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Introduction

Silver acetylides, first isolated in 1865,¹ are finding renewed interest in organic synthesis, with recent reports of $C-C^2$ and $C-Si^3$ bond coupling applications and use in copper(I)catalyzed cycloaddition reactions of silver acetylides and azides.⁴ Despite these promising developments, a key challenge in establishing robust synthetic methods involving organosilver reagents is that the relationship between structure and reactivity is generally ill defined. Thus the role of auxiliary ligands, solvent and the nature of the reactive organosilver species (*e.g.* monomer *versus* cluster) are not well understood. Indeed a similar situation holds true for the C-C bond coupling reactions of copper acetylides, with examples of welldefined clusters giving rise to products being rare. Exceptions include reductive elimination of the mixed coupling product

ArC \equiv CR *via* thermolysis of mixed aryl-alkynyl copper clusters Ar₄Cu₆(C \equiv CR)₂⁵ and Glaser⁶ coupling reactions of di-copper substituted silicotungstates.⁷

Electrospray ionisation (ESI) in conjunction with multistage mass spectrometry (MS^n) experiments⁸ to has been used to examine the fundamental unimolecular and bimolecular C-C bond coupling reactions of size selected silver cluster ions.9-11 In an earlier study the silver hydride cluster Ag₄H⁺ was shown to mediate Wurtz coupling¹² of allylbromide via the sequential reactions shown in eqn 1-3.9a Subsequent work highlighted that this and other silver clusters can also promote C-C bond coupling of allyl iodide^{9d,e} and allyl bromide,^{9e} as shown for allyliodide reacting with Ag_5^+ (eqn 4 and 5) and Ag_4H^+ (eqn 6–8, where R = allyl). The organometallic cations, (C_3H_5) - Ag_x^+ (where x = 2 and 4), play a key role in the final sp^3-sp^3 C-C bond coupling step (eqn 5 and 8). In order to better understand this final step, the reactions of CH₃Ag₂⁺ and allyliodide (eqn (8), where R = Me) were studied using a combination of experiment and Density Functional Theory (DFT) calculations, which highlighted that these reactions involved oxidative addition followed by reductive elimination, with the second silver centre playing a key role in oxidative addition.¹⁰ Finally, ESI of silver hexynyl produces silver hexynyl cluster cations, $[(C_4H_9C = CAg)_nAg]^+$, which upon collision-induced dissociation (CID) undergo a range of reactions including

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sp–sp³ Coupling reactions of alkynylsilver cations, RC \equiv CAg₂⁺ (R = Me and Ph) with allyliodide[†]

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Alkynylsilver cations, $RC \equiv CAg_2^+$ (where R = Me and Ph) have been prepared in the gas phase using multistage mass spectrometry experiments in a quadrupole ion trap mass spectrometer. Two methods were used: (i) electrospray ionisation (ESI) of a mixture of AgNO₃ (in MeOH/H₂O/acetic acid) and the alkyne carboxylic acid to yield the appropriate silver acetylide cations RC=CAq2+, via a facile decarboxylation of the RC=CCO₂Ag₂⁺ precursor; (ii) ESI of silver acetylides, RC=CAg, which yields a cluster of the type, [(RC=CAq)₁₂Aq₂CI]⁺. Regardless of the method of preparation, these alkynylsilver cations, RC=CAq₂⁺, undergo ion-molecule reactions with allyliodide to yield the ionic products Ag_2^{\dagger} and [(RC==CCH₂CH==CH₂)Ag]⁺. The CID spectrum of [(PhC==CCH₂CH==CH₂)Ag]⁺ was compared to that of an authentic sample of the silver adduct of 5-phenyl-1-penten-4-yne. Both ions fragment to yield Ag⁺ and the radical cation, PhC=CCH₂CH=CH₂+', confirming that C-C bond coupling has taken place in the gas phase. DFT calculations were carried out on these C-C bond coupling reactions for the system R = Me. The reaction is highly exothermic and involves the initial coordination of the allyliodide to both silver atoms, with the iodine coordinating to one atom and the alkene moiety coordinating to the other. The overall mechanism of C-C bond coupling involves oxidative addition of the allyliodide followed by reductive elimination of RC=CCH₂CH=CH₂, to ultimately yield two sets of reaction products: (i) Aq_2I^+ and RC=CCH₂CH=CH₂; and (ii) [(RC=CCH₂CH=CH₂)Ag]⁺ and AgI.

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[†]Electronic supplementary information (ESI) available: (a) Cartesian coordinates for structures of ions and neutrals; (b) Fig. S1 and S2. See DOI: 10.1039/c2dt32143b

reductive elimination to give the Glaser product *via* sp-sp C–C bond coupling (eqn 9, for n = 3 and 4).^{11,13}

$$Ag_4H^+ + CH_2 = CHCH_2Br \rightarrow Ag_4Br^+ + CH_2 = CHCH_3$$
(1)

$$Ag_4Br^+ + CH_2 = CHCH_2Br \rightarrow Ag_4Br_2(C_3H_5)^+$$
(2)

$$\begin{array}{l} \operatorname{Ag_4Br_2(C_3H_5)^+} + \operatorname{CH_2=CHCH_2Br} \to \\ \operatorname{Ag(1, 5-hexadiene)^+} + \operatorname{Ag_3Br_3} \end{array} \tag{3}$$

$$Ag_5^+ + CH_2 = CHCH_2I \rightarrow Ag_4(C_3H_5)^+ + AgI$$
 (4)

$$C_{3}H_{5})Ag_{4}^{+} + CH_{2} = CHCH_{2}I \rightarrow Ag_{4}I^{+} + (CH_{2} = CHCH_{2})_{2} (5)$$

$$Ag_4H^+ + CH_2 = CHCH_2I \rightarrow Ag_4I^+ + CH_2 = CHCH_3$$
 (6)

$$Ag_4I^+ + CH_2 = CHCH_2I \rightarrow Ag_2(C_3H_5)^+ + Ag_2I_2$$
(7)

$$RAg_{2}^{+} + CH_{2} = CHCH_{2}I \rightarrow Ag_{2}I^{+} + RCH_{2}CH = CH_{2}$$
 (8)

$$(C_4H_9C \equiv CAg)_n Ag^+ \rightarrow (C_4H_9C \equiv CAg)_{n-2} Ag_3^+ + (C_4H_9C \equiv C)_2$$
(9)

Here we use a combination of mass spectrometry experiments and DFT calculations to explore the bimolecular sp-sp³ C-C bond coupling reactions between alkynylsilver cations, $RC \equiv CAg_2^+$ and allyliodide.

Experimental

A

Reagents

Silver nitrate, 2-butynoic acid, phenyl propiolic acid and allyl iodide were obtained from Aldrich and used without further purification and dissolved in appropriate solvents (MeOH). The following gases were used in the mass spectrometry experiments: helium (Ultra High Purity, BOC) as the bath gas; nitrogen (High purity, BOC) as the auxiliary gas.

Synthesis

Silver phenylacetylide was synthesized by the method of Létinois-Halbes et al.13 1-(Pent-4-en-1-ynyl)benzene was prepared via the procedure of Bieber and co-workers.^{14a} Briefly, CuI (22 mg, 12 mmol), K₂CO₃ (0.65 g, 4.7 mmol) and Na₂SO₃ (0.30 g, 2.4 mmol) were suspended in DMSO (4.5 mL). To this was added phenylacetylene (0.50 mL, 4.6 mmol) and allyl bromide (0.59 mL, 6.8 mmol) respectively. The mixture was stirred in a closed atmosphere for 40 h, where the colour turned from bright yellow to dull brown. The mixture was then partitioned between water (15 mL) and pentane (3×15 mL). The combined organic layers were dried over Na₂SO₄, and concentrated under reduced pressure. ¹H NMR of the residue indicated the product and starting acetylene ratio as 2:1. The residue was passed through a plug of silica gel (pentane), followed by removal of starting acetylene under high vacuum, to give the desired ene-yne as a colourless liquid (0.24 g, 37%). ¹H NMR (400 MHz, CDCl₃) δ 3.18 (dt, J 5.3, 1.8, 2H), 5.15 (dq, J 10.0, 1.7, 1H), 5.39 (dq, J 17.0, 1.8, 1H), 5.89 (ddt, J 16.9, 10.0, 5.3, 1H), 7.25-7.30 (m, 3H), 7.39-7.43 (m, 2H). ¹³C NMR

(100 MHz, CDCl₃) δ 23.7, 82.9, 86.5, 116.2, 123.7, 127.7, 128.2, 131.6, 132.4. These spectral data matched the literature values.^{14b}

Mass spectrometry

Mass spectrometry experiments were conducted using a modified Finnigan LCQ quadrupole ion trap mass spectrometer equipped with a Finnigan ESI source, as described previously.¹⁵ Two different types of ESI solutions were prepared:

Method (a) AgNO₃/RC \equiv CCO₂H: a mixture of AgNO₃ (in MeOH), and the appropriate propiolic acid, RC \equiv CCO₂H (R = Me or Ph), in MeOH was prepared at a ratio of *ca.* 1:2. The resulting mixture was diluted with methanol to a maximum concentration of *ca.* 1 mM of the acid.

Method (b): the silver phenylacetylide, PhC=CAg, (*ca.* 10 mg) was dissolved in acetonitrile/H₂O (50 to 50 ratio, 10 mL) and the resulting mixture was diluted to a maximum concentration of *ca.* 1 mM of silver phenylacetylide.

The resultant ESI solutions were injected into the ESI source at a flow rate of approximately 5 μ L min⁻¹. Typical electrospray source conditions involved needle potentials of 4.5–5.0 kV and heated capillary temperatures of 180–200 °C. Extensive tuning of the electrospray conditions was often required due to the low signal-to-noise ratio and/or low abundance of some species. Mass selection, collisional activation and ion-molecule reactions were carried out using the 'advanced scan' function of the LCQ software, which allows the Q value and the reaction time to be varied.

Gas phase synthesis of the alkynylsilver cations, $RC \equiv CAg_2^{+1}$ (WHERE R = Me, AND Ph). Two methods were used: (i) $[(RC \equiv CAg)_n Ag]^+$ cluster ions were formed from the ESI solution [method (a)] described above and arise from a facile decarboxylation of the carboxylate precursors $[(RC \equiv CCO_2Ag)_nAg]^{\dagger}$ (e.g. ESI Fig. S1⁺). The facile decarboxylation of copper and silver acetylides have been previously studied¹⁵ and the reverse reaction, carboxylation of copper and silver acetylides has also been studied.16 Decarboxylation of metal carboxylates has been extensively used previously to make coinage metal organometallic anions and cations^{10,17} and was used here to prepare R = Me and Ph (eqn 10); (ii) CID of the silver acetylide cluster [(RC=CAg)₁₂Ag₂Cl]^{+,11} formed from ESI solution in section (b) described above, to form smaller clusters $[(RC \equiv CAg)_n Ag]^+$ (where n = 4-6) and subsequent CID on these clusters (eqn 11) generates RC=CAg2⁺ amongst others. We have previously described the CID reactions of silver acetylides clusters ions (where R = Bu)¹¹ and this method was used to prepare R = Ph.

$$RC \equiv CCO_2 Ag_2^+ \to RC \equiv CAg_2^+ + CO_2$$
(10)

$$(\mathbf{RC} = \mathbf{CAg})_n \mathbf{Ag}^+ \to \mathbf{RC} = \mathbf{CAg_2}^+ + (\mathbf{RC} = \mathbf{CAg})_{n-1}$$
(11)

ION-MOLECULE REACTIONS. The instrument has been modified to permit introduction of neutral reagents into the ion trap, allowing the measurement of ion-molecule reactions, these modifications and experimental procedures have been described in detail previously.¹⁸ It is worth noting that Gronert's pioneering studies suggest that ions undergoing ionmolecule reactions in the LCQ are essentially at room temperature.¹⁹

DFT calculations

In order to gain insights into the mechanism of the reaction of $CH_3CCAg_2^+$ with allyliodide, we have carried out DFT calculations using Gaussian 03²⁰ using the B3LYP level of theory with a 6-31+G* basis set for C, H and O and the Stuttgart (SDD) effective core potential (ECP) for Ag.²¹ Vibrational frequency calculations were carried out on each optimized structure at the same level of theory. This level of theory was chosen to allow direct comparison to the related reaction of CH₃Ag₂⁺ with allyliodide.¹⁰ Reaction energetics were calculated by using the energies listed in the ESI.[†] Full data (Cartesian coordinates, energies and imaginary frequencies for transition states) are given in the ESI.[†] Since the intermediate product of C-C bond coupling in our calculations is a π -complex between 1-hexen-4-yne and the cation Ag₂I⁺, we have carried out a manual search for conformations followed by geometry optimisations as well as an intrinsic reaction coordinate (IRC) calculation followed by a geometry optimisation. The same π -complex was located from both procedures.

Results and discussion

(a) Ion-molecule reactions of $RC \equiv CAg_2^+$ with allyliodide

In a recent study we have shown that CH₃Ag₂⁺ reacts with allyliodide via a sp^3-sp^3 C-C bond coupling reaction (eqn 8, R = Me).¹⁰ Thus we were interested in establishing whether the silver acetylide clusters $RC \equiv CAg_2^+$ (where R = Me and Ph) undergo related sp-sp³ C-C bond coupling reactions with allyliodide. The acetylide clusters $RC \equiv CAg_2^+$, formed via method (a) (R = Me, Ph) were individually mass selected and allowed to react with allyl iodide (CH2=CHCH2I). The resultant product ion spectra, which involve the same reaction conditions (allyl iodide concentration and reaction time), are shown in Fig. 1 and ESI Fig. S2.[†] The major pathway in each case corresponds to the C-C bond coupling to form RC=CCH2CH=CH2 (eqn 12a) along with the corresponding Ag_2I^+ (*m*/*z* 343) (Fig. 1a) and b, eqn 12a). In addition, a minor amount of the C-C bond coupled product complexed to a silver cation, $[(RC \equiv CCH_2CH = CH_2)Ag]^+$ (*m*/*z* 187/189, Fig. 1a and *m*/*z* 249/ 251, Fig. 1b), was observed (eqn 12b). Interestingly, this product was not observed in the reaction of CH₃Ag₂⁺ with allyl iodide, suggesting that the presence of the alkyne functional group facilitates coordination to the silver cation. Finally a range of other peaks due to the addition of background solvents H₂O and CH₃OH as well as further adsorption of the neutral substrate (allyl iodide) are also observed.

$$\begin{array}{l} \text{RC} = \text{CAg}_2^+ + \text{CH}_2 = \text{CHCH}_2 \text{I} \rightarrow \\ \text{Ag}_2 \text{I}^+ + \text{RC} = \text{CCH}_2 \text{CH} = \text{CH}_2 \end{array} \tag{12a}$$

$$\rightarrow [(\mathbf{RC} = \mathbf{CCH}_2\mathbf{CH} = \mathbf{CH}_2)\mathbf{Ag}]^+ + \mathbf{AgI}$$
(12b)



Fig. 1 Ion-molecule reactions of allyl iodide with mass selected $RC \equiv CAg_2^+$: (a) R = Me (Method (a)); (b) R = Ph (Method (a)). A concentration of allyliodide of ~10⁹ molecules cm⁻³ and reaction time = 100 ms was used for all the ion-molecule reactions. A * represents the mass selected precursor ion, while a [§] represents the C-C coupled product ion, [(RC = CCH₂CH=CH₂)Ag]⁺. A ## represents the further addition of the substrate C₃H₅I.

In order to further confirm the presence and identity of a C-C bond coupled product in the case of $[(PhC \equiv CCH_2CH = CH_2)Ag]^+$ (m/z 249/251) this ion was mass selected and subjected to CID (Fig. 2a). Two fragmentation reactions were observed: formation of Ag⁺ (eqn 13a) and loss of a silver atom to form the radical cation $[(PhC \equiv CCH_2CH = CH_2)]^+$ (eqn 13b). The observation of both $(PhC \equiv CCH_2CH = CH_2)^+$ and Ag^+ as fragments not only confirms the formation of a C-C bond coupled product, but it also suggests that the ene-yne PhC=CCH2CH=CH2 has an ionisation energy of the same order as the silver atom. The identity of the C-C product formed was further explored by subjecting the ion formed upon the mixing of a silver salt with an authentic sample of PhC=CCH₂CH=CH₂ to CID. Thus CID of $[(PhC \equiv CCH_2CH = CH_2)Ag]^+$ (Fig. 2b, m/z 249) gives the same fragments (eqn 13a and 13b) in similar abundances, further supporting the formation of a C-C bond coupled product.

$$[(RC \equiv CCH_2CH = CH_2)Ag]^+ \rightarrow Ag^+ + RC \equiv CCH_2CH = CH_2$$
(13a)

$$\rightarrow [(\mathbf{RC} = \mathbf{CCH}_2\mathbf{CH} = \mathbf{CH}_2)]^+ + \mathbf{Ag}$$
(13b)

(B) Insights into the mechanisms of C-C bond coupling between allyl iodide and $CH_3C \equiv CAg_2^+ via$ DFT Calculations

We used the previously published DFT calculated potential energy diagram for the C-C bond coupling of $CH_3Ag_2^+$ with allyl iodide as a starting point to explore the related potential energy diagram for the reaction of $CH_3C \equiv CAg_2^+$ with allyl iodide. The results of these calculations are shown in Fig. 3.



Fig. 2 CID of the C–C bond coupled product $[(RC=CH_2CH_2CH_2Ag]^+: (a) R = Ph formed in Fig. 1b; (b) spectrum of authentic product <math>[(PhC=CCH_2CH=CH_2)-Ag]^+$. All spectra were generated with an activation time of 30 ms and a *Q* value of 0.25. A * represents the mass selected precursor ion.

An examination of the potential energy diagram (Fig. 3) indicates that all the reactions are exothermic and that the energies associated with all the transition states [TS (A-B) and TS (B-C)] are less than the energies of the separated reactants. This is consistent with the experimental occurrence of C-C bond coupling under the near thermal conditions of the quadrupole ion trap.¹⁹ The first transition state TS(A-B) lying 0.79 eV below the entrance channel, involves C-I bond breaking and metal-C bond making associated with the formation of the three-coordinate organometallic (III) intermediate, B, via oxidative addition. The second transition state TS(B-C) lying 0.71 eV below the entrance channel, is associated with the reductive elimination reaction in which the C-C bond is formed. The resultant, and final intermediate, C, is the π -complexes between 1-hexen-4-yne and the silver iodide cation, Ag_2I^+ . Loss of 1-hexen-4-yne from this intermediate results in formation of the experimentally observed Ag₂I⁺ products, D, (eqn 12a) while loss of AgI yields the other observed ionic product, $[(CH_3C \equiv CCH_2CH = CH_2)Ag]^+$ (D) (eqn 12b). Although the loss of AgI (eqn 12b) is predicted to be slightly favoured energetically over formation of Ag₂I⁺ (eqn 12a), experimentally Ag_2I^+ is observed to be the major product ion (Fig. 1a). The origin of this discrepancy is not clear, but maybe due to the fact that extrusion of AgI from C requires a conformational change of the ene-yne



Fig. 3 DFT calculations relevant to C–C coupling between $CH_3C \equiv CAg_2^+$ and $CH_2 \equiv CHCH_2I$ to form Ag_2I^+ and $CH_3C \equiv CCH_2CH \equiv CH_2$: (a) potential energy diagram, (b) relevant structures and energies for intermediates, transition states and products relative to reactants. Absolute energies and Cartesian coordinates for all structures are provided in the ESI.†

CH₃C \equiv CCH₂CH=CH₂CH=CH₂ to form $[(CH_3C \equiv$ CCH₂CH=CH₂)Ag]⁺ (**D**), which may influence the reaction dynamics and hence the product branching ratios.²² Despite numerous attempts we have not been able to locate a transition state for extrusion of AgI from **C**.

(c) Gas phase studies highlight the role of the R group in C-C bond coupling of RAg₂⁺ with allyliodide

How does this study shed light on the "role of auxiliary ligands, solvent and the nature of the reactive organosilver species"? By removing two of these variables (auxiliary ligands and solvent), we have been able to focus on the nature of the reactive organosilver species, and are able to answer the fundamental question "how does the *R* group in RAg_2^+ influence the *C*-*C* bond coupling reaction with allyliodide?".[‡] Both the MS experiments and the DFT calculations highlight that while C-C bond coupling occurs for $CH_3Ag_2^+$ and $CH_3C\equiv CAg_2^+$,

[‡]While cationic silver acetylide clusters are known in solution (*e.g.* $[Ag_{14}(C \equiv CR)_{12}CI]^{+4a})$, the simple clusters studied here may not play any significant role in C–C bond coupling reactions in solution.

there are some differences. The presence of the triple bond in the coupled product provides an additional coordination site, which is why the additional reaction product $[(CH_3C \equiv CCH_2CH = CH_2)Ag]^+$ is observed experimentally (eqn 12b and Fig. 1a, m/z 187/189). Furthermore, the DFT calculations reveal that while both $CH_3Ag_2^+$ and $CH_3C \equiv CAg_2^+$ react via oxidative addition and reductive elimination, there are subtle differences in the structures and energies of key species involved. For CH₃Ag₂⁺, the highest barrier corresponds to oxidative addition, while for $CH_3C \equiv CAg_2^+$ it corresponds to reductive elimination. The acetylide influences the geometry of the allyl group in the intermediate, B, formed upon oxidative addition, which changes from a η^1 -allyl geometry for $CH_3Ag_2^+$ to a η^3 -allyl geometry for $CH_3C \equiv CAg_2^+$. Finally, the presence of the second acetylide binding site in CH₃C=CCH₂CH=CH₂ changes the structure of the product complex, C, formed from reductive elimination. For $CH_3Ag_2^+$, 1-butene binds to only one Ag of Ag₂I⁺, while for the ene-yne $CH_3C \equiv CCH_2CH = CH_2$ the alkene binds to one Ag and the alkyne to the other Ag of Ag_2I^+ .

Conclusions

A key ongoing research front in organometallic chemistry is the development of robust methods for C-C bond coupling reactions of all variants of $sp^x - sp^y$ bonds (where x, y = 1-3). Thus there has been considerable interested in extending the widely used palladium catalyzed Sonagashira sp-sp² C-C coupling reactions between terminal alkynes and aryl or vinyl halides²³ to a sp-sp³ C-C coupling variant with alkyl halides as the substrate.²⁴ Stoichiometric versions involving silver acetylides and allyl iodides were reported some time ago,²⁵ which has prompted us to examine these reactions in the gas phase. We have found that $RC \equiv CAg_2^+$ ions (R = CH₃ and Ph) react with allyl iodide to produce two ionic products that are signatures of C-C bond coupling: Ag₂I⁺ and [(RC=CCH₂CH=CH₂)- Ag^{\dagger} . CID was used to confirm that [(PhC=CCH₂CH=CH₂)- Ag^{\dagger} corresponds to a C-C coupled product *via* comparison to an "authentic", independently synthesized sample. DFT calculations on the reactions of $CH_3C \equiv CAg_2^+$ with allyliodide support the experiments and highlight that these reactions proceed via oxidative addition/reductive elimination steps, in a similar manner to the previously studied sp³-sp³ C-C coupling reaction between CH3Ag2+ and allyliodide.10 Our observation of facile decarboxylation of silver complexes of propiolic acids and the fact that the C-C bond coupling with allyliodide is stoichiometric, suggests future work focused on two fronts involving the examination of: (i) a potential gas phase catalytic cycle for decarboxylative C-C bond coupling of allyl propiolate catalyzed by $RC \equiv CAg_2^+$ ions and other coinage metal acetylide ions (we note the recent report of the extension of the C-C bond coupling reaction of dimethylcuprate with allyl iodide^{17h} to a catalytic variant with allyl acetate^{17m}); (ii) related silver catalyzed decarboxylative coupling of allyl carboxylates in the condensed phase.

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References

- 1 M. Berend and C. Liebermann, Justus Liebigs Ann. Chem., 1865, 135, 259.
- 2 (a) U. Halbes-Letinois, J.-M. Weibel and P. Pale, Chem. Soc. Rev., 2007, 36, 759; (b) R. H. Pouwer, C. M. Williams, A. L. Raine and J. B. Harper, Org. Lett., 2005, 7, 1323; (c) R. H. Pouwer, J. B. Harper, K. Vyakaranam, J. Michl, C. M. Williams, C. H. Jessen and P. V. Bernhardt, Eur. J. Org. Chem., 2007, 2, 241; (d) Y. Yamamoto, Chem. Rev., 2008, 108, 3199–3222; (e) X. Liu, Z. Wang, X. Cheng and C. Li, J. Am. Chem. Soc., 2012, 134, 14330–14333; (f) R. H. Pouwer and C. M. Williams, in Silver in Organic Chemistry, ed. M. Harmata, Wiley, New Jersey, 2010, p. 1.
- 3 K. Murakami, K. Hirano, H. Yorimitsu and K. Oshima, Angew. Chem., Int. Ed., 2008, 47, 5833.
- 4 (a) I. P. Silvestri, F. Andemarian, G. N. Khairallah, S. W. Yap, T. Quach, S. Tsegay, C. M. Williams, R. A. J. O'Hair, P. S. Donnelly and S. J. Williams, *Org. Biomol. Chem.*, 2011, 9, 6082–6088; (b) J. McNulty, K. Keskar and R. Vemula, *Chem.–Eur. J.*, 2011, 17, 14727– 14730.
- 5 (*a*) G. Van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 1974, 575; (*b*) G. Van Koten, R. W. M. ten Hoedt and J. G. Noltes, *J. Org. Chem.*, 1977, 42, 2705.
- 6 (a) C. Glaser, Ber. Dtsch. Chem. Ges., 1869, 2, 422; For a review see: (b) P. Siemsen, R. C. Livingston and F. Diederich, Angew. Chem., Int. Ed., 2000, 39, 2633–2657.
- 7 K. Kamata, S. Yamaguchi, M. Kotani, K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2008, 47, 2407.
- 8 R. A. J. O'Hair, Chem. Commun., 2006, 1469.
- 9 (a) G. N. Khairallah and R. A. J. O'Hair, Angew. Chem., Int. Ed., 2005, 44, 728; (b) G. N. Khairallah and R. A. J. O'Hair, Dalton Trans., 2005, 2702; (c) G. N. Khairallah and R. A. J. O'Hair, Dalton Trans., 2007, 3149; (d) G. N. Khairallah and R. A. J. O'Hair, Dalton Trans., 2008, 2956; (e) F. Q. Wang, G. N. Khairallah and R. A. J. O'Hair, Int. J. Mass Spectrom., 2009, 283, 17–25.
- 10 G. N. Khairallah, T. Waters and R. A. J. O'Hair, *Dalton Trans.*, 2009, 2832–2836.
- 11 F. Q. Wang, G. N. Khairallah, G. A. Koutsantonis, C. M. Williams, D. L. Callahan and R. A. J. O'Hair, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4132–4135.
- 12 (a) A. Wurtz, Ann. Chim. Phys., 1855, 44, 275–312; for a review see: (b) T. Laue and A. Plagens, Named Organic Reactions, John Wiley & Sons, 2nd edn, 2005, pp. 147, 304–305.

- 13 U. Létinois-Halbes, P. Pale and S. Berger, *J. Org. Chem.*, 2005, **70**, 9185.
- 14 (a) L. W. Bieber and M. F. Da Silva, *Tetrahedron Lett.*, 2007,
 48, 7088–7090; (b) X.-F. Ren, M. I. Konaklieva, E. Turos,
 L. M. Krajkowski, C. H. Lake, T. S. Janik and M. R. Churchill, *J. Org. Chem.*, 1995, 60, 6484–6495.
- 15 For Cu: (a) A. Kolarovič and Z. Fáberová, J. Org. Chem., 2009,
 74, 7199–7202; (b) A. Kolarovič, M. Schnürch and
 M. D. Mihovilovic, J. Org. Chem., 2011, 76, 2613–2618; For Ag:
 (c) A. Ruaudel-Teixier, Mol. Cryst. Liq. Cryst., 1983, 96, 365–372.
- 16 F. Manjolinho, M. Arndt, K. Gooßen and L. J. Gooßen, ACS Catal., 2012, 2, 2014–2012.
- 17 (a) R. A. J. O'Hair, Chem. Commun., 2002, 20-21; (b) P. F. James and R. A. J. O'Hair, Org. Lett., 2004, 6, 2761; (c) N. J. Rijs, T. Waters, G. N. Khairallah and R. A. J. O'Hair, J. Am. Chem. Soc., 2008, 130, 1069; (d) N. J. Rijs and R. A. J. O'Hair, Organometallics, 2009, 28, 2684-2692; (e) N. J. Rijs, B. F. Yates and R. A. J. O'Hair, Chem.-Eur. J., 2010, 16, 2674-2678; (f) N. J. Rijs and R. A. J. O'Hair, Organometallics, 2010, 29, 2282-2291; (g) N. J. Rijs, G. B. Sanvido, G. N. Khairallah and R. A. J. O'Hair, Dalton Trans., 2010, 8655-8662; (h) N. J. Rijs, N. Yoshikai, E. Nakamura and R. A. J. O'Hair, J. Am. Chem. Soc., 2012, 134, 2569-2580; (i) N. J. Rijs and R. A. J. O'Hair, Dalton Trans., 2012, 3395-3406; (j) L. O. Sraj, G. N. Khairallah, G. da Silva and R. A. J. O'Hair, Organometallics, 2012, 31, 1801-1807; (k) C. Brunet, R. Antoine, M. Brover, P. Dugourd, A. Kulesza, J. Petersen, M. I. S. Röhr, R. Mitrić, V. Bonačić-Koutecký and R. A. J. O'Hair, J. Phys. Chem. A, 2011, 115, 9120-9127; (l) M. I. S. Röhr, J. Petersen, C. Brunet, R. Antoine, M. Broyer, P. Dugourd, V. Bonačić-Koutecký, R. A. J. O'Hair and R. Mitrić, J. Phys. Chem. Lett., 2012, 3, 1197-1201; (m) N. J. Rijs and R. A. J. O'Hair, Organometallics, 2012, DOI: 10.1021/om300717g.
- 18 T. Waters, R. A. J. O'Hair and A. G. Wedd, J. Am. Chem. Soc., 2003, 125, 3384.
- 19 S. Gronert, J. Am. Soc. Mass Spectrom., 1998, 9, 845.
- 20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi,

G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, Yazyev, A. J. Austin, R. Cammi, C. Pomell, О. J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, Salvador, J. J. Dannenberg, V. G. Zakrzewski, P. S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, K. Malick, A. D. Rabuck, K. Raghavachari, D. J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, Al-Laham, C. Y. Peng, A. Nanavakkara. M. Α. M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian_03, Gaussian, Inc., Pittsburgh, PA, 2003.

- 21 M. Dolg, U. Wedig, H. Stoll and H. Preuss, J. Chem. Phys., 1987, 86, 866.
- 22 (a) B. K. Carpenter, Annu. Rev. Phys. Chem., 2005, 56, 57–89;
 D. H. Ess, S. E. Wheeler, R. G. Iafe, L. Xu, N. Celebi-Olçüm and K. N. Houk, Angew. Chem., Int. Ed., 2008, 47, 7592–7601; (b) U. Lourderaj and W. L. Hase, J. Phys. Chem. A, 2009, 113, 2236–2253; (c) J. Rehbein and B. K. Carpenter, Phys. Chem. Chem. Phys., 2011, 13, 20906–20922.
- 23 (a) K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 16, 4467–4470; (b) K. Sonogashira, *J. Organomet. Chem.*, 2002, 653, 46–49; (c) R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, 107, 874; (d) R. Chinchilla and C. Nájera, *Chem. Soc. Rev.*, 2011, 40, 5084.
- 24 (a) M. Eckhardt and G. C. Fu, J. Am. Chem. Soc., 2003, 125, 13642–13643; (b) M. Chen, X. Zheng, W. Li, J. He and A. Lei, J. Am. Chem. Soc., 2010, 132, 4101–4103; (c) T. Hatakeyama, Y. Okada, Y. Yoshimoto and M. Nakamura, Angew. Chem., Int. Ed., 2011, 50, 10973–10976; (d) O. Vechorkin, A. Godinat, R. Scopelliti and X. L. Hu, Angew. Chem., Int. Ed., 2011, 50, 11777–11781; (e) F. Ye, X. S. Ma, Q. Xiao, H. Li, Y. Zhang and J. B. Wang, J. Am. Chem. Soc., 2012, 134, 5742–5745.
- 25 M. E. Isabelle and L. C. Leitch, Can. J. Chem., 1958, 36, 440-448.