

**Sonogashira coupling on an extended gold surface *in vacuo*:
reaction of phenylacetylene with iodobenzene on Au(111)**

Vijay K. Kanuru, Georgios Kyriakou, Simon K. Beaumont, Anthoula C. Papageorgiou,

*David J. Watson[†] and Richard M. Lambert**

Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom.

[†]Present address: Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD
United Kingdom.

**RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required
according to the journal that you are submitting your paper to)**

- Corresponding author. Email: rml1@cam.ac.uk; Tel.: +44 1223 336467; Fax: +44 1223 336362.

Abstract

Temperature programmed reaction measurements supported by STM show that phenylacetylene and iodobenzene react on smooth Au(111) under vacuum conditions to yield biphenyl and diphenyldiacetylene, the result of homocoupling of the reactant molecules. They also produce *diphenylacetylene*, the result of Sonogashira cross-coupling, prototypical of a class of reactions that are of paramount importance in synthetic organic chemistry and whose mechanism remains controversial. Roughened Au(111) is completely inert towards all three reactions indicating that the availability of crystallographically well-defined adsorption sites is crucially important. High resolution XPS and NEXAFS spectroscopy show that the reactants are initially present as intact, essentially flat-lying molecules, and that the temperature threshold for Sonogashira coupling coincides with that for C-I bond scission in the iodobenzene reactant. The fractional order kinetics and low temperature associated with desorption of the Sonogashira product suggest that the reaction occurs at the boundaries of islands of adsorbed reactants and that its appearance in the gas phase is surface reaction rate limited. These findings demonstrate unambiguously, and for the first time, that this heterogeneous cross-coupling chemistry is an intrinsic property of extended, metallic pure gold surfaces: no other species, including solvent molecules, basic or charged (ionic) species are necessary to mediate the process.

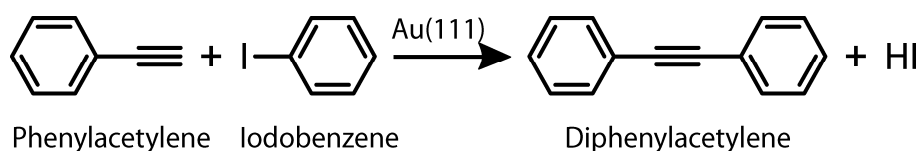
KEYWORDS: Gold; Sonogashira; Coupling; Heterogeneous; Au(111); NEXAFS; XPS.

Introduction:

The metal-catalyzed Sonogashira, Heck and Suzuki coupling reactions that lead to the formation of new carbon-carbon bonds¹⁻⁴ are of major importance in synthetic organic chemistry. Often, metal nanoparticles are used as the source of catalytic material,⁵⁻⁷ although it is a matter for continuing debate as to whether the active sites are present at the nanoparticle surfaces or reside in solution as molecular species leached from the solid phase.^{5,7-9}

This remains a controversial issue, not least in the case of Sonogashira coupling.^{1,4,5,7} Even though a very large number of investigations have been carried out, few of these have directly addressed the identity of the catalytically active species; not infrequently, it is tacitly assumed or otherwise inferred that the reaction occurs homogeneously. In part, this reflects the difficulty of carrying out unambiguous analytical measurements that could provide an answer, and of course it is always possible that the extent to which homogeneous and heterogeneous pathways contribute may vary from case to case. Suffice to say that evidence has been presented in favor of both points of view.^{5,7,10-12} In the case of Pd, catalysis by leached species has been demonstrated,^{13,14} whereas for other metals the issue is more complex.¹⁵ Using supported gold nanoparticles, Gonzalez-Arellano *et al.* reported leaching under reaction conditions but took the view that the catalysis was heterogeneous;¹² they also found no significant solvent effects.

Here we report on the interaction of phenylacetylene (PA) and iodobenzene (IB), prototypical of Sonogashira coupling, on an extended Au(111) surface under conditions of ultra high vacuum where there is no possibility of homogeneous chemistry and the overall reaction may be written formally as shown in Scheme 1. Gold was chosen in view of current interest in this metal as a catalyst for an ever-widening range of organic reactions.¹⁶



Scheme 1. Sonogashira coupling of phenylacetylene and iodobenzene.

By means of temperature programmed reaction, STM, high resolution synchrotron fast XPS and NEXAFS spectroscopy, it was found that the reactant molecules are adsorbed intact, lie flat, and, in addition to undergoing homo-coupling, Sonogashira cross-coupling to yield diphenylacetylene *does* occur with extreme sensitivity to the morphology of the gold surface.

Experimental Methods

Temperature programmed reaction experiments were conducted in Cambridge in an ultra-high vacuum (UHV) chamber operated at a base pressure of 1×10^{-10} torr. Reagent grade phenylacetylene 98% (Sigma Aldrich) and iodobenzene 99% (Fluka) were dosed onto the sample by backfilling the chamber which was equipped with an Omicron 3 grid retarding field analyser for LEED/AES analysis and a VG 300 quadrupole mass spectrometer whose ionizer was positioned 5 mm from the front face of the sample. The Au(111) single crystal (10 mm \times 15 mm \times 1.0 mm) could be cooled to 100 K and heated to 1200 K, monitored by a T1T2 thermocouple attached directly to the sample. The TPR heating ramp used was 4 K s^{-1} and the data presented here are corrected for mass spectrometer sensitivity and molecular ionization cross-sections. STM experiments were carried out in Cambridge in an Omicron variable-temperature UHV STM, which was operated in the constant current mode using etched tungsten tips.

High resolution XPS and NEXAFS measurements were carried out on the SuperESCA beamline at the ELETTRA synchrotron radiation source in Trieste, Italy. Spectra were collected using a single-pass 32-channel concentric hemispherical electron analyzer. The excitation energies used for the acquisition of the C 1s, I 3d, and Au 4f spectra were 380 eV, 720 eV, and 180 eV, respectively. The angle between the analyzer entrance lens and the incoming photon beam was 70° in the horizontal plane. The Au(111) crystal was attached to a motorized manipulator *via* a tantalum back plate fitted with a T1T2 thermocouple and could be heated resistively to 900 K or cooled to 90 K.

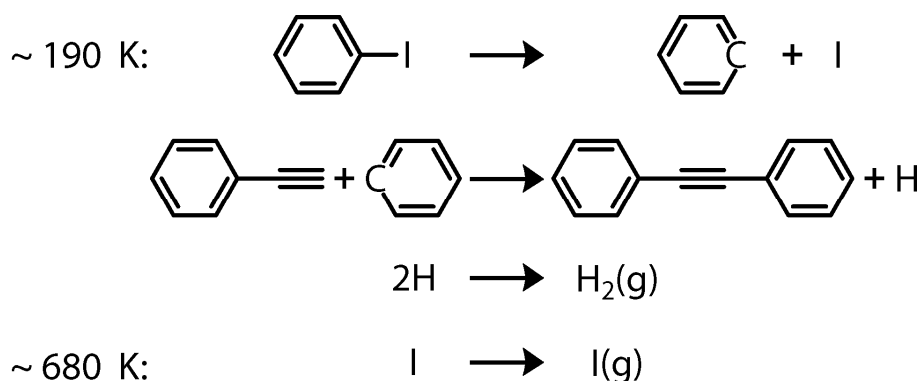
The Au(111) sample was cleaned by repeated cycles of Ar^+ sputtering (99.999% Messer) followed by annealing at 550 K until a clean, atomically flat surface was obtained, as monitored by XPS and LEED (Trieste) or LEED, and Auger electron spectroscopy or STM (Cambridge). Quoted coverages for NEXAFS and XPS are based on estimation of the monolayer point (one monolayer = 1 ML) from the associated shift in C 1s binding energy that is apparent in the high resolution XP spectra for uptakes of each molecule and from the appearance of a multilayer peak in the thermal desorption data.

Results and Discussion

First, we present reaction data obtained using smooth and deliberately roughened Au(111) surfaces. Then we provide and analyze corresponding NEXAFS and fast XPS data and discuss the reaction results in the light of these.

Temperature programmed reaction measurements

Figure 1a shows typical TPR spectra obtained after dosing 0.55 ML of IB and 0.25 ML of PA onto the smooth clean Au(111) surface (Figure 1b) at 90 K. The only gaseous organic products observed were (i) the Sonogashira cross coupling product diphenylacetylene ($m/z = 178$) at ~ 190 K, and (ii) both homo-coupling products dipenyldiacetylene ($m/z = 202$) at ~ 330 K and biphenyl ($m/z = 154$) at ~ 390 K. Unreacted PA ($m/z = 102$) and IB ($m/z = 204$) desorbed at ~ 300 K and ~ 310 K respectively.¹⁷ Note that these results were obtained in the absence of any basic species (for example, tetrabutyl ammonium acetate or K_2CO_3) which are invariably employed when Sonogashira coupling is carried out under practical conditions in solution. The diphenylacetylene peak shape is characteristic of fractional order kinetics¹⁸ suggesting that under our conditions Sonogashira coupling takes place at the boundaries of islands of one or both reactants. Its low temperature indicates that appearance of gaseous diphenylacetylene is a surface reaction rate limited process.¹⁹ The peak shapes of the homo-coupling products (dipenyldiacetylene, biphenyl) are quite different and consistent with self-reaction of PA and IB either within islands or within a dispersed phase. In order to aid the discussion which follows, Scheme 2 shows a simple reaction scheme that is consistent with our findings.



Scheme 2. Sonogashira coupling in vacuum on Au(111); all species to be taken as adsorbed unless stated otherwise.

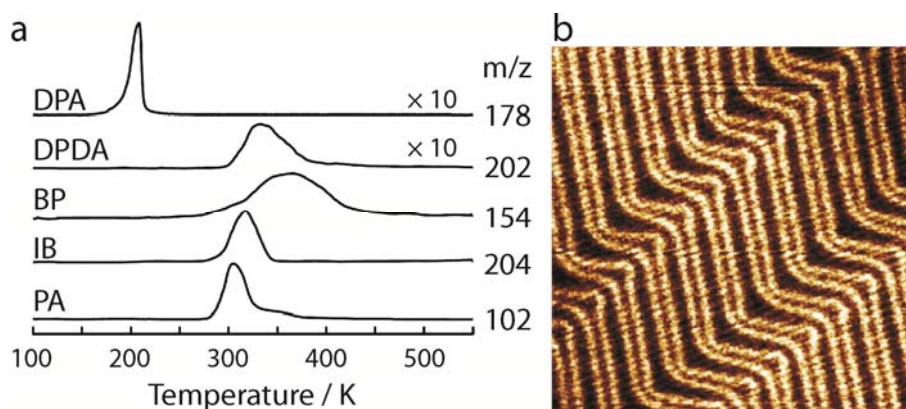


Figure 1. (a) TPR spectra of PA, IB, Diphenylacetylene (DPA), Diphenyldiacetylene (DPDA) and Biphenyl (BP) reactants and products after adsorption of 0.55 ML IB + 0.25 ML PA on Au(111) at 90 K. (b) Typical clean Au(111) surface showing the herringbone reconstruction ($65 \times 65 \text{ nm}^2$, $V_{\text{gap}} = 2.41 \text{ V}$, $I = 0.21 \text{ nA}$).

An estimate of reaction selectivity towards the Sonogashira product, diphenylacetylene, was carried out by calibrating the quadrupole mass spectrometer, allowing for mass discrimination effects characteristic of these instruments, and correcting for ionization gauge sensitivities (see supporting information). This procedure gave a lower limit for the selectivity toward diphenylacetylene formation of at least $\sim 10\%$. The selectivity towards Hay coupling was similarly estimated as $\sim 10\%$, the conversion of iodobenzene being $\sim 60\%$. Although relatively modest, the Sonogashira is in the order of reported selectivities for the same reaction carried out *in solution and in the presence of base*, catalyzed by supported Au nanoparticles. Basic species are known to promote Sonogashira reactions,²⁰ possibly by facilitating abstraction of the weakly acidic hydrogen atom on the alkyne.

How fast is this chemistry? It is not possible to specify a turnover frequency (TOF) in the normally understood sense because in a one-shot TPR experiment there is no incident flux of reactant molecules, the system is not isothermal nor is it in steady state. However, subject to certain assumptions (see

supporting information) one may obtain a lower limit for a kind of pseudo-TOF of $\sim 30 \text{ h}^{-1}$, which is in the range of values reported for coupling reactions catalyzed by organometallic complexes.

As shown below by the XPS results, iodine was retained on the surface immediately after reaction, as indeed expected, given the strength of iodine/gold chemisorption. It could subsequently be desorbed (activation energy $\sim 180 \text{ kJ mol}^{-1}$) at $\sim 680 \text{ K}$ and the corresponding desorption data are shown in the supporting information. HI desorption was not detected nor is it expected on thermodynamic grounds (see supporting information). Hydrogen, the remaining possible product, was not detected due to its small yield and limited instrumental sensitivity at low m/z , exacerbated by the presence of a very small background hydrogen partial pressure, always present in stainless steel UHV systems.

Figure 2 illustrates the morphology and reactive behavior towards Sonogashira coupling of the deliberately roughened surface (Ar^+ , 1 keV, 8.0 μA , 90 min, no annealing) using the same reactant doses as for the smooth surface. It is evident that diphenylacetylene formation was totally quenched, as was that of the homocoupling products biphenyl and diphenyldiacetylene (not shown). A small amount of reactant desorption occurred, accompanied by extensive decomposition (XPS). Clearly, coupling reactions on gold are very sensitive to the details of surface structure. The inactivity of the rough Au surface may be due to unavailability of well defined crystal facets of sufficient size. It may also be the case that the presence of low co-ordinate Au sites on the roughened surface causes decomposition of the adsorbed reactants.

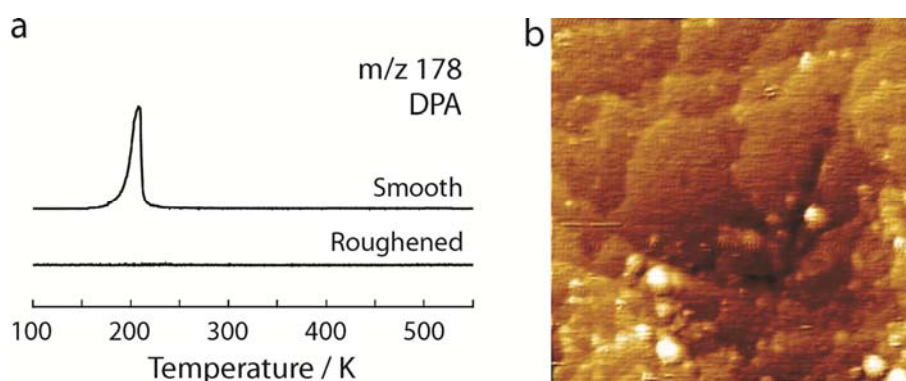


Figure 2. (a) Diphenylacetylene (m/z 178, DPA) TPR spectra after dosing 0.55 ML IB + 0.25 ML PA on smooth and roughened Au(111) surface. (b) STM image of roughened Au(111) surface (65×65 nm², $V_{\text{gap}} = -1.00$ V, $I = 0.87$ nA).

These findings demonstrate unambiguously that PA and IB undergo Sonogashira coupling on a well-ordered extended gold surface in vacuum. They also show that reaction efficiency is sensitive to the details of surface structure, only smooth surfaces with well-developed crystal planes being effective under our conditions. This observation suggests that metal particle size effects are likely to be significant when Sonogashira coupling of these reactants is carried out in solution in the presence of Au nanoparticles. Specifically, large particles should be more effective catalysts than small ones, *if* the reaction occurs heterogeneously.

High resolution XPS

Figure 3a shows C 1s XP spectra acquired during the uptake at 90 K of ~ 0.5 ML of IB followed by ~ 0.5 ML of PA. The IB spectrum is characterized by a major component at 284.3 eV associated with the phenyl ring and a smaller feature at 285.0 eV due to the carbon atom bonded to iodine. These features are more clearly apparent in Figure 3b which shows the C 1s spectrum from a 0.9 ML of IB at 90 K. The relative intensity of the two components is $\sim 1:5$ which is consistent with non-dissociative adsorption of IB, a conclusion that is confirmed by the I 3d_{5/2} spectra discussed below. Addition of ~ 0.5 ML PA to the 0.5 ML IB resulted in the composite spectra shown in the upper part of Figure 3a. The principal component at ~ 284.3 eV increased in intensity, broadened, and its apparent binding energy downshifted slightly. A broad feature at ~ 285.0 eV binding energy also appeared, most likely due to the alkyne group. Interpretation is made possible by the results shown in Figure 3c which refers to ~ 0.9 ML of pure PA. Two components are present with an intensity ratio of $\sim 2:6$, again consistent with non-dissociative molecular adsorption. The identical binding energy of 284.3 eV observed for both molecules in the co-adsorbed spectra (Figure 3a) and in the submonolayer spectra of the pure reactants (Figure 3b and 3c) confirms that when coadsorbed at a total coverage of ~ 1 ML, both PA and IB were

in contact with the Au(111) surface: multilayer adsorption would have resulted in a measurable shift to higher binding energy if this were not the case.

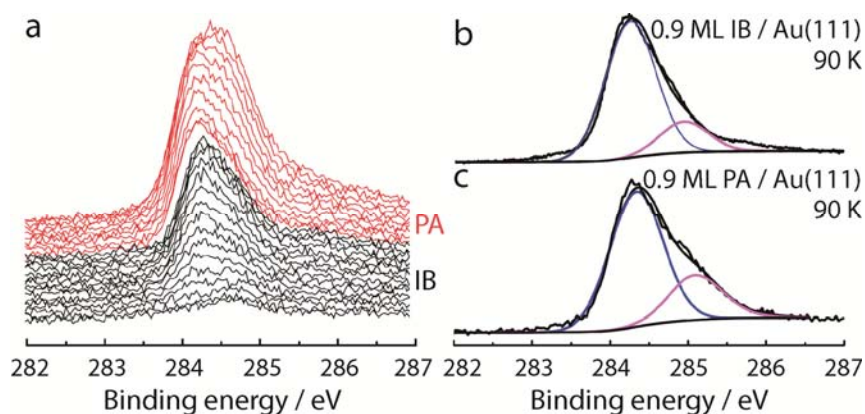


Figure 3. (a) Temperature dependence of C 1s spectra resulting from exposure of Au(111) to ~ 0.5 ML IB followed by ~ 0.5 ML PA at 90 K (b) C 1s spectrum of 0.9 ML IB. (c) C 1s spectrum 0.9 ML of PA.

Figure 4a and 4b show subsets of C 1s and I 3d data acquired in a separate experiment in which a ~ 1 ML mixed adsorbed layer of IB and PA was annealed at 5 K min^{-1} . In this case an amount of PA was initially present in a second layer, resulting in the C 1s high energy shoulder at $\sim 284.7 \text{ eV}$; it had disappeared by 173 K resulting in a downshift of the C 1s emission maximum by 0.3 eV. The corresponding I $3d_{5/2,3/2}$ spectrum increased in intensity due to desorption of the overlying PA multilayer and the observed binding energies correspond to organically bound iodine (I $3d_{5/2} = 618.4 \text{ eV}$). Further increase of temperature to 266 K shifted the C 1s envelope to lower binding energy, consistent with scission of the C-I bond in the iodobenzene, a process analogous to oxidative addition of an organic halide to an organometallic complex, as noted by Celio et al.²¹ This conclusion is strongly confirmed by the corresponding iodine spectrum which exhibits emission due to two chemically distinct forms of I: the original component at 618.4 eV and a new feature shifted to lower binding energy by 1.7 eV, as expected for I_{ads} resulting from C-I bond scission,²² a process that was complete by $\sim 373 \text{ K}$. Note that the onset of IB dissociation ($\sim 266 \text{ K}$) corresponds well with the onset of Sonogashira coupling observed in the Cambridge TPR experiments (Figure 1). Additionally, the overall loss of C 1s intensity

between 266 K and 373 K agrees with the desorption of un-reacted IB, PA and of biphenyl, as shown in Figure 1. The residual C 1s peak at 373 K centered at ~ 284.0 eV was almost certainly due to biphenyl, as will be confirmed by the NEXAFS results.

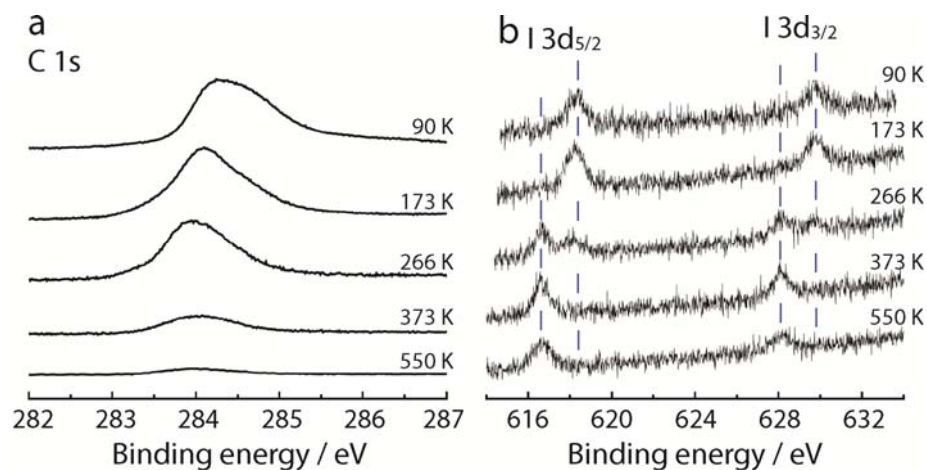


Figure 4. (a) Time and temperature dependent C 1s spectra resulting from annealing mixed layer of ~ 0.5 ML IB + 0.7 ML PA at 5 K min^{-1} . (b) Corresponding I 3d spectra.

Given the above results and that it seems at least plausible that Sonogashira coupling is preceded by C-I scission in IB, it is of interest to examine the latter process in more detail by means of the C 1s spectrum. Figure 5a shows the time and temperature dependence of the C 1s spectrum, starting with a multilayer of pure IB; a subset of these data is presented in Figure 5b. Between 90 K and 180 K the main C 1s component shifted from 284.7 eV to 284.4 eV, indicative of multilayer desorption. Between 180 K and 220 K there was no significant shift. Between 220 K and 316 K a progressive downshift of the C 1s intensity maximum to lower binding energies occurred, accompanied by loss of the characteristic shoulder at 284.9 eV, corresponding to scission of the C-I bond. This more accurate result corroborates the temperature dependence of the iodine spectra observed for a mixed IB + PA layer. Specifically, the C 1s data show that the threshold for C-I scission in IB is ~ 220 K in very good agreement with the temperature regime over which the Sonogashira cross-coupling product was observed in the TPR measurements (Figure 1). In this connection, Syomin and Koel²³ studied the adsorption and reaction of IB on Au(111) by TPD and IRAS and also found that scission of the C-I

bond takes place around 200 – 250 K, resulting in immediate formation of biphenyl. The latter observation is of relevance in the present case as it suggests an explanation for the relatively limited Sonogashira selectivity we find: in the absence of base, which serves to activate PA, phenyl species resulting from C-I scission tend to undergo homo-coupling to yield biphenyl before they can be captured by PA to yield the Sonogashira product. This effect would presumably be accentuated if the IB molecules tended to form islands as is reported for IB on Cu(110),²⁴ and, indeed, we found that biphenyl was the main product in the TPR experiments (Figure 1).

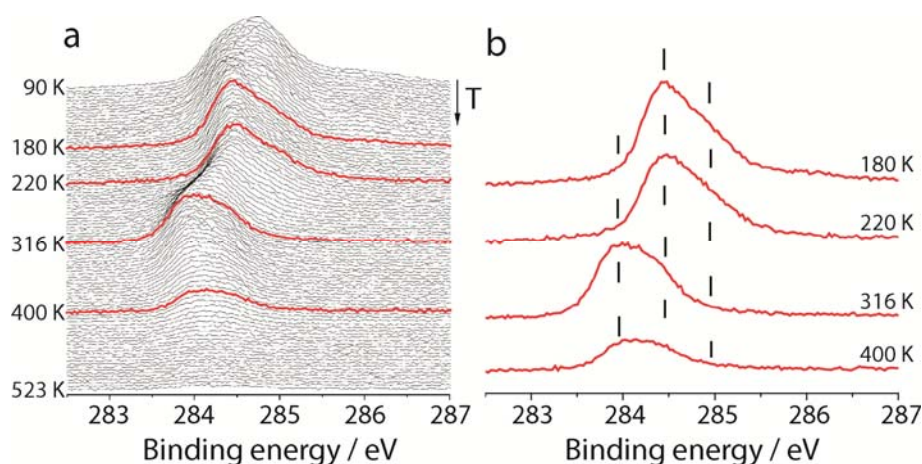


Figure 5. (a) Time and temperature dependence of C 1s spectrum commencing with multilayers of IB adsorbed at 90 K. (b) Data subset extracted from (a).

NEXAFS spectroscopy of individual reactants, co-adsorbed reactants, and reaction

NEXAFS measurements were carried out on IB and PA separately adsorbed, co-adsorbed and as a function of temperature. Figure 6a shows C K-edge NEXAFS spectra of 0.5 ML of PA on Au(111) at 90 K recorded at five photon incidence angles (θ , defined relative to the surface plane). Prominent resonances due to C 1s \rightarrow π^* and C 1s \rightarrow σ^* transitions are apparent and a summary of assignments and the associated transitions is given in Table 1.

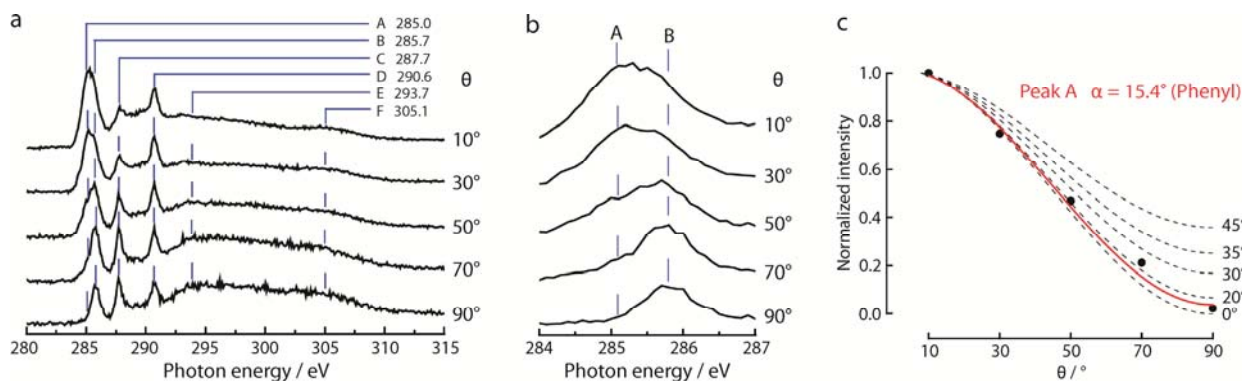


Figure 6. (a) C K-edge NEXAFS spectra acquired at five angles of photon incidence θ for a ~ 0.5 ML coverage of PA on Au(111) at 90 K. (b) Expanded scale for leading π^* resonances A and B. (c) Curve fitting analysis of θ dependence of π^* resonance A to estimate the phenyl ring tilt angle, α .

Table 1. Resonance assignments for the C K-edge NEXAFS of PA on Au(111)^[25-28]

Peak	Energy / eV	Assignment
A	285.0	C1s $\rightarrow \pi^*$ (phenyl) PA
B	285.7	C1s $\rightarrow \pi^*$ (alkyne) PA
C	287.7	C1s $\rightarrow \sigma^*$ C-H
D	290.6	C1s $\rightarrow \pi^*b_{2g} + \sigma^*$ C-H
E	293.7	C1s $\rightarrow \sigma^*$ C-C
F	305.1	C1s $\rightarrow \sigma^*$ C-C

Resonances A and B at 285.0 eV and 285.7 eV correspond to C 1s $\rightarrow \pi^*$ transitions and are crucial for estimating the orientation of PA on Au(111): Figure 6b clarifies the different θ dependences of resonance A (phenyl group) and B (alkyne group which contains π_x and π_y components that exhibit opposite angular variation and therefore no net change). Note that the C K-edge NEXAFS spectrum of gaseous PA^[25,26] exhibits a clear and characteristic splitting of the C 1s $\rightarrow \pi^*$ resonance at ~ 285.5 eV which results from conjugation of the alkyne and phenyl groups in the molecule. To a first approximation, the lower energy resonance may be considered as phenyl-like whilst that at higher

energy includes contributions both from the phenyl and the alkyne groups. This splitting disappears upon adsorption of PA on Cu and Pt surfaces,^{26,28} due to appreciable rehybridization of the molecular orbitals of the alkyne group which adopts a distorted sp^2 configuration. However in the present case the characteristic split of the C 1s $\rightarrow \pi^*$ resonance is still apparent, indicating preservation of the molecular geometry and consistent with the XPS results. Five more transitions are resolved at higher photon energies, assigned in Table 1, but not required for analysis.²⁵⁻²⁸

The angular dependence of the C 1s $\rightarrow \pi^*$ resonance A provides a means of determining the orientation of the molecules with respect to the surface.²⁹ Figure 6c shows the observed normalized intensities overlaid with a series of theoretical curves,²⁹ the least squares best fit yielding a tilt angle of $\alpha = 15^\circ$ with an uncertainty of 5° for the orientation of the phenyl group with respect to the surface: i.e., the molecule lies almost flat.

Similarly, Figure 7a shows C *K*-edge NEXAFS spectra for 0.5 ML of IB acquired at five photon incidence angles. Seven resonances are resolved and their assignment is summarized in Table 2. The first two resonances at 285.1 eV and 286.0 eV are assigned to the C 1s $\rightarrow \pi^*$ transition, split into two components due to the presence of the heteroatom as a result of the reduction in symmetry from D_{6h} to C_{2v} ,^{30,31} more clearly apparent in Figure 7b. This splitting provides strong confirmation that adsorption of IB at 90 K is non-dissociative, again in good accord with the XPS data. At higher photon energies five more transitions are clearly resolved and can be assigned (Table 2).

The angular dependence of resonance A at 285.1 eV was used to calculate the orientation of IB with respect to the surface as before²⁹ and the results are shown in Figure 7c: IB also adsorbs relatively flat on the surface, with tilt angle $\alpha = 15^\circ$, which agrees well with the observations of Syomin and Koel²³ who used IRAS to show that at submonolayer coverages IB adsorbs almost flat on Au(111).

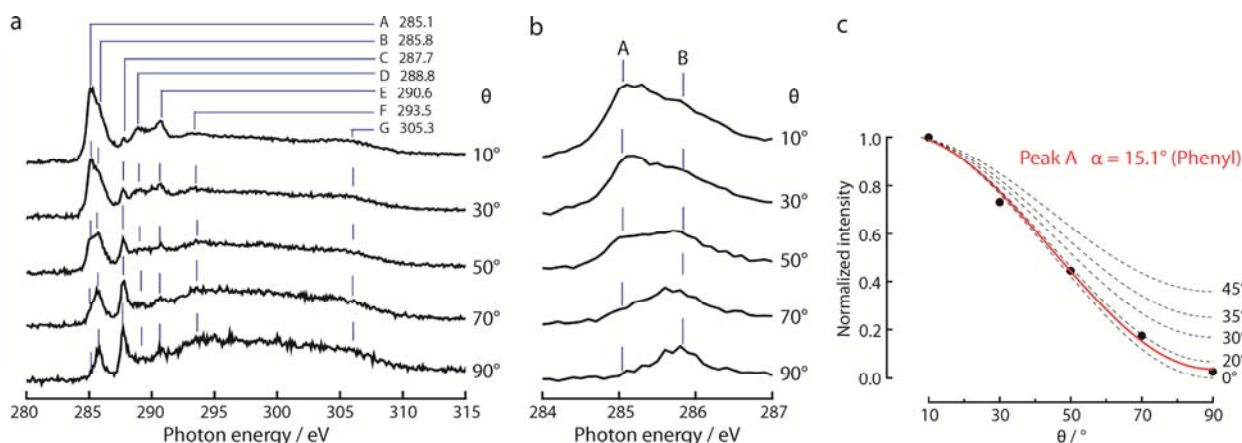


Figure 7. (a) C K-edge NEXAFS spectra acquired at five photon incidence angles θ for a ~ 0.5 ML coverage of IB on Au(111). (b) A close up of principle π^* resonances A and B. (c) Curve-fitting analysis of the photon angle dependence of π^* resonance A to estimate the corresponding phenyl ring tilt angle, α .

Table 2. Resonance assignments for C K-edge NEXAFS of IB on Au(111)^[30,31]

Peak	Energy / eV	Assignment
A	285.1	C1s \rightarrow π^* phenyl
B	285.8	C1s \rightarrow π^* phenyl
C	287.7	C1s \rightarrow σ^* C-H
D	288.8	C1s \rightarrow π^*b_{2g}
E	290.6	C1s \rightarrow σ^* C-H
F	293.5	C1s \rightarrow σ^* C-C
G	305.3	C1s \rightarrow σ^* C-C

Finally, we used NEXAFS to try and examine co-adsorption of PA and IB at 90 K and the subsequent reaction and evolution of the mixed layer with increasing temperature. Beam time limitation allowed acquisition of data at only two temperatures, 90 K and 373 K as shown in Figure 8. At 90 K the superposition of resonances and possible masking of some resonances by a contribution from a partial multilayer^{32,33} makes identification of these features unreliable. However, according to the TPR results

(Figure 1) the only species surviving on the surface at 373 K should have been the reaction product biphenyl, and indeed this fits well with the single resonance observed at that temperature. Analysis of this feature as a function of photon incidence angle was carried out (see supporting information) and gave a tilt angle of $\sim 0^\circ$. That is, biphenyl lies absolutely flat, as might be expected.²³

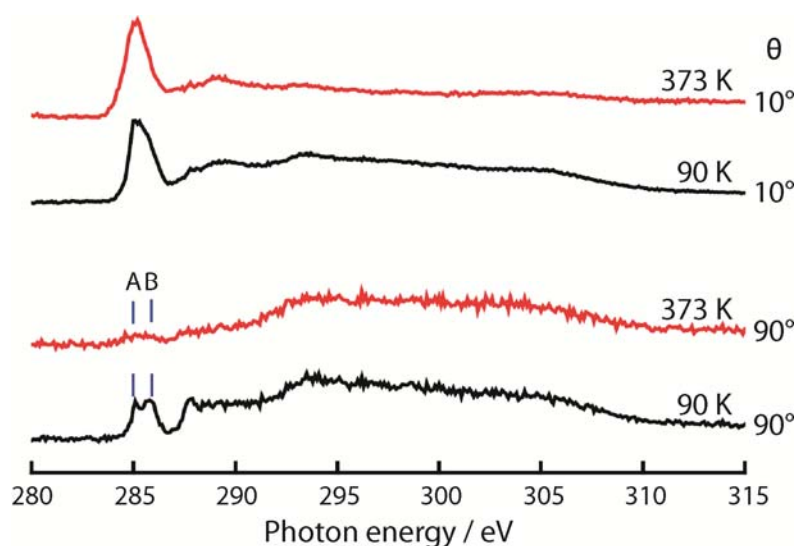


Figure 8. C K-edge NEXAFS spectra acquired at 10° and 90° angles of photon incidence θ for the co-adsorption of ~ 0.5 ML and ~ 0.7 ML of IB and PA on Au(111) at 90 K followed by annealing to 373 K.

Conclusions

In summary, phenylacetylene and iodobenzene react on smooth Au(111) under vacuum conditions to yield biphenyl and diphenyldiacetylene, the result of homocoupling, and, with appreciable selectivity, diphenylacetylene, the result of Sonogashira cross-coupling and the process of paramount interest in this work. These findings provide the first unambiguous demonstration that this heterogeneous cross-coupling chemistry is an intrinsic property of extended, metallic pure gold surfaces. The minimum necessary and sufficient conditions are co-adsorbed reactants on a clean well ordered gold surface: no other species, including charged (ionic) species are necessary to mediate the process. Roughened Au(111) is completely inactive towards all three reactions indicating that the availability of crystallographically well-defined adsorption sites is crucially important. In view of the many reported

correlations between single crystal reaction data and nanoparticle catalysis at the gas/solid interface (see for example the reviews by Ertl and Freund³⁴ and Somorjai et al.³⁵ it seems possible that pronounced particle size effects may arise when these coupling reactions are catalyzed by gold nanoparticles under practical conditions. Indeed Besson *et al.* have reported superior catalytic performance for larger Pt nanoparticles in solution compared to smaller ones.³⁶ High resolution XPS and NEXAFS spectroscopy demonstrate that the reactants are initially present as essentially flat-lying intact molecules. The temperature threshold for Sonogashira coupling coincides with that for C-I bond scission in the biphenyl, although this does not prove that C-I scission is the reaction-initiating step. The fractional order kinetics and low temperature associated with desorption of the Sonogashira product suggest that under our conditions it is formed at the boundaries of islands of adsorbed reactants and that its appearance in the gas phase is reaction rate limited.

Acknowledgments

The authors thank Silvano Lizzit, Sandra Gardonio and Michele Tranquillin for their assistance during the synchrotron experiments. V.K.K. acknowledges the award of a Gates Cambridge Scholarship. G.K. and A.C.P. acknowledge financial support from the UK Engineering and Physical Sciences Research Council. S.K.B. acknowledges financial support from Cambridge University; Trinity Hall, Cambridge; the UK Society of the Chemical Industry and the International Precious Metals Institute.

Supporting information available: Experimental methodology and calibration procedure used for estimating reaction selectivity; angle-resolved C K-edge NEXAFS spectra of the biphenyl homocoupling product at 373 K; iodine desorption spectrum; thermochemistry of H₂ vs HI desorption; thermochemistry of I atoms vs I₂ molecules desorption; pseudo-TOF estimation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874-922.
- (2) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133-173.
- (3) Hartwig, J. F. *Nature* **2008**, *455*, 314-322.
- (4) Plenio, H. *Angew. Chem. Int. Ed.* **2008**, *47*, 6954-6956.
- (5) Durand, J.; Teuma, E.; Gomez, M. *Eur. J. Inorg. Chem.* **2008**, 3577-3586.
- (6) de Souza, R.; Bittar, M. S.; Mendes, L. V. P.; da Silva, C. M. F.; da Silva, V. T.; Antunes, O. A. C. *Synlett* **2008**, 1777-1780.
- (7) Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 2886-2890.
- (8) Widegren, J. A.; Finke, R. J. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317-341.
- (9) Phan, N. T. S.; van der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609 – 679.
- (10) Kohler, K.; Kleist, W.; Prockl, S. S. *Inorg. Chem.* **2007**, *46*, 1876-1883.
- (11) Kanuru, V. K.; Humphrey, S. M.; Kyffin, J. M. W.; Jefferson, D. A.; Burton, J. W.; Armbrüster, M.; Lambert, R. M. *Dalton Trans.* **2009**, 7602-7605.
- (12) Gonzalez-Arellano, C.; Abad, A.; Corma, A.; Garcia, H.; Iglesias, M.; Sanchez, F. *Angew. Chem. Int. Ed.* **2007**, *46*, 1536-1538.
- (13) Gaikwad, A. V.; Holuigue, A.; Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G. *Chem. Eur. J.* **2007**, *13*, 6908-6913.

- (14) Thathagar, M. B.; Kooyman, P. J.; Boerleider, R.; Jansen, E.; Elsevier, C. J.; Rothenberg, G. *Adv. Synth. Catal.* **2005**, *347*, 1965-1968.
- (15) Durán Pachón, L.; Rothenberg, G. *Appl. Organomet. Chem.* **2008**, *22*, 288-299.
- (16) (a) He, L.; Wang, L. -C.; Sun, H.; Ni, J.; Cao, Y.; He, H. -Y.; Fan, K. -N. *Angew. Chem. Int. Ed.* **2009**, *48*, 9538-9541. (b) Fujitani, T.; Nakamura, I.; Akita, T.; Okumura, M.; Haruta, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 9515-9518. (c) Raptis, C.; Garcia, H.; Stratakis, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3133-3136. (d) Zhang, G.; Peng, Y.; Cui, L.; Zhang, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 3112-3115.
- (17) Stein, S. E. "Mass Spectra" in *NIST Chemistry WebBook*, Linstrom P.J.; Mallard, W.G., Eds.; NIST Standard Reference Database Number 69; National Institute of Standards and Technology, Gaithersburg MD, <http://webbook.nist.gov>, (retrieved January 10, 2010).
- (18) Wu, H. -J.; Hsu, H. -K.; Chiang, C. -M. *J. Am. Chem. Soc.* **1999**, *121*, 4433-4442.
- (19) Woodruff, D. P.; Delchar, T. A. *Modern Techniques of Surface Science*, 2nd ed.; Cambridge University Press: Cambridge, UK, 1994; pp 375-377.
- (20) Thathagar, M. B.; Beckers, J.; Rothenberg, G. *Green Chem.* **2004**, *6*, 215-218.
- (21) Celio, H.; Smith, K. C.; White, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 10422-10423.
- (22) Bugyi, L.; Oszkó, A.; Solymosi, F. *Surf. Sci.* **2003**, *539*, 1-13.
- (23) Syomin, D.; Koel, B. E. *Surf. Sci.* **2001**, *490*, 265-273.
- (24) Dougherty, D. B.; Lee, J.; Yates, J. T., Jr. *J Phys. Chem. B* **2006**, *110*, 20077-20080.
- (25) Carravetta, V.; Polzonetti, G.; Iucci, G.; Russo, M. V.; Paolucci, G.; Barnaba, M. *Chem. Phys. Lett.* **1998**, *288*, 37-46.

- (26) Polzonetti, G.; Carravetta, V.; Russo, M. V.; Contini, G.; Parent, P.; Laffon, C. *J. Electron. Spectrosc. Relat. Phenom.* **1999**, *98-99*, 175-187.
- (27) Iucci, G.; Carravetta, V.; Paolucci, G.; Goldoni, A.; Russo, M. V.; Polzonetti, G. *Chem. Phys.* **2005**, *310*, 43-49.
- (28) Iucci, G.; Carravetta, V.; Altamura, P.; Russo, M. V.; Paolucci, G.; Goldoni, A.; Polzonetti, G. *Chem. Phys.* **2004**, *302*, 43-52.
- (29) Stöhr, J.; Outka, D. A. *Phys. Rev. B* **1987**, *36*, 7891-7905.
- (30) Yang, M. X.; Xi, M.; Yuan, H. J.; Bent, B. E.; Stevens, P.; White, J. M. *Surf. Sci.* **1995**, *341*, 9-18.
- (31) Lee, A. F.; Chang, Z. P.; Hackett, S. F. J.; Newman, A. D.; Wilson, K. *J. Phys. Chem. C* **2007**, *111*, 10455-10460.
- (32) Solomon, J. L.; Madix, R. J.; Stöhr, J. *Surf. Sci.* **1991**, *255*, 12-30.
- (33) Kong, M. J.; Teplyakov, A. V.; Lyubovitsky, J. G.; Bent, S. F. *Surf. Sci.* **1998**, *411*, 286-293.
- (34) Ertl, G.; Freund, H. -J. *Phys. Today* **1999**, *52*, 32-38.
- (35) Somorjai, G. A.; Frei, H.; Park, J. Y. *J. Am. Chem. Soc.* **2009**, *131*, 16589-16605.
- (36) Besson, C.; Finney, E. E.; Finke R. G. *Chem. Mater.* **2005**, *17*, 4925-4938.

TOC GRAPHIC

