Angewandte
Communications

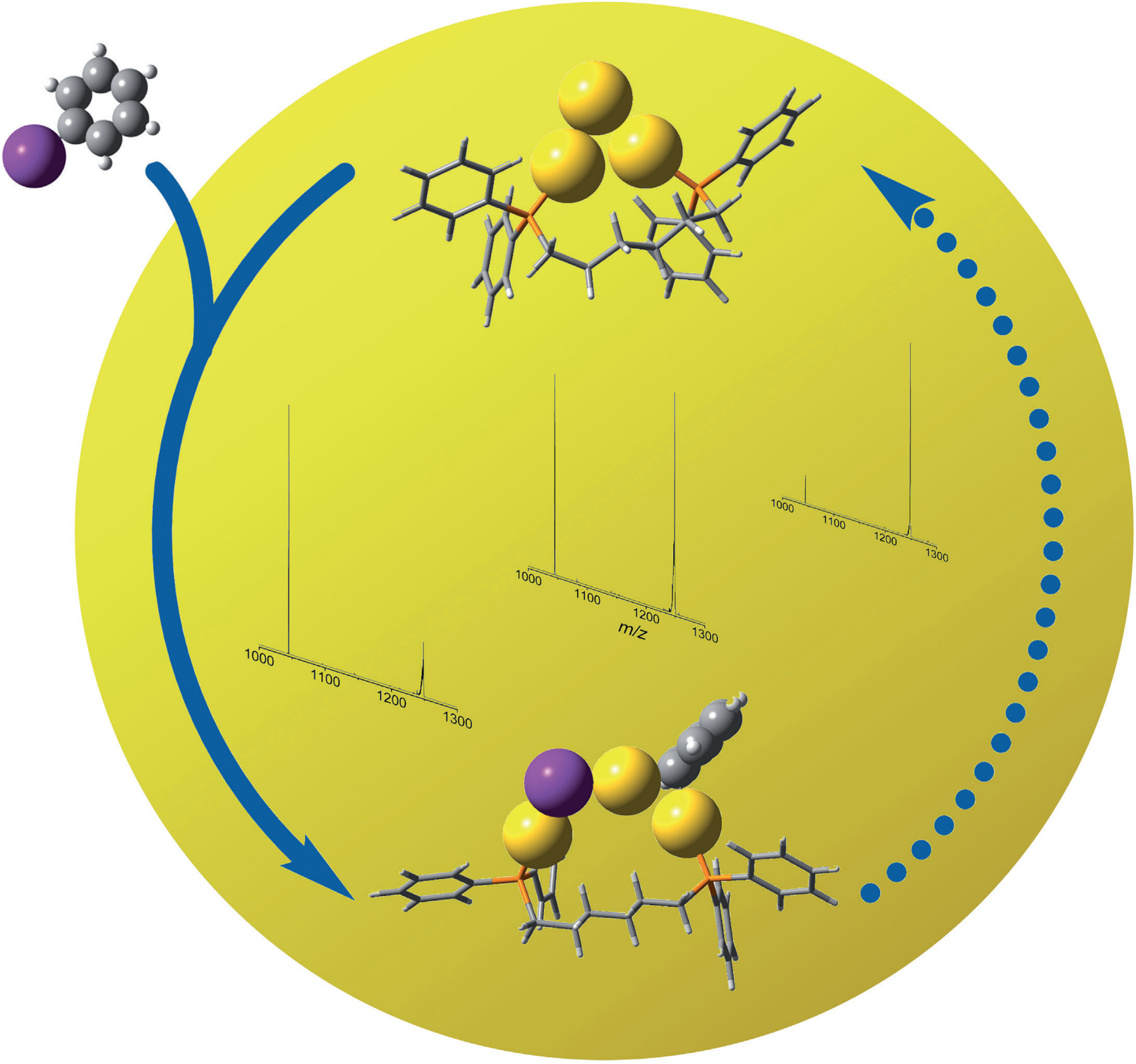
Sonogashira Coupling

DOI: 10.1002/anie.201108502

Gold-Mediated C–I Bond Activation of Iodobenzene**

Peter S. D. Robinson, George N. Khairallah, Gabriel da Silva, Hadi Lioe, and Richard A. J. O'Hair**

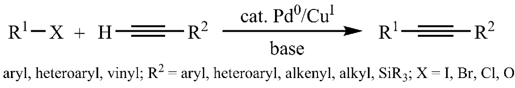
Dedicated to Professor Charles H. DePuy on the occasion of his 85th birthday



Angewandte
Chemie

WILEY
ONLINE LIBRARY

The key challenges in unequivocally assigning the active catalyst in homogenous transition-metal catalysis was recently covered in a review by Crabtree.[1] These include the need to rule out the possibility of 1) nanoparticles being the active catalyst and 2) artifacts owing to low-levels of highly reactive metal impurities. A key case study that Crabtree highlighted is the recent controversy surrounding the use of gold[2] as an alternative catalyst to palladium in the Sonogashira coupling reaction (Scheme 1), which is widely used in synthetic organic chemistry.[3–5]

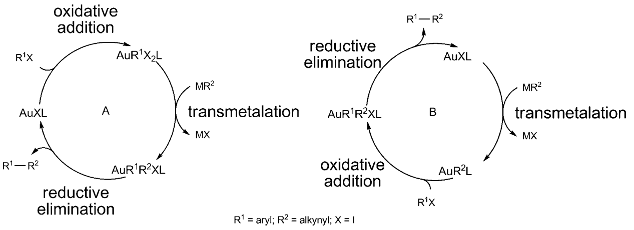


$$R^1{-}X + H{-}{\equiv}{-}R^2 \xrightarrow[\text{base}]{\text{cat. Pd}^0/\text{Cu}^\text{I}} R^1{-}{\equiv}{-}R^2$$

R^1 = aryl, heteroaryl, vinyl; R^2 = aryl, heteroaryl, alkenyl, alkyl, SiR_3; X = I, Br, Cl, OTf

Scheme 1. The Sonogashira sp–sp^2 C–C cross-coupling reaction (adapted from Chinchilla and Nájera).[3b]

Corma and co-workers reported that gold supported on nanocrystalline CeO_2 provides excellent selectivity for cross-coupling (89 %).[2a] As Au^0, Au^I, and Au^{III} are all present on the nanoparticle surface, they performed a series of kinetic studies on colloidal gold and various Schiff base complexes, and suggested that it is the Au^I oxidation state that mediates the Sonogashira reaction.[2a] To explain the apparent catalytic activity of Au^I complexes for the Sonogashira reaction, Lauterbach et al. attempted a series of experiments to test two potential catalytic cycles shown in Scheme 2.[2b] They found that a range of two-coordinate Au^I complexes are unable to activate aryl iodide by oxidative addition; they suggested that the observed catalytic activity of Corma and co-workers is actually due to the presence of palladium impurities, with Au^I simply replacing the role of Cu^I in traditional Sonogashira coupling.



Scheme 2. Catalytic cycles proposed by Lauterbach et al. for an Au^I complex mediated Sonogashira cross-coupling.[2b] A key requirement for both cycles is oxidative addition. R^1X is an aryl halide and MR^2 is a metal acetylide.

Very recently Corma and co-workers have carried out carefully controlled kinetic studies to show that the catalytic activity is not due to palladium impurities.[2c] Instead, catalytic activity was attributed to the in situ formation of gold clusters by degradation of the Au^I complex. This was supported by DFT calculations, which showed that while oxidative addition of iodobenzene to the mononuclear complex Me_3PAuI has a high activation barrier (132.2 kJ mol^{-1}), the related reaction for the bare gold cluster Au_{38} has a substantially lower barrier (47.3 kJ mol^{-1}).[2c]

Gas-phase studies represent a powerful way of uncovering the intrinsic reactivity of metallic ions[6,7] and the mechanisms of their C–X bond activation reactions.[8] The stoichiometry of the metallic reactant ion can be confidently assigned by the unique mass and often-distinctive isotopic signature of the metal. It can then be mass-selected using well-established tandem mass-spectrometry-based approaches and its reactivity directly probed by monitoring the changes in its abundance as well as the formation of ionic products. By mass-selecting the reactant ion, the issue of impurities are circumvented, while reactivity as a function of metal cluster size can simply be probed by examining a range of different clusters.[9] Herein a combination of mass-spectrometry-based experiments and DFT calculations are used to examine the gas phase reactions of iodobenzene with the mononuclear gold cations $(R_3P)_nAu^+$ (R = Me, Ph; $n = 1, 2$) and the ligated gold clusters $[Au_3L^n]^+$ ($L = Ph_2P(CH_2)_nPPh_2$; $n = 3$–6) to establish the molecular requirements for C–I bond activation.

Electrospray ionization (ESI) in combination with multistage mass spectrometry (MS^n) experiments were used to generate 1) $(R_3P)Au^+$ (R = Me, Ph) by collision-induced dissociation (CID) of $(R_3P)_2Au^+$; 2) $(R_3P)_2Au^+$ (R = Me, Ph) by ESI/MS on $(R_3P)AuCl$; and 3) $[Au_3L^n]^+$ ($L^n = Ph_2P(CH_2)_nPPh_2$; $n = 3$–6) by CID of larger gold clusters synthesized in the condensed phase and transferred to the gas phase by ESI.[10] Figure 1 a–d shows representative spectra of the ion–molecule reactions of these ions with iodobenzene (for all $[Au_3L^n]^+$, see the Supporting Information, Figure S1). An examination of Figure 1 reveals that the types of reaction products and the overall reactivity depend on the number of gold atoms (compare Figure 1 b to c); the number of ligands present (compare Figure 1 a and b); and the type of bisphosphine ligand (see Figure S1).

As the gas-phase reactivity of bare Au^+ has been previously described, we focused on examining the reactivity of the ligated cations.[11] The monoligated complexes R_3PAu^+

---

[*] P. S. D. Robinson, Dr. G. N. Khairallah, Dr. H. Lioe,
Prof. R. A. J. O'Hair
School of Chemistry, University of Melbourne
Melbourne, Victoria 3010 (Australia)
and
Bio21 Institute of Molecular Science and Biotechnology
University of Melbourne, Melbourne, Victoria 3010 (Australia)
and
ARC Centre of Excellence for Free Radical Chemistry and Biotechnology
E-mail: gkhai@unimelb.edu.au
rohair@unimelb.edu.au

Dr. G. da Silva
Department of Chemical and Biomolecular Engineering
University of Melbourne, Melbourne, Victoria 3010 (Australia)

[**] We thank the Australian Research Council (ARC) for financial support through DP1096134 and the ARC CoE program, the NCI National Facility at the ANU for the allocation of computing resources under the Merit Allocation Scheme, Prof. Paul Mulvaney for his enthusiastic support of this work, Wen Mike Xiao and Dr. Tich-Lam Nguyen for carrying out preliminary experiments on the synthesis of gold clusters, and Dr. Hudgens for providing preprints on the synthesis of gold clusters.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108502.

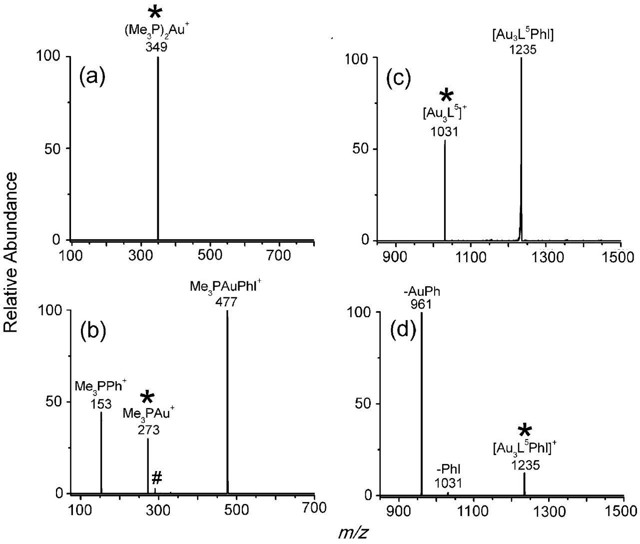


Figure 1. LTQ mass spectra obtained from ion–molecule reactions of iodobenzene (8.36×10^9 molecules cm^{-3}) with a) (Me$_3$P)$_2$Au$^+$ (10 s reaction time), b) Me$_3$PAu$^+$ (200 ms reaction time), and c) [Au$_3$L^5]$^+$ (1 s reaction time). d) CID of [Au$_3$L^{5}PhI]$^+$. A ⋆ represents the mass selected precursor ion. A # represents the addition of adventitious H$_2$O present in the ion trap.

react by adduct formation [Eq. (1)] and P–C bond formation by oxidative addition/reductive elimination [Eq. (2)]. The bisligated complexes (R$_3$P)$_2$Au$^+$ however, are unreactive at the longest reaction time studied [10 s; Eq. (3)]. Finally, all of the [Au$_3$L^n]$^+$ clusters react by adduct formation [Eq. (4)].

$$\mathrm{R_3PAu^+ + PhI \rightarrow R_3PAu(PhI)^+} \quad (1)$$

$$\mathrm{\rightarrow R_3PPh^+ + AuI} \quad (2)$$

$$\mathrm{(R_3P)_2Au^+ + PhI \rightarrow no\ reaction} \quad (3)$$

$$\mathrm{[Au_3L^{\mathit{n}}]^+ + PhI \rightarrow [Au_3L^{\mathit{n}}(PhI)]^+} \quad (4)$$

Although the nature of some of the products clearly highlight that C–I bond activation has occurred [Eq. (2)], we used CID to establish whether C–I bond activation has occurred in the adducts formed in Equations (1) and (4). Thus, these ions were mass selected and subjected to CID (Figure 1 d; Supporting Information, Figure S2, S3). We observed that R$_3$PAu(PhI)$^+$ fragments by loss of PhI [Eq. (5)] and AuI [Eq. (6)], while [Au$_3$L^n(PhI)]$^+$ fragments by a minor loss of PhI [Eq. (7)] and PhAu [Eq. (8)]. When the deuterated adduct [Au$_3$L^n(C$_6$D$_5$I)]$^+$ is subjected to CID, C$_6$D$_5$Au is lost (Supporting Information, Figure S4), showing that C–I bond activation has occurred rather than C–P bond activation of the bisphosphine ligand. A further stage of CID on [L^{n}Au$_2$I]$^+$ results in the loss of AuI [Eq. (9)]. These sequential losses of PhAu and AuI are strong indicators that C–I bond activation has occurred.

$$\mathrm{R_3PAu(PhI)^+ \rightarrow R_3PAu^+ + PhI} \quad (5)$$

$$\mathrm{\rightarrow R_3PPh^+ + AuI} \quad (6)$$

$$\mathrm{[Au_3L^{\mathit{n}}(PhI)]^+ \rightarrow [Au_3L^{\mathit{n}}]^+ + PhI} \quad (7)$$

$$\mathrm{\rightarrow [L^{\mathit{n}}Au_2I]^+ + PhAu} \quad (8)$$

$$\mathrm{[L^{\mathit{n}}Au_2I]^+ \rightarrow [L^{\mathit{n}}Au]^+ + AuI} \quad (9)$$

To quantify the observed reactivities, the branching ratios and rate constants for the reactions were measured, and the data are summarized in Table 1. It is clear that in the case of monoligated complexes R$_3$PAu$^+$, the reaction with PhI is highly efficient owing in part to the presence of a vacant coordination site on gold. The branching ratio for the product of reductive elimination by formation of C–P bond [Eq. (2)] is dependent on the phosphine ligand. When R = Me, the C–P bond formation channel represents 26.5 %, whereas it is only 0.5 % in the case of R = Ph. In the case of [Au$_3$L^n]$^+$, although adduct formation is the only reaction channel observed in all cases, detailed kinetic modeling (Supporting Information) shows that the reaction kinetics for oxidative addition are clearly ligand-dependent, increasing with the increase in the linker size (CH$_2$)$_n$ ($n = 3$: least efficient, 0.04 %; $n = 6$: most efficient, 42 %).

Table 1: Kinetics associated with the ion–molecule reactions of gold cations with iodobenzene.

Reactant	Product (Equation, B.R.)[a]	k_{expt}[b,c]	Reaction efficiency[d]
Me$_3$PAu$^+$	Me$_3$PAu(PhI)$^+$ (1, 73.5 %) Me$_3$PPh$^+$ (2, 26.5 %)	1.09×10^{-9}	100
Ph$_3$PAu$^+$	Ph$_3$PAu(PhI)$^+$ (1, 99.5 %) Ph$_4$P$^+$ (2, 0.5 %)	1.27×10^{-9}	100
(Me$_3$P)$_2$Au$^+$	N.R.		
(Ph$_3$P)$_2$Au$^+$	N.R.		
[Au$_3$L^3]$^+$	[Au$_3$L^3(PhI)]$^+$ (4, 100 %)	3.57×10^{-13}	0.04
[Au$_3$L^4]$^+$	[Au$_3$L^4(PhI)]$^+$ (4, 100 %)	6.55×10^{-12}	0.75
[Au$_3$L^5]$^+$	[Au$_3$L^5(PhI)]$^+$ (4, 100 %)	8.66×10^{-11}	9.9
[Au$_3$L^6]$^+$	[Au$_3$L^6(PhI)]$^+$ (4, 100 %)	3.69×10^{-10}	42

[a] B.R. = branching ratio, N.R. = no reaction. [b] In units of cm^3 molecule^{-1} s^{-1}. [c] Rates for the reaction with iodobenzene to yield the oxidative addition product. Rates were determined by modeling the ion evolution with time (see the Supporting Information). [d] Reaction efficiency = ($k_{\mathrm{expt}}/k_{\mathrm{ADO}}$) 100 %. k_{ADO} is the theoretical ion–molecule collision rate constant obtained from the average-dipole orientation (ADO) theory, which was calculated using the Colrate program.[12]

To gain insights into these C–I bond activation reactions, DFT calculations were carried out on the reactions of iodobenzene and the gold complexes Me$_3$PAu$^+$ and (Me$_3$P)$_2$Au$^+$ (Figure 2) and the clusters [Au$_3$L^n]$^+$ ($n = 3$–6; Figure 3).

The potential energy diagrams for the gold complexes Me$_3$PAu$^+$ and (Me$_3$P)$_2$Au$^+$ are entirely consistent with the experimental results. The monoligated complex, with its vacant coordination site is predicted to readily react (bottom plot of Figure 2 a) by oxidative addition to form the Au$^{\mathrm{III}}$ product (**2**), which can either be collisionally stabilized [Eq. (1)], or can react further by reductive elimination to form AuI and the phosphonium ion, Me$_3$PPh$^+$ [Eq. (2)]. A key point is that the energies of all species (intermediates **1**–**3** and transition states **TS1–2** and **TS2–3** of Figure 2 b) along this

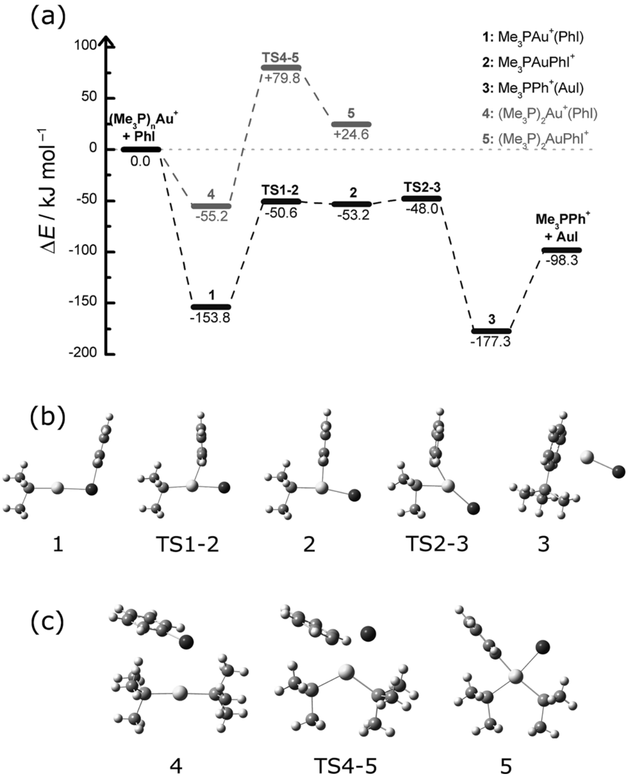


Figure 2. DFT-calculated energy diagrams (at the M06/SDD6-31G-(d,p)//B3LYP/SDD6-31G(d,p) level of theory) for ion–molecule reactions of iodobenzene with a) Me_3PAu^+ and $(Me_3P)_2Au^+$, b) key species for reaction of Me_3PAu^+; c) key species for reaction of $(Me_3P)_2Au^+$.

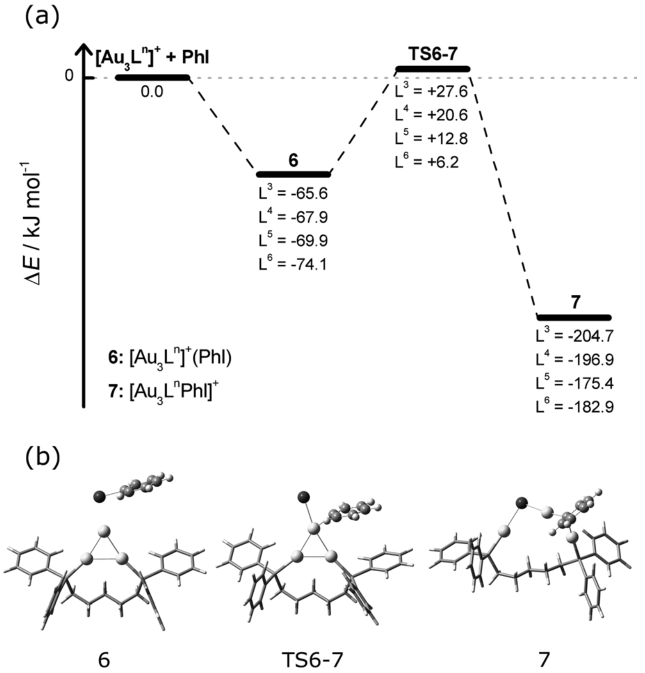


Figure 3. a) DFT-calculated energy diagrams (at the M06/SDD6-31G-(d,p)//B3LYP/SDD6-31G(d,p) level of theory) for ion–molecule reactions of iodobenzene with $[Au_3L^n]^+$ ($n=3$–6); b) key species for reaction of $[Au_3L^5]^+$.

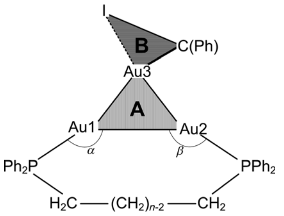
reaction coordinate fall below the energies of the separated reactants, which is consistent with the experimental formation of both products [Eq. (1) and (2), Figure 1 b]. In contrast, for the bisligated complex (top plot of Figure 2 a), formation of the Au^{III} oxidative addition product, **5**, is significantly endothermic ($+24.6\ kJ\,mol^{-1}$), with a substantial barrier associated with **TS4–5** of $+79.8\ kJ\,mol^{-1}$. This is not only consistent with the experiments, which show a complete absence of any products (Figure 1 a), but also with the high activation barrier previously predicted by Corma et al. for the oxidative addition of iodobenzene to the related mononuclear complex Me_3PAuI.[2c]

Although Rahman and co-workers have used DFT calculations to clearly show that the size of the linker n in bisphosphine ligands $H_2P(CH_2)_nPH_2$ helps to select the preferred number of gold atoms x in $[Au_xL^n_y]^{z+}$ clusters,[13] the role of the linker size in tuning chemical reactivity appears to represent unchartered territory in gold cluster chemistry.[14] To confirm the experimentally determined reactivity order for C–I bond activation of iodobenzene by the gold clusters $[Au_3L^n]^+$, DFT calculations were carried out for all four clusters $n=3$–6 (Figure 3). Figure 3 a shows how the energies associated with the potential energy diagram for oxidative addition vary as a function of the linker size n. The energies of both the precomplex **6** and the transition state **TS6–7** directly track the experimental reactivity order. Thus the least reactive cluster ($n=3$: reaction efficiency 0.04 %; Table 1) forms the least stable complex **6** ($-65.6\ kJ\,mol^{-1}$) and the transition state for C–I bond activation **TS6–7** is highest in energy ($+27.6\ kJ\,mol^{-1}$). In contrast, the most reactive cluster ($n=6$, reaction efficiency = 42 %, Table 1) forms the most stable complex **6** ($-74.1\ kJ\,mol^{-1}$) and the transition state for C–I bond activation **TS6–7** is lowest in energy ($+6.2\ kJ\,mol^{-1}$). Furthermore, the overall barrier height is linearly proportional to the natural logarithm of the rate constant for oxidative addition, as would be expected from transition state theory. Interestingly, the stability of complex **7** is reversed with different ligands.

What factors are at play in tuning the chemical reactivity of these bisphosphine ligated gold clusters $[Au_3L^n]^+$? Examination of the structures of each of the four transition states **TS6–7** reveals that key geometric parameters include the P-Au-Au bond angles α and β and the angle γ between the Au-Au-Au plane A and the I-Au-C plane B in Table 2. The transition state barrier height is reduced from L^3 to L^6 as α and β increase toward 180° and γ approaches 0°.

This work resolves a key controversy surrounding the gold mediated Sonogashira coupling reaction,[2] and highlights the value of fundamental gas-phase ion chemistry in organometallic chemistry. By probing the key step of iodobenzene C–I bond activation, we have shown that bisligated mononuclear gold(I) complexes are unreactive towards iodobenzene. In contrast, the bisphosphine ligated gold clusters $[Au_3L^5]^+$ and $[Au_3L^6]^+$ readily react by C–I bond activation. A novel feature of the latter reactions uncovered by both experiment and theory is that the size of the linker n in the bisphosphine ligand $Ph_2P(CH_2)_nPPh_2$ tunes the reactivity of the gold cluster, $[Au_3L^n]^+$, from a nearly unreactive case with $n=3$ to an almost collision-limited reaction when $n=6$. This highlights

Table 2: Key geometrical differences in the transition state **TS6–7** as a function of linker size *n*.



Ligand	α[a]	β[a]	γ[a,b]
L^3	121.7	111.2	52.7
L^4	129.3	121.3	50.0
L^5	141.4	132.6	16.2
L^6	150.2	135.0	9.4

[a] In degrees. [b] γ is the angle between plane A defined by Au1-Au2-Au3 and plane B defined by Au3-C(Ph)-I.

the incredible sensitivity of gold cluster reactivity towards the local chemical structure. Given the intense interest in gold mediated transformations of organic substrates and the ready gas-phase synthesis of a wide range of gold clusters $[Au_xL^n{}_y]^{z+}$, the stage is set to probe reactivity as a function of nuclearity x, ligation (size of the linker n, and number of bisphosphine ligands y) and charge (z). Such studies are underway and will provide valuable information on the potential role of gold nanoclusters in catalysis.[15]

Experimental Section

Ion–molecule reactions were performed using a Finnigan hybrid linear triple-quadrupole (LTQ) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer that was modified to introduce a gaseous mixture containing He and the iodobenzene reagent into the linear ion trap, such that the He pressure is about 2 mTorr and the reagent concentration is about 8.36×10^9 molecules$\,cm^{-3}$ in the ion trap.[16] Ions formed in the linear ion trap resulting from ion–molecule reactions and/or CID were transferred to the FTICR cell for accurate mass measurements. Standard ion isolation and excitation procedures were performed using the LTQ-FTICR software. Ligated gold clusters $[Au_{11}L^3{}_5]^{3+}$ and $[Au_8L^n{}_4]^{2+}$ ($n=4$–6) were synthesized in solution using published methods.[10]

ESI solutions were introduced into the mass spectrometer using a syringe pump operating at 5 μL min^{-1} and by applying 3.3–4.8 kV to the ESI capillary relative to the heated capillary entrance to the mass spectrometer (300 °C). To obtain ion–molecule reaction efficiencies, the experimentally measured rate constant is divided by the theoretical ion–molecule collision rate constant that is obtained from the average-dipole orientation (ADO) theory[12].

Theoretical calculations were performed using the Gaussian 09 software package.[17] A range of different starting structures were considered. For $[Au_3L^n]^+$, different conformations of the bisphosphine ligand were examined (data not shown), and we determined that the most stable clusters were those in which each P atom coordinated to a different gold atom (see **6** of Figure 3). All structures of all species were optimized using the B3LYP level of theory, with the SDD basis set for Au and I, and the 6-31G(d,p) basis set for C, H, and P. Frequency calculations were carried out on all of the optimized structures to confirm they correspond to either minima (no imaginary frequencies) or transition states (one imaginary frequency). Single point energy calculations were carried out with the M06 functional[18] with the same basis set as above, and these energies are reported here. The M06 method is well-suited to main-group and transition-metal reaction thermochemistry, and energies quoted in this study are expected to be accurate to around ±10 kcal mol^{-1} on average. Cartesian coordinates and energies for all of the species are given in the Supporting Information.

Received: December 2, 2011

Keywords: bond activation · density functional calculations · gas-phase reactions · gold · mass spectrometry

[1] "Resolving Heterogeneity Problems and Impurity Artifacts in Operationally Homogeneous Transition Metal Catalysts": R. H. Crabtree, *Chem. Rev.* **2012**, DOI: 10.1021/cr2002905.

[2] a) C. González-Arellano, A. Abad, A. Corma, H. García, M. Iglesias, F. Sánchez, *Angew. Chem.* **2007**, *119*, 1558; *Angew. Chem. Int. Ed.* **2007**, *46*, 1536; b) T. Lauterbach, M. Livendahl, A. Rosellon, P. Espinet, A. M. Echavarren, *Org. Lett.* **2010**, *12*, 3006; c) A. Corma, R. Juárez, B. Boronat, F. Sánchez, M. Iglesias, H. García, *Chem. Commun.* **2011**, *47*, 1446; d) M. Livendahl, P. Espinet, A. M. Echavarren, *Platinum Met. Rev.* **2011**, *55*, 212.

[3] a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467; b) R. Chinchilla, C. Nájera, *Chem. Rev.* **2007**, *107*, 874; c) R. Chinchilla, C. Nájera, *Chem. Soc. Rev.* **2011**, *40*, 5084.

[4] Sonogashira cross-coupling occurs on smooth Au(111) surfaces, with some formation of the homocoupling byproducts: V. K. Kanuru, G. Kyriakou, S. K. Beaumont, A. C. Papageorgiou, D. J. Watson, R. M. Lambert, *J. Am. Chem. Soc.* **2010**, *132*, 8081.

[5] Catalytic activity for Sonogashira cross-coupling has also been reported for gold supported on Ce_2O_3, Nb_2O_5, SiO_2, and La_2O_3 nanoparticles: a) R. O. M. A. de Souza, M. S. Bittar, L. V. P. Mendes, C. M. F. da Silva, V. T. da Silva, O. A. C. Antunes, *Synlett* **2008**, 1777; b) G. Kyriakou, S. K. Beaumont, S. M. Humphrey, C. Antonetti, R. M. Lambert, *ChemCatChem* **2010**, *2*, 1444; c) S. K. Beaumont, G. Kyriakou, R. M. Lambert, *J. Am. Chem. Soc.* **2010**, *132*, 12246.

[6] a) D. K. Böhme, H. Schwarz, *Angew. Chem.* **2005**, *117*, 2388; *Angew. Chem. Int. Ed.* **2005**, *44*, 2336; b) R. A. J. O'Hair, *Chem. Commun.* **2006**, 1469.

[7] For recent MS studies on palladium-catalyzed Sonogashira cross-coupling, see: a) K. L. Vikse, M. A. Henderson, A. G. Oliver, J. S. McIndoe, *Chem. Commun.* **2010**, *46*, 7412; b) K. L. Vikse, Z. Ahmadi, C. C. Manning, D. A. Harrington, J. S. McIndoe, *Angew. Chem.* **2011**, *123*, 8454; *Angew. Chem. Int. Ed.* **2011**, *50*, 8304.

[8] For reviews on C−X bond activation, see: a) H. Schwarz, *Angew. Chem.* **2011**, *123*, 10276; *Angew. Chem. Int. Ed.* **2011**, *50*, 10096; b) J. Roithová, D. Schröder, *Chem. Rev.* **2010**, *110*, 1170; c) U. Mazurek, H. Schwarz, *Chem. Commun.* **2003**, 1321; d) K. Eller, *Coord. Chem. Rev.* **1993**, *126*, 93.

[9] Gas-phase studies have shown that the silver-cluster-mediated Wurtz-like coupling of allyhalides is influenced by the size of the cluster and the nature of the halide: a) G. N. Khairallah, R. A. J. O'Hair, *Angew. Chem.* **2005**, *117*, 738; *Angew. Chem. Int. Ed.* **2005**, *44*, 728; b) F. Q. Wang, G. N. Khairallah, R. A. J. O'Hair, *Int. J. Mass Spectrom.* **2009**, *283*, 17.

[10] Gold clusters were formed by ESI/MS of preformed clusters in combination with cluster fragmentation by CID. Details will be reported in a full paper. This approach is inspired by previous studies: a) M. Bertino, Z. Sun, R. Zhang, L. Wang, *J. Phys. Chem. B* **2006**, *110*, 21416; b) D. E. Bergeron, J. W. Hudgens, *J. Phys. Chem. C* **2007**, *111*, 8195; c) J. S. Golightly, L. Gao, A. W. Castleman, Jr., D. E. Bergeron, J. W. Hudgens, R. J. Magyar, C. A. Gonzalez, *J. Phys. Chem. C* **2007**, *111*, 14625. For previous gas phase studies of the reactions of $(R_3P)Au^+$, see: d) J.

Roithová, J. Hrusak, D. Schröder, H. Schwarz, *Inorg. Chim. Acta* **2005**, *358*, 4287; e) G. N. Khairallah, R. A. J. O'Hair, M. I. Bruce, *Dalton Trans.* **2006**, 3699.

[11] Previous gas phase studies using FTICR experiments have shown that Au^+ reacts with iodobenzene by iodide abstraction, phenyl group abstraction, and electron transfer: J. R. Brown, P. Schwerdtfeger, D. Schröder, H. Schwarz, *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 485. Our results are fully consistent with these reaction channels and we have measured the rate of reaction (see the Supporting Information).

[12] a) T. Su, M. T. Bowers in *Gas-Phase Ion Chemistry* (Ed.: M. T. Bowers), Academic Press, New York, **1979**, p. 83; b) K. F. Lim, *Quantum Chem. Program Exch.* **1994**, *14*, 3.

[13] S. Hong, G. Shafai, M. Bertino, T. S. Rahman, *J. Phys. Chem. C* **2011**, *115*, 14478.

[14] This contrasts with the well-known concept of bite angle in catalysis by mononuclear bisphosphine-ligated transition-metal complexes; for a review see: Z. Freixa, P. W. N. M. van Leeuwen, *Dalton Trans.* **2003**, 1890.

[15] For a rare recent example, see: Y. Zhu, H. Qian, B. A. Drake, R. Jin, *Angew. Chem.* **2010**, *122*, 1317; *Angew. Chem. Int. Ed.* **2010**, *49*, 1295.

[16] W. A. Donald, C. J. McKenzie, R. A. J. O'Hair, *Angew. Chem.* **2011**, *123*, 8529; *Angew. Chem. Int. Ed.* **2011**, *50*, 8379.

[17] Gaussian 09 (Revision B.01). Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, **2009**.

[18] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.