ChemComm

Coordination of gold cations to alkynyl ligands: - the role of metals, vinylidenes, di- and tri-auration

Journal:	*ChemComm*
Manuscript ID:	CC-COM-03-2015-002629.R1
Article Type:	Communication
Date Submitted by the Author:	29-Apr-2015
Complete List of Authors:	Ciano, Luisa; University of York, Chemistry Milner, Lucy; University of York, Department of Chemistry Mistry, Nimesh; University of York, Department of Chemsitry Pridmore, Natalie; University of York, Chemistry Townsend, Nell; University of Bristol, School of Chemistry Halliday, Connor; University of York, Chemistry Whitwood, Adrian; University of York, Department of Chemsitry Fey, Natalie; University of Bristol, School of Chemistry Lynam, Jason; University of York,

SCHOLARONE™
Manuscripts

Journal Name RSCPublishing

COMMUNICATION

Dispersion, solvent and metal effects in the binding of gold cations to alkynyl ligands:implications for Au(I) catalysis

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Luisa Ciano, [a] Natalie Fey[b*], Connor J. V. Halliday,[a] Jason M. Lynam[a*], Lucy M. Milner,[a] Nimesh Mistry,[a] Natalie E. Pridmore,[a] Nell S. Townsend[b] and Adrian C. Whitwood.[a]

The coordination modes of the $[Au(PPh_3)]^+$ cation to metal alkynyl complexes have been investigated. On addition to ruthenium, a vinylidene complex, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CPh\{AuPPh_3\})]^+$, is obtained while addition to a gold(III) compound gives di- and trinuclear gold complexes depending on the conditions employed. In the trinuclear species, a gold(I) cation is sandwiched between two gold(III) alkynyl complexes, suggesting that coordination of multiple C-C triple bonds to gold is facile.

Gold catalysts are effective reagents for activating multiple bonds towards intramolecular cycloaddition and nucleophilic attack. In addition to the growing number of synthetic applications of gold complexes in both the +1 and +3 oxidation states,[1] there is clear evidence that binding of two gold atoms to the unsaturated substrate (diauration) plays an important role in catalysis.[2] In the case of binding to arenes or alkenyl groups, two gold atoms may bind to form a "gem-diaurate" **A**,[2a, 3] terminal alkynes may be activated by formation of σ–π complex, **B**,[4] and it has been proposed that vinylidene complexes, **C**,[5] are key intermediates in the cyclisation of diynes. Indeed, all three binding modes have been proposed within a single catalytic cycle,[6] illustrating the flexibility of digold coordination to support key intermediates in C-C bond forming reactions.

Vinylidene complexes are important intermediates in a number of transition metal-mediated processes,[7] notably those involving the functionalisation of terminal alkynes, although typically these reactions have involved elements from Groups 6-9.[7-8] In these cases, the conversion of alkynes to their vinylidene tautomers has been shown to generate stable complexes, whereas this is not the case for gold.[9] There is, however, a continuum in behaviour between gem-diaurate-type structures, **D**, dinuclear σ-π complexes, **E**, and vinylidenes, **F**, which differ only in terms of the relationship between the position of $[M^2]$ and the alkynyl system. In the case where $[M^1]$ = Au, no structures of type **F** have been isolated and in the solid state σ-π complexes **E** are observed and **D** is a probable transition state for the exchange of gold atoms.[4f] However, evidence for mono-nuclear gold vinylidene complexes as intermediates in metal-catalysed reactions has been presented recently.[10] Insight into how a given combination of $[M^1]$ and $[M^2]$ affect relative stability of forms **D**, **E** and **F** will aid in the selection and optimisation of catalysts promoting reaction pathways involving these intermediates.

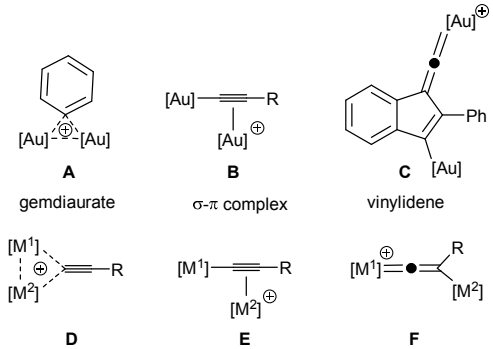
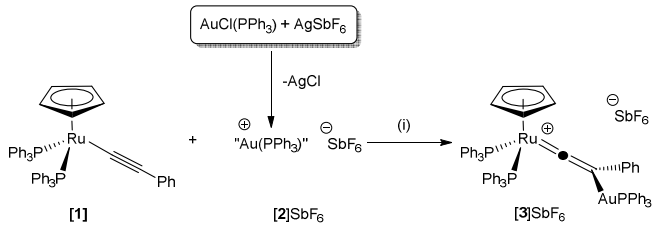


Figure 1. Binding modes of gold to unsaturated substrates

It was envisaged that by making the isolobal substitution of a proton by $[Au(PPh_3)]^+$ a vinylidene complex of type **F** with $[M^1]$ = Ru, $[M^2]$ = Au, $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CH\{AuPPh_3\})]^+$ would be a viable target. As complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CHR)]^+$ may be prepared from protonation of alkynyl complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(\text{-}C\equiv CR)]$,[11] a related reaction with "$[Au(PPh_3)]^+$" would provide a straightforward route to the desired complex.

Addition of the cationic species $[Au(PPh_3)]SbF_6$, [**2**]SbF_6, (generated *in situ* from the reaction of $[AuCl(PPh_3)]$ with $AgSbF_6$) to $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(\text{-}C\equiv CPh)]$, [**1**], in CH_2Cl_2 solution resulted in a colour change from yellow to orange (Scheme 1). Addition of Et_2O gave an orange precipitate identified as $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CPh\{AuPPh_3\})]SbF_6$, [**3**]$SbF_6$. The $^{13}C\{^1H\}$ NMR spectrum of $[\mathbf{3}]^+$ exhibited resonances typical of a vinylidene ligand, with a triplet observed for the ruthenium-bound carbon atom at δ 354.1 (t, $^2J_{PC}$ = 15.7 Hz), whereas the β-carbon atom was observed at δ 118.8 (d, $^2J_{PC}$ = 15.4 Hz) with the doublet coupling presumably arising from the single PPh_3 ligand bound to gold. A peak in the ESI-MS at *m/z* 1251.2225 with the correct isotope pattern confirmed the presence of a complex containing both ruthenium and gold atoms as well as the additional ancillary ligands.

This journal is © The Royal Society of Chemistry 2012



Scheme 1. (i) CH_2Cl_2 solution, 1 hr, r.t.

The postulated structure of [**3**]$^+$ was further supported by DFT calculations (see ESI† for computational details), finding geometry **F** lowest in energy, with **E** 19 kJ mol^{-1} higher in energy, while optimisation of **D** remained unsuccessful; with restraints, this lies 90 kJ mol^{-1} above **F** (Table 1). The formation of [**3**]SbF_6 demonstrates that it is possible to form vinylidene complexes **F** with [M^1] = Ru and [M^2] = Au and that the reaction with [Au(PPh$_3$)]$^+$ is analogous to the addition of other electrophiles to [**1**].[11-12]

Table 1: Metal effect on preferred coordination mode with [M^2] = [Au(PPh$_3$)]$^+$, BP86 calculated relative potential energies (kJ mol^{-1})

[M^1] =	CpRu(PPh$_3$)$_2$]$^+$	[Au(PPh$_3$)]$^+$	[Au(^{t}BuC^N^C^{t}Bu)]$^+$
D	(90)[a]	0	(10)[a]
E	19	10	0.0
F	0	(78)[a]	(59)[a]

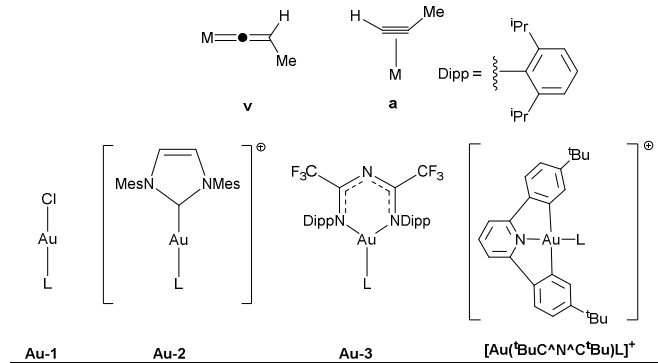
[a] Angle restraints used, see Table S3.2.† for B3LYP energies.

For gold(I) alkynyl complexes with coordinated gold cations, the σ-π binding of type **E** is observed most frequently in the solid state,[4] and rapid exchange of environments through a low energy gem-diaurate species **D** has been proposed.[4f] Indeed, an examination of the structure of σ-π complexes, **E**, indicates that in most cases a distortion is observed, with the π-bound gold atom being closer to the gold-bound carbon of the alkynyl group (see S2.5†). Furthermore, our calculations (Table 1) indicate that when [M^1] = [M^2] = Au(PPh$_3$) the gem-diaurate complex **D** is actually lower in energy than isomer **E**. For this complex, powder X-ray diffraction experiments predict an Au-Au distance of 3.08 Å,[13] in excellent agreement with that found in the calculated structure of **D** (3.09 Å); in DFT-calculated structure **E** it is predicted to be 3.24 Å.

The effect of the gold oxidation state on the relationship between **D**, **E**, and **F** has not been explored so far. Our recent calculations have indicated that d^8 systems are better at stabilising vinylidene ligands than their d^{10} analogues, so gold(III) might be more effective at stabilising vinylidene ligands than gold(I).[9a] Further calculations, summarised in Table 2 for a methyl-substituted model alkyne, also suggested that a smaller energy difference between alkyne and vinylidene tautomers could be achieved for gold(III) than for gold(I). However, the calculated predictions for other substitution patterns were less clear, with carbocationic species observed instead of alkynes (Table S3.2†). Comparing the three binding modes computationally for two gold complexes (Table 1), the simple gold(I) alkynyl favours **D**, while the gold(III) complex favours **E**, and **F** becomes comparatively less unfavourable. Experimental confirmation of the favoured form would provide validation for our computational predictions, as well as giving insight into the role of [M^1] in determining the relative preference.

The cyclometallated gold(III) alkynyl complex [Au(^{t}BuC^N^C^{t}Bu)(C≡CPh)], [**4**], previously prepared by Yam and co-workers was selected as a precursor for this study (Scheme 2).[14] In addition, Bochmann has demonstrated that this pincer ligand is effective at stabilising gold complexes with hydride[15] and η^2-alkene ligands.[16] Furthermore, Tilset and co-workers have shown that

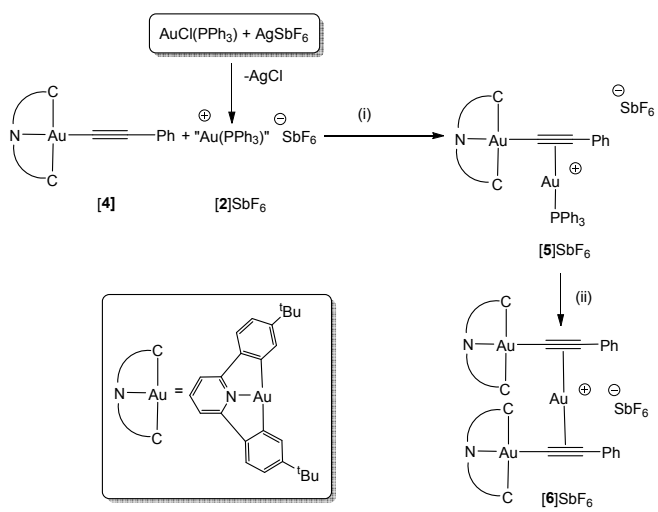
Table 2: Calculated tautomer energy differences, $\Delta E_{v\text{-}a}$ (kJ mol^{-1}) for different metal complexes.[9a] (See also Table S3.2.†)



	Au-1[9a]	Au-2[9a]	Au-3[9a]	[Au(^{t}BuC^N^C^{t}Bu)L]$^+$
$\Delta E_{v\text{-}a}$ / kJ mol^{-1}	39	61	36	13

cationic Au(III) alkene complexes may be prepared,[17] and that a cyclometallated gold(III) complex may promote the insertion of ethene into a metal-oxygen bond.[18]

Reaction of a toluene solution of [**4**] with [**2**]SbF_6 resulted in the formation of a yellow precipitate of the Au(III)-Au(I) σ-π complex, [**5**]SbF_6 (Scheme 2). Although the poor solubility of [**5**]SbF_6 in C_6D_6 and subsequent reactivity observed in CD_2Cl_2 (*q.v.*) precluded a detailed NMR study, the identity of the complex was confirmed by HR-MS (where a peak for the molecular ion was observed) and single crystal X-ray diffraction of the C_6D_6 (Figure 2a) and $C_6H_5CH_3$† solvates.



Scheme 2. (i) Toluene 16 hrs, r.t., (ii) CH_2Cl_2, 16 hrs, r.t. - [Au(PPh$_3$)$_2$]SbF_6.

Repeating the reaction but using CH_2Cl_2 as solvent for [**4**], or dissolving isolated [**5**]SbF_6 in CD_2Cl_2, resulted in a colour change from yellow to green, indicating formation of a different product, identified as [**6**]SbF_6 (Scheme 2). Slow diffusion of Et_2O into these solutions afforded green crystals suitable for study by X-ray diffraction. The resulting structural determination (Figure 2b) demonstrated that an unusual reaction had occurred to give a trimetallic complex, [**6**]SbF_6, in which a single Au(I) cation was sandwiched between two Au(III) alkynyl groups. In the $^{13}C\{^1H\}$ NMR spectrum, resonances for the two alkynyl carbon atoms were observed at δ 92.8 (Au-*C*≡) and δ 114.8 (C≡*C*-Ph) that exhibited small coordination shifts (Δδ 0.1 and 13.4 respectively, identified

This journal is © The Royal Society of Chemistry 2012

with the aid of a ^{13}C-enriched sample). A peak in the ESI-MS of [**6**]SbF_6 at *m/z* 1475.4042, with the correct isotopic distribution pattern, confirmed the presence of the trinuclear framework. Analysis of the supernatant demonstrated that $[Au(PPh_3)_2]^+$ has been formed accounting for the mass balance of the reaction.

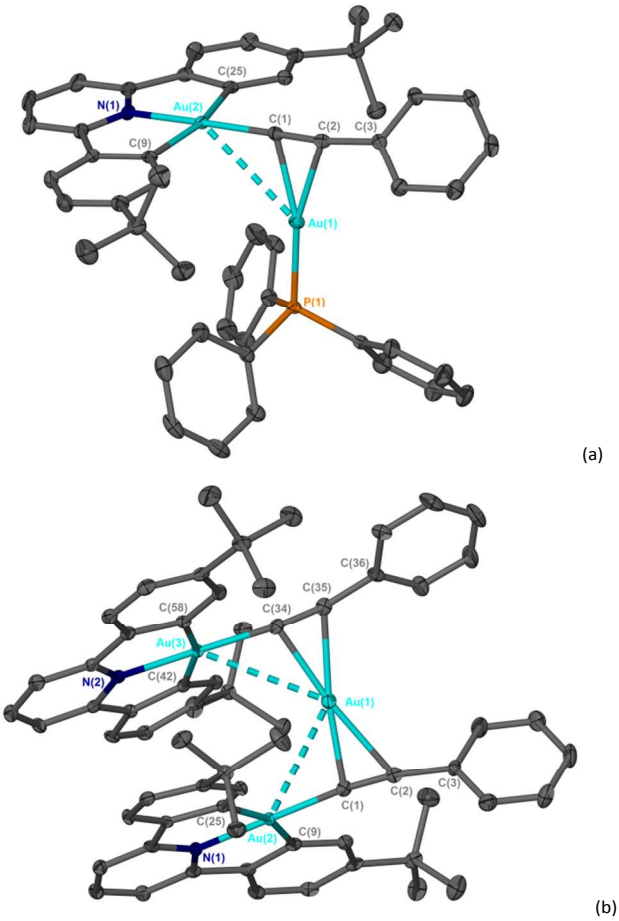


Figure 2. X-ray structure of (a) the [**5**]$^+$ cation and (b) the [**6**]$^+$ cation. Thermal ellipsoids are shown at the 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths for [**5**]$^+$ / Å Au(1)-Au(2) 3.29377(14), Au(1)-C(1) 2.221(3), Au(1)-C(2) 2.256(3), Au(2)-C(1) 1.984(3). Selected bond lengths for [**6**]$^+$ / Å Au(1)-Au(2) 3.2477(5), Au(1)-Au(3) 3.3687(5), Au(1)-C(1) 2.145(4), Au(1)-C(2) 2.357(4), Au(1)-C(34) 2.175(4), Au(1)-C(35) 2.255(4), Au(2)-C(1) 1.975(4), Au(3)-C(34) 1.977(4).

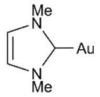
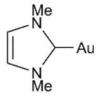
In the structure of [**6**]$^+$ observed crystallographically, the Au(I) cation is bound asymmetrically to the two alkynyl ligands; in both cases the Au(I) is closer to the Au(III)-coordinated carbon atom, but one of these interaction is more marked than any example reported to date [Au(1)-C(1) 2.145(4) Å, Au(1)-C(2) 2.357(4) Å]. In [**5**]$^+$ and [**6**]$^+$ there are intermolecular π–π interactions between the C^N^C-pincer ligands, however, in the case of [**6**]$^+$ there is also evidence for intramolecular interactions between the pyridyl and aryl groups (S2.4†). It seems likely that these intramolecular π–π interactions (along with the formation of $[Au(PPh_3)_2]^+$) are favouring formation of the trinuclear gold complex.

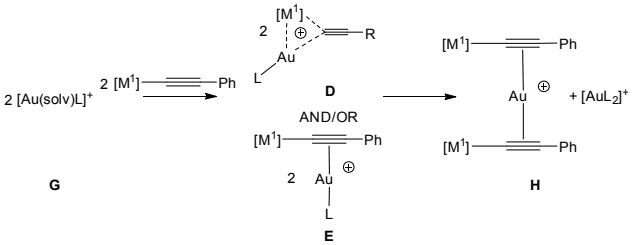
To the best of our knowledge [**6**]$^+$ is the first example of a species with three gold atoms in a "σ–π^2–σ-complex".[19] A single gold(I) binding two alkyne ligands has been reported with the strained cyclooctyne,[20] and when a preorganised supramolecular diyne is used.[21] These factors presumably facilitate binding to the gold by compensating for the bonding of the alkyne to such a weakly π-basic metal and help to overcome the entropic penalty. In addition, a structure in which a gold(I) cation is coordinated between two alkyne units has been shown to be a transition state for the exchange of gold between two alkyne units in a mechanistic study of gold(I) catalysis.[5d] This, together with the analysis of complexes of form **D** and **E** reported here, suggests that the potential energy surface for the binding of gold to alkynes is likely to be flat, with small perturbations determining whether a given species is a minimum or a transition state. Therefore, the factors controlling the coordination of gold to alkynes were investigated in more detail.

Calculations of simple fragment binding energies illustrate that the binding of $[Au(PPh_3)]^+$ to [**4**], giving [**5**]$^+$, is more favourable than binding to benzene and PhC≡CH (Table S3.4†) reinforcing the notion that binding of gold cations to alkynyl ligands is more favourable than binding to alkynes.[3a] The calculations also show clear energy differences between the binding of benzene and CH_2Cl_2, helping to explain the observed experimental solvent effect.

The difference in the calculated energies of [**5**]$^+$ and [**6**]$^+$ is small and dispersion corrections favour [**6**]$^+$ slightly (by 4-6 kJ mol^{-1}), while [**5**]$^+$ is favoured if such corrections are not included (Tables S3.5, S3.6†). The effect of dispersion corrections on the thermodynamic preference for [**6**]$^+$ support the hypothesis that intramolecular π–π interactions are responsible for favouring the formation of the trinuclear scaffold.

Table 3: Calculated energy balance between complexes **D/E** and **H** (Scheme 3) with different substituents [M^1] in kJ mol^{-1}. (BP86-D3BJ ΔG + ΔE_{solv}, kJ mol^{-1} see Table S3.8† for B3LYP-D3BJ data.)

Solvent	L	[M^1]	G	D/E	H	D/E-H
C_6H_6	PPh_3	[Au(^{t}BuC^N^C^{t}Bu)]$^+$	0	-207	-211	+4
CH_2Cl_2	PPh_3	[Au(^{t}BuC^N^C^{t}Bu)]$^+$	0	-234	-240	+6
C_6H_6	PPh_3	H	0	-47	-43	-4
CH_2Cl_2	PPh_3	H	0	-100	-99	-1
C_6H_6	PPh_3	Au(PPh_3)	0	-200	-192	-8
CH_2Cl_2	PPh_3	Au(PPh_3)	0	-219	-213	-6
C_6H_6	PPh_3		0	-184	-196	+12
CH_2Cl_2	PPh_3		0	-202	-216	+14
C_6H_6	PPh_3	Au(IPr)	0	-225	-211	-14
CH_2Cl_2	PPh_3	Au(IPr)	0	-233	-223	-10



Scheme 3. Model reaction used to explore preference for gold(I) complexes.

We have also explored the energy balance between the σ-π complex **E** (for some complexes, this optimises to the gem complex **D**, discussed in greater detail in the ESI) and the trinuclear gold(I) complex **H** with a range of different substituents and ligands (Scheme 3, Tables 4 and S3.8†). Remarkably, the calculations predict that for other compounds with gold in the +1 oxidation state and supported by phosphine or *N*-heterocyclic ligands, σ–π^2–σ

complexes **H** might also be accessible. Indeed, the predicted energy balance between these species and **D**/**E**, are small and probably within the limits of reliability of the theoretical method used. The calculations therefore predict that it should be possible to observe complexes of type **H** in other ligand systems.

To test this hypothesis, a sample of [Au(-C≡CPh)(PPh_3)], [**7**], was treated with [**2**]SbF_6 in CD_2Cl_2 solution. An ESI-MS spectrum of the reaction mixture confirmed the presence of $[Au(PPh_3)_2]^+$ and an intense peak at *m/z* 1019.1556 was consistent with the formation of either **D** or **E** with $[M^1] = [M^2] = AuPPh_3$. A less intense peak at *m/z* 1317.1643 was assigned to the trinuclear complex **H** ($[M^1]$ = Au(I){PPh_3}), supporting predictions from the DFT calculations that the trinuclear framework may not be limited to the gold(III) example. The $^{31}P\{^1H\}$ NMR spectrum exhibited a sharp resonance for $[Au(PPh_3)_2]^+$ and a very broad feature at δ 37.5 which on cooling to 195 K decoalesced to a number of new resonances. Repeating the reaction with a ^{13}C-enriched sample, [Au(-^{13}C≡CPh)(PPh_3)], [**7-^{13}C**], resulted in a number of these resonances exhibiting P-C couplings (S1.8†). Although the NMR data do not unambiguously demonstrate the formation of a trinuclear complex, they do indicate that a number of gold alkynyl phosphine complexes are present and undergoing rapid exchange. A detailed investigation of this behaviour is currently underway.

These results have demonstrated that the key factor controlling the preference between isomers **D**, **E** or **F** is the nature of $[M^1]$. Presumably, the more π-basic ruthenium(II) and crowded environment in $[\mathbf{3}]^+$ effectively stabilizes the vinylidene ligand, whereas (at least in the systems explored to date) neither Au(I) nor Au(III) are suitably π-basic and/or bulky. The observation of trinuclear complexes for both gold(I) and gold(III) complexes raises the possibility that coordination by more than two gold atoms to a substrate may be involved in catalytic processes. In the case of the gold(III) complexes, dispersion interactions between the two pincer ligands ensure that the trinuclear complex is the lowest energy structure, and although these effects are not as pronounced in the gold(I) analogue, there is only a small difference in energy between complexes of type **D**/**E** and **H**. Furthermore, our data suggest that the solvent may play a key role in determining the nuclearity of gold-containing complexes and this should also be considered as an important factor in catalysis.

Notes and references

[a] Department of Chemistry, University of York, York, YO10 5DD. E-mail: jason.lynam@york.ac.uk
[b] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS. E-mail natalie.fey@bristol.ac.uk.

† Electronic Supplementary Information (ESI) available: Experimental and computational details, X-ray structure determinations including a comparison of structural metrics of this class of compounds, further discussion of computational data including a more complete evaluation of method effects and xyz coordinates of optimised geometries. See DOI: 10.1039/c000000x/

We thank the University of York (pump-prime funding) and the EPSRC (studentship to LMM) for funding and the Centre for Computational Chemistry, University of Bristol, for computing resources. We are grateful to Professor Paul Low (University of Western Australia) for helpful discussions.

1. (a) A. S. K. Hashmi, T. D. Ramamurthi and F. Rominger, *J. Organomet. Chem.*, 2009, **694**, 592; (b) G. Zhang, Y. Peng, L. Cui and L. Zhang, *Angew. Chem. Int. Ed.*, 2009, **48**, 3112. (c) L. T. Ball, G. C. Lloyd-Jones and C. A. Russell, *J. Am. Chem. Soc.*, 2013, **136**, 254; (d) W. J. Wolf, M. S. Winston and F. D. Toste, *Nat. Chem.*, 2014, **6**, 159;
2. (a) A. Gomez-Suarez and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2012, **51**, 8156 (b) D. Weber and M. R. Gagne, *Chem. Sci.*, 2013, **4**, 335; (c) I. Braun, A. M. Asiri and A. S. K. Hashmi, *ACS Catalysis*, 2013, **3**, 1902; (d) C. Obradors and A. M. Echavarren, *Chem. Commun.*, 2014, **50**, 16; (d); (e) A. S. K. Hashmi, *Acc. Chem. Res.*, 2014, **47**, 864.
3. (a) P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk and F. D. Toste, *J. Am. Chem. Soc.*, 2008, **130**, 4517; (b) S. Flugge, A. Anoop, R. Goddard, W. Thiel and A. Furstner, *Chem. Eur. J.*, 2009, **15**, 8558; (c) D. Weber, M. A. Tarselli and M. R. Gagne, *Angew. Chem. Int. Ed.*, 2009, **48**, 5733; (d) H. Schmidbaur and A. Schier, *Organometallics*, 2010, **29**, 2.
4. (a) T. N. Hooper, M. Green and C. A. Russell, *Chem. Commun.*, 2010, **46**, 2313; (b) A. Himmelspach, M. Finze and S. Raub, *Angew. Chem. Int. Ed.*, 2011, **50**, 2628; (c) T. J. Brown and R. A. Widenhoefer, *J. Organomet. Chem.*, 2011, **696**, 1216; (d) T. J. Brown and R. A. Widenhoefer, *Organometallics*, 2011, **30**, 6003; (e) A. Grirrane, H. Garcia, A. Corma and E. Álvarez, *ACS Catalysis*, 2011, **1**, 1647; (f) R. E. M. Brooner, T. J. Brown and R. A. Widenhoefer, *Chem. Eur. J.*, 2013, **19**, 8276; (g) R. E. M. Brooner and R. A. Widenhoefer, *Angew. Chem. Int. Ed.*, 2013, **52**, 11714; (h) A. S. K. Hashmi, T. Lauterbach, P. Noesel, M. H. Vilhelmsen, M. Rudolph and F. Rominger, *Chem. Eur. J.*, 2013, **19**, 1058. (i) C. Obradors and A. M. Echavarren, *Chem. Eur. J.*, 2013, **19**, 3547; (j) A. Gomez-Suarez, S. Dupuy, A. M. Z. Slawin and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2013, **52**, 938; (k) A. Grirrane, H. Garcia, A. Corma and E. Alvarez, *Chem. Eur. J.*, 2013, **19**, 12239; (l) L. Jasikova and J. Roithova, *Organometallics*, 2013, **32**, 7025; (m) A. Homs, C. Obradors, D. Lebœuf and A. M. Echavarren, *Adv. Synth. Catal.*, 2014, **356**, 221; (n) (k) A. Gimeno, A. B. Cuenca, S. Suarez-Pantiga, C. R. de Arellano, M. Medio-Simon and G. Asensio, *Chem. Eur. J.*, 2014, **20**, 683; (l)
5. (a) L. W. Ye, Y. Z. Wang, D. H. Aue and L. M. Zhang, *J. Am. Chem. Soc.*, 2012, **134**, 31; (b) A. S. K. Hashmi, I. Braun, M. Rudolph and F. Rominger, *Organometallics*, 2012, **31**, 644; (c) M. M. Hansmann, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2013, **52**, 2593; (d) M. H. Vilhelmsen and A. S. K. Hashmi, *Chem. Eur. J.*, 2014, **20**, 1901; (e) J. Bucher, T. Stößer, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2015, **54**, 1666; (f) P. Nösel, V. Müller, S. Mader, S. Moghimi, M. Rudolph, I. Braun, F. Rominger and A. S. K. Hashmi, *Adv. Synth. Catal.*, 2015, **357**, 500; (g) J. Bucher, T. Stosser, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2015, **54**, 1666.
6. K. Graf, P. D. Hindenberg, Y. Tokimizu, S. Naoe, M. Rudolph, F. Rominger, H. Ohno and A. S. K. Hashmi, *Chemcatchem*, 2014, **6**, 199.
7. (a) B. M. Trost and A. McClory, *Chem. Asian J.*, 2008, **3**, 164; (b) J. M. Lynam, *Chem. Eur. J.*, 2010, **16**, 8238.
8.(a) B. M. Trost, M. U. Frederiksen and M. T. Rudd, *Angew. Chem. Int. Ed.*, 2005, **44**, 6630; (b) C. Bruneau and P. H. Dixneuf, *Angew. Chem. Int. Ed.*, 2006, **45**, 2176; (c) D. G. Johnson, J. M. Lynam, N. S. Mistry, J. M. Slattery, R. J. Thatcher and A. C. Whitwood, *J. Am. Chem. Soc.*, 2012, **135**, 2222.
9. (a) M. M. Hansmann, F. Rominger and A. S. K. Hashmi, *Chem. Sci.*, 2013, **4**, 1552; (b) O. J. S. Pickup, I. Khazal, E. J. Smith, A. C. Whitwood, J. M. Lynam, K. Bolaky, T. C. King, B. W. Rawe and N. Fey, *Organometallics*, 2014, **33**, 1751.
10.V. Lavallo, G. D. Frey, S. Kousar, B. Donnadieu and G. Bertrand, *P. Natl. Acad. Sci. USA*, 2007, **104**, 13569.
11. M. I. Bruce and R. C. Wallis, *Aust. J. Chem.*, 1979, **32**, 1471.
12. (a) M. I. Bruce, A. G. Swincer and R. C. Wallis, *J. Organomet. Chem.*, 1979, **171**, C5; (b) M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, 1980, **33**, 1471.
13.V. L. Korsunsky, K. I. Grandberg, E. I. Smyslova and T. V. Baukova, *J. Organomet. Chem.*, 1987, **335**, 277.
14.(a) K. M.-C. Wong, L.-L. Hung, W. H. Lam, N. Zhu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2007, **129**, 4350; (b) V. W.-W. Yam, K. M.-C. Wong, L.-L. Hung and N. Zhu, *Angew. Chem. Int. Ed.*, 2005, **44**, 3107.
15. D.-A. Roşca, D. A. Smith, D. L. Hughes and M. Bochmann, *Angew. Chem. Int. Ed.*, 2012, **51**, 10643.
16. N. Savjani, D.-A. Roşca, M. Schormann and M. Bochmann, *Angew. Chem. Int. Ed.*, 2013, **52**, 874.
17. E. Langseth, M. L. Scheuermann, D. Balcells, W. Kaminsky, K. I. Goldberg, O. Eisenstein, R. H. Heyn and M. Tilset, *Angew. Chem. Int. Ed.*, 2013, **52**, 1660.
18. E. Langseth, A. Nova, E. A. Tråseth, F. Rise, S. Øien, R. H. Heyn and M. Tilset, *J. Am. Chem. Soc.*, 2014, **136**, 10104.
19. Examples of gold bridging ruthenium and rhenium alkynyl complexes have been reported see C. S. Griffith and G. E. Koutsantonis, *Aust. J. Chem.*, 2012, **65**, 698 and G A. Carriedo, D. Miguel, V. Riera and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1987, 2867 respectively.
20. (a) A. Das,C. Dash, M. Yousufuddin, M. A.Celik, G. Frenking and H. V. R Dias, *Angew. Chem. Int. Ed.*, 2012, **51**, 3940. (b) A. Das, C. Dash, M. A. Celik, M. Yousufuddin, G. Frenking and H. V. R. Dias, *Organometallics*, 2013, **32**, 3155.
21. S.-Kong Yip, E. C.-C. Cheng, L.-H. Yuan, N. Zhu and V. W.-W. Yam, *Angew. Chem. Int. Ed.*, 2004, **43**, 4957.

This journal is © The Royal Society of Chemistry 2012