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[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]chloridogold(I)

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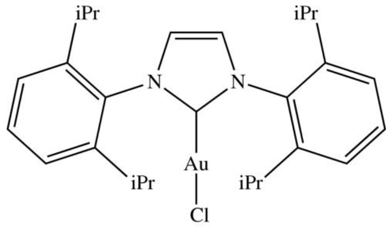
The molecule of the title compound, [AuCl($C_{27}H_{36}N_2$)], which belongs to a class of potentially catalytically active N-heterocyclic carbene complexes, has crystallographic C_2 symmetry and approximate C_{2v} symmetry. The structure is isostructural with the Cu^I and Ag^I analogues. A previous report of the structure of the title compound as its toluene solvate [Fructos *et al.* (2005). *Angew. Chem. Int. Ed.* **44**, 5284–5288] has inaccurate geometry for the complex molecule as a consequence of probable incorrect refinement in the space group *Cc*, instead of *C*2/*c* [Marsh (2009). *Acta Cryst.* B**65**, 782–783]. The Au—C bond length of 1.998 (4) Å in the title compound is more consistent with the mean distance of 1.979 (14) Å found in 52 other reported [AuCl(carbene)] complexes than with the shorter distance of 1.942 (3) Å given for the refinement in the space group *Cc* for the toluene solvate and the value of 1.939 Å obtained from the recalculation of that structure in *C*2/*c*.

Comment

In recent years, the popularity of gold(I) and gold(III) complexes has developed exponentially due to their very broad catalytic activity (Fürstner & Davies, 2007; Hashmi, 2007; Jiménez-Nuñez & Echavarren, 2008; Li *et al.*, 2008; Michelet *et al.*, 2008). The use of N-heterocyclic carbenes (NHCs) as ancillary ligands in gold(I) complexes has received considerable attention, as they provide unique properties due to their unprecedented σ-donation and significant steric bulk (Marion & Nolan, 2008; Nolan, 2011). In addition, gold(I) complexes based on N-heterocyclic carbenes have attracted increased attention in medicinal chemistry (Hindi *et al.*, 2009) where they display anti-arthritic (Gunatilleke & Barrios, 2006), antitumour (Barnard *et al.*, 2004) and antimicrobial activity (Özdemir *et al.*, 2010).

During our study of a gold-catalysed 1,2/1,2-bisacetoxy migration of 1,4-bispropargyl acetates to form (1*Z*,3*Z*)-2,3-diacetoxy-1,3-dienes (Huang *et al.*, 2009), we synthesized and crystallized the title complex, (I).

The crystal structure of (I) as its toluene solvate was reported by Fructos *et al.* (2005) and discussed again by de Frémont, Scott, Stevens & Nolan (2005). The structure was reported in the space group *Cc* with $Z' = 1$. It was subsequently proposed by Marsh (2009) that the originally reported space group was probably incorrect and that the space group should be *C*2/*c* with $Z' = \frac{1}{2}$, the complex molecule sitting on a C_2 axis and the solvent molecule disordered about a centre of inversion. Marsh noted from the originally deposited CIF [Cambridge Structural Database (CSD; Allen, 2002) refcode NATLAW, deposition No. 258274] that the original refinement was apparently unstable, as it had not converged, required many geometric restraints and had quite a wide range of C—C distances in the benzene rings (1.21–1.54 Å). This behaviour is consistent with attempting to refine a structure in a space group with lower symmetry than the true space group, especially when the molecule would have crystallographic symmetry but the chosen space group does not impose that symmetry on the molecule. The revised structure proposed by Marsh has more reasonable geometry, but that result was based on symmetrizing the geometry of the molecule refined in the original *Cc* structure. It was not refined against the original reflection data, so an accurate determination of the geometry of the title complex molecule was hitherto not available.



(I)

In view of the absence of a fully refined structure in the correct space group for the toluene solvate of (I), we determined the structure in its unsolvated form. A view of the

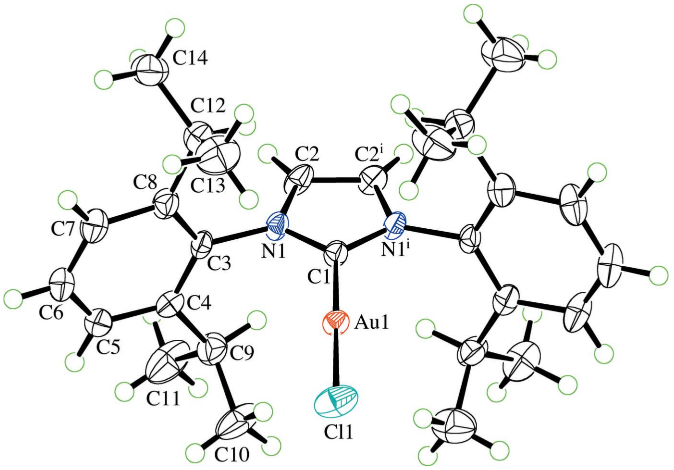


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z$.]

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molecular structure is shown in Fig. 1. The molecule of (I) has crystallographic C_2 symmetry and approximate C_{2v} symmetry, where the root-mean-square fit of the non-H atoms to perfect C_{2v} symmetry is 0.11 Å. Consequently, the planes of the benzene and imidazolylidene rings are nearly perpendicular to each other, with a dihedral angle between them of 87.39 (15)°, and the isopropyl groups are oriented similarly on each side of the unique benzene ring. The C_2 axis passes through the Au, Cl and coordinated C atoms, so that atom Au1 necessarily has perfect linear coordination geometry. The Au1—C1 bond length of 1.998 (4) Å is more consistent with this distance in other [AuCl(NHC)] complexes [mean of 1.979 (14) Å over 52 entries in the CSD; Version 5.32 with November 2011 updates] than with the value of 1.942 (3) Å given for the refinement in the space group *Cc* for the toluene solvate of (I) (de Frémont, Scott, Stevens & Nolan, 2005) and the value of 1.939 Å obtained from the recalculation of that structure in *C*2/*c* (Marsh, 2009). The Au1—Cl1 distance of 2.2718 (11) Å in (I) does not differ significantly from that obtained in the *Cc* refinement [2.2698 (11) Å].

The structure of the analogue of (I) in which the five-membered ring is saturated has also been reported by de Frémont, Scott, Stevens & Nolan (2005). This structure is virtually isostructural with that of (I) and the unit-cell dimensions are very similar. The Au—C and Au—Cl distances in that structure [1.982 (2) and 2.2760 (8) Å, respectively] are also very similar to those in (I).

The structure of (I) is isostructural with the Cu^{I} and Ag^{I} analogues [CSD refcodes EVAHEO (Kaur *et al.*, 2004) and NEHBIM (Yu *et al.*, 2006), respectively]. The carbene N—C bonds have a similar length in all three structures, being 1.338 (3), 1.320 (7) and 1.3485 (17) Å for (I) and the Cu^{I} and Ag^{I} analogues, respectively. The metal–C bond lengths vary in the sequence Cu < Au < Ag [1.953 (8), 1.998 (4) and 2.077 (2) Å, respectively]. A similar trend is found for the corresponding metal–Cl bond lengths, *viz.* 2.089 (4), 2.2718 (11) and 2.3038 (7) Å, respectively. Although the Ag—C bond here is longer than the Au—C bond and seems counter-intuitive, considering that Au^{I} would be expected to have a larger ionic radius than Ag^{I}, it is not unusual. The mean Ag—C bond length from 51 entries for [AgCl(NHC)] complexes in the CSD is 2.079 (13) Å, while the mean Au—C distance, as mentioned above, is 1.98 (2) Å. Calculations on the $[M(\mathrm{CN})_2]^-$ anion [M = Ag^{I} or Au^{I}; Zaleski-Ejgierd *et al.*, 2008; Wang *et al.*, 2009] have found that the Au—C bond is shorter than the Ag—C bond, and this has been attributed to increased covalency in the Au—C bond on account of strong relativistic effects in Au (Wang *et al.*, 2009).

The analogous Cu^{I} and Ag^{I} structures have also been determined as their dichloromethane solvates [CSD refcodes EVICER (Mankad *et al.*, 2004) and HEBLUW (de Frémont, Scott, Stevens, Ramnial *et al.*, 2005), respectively]. While the M—Cl bond lengths [2.106 (2) and 2.3135 (18) Å for the Cu^{I} and Ag^{I} dichloromethane solvates, respectively] and the Ag—C distance [2.056 (7) Å] are similar to the corresponding distances in the unsolvated structures mentioned above, the Cu—C bond length of 1.881 (7) Å is 0.07 Å shorter in the dichloromethane solvate than in the unsolvated case. The mean Cu—C distance from 15 entries for [CuCl(NHC)] complexes in the CSD is 1.90 (4) Å, but this set has three structures, of which the unsolvated Cu^{I} structure (CSD refcode EVAHEO) is one, in which the Cu—C bond is up to 0.1 Å longer than for the other structures. Discarding these three outliers, the 12 remaining [CuCl(NHC)] structures have a mean Cu—C bond length of 1.88 (1) Å, which is very close to the corresponding bond length observed in the Cu^{I} dichloromethane solvate.

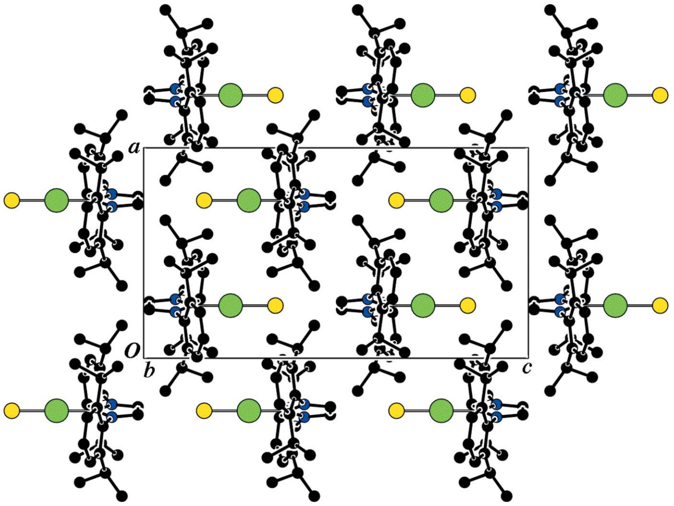

Figure 2
The crystal packing of (I), projected down the *b* axis, showing the columns of aligned molecules progressing horizontally. All H atoms have been omitted for clarity.

There are no significant intermolecular interactions in the structure of (I). The molecules stack in columns parallel to the [001] axis in which the C—Au—Cl vector points directly along the column axis and all molecules in the column are aligned unidirectional. Adjacent columns are antiparallel (Fig. 2).

Experimental

The title compound was prepared according to a previously reported procedure (de Frémont, Scott, Stevens & Nolan, 2005). Colourless single crystals suitable for crystal structure analysis were grown in an NMR tube from a solution of (I) (10 mg) in CD_2Cl_2 (0.1 ml) and pentane (2 ml) that was cooled slowly to 273 K over a period of one week.

Crystal data

$[\mathrm{AuCl(C_{27}H_{36}N_2)}]$
M_r = 621.01
Orthorhombic, *Pccn*
a = 10.6655 (2) Å
b = 12.6641 (2) Å
c = 19.5145 (4) Å
V = 2635.82 (8) Å^3
Z = 4
Mo *Kα* radiation
μ = 5.72 mm^{-1}
T = 160 K
0.18 × 0.15 × 0.12 mm

Data collection

Agilent SuperNova dual radiation diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{\min}$ = 0.894, $T_{\max}$ = 1.000
17748 measured reflections
3631 independent reflections
2389 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	146 parameters
$wR(F^2) = 0.050$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\max} = 0.57$ e Å^{-3}
3630 reflections	$\Delta\rho_{\min} = -1.03$ e Å^{-3}

Methyl H atoms were constrained to ideal geometry, with C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C), but were allowed to rotate freely about the C—C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 (aromatic) or 1.00 Å (methine) and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). One reflection, the intensity of which was considered to be an extreme outlier, was omitted from the final refinement.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3424). Services for accessing these data are described at the back of the journal.

References

Agilent (2011). *CrysAlis PRO*. Version 1.171.35.15. Agilent Technologies, Yarnton, Oxfordshire, England.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Barnard, P. J., Baker, M. V., Berners-Price, S. J. & Day, D. A. (2004). *J. Inorg. Biochem.* **98**, 1642–1647.

Frémont, P. de, Scott, N. M., Stevens, E. D. & Nolan, S. P. (2005). *Organometallics*, **24**, 2411–2418.

Frémont, P. de, Scott, N. M., Stevens, E. D., Ramnial, T., Lightbody, O. C., Macdonald, C. L. B., Clyburne, J. A. C., Abernethy, C. D. & Nolan, S. P. (2005). *Organometallics*, **24**, 6301–6309.

Fructos, M. R., Belderrain, T. R., Nicasio, M. C., de Frémont, P., Scott, N. M., Nolan, S. P., Díaz-Requejo, M. M. & Pérez, P. J. (2005). *Angew. Chem. Int. Ed.* **44**, 5284–5288.

Fürstner, A. & Davies, P. W. (2007). *Angew. Chem. Int. Ed.* **46**, 3410–3449.

Gunatilleke, S. S. & Barrios, A. M. (2006). *J. Med. Chem.* **49**, 3933–3937.

Hashmi, A. S. K. (2007). *Chem. Rev.* **107**, 3180–3211.

Hindi, K. M., Panzner, M. J., Tessier, C. A., Cannon, C. L. & Youngs, W. (2009). *Chem. Rev.* **109**, 3859–3884.

Huang, X., de Haro, T. & Nevado, C. (2009). *Chem. Eur. J.* **15**, 5904–5908.

Jiménez-Nuñez, E. & Echavarren, A. M. (2008). *Chem. Rev.* **108**, 3326–3350.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kaur, H., Zinn, F. K., Stevens, E. D. & Nolan, S. P. (2004). *Organometallics*, **23**, 1157–1160.

Li, Z., Brouwer, C. & He, C. (2008). *Chem. Rev.* **108**, 3239–3265.

Mankad, N. P., Gray, T. G., Laitar, D. S. & Sadighi, J. P. (2004). *Organometallics*, **23**, 1191–1193.

Marion, N. & Nolan, S. P. (2008). *Chem. Soc. Rev.* **37**, 1776–1782.

Marsh, R. E. (2009). *Acta Cryst.* B**65**, 782–783.

Michelet, V., Toullec, P. Y. & Genêt, J. P. (2008). *Angew. Chem. Int. Ed.* **47**, 4268–4315.

Nolan, S. P. (2011). *Acc. Chem. Res.* **44**, 91–100.

Özdemir, İ., Temelli, N., Günal, S. & Demir, S. (2010). *Molecules*, **15**, 2203–2210.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Wang, X.-B., Wang, Y.-L., Yang, J., Xing, X.-P., Li, J. & Wang, L.-S. (2009). *J. Am. Chem. Soc.* **131**, 16368–16370.

Yu, X.-Y., Patrick, B. O. & James, B. R. (2006). *Organometallics*, **25**, 2359–2363.

Zaleski-Ejgierd, P., Patzschke, M. & Pyykkö, P. (2008). *J. Chem. Phys.* **128**, 224303.