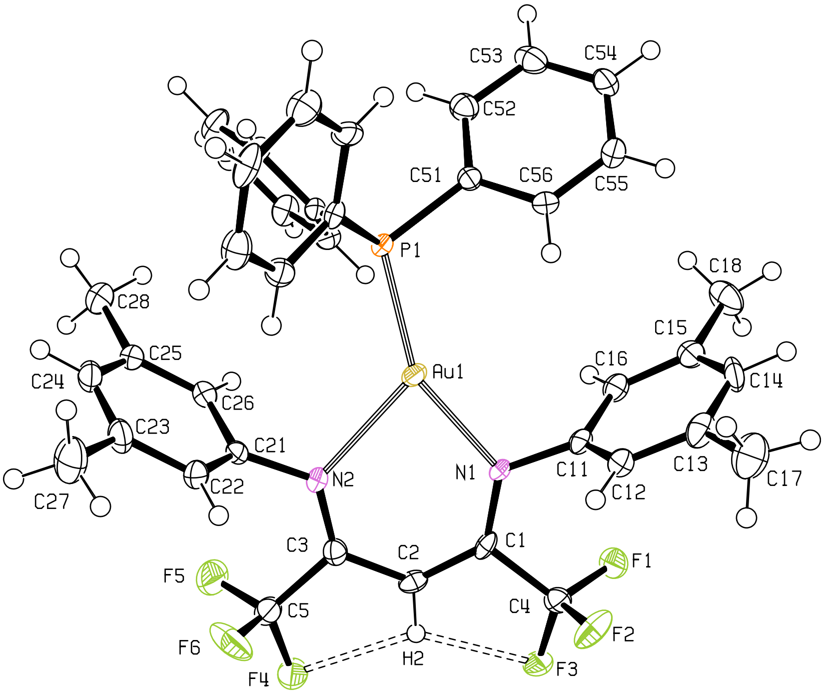


Fig. 1. Molecular structure of **2**. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): Au(1)–N(1) 2.137(4), Au(1)–N(2) 2.384(4); N(1)–C(1) 1.339(7), N(2)–C(3) 1.308(7); C(1)–C(2) 1.382(7), C(2)–C(3) 1.416(7); N(1)–Au–P(1) 151.91(12); N(2)–Au–P(1) 123.68(10); N(1)–Au–N(2) 84.41(15); F(3)···H(2) 2.20(5); F(4)···H(2) 2.20(6); F(3)···H(2)···F(4) 143(3).

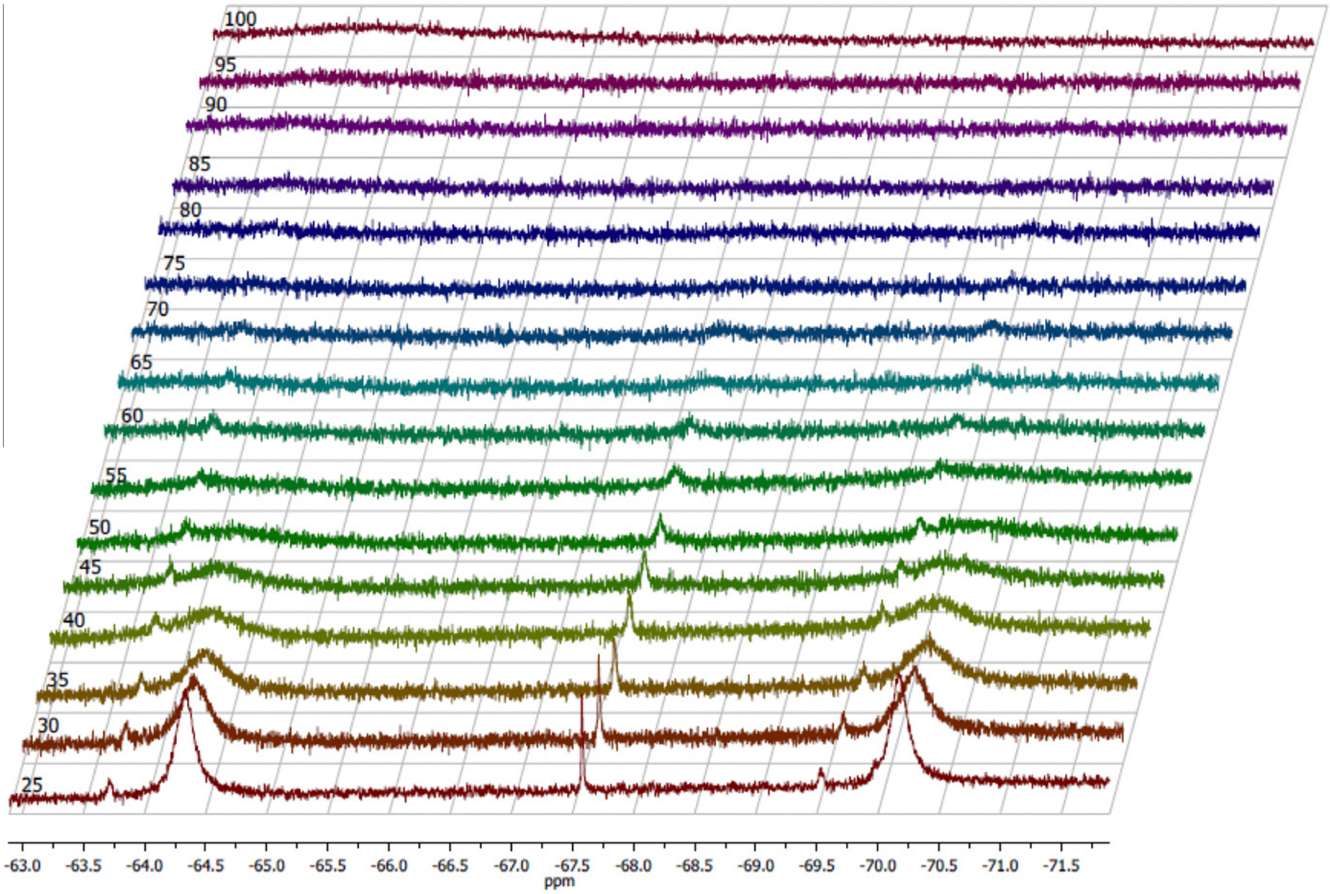


Fig. 2. ^{19}F NMR spectra of **2** over the temperature range 25–105 °C (toluene-d_8).

5.81 (1H, s, C*H*), 2.27 (12H, s, CH_3-Ar). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −62.76 (6F, s, CF_3). *Anal.* Calc. for $C_{21}H_{19}F_6KN_2$: C, 55.74; H, 4.23; N, 6.19. Found: C, 55.67; H, 4.35; N, 6.11%.

3.2. Synthesis of [RN=C(CF$_3$)CH=(CF$_3$)CNR)AuPPh$_3$] (R = 3,5-C$_6$H$_3$Me$_2$) (**2**)

An orange-red solution of **1**-K (226 mg, 0.50 mmol) in dry THF (15 mL) was added by syringe to a colourless solution of AuCl(PPh_3) (247 mg, 0.50 mmol) in dry THF (20 mL) cooled on an ice bath. After 1 h at 0 °C and 1 h at room temperature the THF was removed to leave an orange-red solid, which was recrystallized from light petroleum at −28 °C. Orange crystals of **2** were obtained (371 mg, 0.43 mmol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (15H, m, P*Ph*$_3$), 6.53 (4H, s, *o*-Ar), 6.43 (2H, s, *p*-Ar), 5.51 (s, 1H, C*H*), 2.07 (12H, s, CH_3-Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 142.6 (s), 148.6 (s) 138.4 (d, *J* = 13.6 Hz), 134.2 (s), 131.8 (s), 129.2 (br. s), 127.2 (s), 125.0 (br. s), 121.2 (br. s), 120.2 (br. s), 119.0 (br. s), 114.3 (br. s), 21.2 (s). ^{19}F NMR (300 MHz, $CDCl_3$, 20 °C): δ −66.17 (br, 3F, 4-CF_3), −71.14 (br, 3F, 2-CF_3). ^{31}P NMR ($CDCl_3$): δ 31.02 (s). *Anal.*Calc. for $C_{39}H_{34}AuF_6N_2P$: C, 53.68; H, 3.93; N, 3.21. Found: C, 53.52; H, 3.78; N, 3.33%.

3.3. X-ray crystallography

Crystal data were collected at 120(1) K on a Bruker-Nonius Roper CCD diffractometer at the EPSRC National Crystallography Service. Data were processed using DENZO/SCALEPACK [12] programs. The structure was solved by direct methods in the SHELXS program [13] and refined by full-matrix least-squares methods, on F^2's, in SHELXL [13]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Except for the methyl groups C(17), C(18), C(27) and C(28) that were allowed to rotate about the C–C bond and the coordinates of H(2) that were refined freely.

3.3.1. Crystal data

$C_{39}H_{34}AuF_6N_2P$, $M = 872.62$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.2054(4)$, $b = 12.7181(4)$, $c = 13.6002(4)$ Å, $\alpha = 101.607(2)$, $\beta = 111.625(2)$, $\gamma = 108.416(2)°$, $V = 1737.12(9)$ Å^3. $Z = 2$, $D_{calc} = 1.668$ g cm^{-3}, $F(000) = 860$, $T = 120(1)$ K, λ(Mo Kα) = 0.71069 Å. $wR_2 = 0.0904$ and $R_1 = 0.0654$ for all 7939 reflections – for the 'observed' data only, $R_1 = 0.0450$.

Acknowledgements

NS thanks the University of East Anglia for a studentship. This work was supported by Johnson Matthey plc and the Engineering and Physical Sciences Research Council. We thank the National Crystallography Service for the data collection of **2**.

Appendix A. Supplementary data

CCDC 865393 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.
[2] H.V.R. Dias, J.A. Flores, Inorg. Chem. 46 (2007) 5841.
[3] A.A. Mohamed, Coord. Chem. Rev. 254 (2010) 1918.
[4] N. Carrera, N. Savjani, J. Simpson, D.L. Hughes, M. Bochmann, Dalton Trans. 40 (2011) 1016.
[5] A. Venugopal, M.K. Ghosh, H. Jürgens, K.W. Törnroos, O. Swang, M. Tilset, R.H. Heyn, Organometallics 29 (2010) 2248.
[6] For a discussion of CH-F bonding criteria see for example: A.J. Mountford, D.L. Hughes, S.J. Lancaster, Chem. Commun. (2003) 2148.
[7] J.A. Flores, H.V.R. Dias, Inorg. Chem. 47 (2008) 4448.
[8] H.V.R. Dias, J.A. Flores, J. Wu, P. Kroll, J. Am. Chem. Soc. 131 (2009) 11249.
[9] A.D. Phillips, O. Zava, R. Scopilitti, A.A. Nazarov, P.J. Dyson, Organometallics 29 (2010) 417.
[10] S. Hong, L.M.R. Hill, A.K. Gupta, B.D. Naab, J.B. Gilroy, R.G. Hicks, C.J. Cramer, W.B. Tolman, Inorg. Chem. 48 (2009) 4514.
[11] D.S. Laitar, C.J.N. Mathison, W.M. Davis, J.P. Sadighi, Inorg. Chem. 42 (2003) 7354.
[12] Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography Part A, vol. 276, Academic Press, 1997, p. 307.
[13] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.