Gold Cations

DOI: 10.1002/anie.201102750

The Interaction of Gold(I) Cations with 1,3-Dienes**

*Rajashekharayya A. Sanguramath, Thomas N. Hooper, Craig P. Butts, Michael Green,**
*John E. McGrady, and Christopher A. Russell**

In memory of F. Gordon A. Stone

The activation of C−C multiple bonds by substituted gold cations $[R_3PAu]^+$ is an important theme in contemporary homogeneous catalysis.[1] However, it is interesting to note that studies of the reactivity of conjugated 1,3-dienes using gold catalysts are relatively rare, although Au/ZrO_2 catalysts were found to be effective in the heterogeneous selective hydrogenation of 1,3-butadiene.[2] Furthermore, homogeneous gold catalysts have been used to synthesize functionalized cyclopentadienes[3] and have been employed, for example, in both hydrothiolation[4] and hydroamination[5] of conjugated dienes. In the last of these reactions, a mechanism was suggested whereby the gold center binds η^4 to the diene, which is thus activated towards nucleophilic attack by the amine. Subsequent theoretical studies[6] have refined the mechanism suggesting that the gold actually binds η^2 to the diene prior to attack of the N-nucleophile on the coordinated double bond; protodeauration by proton transfer from the NH_2 group to the unsaturated carbon atom regenerates the catalyst. For further advances to be made, a detailed understanding of the interaction of gold centers with 1,3-dienes would of course be beneficial.[7] Since the submission of this manuscript, a related study of gold cation interactions with 1,3-dienes has been published.[8]

Initially we sought confirmation that the ligand and diene substrates which we employed were active in the hydroamination of 1,3-dienes. Pleasingly, 2,3-dimethylbuta-1,3-diene undergoes near-quantitative hydroamination (by NMR spectroscopy) with both benzylcarbamate and *p*-toluenesulfonamide in 1,2-dichloroethane in the presence of 10 mol% $[tBu_3PAuCl]/AgSbF_6$ catalyst under mild conditions to form an allylic amine; similar results were observed under the same conditions using the combination of 2,5-dimethylhexa-2,4-diene with $[(tBu_2(\text{o-biphenyl})PAuCl]/AgSbF_6$. We also noted that under the same conditions, the normally highly reactive 2,3-dimethoxybuta-1,3-diene did not show any evidence of reaction (^1H NMR spectroscopy), which suggested to us that the interaction of this substrate and gold may be rather different to its counterparts.

The nature of the interaction between gold and the 1,3-diene substrate was then probed using the room-temperature reaction of a slurry of [LAuCl] ($L = tBu_3P$; $tBu_2(o\text{-biphenyl})P$) and $AgSbF_6$ in CH_2Cl_2 with a series of symmetric conjugated dienes $R_2C{=}CR'{-}CR'{=}CR_2$ (Scheme 1). Filtration of the resulting white precipitate of AgCl and recrystallisation of the product yielded the cationic gold butadiene products $[(\eta^2\text{-1,3-diene})Au(L)]^+$. The mixing time for the initial reaction was found to be critical in determining the outcome of the reaction: Whereas the reaction using 2,3-dimethylbuta-1,3-diene was invariant to long reaction times (typically 16 h), side reactions were seen (by ^{31}P NMR spectroscopy) for 2,5-dimethylhexa-2,4-diene after only 15 minutes. Most strikingly, immediate filtration of the mixture using 2,3-dimethoxylbuta-1,3-diene (typically within 30 seconds) was necessary to avoid intense colorations typically associated with the formation of colloidal gold solutions.

$$\begin{array}{c}[LAuCl]\\ +\\ Ag[SbF_6]\end{array} \xrightarrow[\text{- AgCl}]{R_2CC(R')C(R')CR_2} [(\eta^2\text{-1,3-diene})AuL]^+\,[SbF_6]^-$$

1 (R = H, R' = Me, L = P*t*Bu$_3$);
2 (R = Me, R' = H, L = P*t*Bu$_2$(*o*-biphenyl))
3 (R = H, R' = OMe, L = P*t*Bu$_2$(*o*-biphenyl))

Scheme 1. Synthesis of compounds **1**–**3**.

A series of cationic gold–η^2-alkene complexes has been recently reported which were prepared from the interaction of an alkene with either "free" $[Au]^+$ or $[AuL]^+$ centers and employing a suitable weakly-coordinating anion;[9] similar methods have also been used to generate the corresponding silver salts.[10] In common with these limited examples of cationic gold(I) alkene complexes, both **1** and **2** are remarkably stable, being ostensibly air- and moisture-stable and showing no sign of decomposition (^1H and ^{31}P NMR spectroscopy) after 2 h reflux in $CDCl_3$. The onset of decomposition upon heating in the solid state does not occur until 158 °C for **1** and 218 °C for **2**. Futhermore, both compounds are indefinitely stable to light (daylight) and show no sign of decomposition when the solid is subjected to a vacuum (ca. 10^{-2} torr, 30 min). In contrast, **3** is sensitive to air and moisture, decomposing upon brief exposure to air to form unidentified product(s).

---

[*] R. A. Sanguramath, Dr. T. N. Hooper, Dr. C. P. Butts, Prof. M. Green, Dr. C. A. Russell
School of Chemistry, University of Bristol
Cantock's Close, Bristol, BS8 1TS (U.K.)
E-mail: chris.russell@bristol.ac.uk
Homepage: http://www.inchm.bris.ac.uk/people/russell.shtm
Prof. J. E. McGrady
Department of Chemistry, Inorganic Chemistry Laboratory
University of Oxford, South Parks Road, Oxford OX1 3QR (U.K.)

[**] We thank the University of Bristol (M.G., C.A.R., T.N.H., R.A.S.) for financial support. We thank Umicore AG & Co. KG for the generous donation of $HAuCl_4$.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102750.

Single crystals of **1**–**3** suitable for analysis by X-ray diffraction[11] were grown from saturated CH_2Cl_2 solutions layered with either Et_2O (**1**) or *n*-hexane (**2** and **3**). Whereas the diffraction data for **2** and **3** are very good, the data for **1** showed that the crystals were non-merohedrally twinned and displayed significant disorder in the diene unit. Whilst the disorder in the diene unit for **1** means a detailed analysis of the bond lengths and angles would be inappropriate, it is sufficient to show that the diene adopts a planar *trans*-conformation with the gold binding in η^2-fashion to only one of the C=C double bonds (Supporting Information, Figure S1).

The same bonding mode is also observed in the structure of **2** (Figure 1), with the gold bonding in an asymmetric fashion to one alkene (8 % slippage towards the C–H end of a C=C double bond). The coordinated C=C bond (1.391(4) Å) is longer than its uncoordinated counterpart (1.349(5) Å). Although superficially similar, the structure of **3** is rather different to those of **1** and **2** (Figure 2). The C–C distances within the diene backbone show more pronounced variations compared to **2**, with quite distinct alkene groups (C1–C2 1.384(4) Å, C4–C5 1.325(4) Å). Moreover the linking C2–C4 bond (1.492(4) Å) approaches the value associated with non-conjugated C–C single bonds.

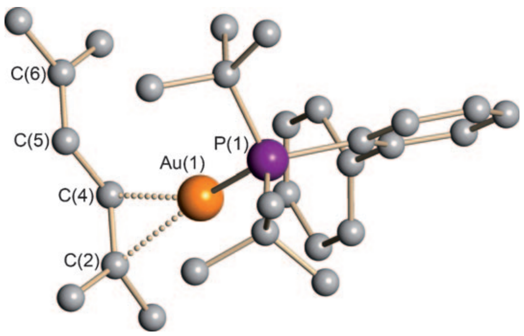

Figure 1. Molecular structure of [Au{P*t*Bu$_2$(*o*-biphenyl)}{$Me_2CC(H)C(H)CMe_2$}]$^+$ (**2**); the [SbF_6]$^-$ anion and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Au1–C4 2.270(3), Au1–C2 2.335(3), C2–C4 1.391(4), C4–C5 1.464(5), C5–C6 1.349(5).

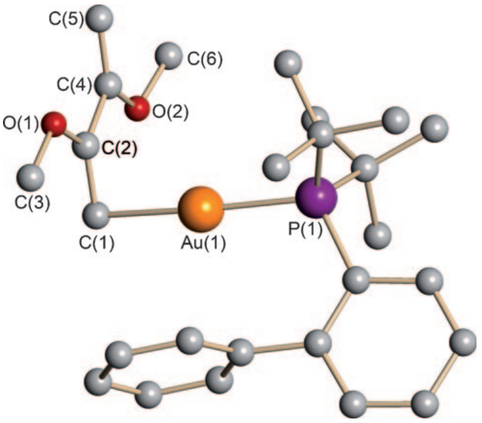

Figure 2. Molecular structure of [Au{P*t*Bu$_2$(*o*-biphenyl)}{$H_2CC(OMe)C(OMe)CH_2$}]$^+$ (**3**); the [SbF_6]$^-$ anion and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Au1–C1 2.175(2), Au1–C2 2.543(2), C1–C2 1.384(4), C2–C4 1.492(4), C4–C5 1.325(4), O1–C2 1.319(3), O2–C4 1.353(3).

The most striking observation, however, relates to the orientation of the gold center. As with **1** and **2**, the heavy metal is associated with only one of the C=C bonds, but in this case it has slipped so significantly (45 %) towards the CH_2 end of the olefin so that it is perhaps better described as being σ-bonded to the carbon atom, giving a near linear geometry at gold (C1-Au1-P1 171.89(8)°). This description is also reflected in the ^{1}H NMR spectrum of **3**, which shows four peaks for the alkene hydrogen atoms, two in the region normally associated with C(sp^2)–H ($\delta = 5.21$ and 4.60 ppm), and two which are significantly upfield ($\delta = 3.56$ and 2.68 ppm). This extreme slippage can be rationalized in terms of the π-donor OMe groups on the diene backbone, which can stabilize the carbocationic center generated by the π-bonded gold fragment, an observation which has precedent in gold–alkene chemistry.[12]

Whereas the experimental evidence suggests that the solid-state structure of **3** is maintained in solution, a rather different picture emerges for **1** and **2**. The room-temperature ^{13}C NMR spectrum of **1** and **2** showed only three and four resonances respectively for the 1,3-diene component, suggesting dynamic behavior consistent with one of three possible scenarios: 1) In solution, the gold–phosphine unit is bound to both alkene sites creating a symmetric *cis*-1,3-diene and therefore giving three resonances; 2) the gold–phosphine unit is only bound to one alkene but is involved in intramolecular exchange with the uncoordinated alkene site, which is fast on the NMR timescale; and 3) the gold–phosphine unit is only bound to one alkene but is involved in an intermolecular exchange process with uncoordinated alkenes, which is fast on the NMR timescale. To differentiate these possibilities, variable-temperature ^{1}H and ^{13}C NMR spectra of **1** and **2** were recorded. The resonances for the 1,3-diene unit of **2** remain invariant in both the ^{1}H and ^{13}C NMR spectra upon cooling to −80 °C. However, the room-temperature ^{1}H NMR spectrum of **1** shows three resonances (one each for the *cis*- and *trans*-alkene protons and one for the methyl group) that broaden upon cooling and ultimately (at −80 °C) separate into five signals, three in the alkene region (in ratio 1:1:2) and two for the now distinct methyl groups. The alkene signals were assigned to the *cis* and *trans* hydrogen atoms of the metal-coordinated alkene. The chemically independent uncoordinated hydrogen atoms, assigned based on the similarity of their chemical shift compared to the free diene, are unresolved owing to the broadness of the signals at this low temperature.

At −90 °C, the ^{13}C{^{1}H} NMR spectrum showed four signals in the alkene region, two for the uncoordinated alkene (in similar positions to those observed for free 2,3-dimethyl-1,3-butadiene) at $\delta = 140.14$ (=*C*Me–) and 124.81 ppm (=*C*H$_2$) and two for the coordinated alkene at δ 153.14 (=*C*Me–) and 93.03 ppm (=*C*H$_2$). Separate peaks were also observed for each methyl group. These findings suggest the structure in solution at −90 °C is similar to that determined by X-ray crystallography and therefore that the gold is coordinated to only one of the alkenes with a rapid exchange

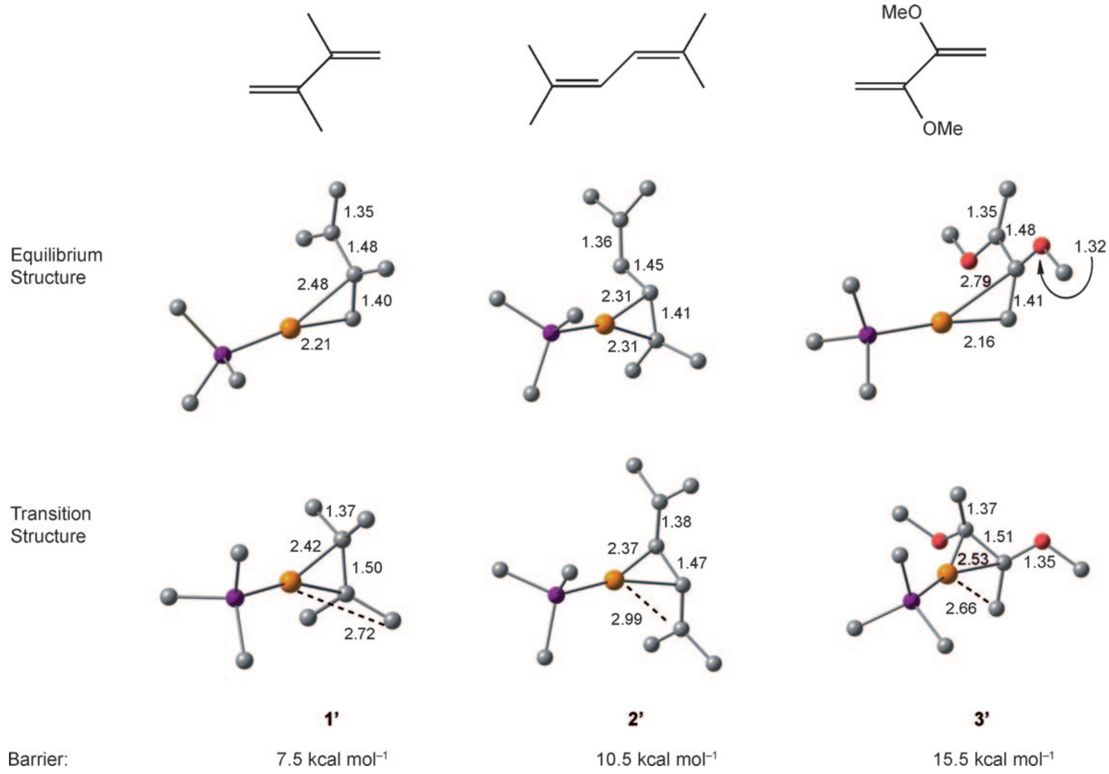

Figure 3. Equilibrium and transition structures and migration barriers for compounds **1′**–**3′**.

process. Furthermore, the low-temperature NMR spectra at two further concentrations of **1** (CD_2Cl_2) showed the rate of exchange of coordinated and uncoordinated arms to be independent of concentration, suggesting the exchange process proceeds by an intra- rather than intermolecular process.

To obtain greater insight into the bonding and dynamics of these species we have used density functional theory to explore the potential energy surfaces for migration of the metal along the butadiene chain. The results of calculations (where the phosphine ligand is modeled as PMe_3) are given in Figure 3. A parallel series of calculations using the full ligand ($PtBu_3$ for **1** and $PtBu_2$(*o*-biphenyl) for **2** and **3**) yielded very similar structural results (see the Supporting Information), but the large number of low-frequency vibrational modes in the complete ligands prevented the location of the corresponding transition structures. The optimized bond lengths summarized in Figure 3 are fully consistent with the trends observed experimentally for **2** and **3**, and suggest that the complete series **1**→**2**→**3** maps a low-energy migration pathway for the $[Au(PR_3)]^+$ unit along the C=C bond.

At one extreme (**2′**), the gold is symmetrically disposed towards both carbon atoms (Au−C 2.31 Å). However, adding electron donating groups at the C2 and C3 positions results in a shift towards the terminal carbon that is marginal in **1′** (2.21 Å vs. 2.48 Å) and dramatic in **3′** (2.16 Å vs 2.79 Å). In **2′**, the incipient positive charge at the coordinated carbon centers is stabilized either by the inductive effects of two methyl groups (C2) or by resonance with the uncoordinated C=C bond (C4), and it appears that these two factors offset each other, leading to an almost symmetric η^2-coordination mode. In **1′**, the developing positive charge at the central carbon is again stabilized by resonance with the residual C=C double bond but also by the inductive effects of the methyl groups, giving greater asymmetry. We note in this context that in their study of gold-catalyzed hydroamination of *cis*-3-methyl-1,3-pentadiene,[6] Lledós and co-workers also reported a strongly slipped η^2-coordination mode where the metal binds to the least substituted CH_2=CHR moiety. The optimized Au−C bond lengths of 2.283 Å and 2.455 Å in this system are very similar to those in **1′**. In **3′**, the resonance with the C=C double bond is supplemented by conjugation with the methoxy oxygen atoms, leading to the dramatically slipped structure and also a distinct asymmetry in the corresponding C−O bond lengths (1.32 Å and 1.36 Å), a feature which is apparent in the solid-state structure of **3** (1.319(3), 1.353(3) Å). We also note that attempts to locate a minimum where the metal coordinates to both double bonds of a *cis*-buta-1,3-diene unit were unsuccessful: in all cases the metal slipped towards one C=C terminus of the ligand to give structures analogous to **1′**, **2′**, and **3′** but with a *cis* disposition of the butadiene. The tendency of Au^I to adopt linear geometries is well-established[13] and the resultant preference for coordination of only one C=C unit of a diene moiety has been noted by Lledós.[6] The calculations also shed some light on the relationship between gold–alkene bonding in the ground state and the barriers to migration from one end of the diene to the other. In all three cases, a C_2-symmetric transition state has been located where the gold center is coordinated to the central C−C unit. The Au−C bond lengths of 2.42 Å and 2.37 Å in **1′** and **2′**, respectively, are marginally longer than in the equilibrium structure. The coordinated C=C bond shortens in the transition structure (1.37 vs. 1.40 Å in **1′**) while the central C–C bond of the butadiene unit lengthens by a small amount. The changes relative to the equilibrium structure are, however, not dramatic, and as a result the computed barriers are low (7.5 kcal mol^{-1} and 10.5 kcal mol^{-1} for **1′** and **2′**, respectively), consistent with their observed fluxionality. In **3′**, in contrast, the terminal Au–C bond length in the transition state is considerably longer than in the equilibrium structure (2.66 vs. 2.16 Å), and so the early part of the reaction coordinate involves almost complete cleavage of the Au–C bond. As a result, the strong C–O π bonding apparent in the equilibrium structure (C–O 1.32 Å) is much reduced in the transition structure, where the corresponding bond length is 1.35 Å. The net effect of these substantial structural modifications along the reaction coordinate is a much larger barrier of 15.5 kcal mol^{-1}, and the molecule is indeed static under all conditions used in our experiments.

In summary, we have isolated three gold–buta-1,3-diene complexes. Two of the complexes have solid-state structures with η^2-bonding to the butadiene for which VT-NMR spectroscopy indicates fluxionality via an intramolecular pathway that is frozen out (in one example) at low temperatures. Calculations reveal a low-energy rearrangement pathway ($\Delta E^{+} = 10.5$ kcal mol^{-1}) is present in **2′**, wherein the gold fragment slips along the butadiene unit via a transition state where the metal is weakly coordinated to the central C–C unit. The third complex, with π-donating OMe groups in the 2- and 3-positions of the diene, is best described as containing an Au–C σ bond to one of the alkene groups, the strong resonance stabilization of the resulting carbocationic center by the methoxy groups effectively preventing the movement of the gold unit over the diene manifold.

Received: April 20, 2011

Keywords: cations · density functional calculations · dienes · gold · X-ray diffraction

---

[1] For dedicated Review volumes, see: a) *Chem. Rev.* **2008**, *108*, 2793; b) *Chem. Soc. Rev.* **2008**, *37*, 1745; c) *Tetrahedron* **2009**, *65*, 1747; d) *J. Organomet. Chem.* **2009**, *694*, 4981.

[2] X. Zhang, H. Shi, B.-Q. Xu, *Angew. Chem.* **2005**, *117*, 7294; *Angew. Chem. Int. Ed.* **2005**, *44*, 7132.

[3] a) J. H. Lee, F. D. Toste, *Angew. Chem.* **2007**, *119*, 930; *Angew. Chem. Int. Ed.* **2007**, *46*, 912; b) M. Melchionna, M. Nieger, J. Helaja, *Chem. Eur. J.* **2010**, *16*, 8262.

[4] C. Brouwer, R. Rahatrian, C. A. He, *Synlett* **2007**, 1785.

[5] C. Brouwer, C. He, *Angew. Chem.* **2006**, *118*, 1776; *Angew. Chem. Int. Ed.* **2006**, *45*, 1744.

[6] G. Kovács, G. Ujaque, A. Lledós, *J. Am. Chem. Soc.* **2008**, *130*, 853.

[7] A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232.

[8] R. E. M. Brooner, R. A. Widenhoefer, *Organometallics* **2011**, *30*, 3182.

[9] a) N. D. Shapiro, F. D. Toste, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 2779; b) H. V. R. Dias, M. Fianchini, T. R. Cundari, C. F. Campana, *Angew. Chem.* **2008**, *120*, 566; *Angew. Chem. Int. Ed.* **2008**, *47*, 556; c) T. N. Hooper, M. Green, J. E. McGrady, J. R. Patel, C. A. Russell, *Chem. Commun.* **2009**, 3877; d) T. N. Hooper, C. P. Butts, M. Green, M. F. Haddow, J. E. McGrady, C. A. Russell, *Chem. Eur. J.* **2009**, *15*, 12196; e) T. J. Brown, M. G. Dickens, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2009**, *131*, 6350; f) T. J. Brown, M. G. Dickens, R. A. Widenhoefer, *Chem. Commun.* **2009**, 6451; g) M. Fianchini, H. X. Dai, H. V. R. Dias, *Chem. Commun.* **2009**, 6373.

[10] a) A. Reisinger, N. Trapp, C. Knapp, D. Himmel, F. Breher, H. Rüegger, I. Krossing, *Chem. Eur. J.* **2009**, *15*, 9505; b) I. Krossing, A. Reisinger, *Angew. Chem.* **2003**, *115*, 5903; *Angew. Chem. Int. Ed.* **2003**, *42*, 5725.

[11] CCDC 821981 (**1**), CCDC 821982 (**2**), and CCDC 821983 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] a) G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.* **2009**, *121*, 2548; *Angew. Chem. Int. Ed.* **2009**, *48*, 2510; b) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. M. Wang, W. A. Goddard, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482; c) G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.* **2010**, *122*, 8644; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466; d) R. L. LaLonde, W. E. Brenzovich, D. Benitez, E. Tkatchouk, K. Kelley, W. A. Goddard III, F. D. Toste, *Chem. Sci.* **2010**, *1*, 226; e) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410.

[13] M. A. Carvajal, J. J. Novoa, S. Alvarez, *J. Am. Chem. Soc.* **2004**, *126*, 1465.