The first gold(III) dinuclear cyclometallated derivatives with a single oxo bridge

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The reaction of the gold(III) cyclometallated complexes [Au(L)Cl][BF_4] [L = $N_2C_{10}H_7(CHMeC_6H_4)$-6 1 or $N_2C_{10}H_7(CMe_2C_6H_4)$-6 2, where $N_2C_{10}H_8$ = 2,2′-bipy] with $AgBF_4$ in acetone solution affords the acetonyl derivatives [Au(L){$CH_2C(O)Me$}][BF_4], 3 and 4, and the dinuclear oxo-bridged complexes [$Au_2(L)_2$(μ-O)][BF_4]$_2$, 5 and 6; the crystal structure of complex 6 gives evidence for an unprecedented unsupported Au–O–Au bridge.

Oxo-bridged units are an important structural feature in the chemistry of early transition metals.[1] These units are also present in the active sites of a number of biological systems such as metalloproteins and metalloenzymes where the μ-oxo bridged moieties are responsible for a wide range of reactions. For this reason the study of synthetic models for these functions has been well developed.[2] In contrast, the chemistry of Group 9–11 late transition metal oxo-complexes has been less investigated[3] despite indications that such complexes may be intermediates in several important catalytic processes.

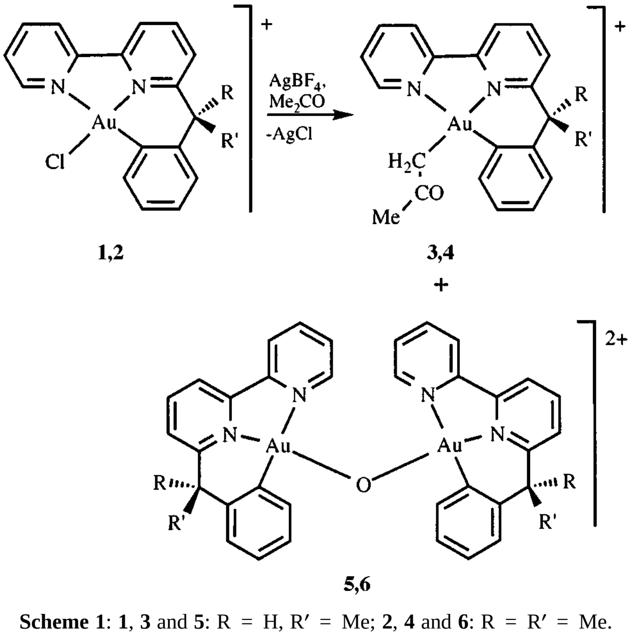
In a recent paper[4] we have reported the syntheses and characterization of a series of stable gold(III) bis oxo-bridged compelxes with 6-alkyl-2,2′-bipyridines. The crystal structures of *trans*-[Au_2{$N_2C_{10}H_7(CH_2CMe_3)$-6}$_2$(μ-O)$_2$][PF_6]$_2$ and *cis*-[Au_2{$N_2C_{10}H_7(CHMe_2)$-6}$_2$(μ-O)$_2$][$AuCl_4$][PF_6], the first gold(III) oxo-complexes, gave evidence for an Au_2(μ-O)$_2$ core. The reactivity of these species is currently under investigation.

In a preliminary study of the reactivity of a series of gold(III) C,N,N cyclometallated derivatives [Au(L)Cl][BF_4][5] (HL = 6-benzyl- and 6-alkyl-2,2′-bipyridines) we have found that in the presence of $AgBF_4$ these species can activate acetone to give the corresponding acetonyl derivatives [Au(L){$CH_2C(O)$-Me}][BF_4], similar to those described by Vicente *et al.* for C,N cycloaurated complexes and reported to be efficient starting materials for the synthesis of ketones *via* C–C coupling.[6] Now we report that from the reaction of [Au(L)Cl][BF_4] [L = $N_2C_{10}H_7(CHMeC_6H_4)$-6 **1** or $N_2C_{10}H_7(CMe_2C_6H_4)$-6 **2**] with $AgBF_4$ in acetone at room temperature, besides the acetonyl derivatives [Au(L){$CH_2C(O)Me$}][BF_4], **3**† and **4**, dinuclear oxo-bridged complexes [$Au_2(L)_2$(μ-O)][BF_4]$_2$, **5** and **6**, are formed.‡

To the best of our knowledge, the latter compounds are the first examples of gold(III) oxo-bridged cyclometallated derivatives. The oxo species are likely to result from aqua complexes [Au(L)(H_2O)]$^{2+}$ due to adventitious water. Deprotonation of the most acidic coordinated water molecule should give mononuclear hydroxo intermediates [Au(L)OH]$^+$. An ‘oxolation’ reaction involving an hydroxo intermediate could give the oxo-bridged species as proposed, *e.g.* in the case of iron(III) oxo complexes.[1]

In the IR spectra a strong absorption at *ca.* 780 cm^{-1} is assigned to the asymmetric stretch of the Au–O–Au moiety by comparison with bent oxo-bridged complexes of other metals.[7] In the FAB mass spectra (positive ions) of compounds **5** and **6** peaks of medium intensity are observed at mass values that correspond to ([M + BF_4]$^+$); in addition, peaks corresponding to the species [Au(L)OH]$^+$ are found in both cases. In the ^1H NMR spectrum of complex **5** [$(CD_3)_2CO$ or CD_2Cl_2, room temperature] two sets of signals are observed, as expected due to the presence of diastereomers. In the spectrum of complex **6** (CD_3CN, room temp.) one set of signals is observed, nevertheless a broad signal (at δ 1.4) for the methyl substituents indicates that either rotation about the Au–O bonds or inversion of the six-membered cyclometallated ring are somewhat slowed down. In fact, two well separated singlets at δ 0.85 and 1.88 appear at −40 °C.

The crystal structure of [Au_2{$N_2C_{10}H_7(CMe_2C_6H_4)$-6}$_2$(μ-O)][$BF_4$]$_2$·MeCN **6**·MeCN, has been determined by single crystal X-ray diffraction.§ It consists of the packing of [$Au_2(L)_2$(μ-O)]$^{2+}$ cations, BF_4^- anions and MeCN molecules in the molar ratio 1 : 2 : 1 with normal van der Waals contacts. A perspective view of the complex dication is shown in Fig. 1 with selected interatomic distances and angles in the caption. The cation displays an idealized C_2 symmetry, with the twofold axis passing through the oxygen atom and the midpoint of the Au(1)···Au(2) vector. The environments of the two gold atoms are very similar to each other; in particular, corresponding bond lengths involving Au(1) and Au(2) are all coincident within three esds. The two gold atoms are in distorted square-planar coordinations, with Au, O, N and N atoms essentially coplanar [maximum deviations from the respective best planes being +0.009(5) for O and −0.016(1) for Au(1), and +0.004(5) for O and −0.008(1) Å for Au(2)], with C(15) and C(35) lying



Scheme 1: **1**, **3** and **5**: R = H, R′ = Me; **2**, **4** and **6**: R = R′ = Me.

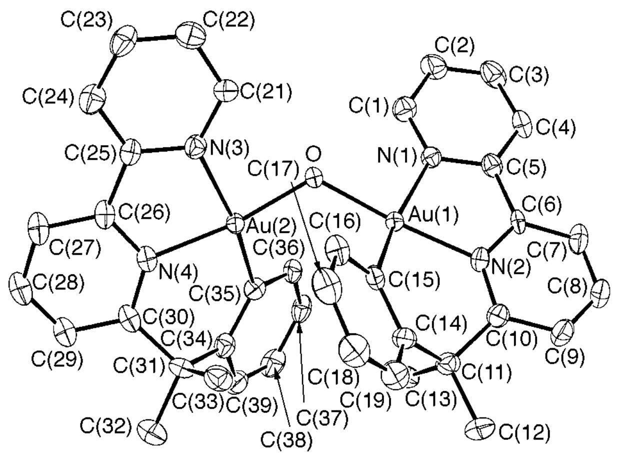


Fig. 1 Perspective view of the complex dication in **6**·MeCN. Selected interatomic distances (Å) and angles (°): Au(1)–O 1.971(5), Au(1)–N(1) 2.103(5), Au(1)–N(2) 2.029(5), Au(1)–C(15) 2.009(6), Au(2)–O 1.956(5), Au(2)–N(3) 2.096(5), Au(2)–N(4) 2.040(5), Au(2)–C(35) 2.009(6), Au(1)$\cdots$Au(2) 3.422(1), Au(1)–O–Au(2) 121.3(2), O–Au(1)–N(1) 91.9(2), O–Au(1)–N(2) 172.7(2), O–Au(1)–C(15) 94.6(2), N(1)–Au(1)–N(2) 80.9(2), N(1)–Au(1)–C(15) 165.4(2), N(2)–Au(1)–C(15) 92.8(2), O–Au(2)–N(3) 90.5(2), O–Au(2)–N(4) 170.7(2), O–Au(2)–C(35) 96.8(2), N(3)–Au(2)–N(4) 80.3(2), N(3)–Au(2)–C(35) 165.9(2), N(4)–Au(2)–C(35) 92.1(2).

0.487(6) and 0.403(6) Å above these planes. The dihedral angle between these best planes is 58.0(1)°. The distortion is very similar to that found in the cation of complex **2**[5] where atom C(15) is displaced 0.417(6) Å out of the best plane of atoms Au, Cl(1), N(1) and N(2). The present Au(1)–O and Au(2)–O bond lengths, 1.971(5) and 1.956(5) Å, can be compared with the Au–O, 1.976(3), and Au–O′, 1.961(3) Å, distances found in *trans*-$[Au_2\{N_2C_{10}H_7(CH_2CMe_3)\text{-}6\}_2(\mu\text{-}O)_2]^{2+}$,[4] The Au–N and Au–C bond lengths are very similar to the corresponding distances found in **2**, *i.e.* Au–N(1) 2.121(5), Au–N(2) 2.009(4), and Au–C(15) 2.009(6) Å. As previously observed in **2**, in the present cation the six-membered metallacycles are in boat conformations, and one of the hydrogen atoms of the Me groups in pseudo-axial position is rather close to the respective gold atom: Au(1)$\cdots$H(131) 2.70 and Au(2)$\cdots$H(331) also 2.70 Å; the corresponding Au$\cdots$H separation in**2** is 2.62 Å. The Au(1)–O–Au(2) angle is 121.3(2)° and the distance Au(1)$\cdots$Au(2) 3.422(1) Å, a distance too long to be considered bonding although slightly shorter than the sum of the estimated van der Waals radii (3.60 Å).[8]

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Notes and references

† Complex **3** has been described in ref. 5. It was obtained from the reaction of complex **1** with $AgBF_4$ in refluxing acetone; under these conditions complex **5** was not isolated.

‡ Reactions of compounds **1** and **2** with $AgBF_4$: to a solution of **1** (0.289 g, 0.5 mmol) in acetone (20 cm^3) was added a solution of $AgBF_4$ (0.097 g, 0.5 mmol) in acetone (10 cm^3): a precipitate of AgCl was formed immediately. The resulting mixture was stirred for 24 h at room temperature and then filtered off. The solution was evaporated to dryness and the residue was extracted with $CHCl_3$ (3 × 10 cm^3). The filtered chloroform solution was concentrated to small volume and diethyl ether was added to give a whitish precipitate of compound **3** (0.120 g). The residue insoluble in $CHCl_3$ was dissolved in CH_2Cl_2, filtered and concentrated to small volume. Addition of diethyl ether gave a white precipitate of compound **5** (0.080 g).

Compounds **4** and **6** were obtained similarly from **2** (0.222 g, 0.37 mmol). Complex **4** was recrystallized from acetone–diethyl ether to give the analytical sample (0.091 g). At variance with complex **5**, complex **6** is insoluble in acetone so it was abstracted with MeCN from the insoluble product containing AgCl, the filtered solution was concentrated to small volume and diethyl ether added to give a white precipitate of **6** (0.098 g).

§ *Crystal data* for **6**·MeCN: $C_{40}H_{37}Au_2B_2F_8N_5O$, M = 1171.3, monoclinic, space group *Cc* (no. 9) (after refinement), a = 12.744(2), b = 22.309(3), c = 14.062(1) Å, β = 96.72(1)°, U = 3970.4(9) $Å^3$, Z = 4, D_c = 1.959 g cm^{-3}, μ = 74.4 cm^{-1}, $F(000)$ = 2240. Reflections measured 23 557, independent (Friedel pairs not merged) 9339 with R_{int} = 0.033. Empirical absorption correction, SADABS (T_{max} = 1.00, T_{min} = 0.66). Final R_2 (F^2, all reflections) = 0.044, R_{2w} = 0.062, conventional R_1 = 0.032 for 506 parameters. For the inverted structure, final R_2 = 0.047, R_{2w} = 0.071. Siemens SMART CCD area-detector, Mo-Kα radiation (λ = 0.710 73 Å), ω scan mode, θ_{min} = 3°, θ_{max} = 26°. Structure solved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic thermal parameters for cation and anions. Cation hydrogen atoms placed in calculated positions, acetonitrile hydrogen atoms ignored. Program used was Personal SDP on a PC-486 computer. An attempt to refine the structure in space group *C*2/*c* was unsuccessful (many thermal parameters of cation atoms were non-positive, heavy disorder was introduced for anions and MeCN with occupancy factors of 0.5, final R_1 was 0.12). CCDC 182/1029.

1 B. O. West, *Polyhedron*, 1989, **8**, 219.

2 Some very recent articles: C. E. Dubé, D. W. Wright, S. Pal, P. J. Bonitatebus, Jr. and W. H. Armstrong, *J. Am. Chem. Soc.*, 1998, **120**, 3704; H. Weihe and H. U. Güdel, *J. Am. Chem. Soc.*, 1998, **120**, 2870; E. C. Wilkinson, Y. Dong, Y. Zang, H. Fujii, R. Fraczkiewicz, G. Fraczkiewicz, R. S. Czernuszewicz and L. Que, Jr., *J. Am. Chem. Soc.*, 1998, **120**, 955; T. K. Lal and R. Mukherjee, *Inorg. Chem.*, 1998, **37**, 2373; O. Horner, M. F. Charlot, A. Boussac, E. Anxolabéhère-Mallart, L. Tchertanov, J. Guilhem and J. J. Girerd, *Eur. J. Inorg. Chem.*, 1998, 721; V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lal, E. I. Solomon and T. D. P. Stack, *J. Am. Chem. Soc.*, 1997, **119**, 11 996; J. E. McGrady and R. Stranger, *J. Am. Chem. Soc.*, 1997, **119**, 8512; C. Kim, Y. Dong and L. Que, Jr., *J. Am. Chem. Soc.*, 1997, **119**, 3635; C. Duboc-Toia, S. Ménage, J. M. Vincent, M. T. Averbuch-Pouchot and M. Fontecave, *Inorg. Chem.*, 1997, **36**, 6148; A. Bérces, *Inorg. Chem.*, 1997, **36**, 4831; N. S. Dean, J. K. Cooper, R. S. Czernuszewicz, D. Ji and C. J. Carrano, *Inorg. Chem.*, 1997, **36**, 2760; H. J. Mok, J. A. Davis, S. Pal, S. K. Mandal and W. H. Armstrong, *Inorg. Chim. Acta*, 1997, **263**, 385; B. H. Ye, X. Y. Li, F. Xue and C. W. Mak, *Chem. Commun.*, 1997, 2407; A. E. M. Boelrijk, T. X. Neenan and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1997, 4561; L. Que, Jr., *J. Chem. Soc., Dalton Trans.*, 1997, 3933; A. K. Bhattyacharya, A. B. Mondal and R. Banarjee, *J. Chem. Soc., Dalton Trans.*, 1997, 2351.

3 H. Shan, Y. Yang, A. J. James and P. R. Sharp, *Science*, 1997, **275**, 1460; J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones and M. C. Ramìrez de Arellano, *Inorg. Chem.*, 1997, **36**, 4438; T. Hosokawa, M. Takano and S. I. Murahashi, *J. Am. Chem. Soc.*, 1996, **118**, 3990; Y. Zhang, R. J. Puddephatt, L. Manojlovic-Muir and K. W. Muir, *Chem. Commun.*, 1996, 2599; H. Schmidbaur, S. Hofreiter and M. Paul, *Nature*, 1995, **377**, 503; K. Angermaier and H. Schmidbaur, *Inorg. Chem.*, 1994, **33**, 2069; Y. Yang, V. Ramamoorthy and P. R. Sharp, *Inorg. Chem.*, 1993, **32**, 1946, and references therein; D. A. Dobbs and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 3836; D. Min, R. D. Larsen, K. Emerson and E. H. Abbott, *Inorg. Chem.*, 1990, **29**, 73; W. D. McGhee, T. Foo, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8543; P. Betz and A. Bino, *J. Am. Chem. Soc.*, 1988, **110**, 602; P. R. Sharp and J. R. Flynn, *Inorg. Chem.*, 1987, **26**, 3231, and references therein.

4 M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1998, 1735.

5 M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1996, 4217.

6 J. Vicente, M. D. Bermudez, M. P. Carrillo and P. G. Jones, *Chem. Ber.*, 1996, **129**, 130; J. Vicente, M. D. Bermudez and F. J. Carrion, *Inorg. Chim. Acta*, 1994, **220**, 1; J. Vicente, M. D. Bermudez, F. J. Carrion and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1975, and references therein.

7 G. S. Brownlee, P. Carty, D. N. Cash and A. Walker, *Inorg. Chem.*, 1975, **14**, 323.

8 D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1996, 561.

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