Electronic Supplementary Information

Argentate(I) and (III) Complexes as Intermediates in Silver-Mediated Cross-Coupling Reactions

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Abstract: Despite the potential of silver to mediate synthetically valuable cross-coupling reactions, the operating mechanisms have remained unknown. Here, we use a combination of rapid-injection NMR spectroscopy, electrospray-ionization mass spectrometry, and quantum chemical calculations to demonstrate that these transformations involve argentate(I) and (III) complexes as key intermediates.

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1) Details of NMR spectroscopic experiments

Rapid-injection NMR experiments were carried out as previously described.¹ Briefly, a suspension of AgI (30 µmol) in dry THF- d_8 (420 µL) in an NMR tube under argon atmosphere was sonicated for 1 min at room temperature. After cooling down to -78 °C, a solution of MeLi (60 µmol) in benzene- d_6 was added to form the argentate(I) in nearly quantitative yield. For the investigation of [RAgMe₃]⁻ complexes (R = allyI), RI was injected at -100 °C and the sample solution was allowed to warm up to -70 °C.

2) Preparation of [(Me₃P)AgMe₃]

A solution of AgI·2PMe₃ (5.0 mmol) in THF (8.5 mL), prepared by the room temperature dissolution of AgI (5.0 mmol) and PMe₃ (10.0 mmol), was added to a 100 mL Schlenk flask containing solid MeLi·THF² (10.0 mmol) at -78 °C under argon atmosphere via a syringe. Upon dissolution of all MeLi, MeI (5.5 mmol) was added via a syringe at -78 °C. The solution was allowed to warm to -30 °C over the course of 2 h whereupon precooled (-30 °C) dry pentane (20 mL) was added. The supernatant was removed cold via a syringe and placed in a fresh 100 mL Schlenk flask at -30 °C under argon atmosphere. Additional precooled (-30 °C) dry pentane (40 mL) was added and the resulting supernatant was filtered via a syringe filter into a 200 mL Schlenk flask at -30 °C under argon atmosphere. The solution was then vacuum concentrated at -30 °C to 8 mL to yield [(Me₃P)AgMe₃] in THF. Titration of the resulting solution with MeLi, observed via NMR spectroscopy, places the yield of the overall preparation at 52%.

3) Details of ESI-mass spectrometric experiments

Standard Schlenk techniques were applied in all cases to exclude traces of moisture. All reagents as well as anhydrous cyclopentyl methyl ether (CPME) and anhydrous methyl *tert*-butyl ether (MTBE) were purchased and used without further purification. Tetrahydrofuran (THF) was dried over sodium/benzophenone and freshly distilled. Solutions of LiAgMe₂·Li(CN) were prepared by transmetallation of Ag(CN) (0.625 mmol) with MeLi (1.25 mmol) in THF (5 mL) at -78 °C under argon. Subsequent reaction with methyl or allyl iodide (0.258 mmol) afforded solutions of the tetraalkylargentates. Sample solutions were diluted by a factor of 5 and then directly injected into a micrOTOF-Q II mass spectrometer (Bruker Daltonik) via gas-tight syringes at a flow rate of 8 μ L min⁻¹. Prior to mass spectrometric experiments, the ESI source including the inlet system was flushed with dry THF for at least 60 min. Nitrogen was used both as drying gas (60 °C, typical flow rate of 5 L min⁻¹) and nebulizer gas (typical backing pressure of 0.7 bar). An ESI voltage of 3.5 kV was applied. In gas-phase fragmentation experiments, ions of interest were mass-selected with an isolation width of 1.0–2.0 u, accelerated to a kinetic energy of E_{LAB} , and allowed to collide with nitrogen gas. The mass spectrometer was externally calibrated with a mixture of CF₃COOH and phosphazenes in H₂O/MeCN. The Bruker DataAnalysis software package was used for the calculation of theoretical *m/z* ratios and isotope patterns.

In order to study the formation of argentate(III) complexes in solvents that are less polar than THF (relative permittivity $\varepsilon^{298 \text{ K}} = 7.42$), ³ analogous experiments were performed in CPME ($\varepsilon^{298 \text{ K}} = 4.76$) ⁴ and MTBE ($\varepsilon^{298 \text{ K}} = 2.60$), ⁴ respectively.

4) Full description of computational details

Except for natural population analysis (NPA),⁵ the program package ORCA 4.0⁶ was used for quantum chemical calculations (VeryTight self-consistent field convergence criteria were applied throughout). Molecular structures were obtained by PBE0⁷ geometry optimizations including Grimme's D3 dispersion correction with Becke-Johnson (BJ) damping.⁸ Within these optimizations (Tight convergence criteria and a DFT integration grid corresponding to Grid7 were applied throughout), the cc-pVDZ basis sets⁹ were used for main group elements and the relativistic ECP28MDF pseudopotential^{10a} together with the cc-pVDZ-PP basis set^{10b} for silver. On the basis of the corresponding analytical harmonic frequency calculations, the optimized structures of reactants and products were confirmed as energy minima, and transition structures were validated as energy saddle points. Moreover, the depicted energy profiles were ensured to correspond to minimum-energy pathways by displacing each transition structure along both directions of the transition mode and conducting PBE0-D3BJ/cc-pVDZ geometry optimizations of the displaced structures, which led to the given energy minima. For the reductive elimination of ethane from [AgMe₄]⁻, NPA charges were determined with Gaussian 09¹¹ on the basis of PBE0-D3BJ/cc-pVDZ single-point energy (SPE) calculations (*Tight* self-consistent field convergence criteria and a DFT integration grid corresponding to *Fine* were applied). For all structures, DLPNO-CCSD(T)¹² SPEs were calculated (NormalPNO truncation thresholds were applied throughout). Within these calculations, the cc-pVTZ basis sets augmented with diffuse functions for carbon and oxygen^{9,13} and the corresponding correlation fitting basis sets¹⁴ were used for main group elements. For silver, the ECP28MDF pseudopotential together with the aug-cc-pVTZ-PP basis set^{10b} and the associated correlation fitting basis set¹⁵ were applied. The gas-phase energy H⁰ for each species was obtained by adding the PBE0-D3BJ/cc-pVDZ zero-point vibrational energy to the DLPNO-CCSD(T)/cc-pVTZ SPE.

In order to determine the G^{298} energy for a particular species in THF at 298 K, thermal energy and entropy corrections as well as the solvation energy ΔG_{solv} were calculated and added to H^0 (THF molecules of the first solvation shell of a coordinatively unsaturated lithium center were explicitly considered). Thermal energy and entropy corrections at 298 K and 1.01325 bar were provided from ORCA 4.0 in the course of the PBE0-D3BJ/cc-pVDZ harmonic frequency calculations on the basis of the statistical mechanics equations for an ideal gas and the quasi-RRHO approach of Grimme.¹⁶ To account for the standard state of a compound in solution (12.3 M for explicitly considered THF molecules and 1 M for all other species), the obtained gas-phase translational entropy was adjusted. For each PBE0-D3BJ/cc-pVDZ gas-phase structure, ΔG_{solv} was calculated as the difference between the corresponding PBE0-D3BJ/cc-pVDZ SPE and the SPE obtained from a PBE0-D3BJ/cc-pVDZ calculation featuring the conductor-like polarizable continuum model (C-PCM)^{17a} for THF (GEPOL^{17b-d} solvent-excluded surfaces were applied and the outlying charge correction was considered throughout). Within these C-PCM calculations, the COSMO^{18a} epsilon function was chosen for neutral species as suggested by Barone and co-workers.^{18b} Our approach for calculating G^{298} energies in solution strictly follows recommendations for the correct use of continuum solvent models.¹⁹ Thus, in line with the conclusion of a recent publication of Plata et al.,²⁰ we did not consider alternative suggestions for calculating entropic contributions in solution.

For comparison, ΔG_{solv} values were determined as described above by using ORCA's default implementation of the SMD model,²¹ which not only considers the electrostatic contribution to ΔG_{solv} , but also explicitly takes into account non-electrostatic contributions. The ΔG^{298} (C-PCM) and ΔG^{298} (SMD) results are in good agreement (Figures S38 and S40, Table S2), which supports that the formation of ethane from [AgMe₄]⁻ + [Li(THF)₄]⁺ in THF proceeds via reductive elimination from the corresponding contact ion-pair argentate(III) complex.

The XYZ coordinates (in Å) of all calculated PBE0-D3BJ/cc-pVDZ structures can be found in the argentates_QCC_structural_data.tar file of the ESI⁺. The symmetry number of a particular structure, which was applied in the calculation of its rotational entropy, is given in the comment line of the corresponding .xyz file.

5) Additional NMR spectra



Fig. S1 Top: ¹H NMR spectrum of dimethylargentate in THF- d_8 at -100 °C. The benzene- d_6 solvent signal is observed at 7.34 ppm, two THF- d_8 solvent signals are observed at 3.6 and 1.7 ppm, and dimethylargentate is observed at -1.25 ppm. Bottom: Expansion of methyl group centered at -1.25 ppm, showing a doublet which is the average of the two ${}^2J_{Ag-H}$ couplings, ${}^2J_{109Ag-H}$ and ${}^2J_{107Ag-H}$. The difference between the two couplings is small enough that only an average coupling of 7.30 Hz is observed.



Fig. S2 ¹³C NMR spectrum of dimethylargentate in THF- d_8 at -100 °C. Both ¹J_{Ag-C} couplings can be observed separately for each isotope of silver. The larger coupling is the ¹J_{109Ag-C} of 92.45 Hz and the smaller coupling belongs to ¹J_{107Ag-C} of 83.69 Hz. The chemical shift is observed to be -8.63 ppm.



Fig. S3 ¹H NMR spectrum measured for the reaction of LiAgMe₂·LiI with allyl iodide (RI) at −100 °C in THF-*d*₈.



Fig. S4 Expanded view (6.3 to 3.4 ppm): ¹H NMR spectrum measured for the reaction of LiAgMe₂·Lil with allyl iodide (RI) at -100 °C in THF- d_8 .



Fig. S5 Expanded view (2.2 to 0.8 ppm): ¹H NMR spectrum measured for the reaction of LiAgMe₂·Lil with allyl iodide (RI) at -100 °C in THF- d_8 .



Fig. S6 Expanded view (0.3 to -1.4 ppm): ¹H NMR spectrum measured for the reaction of LiAgMe₂·Lil with allyl iodide (RI) at -100 °C in THF-*d*₈.



Fig. S7 ¹H NMR spectrum of [(Me₃P)AgMe₃] in THF- d_8 at -100 °C.



Fig. S8 ¹H NMR spectrum of [AgMe₄] prepared via [(Me₃P)AgMe₃] in THF- d_8 at -100 °C.

6) Additional mass spectra



Fig. S9 Negative-ion mode ESI mass spectrum of a solution of the products formed in the reaction of Ag(CN) with methyl lithium (2 eq.) in THF (concentration of the argentate in the sample solution: 25 mM). a: $[\text{LiAg}^{1}\text{Me}(\text{CN})_{2}]^{-}$, b: $[\text{Ag}^{1}_{2}\text{Me}_{3}]^{-}$, c: $[\text{Ag}^{1}_{2}\text{Me}_{2}(\text{CN})]^{-}$, d: $[\text{LiAg}^{1}_{2}\text{Me}_{3}(\text{CN})]^{-}$ + $[\text{LiAg}^{1}_{2}\text{Me}_{2}(\text{OH})(\text{CN})_{2}]^{-}$, f: $[\text{Li}_{2}\text{Ag}^{1}_{2}\text{Me}_{2}(\text{CN})_{3}]^{-}$, g: $[\text{Li}_{2}\text{Ag}^{1}_{3}\text{Me}_{3}(\text{OH})(\text{CN})_{2}]^{-}$.



Fig. S10 Measured (black) and simulated (red) isotopic pattern of [LiAgMe(CN)₂]⁻.



Fig. S11 Measured (black) and simulated (red) isotopic pattern of [Ag¹₂Me₃]⁻.



Fig. S12 Measured (black) and simulated (red) isotopic pattern of $[Ag_2^{l}Me_2(CN)]^{-}$.



Fig. S13 Measured (black) and simulated (red) isotopic pattern of a 9:1 mixture of $[LiAg_2^{l}Me_3(CN)]^{-}$ and $[LiAg_2^{l}Me_2(OH)(CN)]^{-}$.



Fig. S14 Measured (black) and simulated (red) isotopic pattern of $[LiAg_2^IMe_2(CN)_2]^-$.



Fig. S15 Measured (black) and simulated (red) isotopic pattern of $[Li_2Ag_2^{I}Me_2(OH)(CN)_2]^{-1}$.



Fig. S16 Measured (black) and simulated (red) isotopic pattern of $[Li_2Ag_2^{I}Me_2(CN)_3]^{-1}$.



Fig. S17 Measured (black) and simulated (red) isotopic pattern of $[Li_2Ag_3^IMe_6]^-$.



Fig. S18 Measured (black) and simulated (red) isotopic pattern of $[Li_2Ag_3^{I}Me_3(OH)(CN)_2]^{-1}$.



Fig. S19 Measured (black) and simulated (red) isotopic pattern of $[Li_2Ag_3^{I}Me_3(CN)_3]^{-1}$.



Fig. S20 Measured (black) and simulated (red) isotopic pattern of [Ag^lMe₄]⁻.



Fig. S21 Measured (black) and simulated (red) isotopic pattern of [Ag^IMeI]⁻.



Fig. S22 Measured (black) and simulated (red) isotopic pattern of [LiAg^IMe(CN)I]⁻.



Fig. S23 Measured (black) and simulated (red) isotopic pattern of [LiAg^{1/III}₂Me₅(CN)]⁻.



Fig. S24 Measured (black) and simulated (red) isotopic pattern of $[LiAg^{III}_2Me_8]^-$.



Fig. S25 Measured (black) and simulated (red) isotopic pattern of $[LiAg^{III}_{2}Me_{7}(CN)]^{-}$.



 $\label{eq:Fig.S26} \textbf{Fig. S26} \quad \text{Measured (black) and simulated (red) isotopic pattern of } [\text{Li}_2\text{Ag}^l_2\text{Me}_2(\text{CN})_2\text{I}]^-.$



Fig. S27 Negative-ion mode ESI mass spectrum of a solution of the products formed in the reaction of Ag(CN) with methyl lithium (2 eq.) and allyl iodide (0.5 eq) in THF (R = allyl, concentration of the argentate in the sample solution: 25 mM). a: $[Ag^{I}Me_{2}]^{-}$, b: $[Ag^{I}Mel]^{-}$, c: $[Ag^{I}_{2}Me_{3}]^{-}$, d: $[LiAg^{I}_{2}Me_{3}(CN)]^{-}$ + $[LiAg^{I}_{2}Me_{2}(OH)(CN)]^{-}$, e: $[LiAg^{I}_{2}Me_{2}(CN)_{2}]^{-}$, f: $[LiAg^{I/III}_{2}Me_{5}(CN)]^{-}$, g: $[LiRAg^{I/III}_{2}Me_{4}(CN)]^{-}$, h: $[Li_{2}Ag^{I}_{3}Me_{6}]^{-}$.



Fig. S28 Measured (black) and simulated (red) isotopic pattern of [Ag^{III}Me₄]⁻.



Fig. S29 Measured (black) and simulated (red) isotopic pattern of $[RAg^{III}Me_3]^-$ (R = allyl).



Fig. S30 Measured (black) and simulated (red) isotopic pattern of $[LiRAg^{I/III}_2Me_4(CN)]^-$ (R = allyl).



Fig. S31 Measured (black) and simulated (red) isotopic pattern of $[LiRAg^{III}_{2}Me_{7}]^{-}$ (R = allyl).



Fig. S32 Measured (black) and simulated (red) isotopic pattern of $[LiR_2Ag^{III}_2Me_6]^-$ (R = allyl).



Fig. S33 Negative-ion mode ESI mass spectrum of a solution of the products formed in the reaction of Ag(CN) with methyl lithium (2 eq.) and methyl iodide (0.5 eq) in cyclopentyl methyl ether (CPME; concentration of the argentate in the sample solution: 25 mM). a: $[Ag_{2}^{l}Me_{3}]^{-}$, b: $[LiAg_{2}^{l}Me_{3}(CN)]^{-}$, c: $[LiAg_{2}^{l/III}Me_{6}]^{-} + [LiAg_{2}^{l/III}Me_{5}(OH)]^{-}$, d: $[LiAg_{2}^{l/III}Me_{5}(CN)]^{-}$, e: $[LiAg_{2}^{III}Me_{7}(CN)]^{-}$.



Fig. S34 Measured (black) and simulated (red) isotopic pattern of a 6:4 mixture of $[\text{LiAg}^{I/III}_2\text{Me}_6]^-$ and $[\text{LiAg}^{I/III}_2\text{Me}_5(\text{OH})]^-$.



Fig. S35 Negative-ion mode ESI mass spectrum of a solution of the products formed in the reaction of Ag(CN) with methyl lithium (2 eq.) and methyl iodide (0.5 eq) in methyl *tert*-butyl ether (MTBE; concentration of the argentate in the sample solution: 25 mM). a: $[Ag^{I}Me_2]^{-}$, b: $[Ag^{III}Me_4]^{-}$, c: $[LiAg^{I}_2Me_4]^{-} + [LiAg^{I}_2Me_3(OH)]^{-} + [LiAg^{I}_2Me_2(OH)_2]^{-}$, d: $[LiAg^{III}_2Me_8]^{-}$, e: $[Ag^{I}_3Me_4]^{-}$, f: $[Li_4Ag^{I}_5Me_8(OH)_2]^{-} + [Li_4Ag^{I}_5Me_7(OH)_3]^{-}$, g: $[Li_5Ag^{I}_6Me_8(OH)_4]^{-}$.



Fig. S36 Measured (black) and simulated (red) isotopic pattern of $[Ag_{3}^{I}Me_{4}]^{-}$.



Fig. S37 Measured (black) and simulated (red) isotopic pattern of $[Ag_{4}^{I}Me_{5}]^{-}$.



Fig. S38 Measured (black) and simulated (red) isotopic pattern of a 1:9 mixture of $[Li_4Ag_5^{I}Me_8(OH)_2]^{-1}$ and $[Li_4Ag_5^{I}Me_7(OH)_3]^{-1}$.



Fig. S39 Measured (black) and simulated (red) isotopic pattern of [Li₅Ag^l₆Me₈(OH)₄]⁻.



Fig. S40 Mass spectrum of mass-selected $[Ag^{III}Me_4]^-$ and its fragment ions produced upon collision-induced dissociation at $E_{LAB} = 10.0 \text{ eV}$.



Fig. S41 Mass spectrum of mass-selected $[LiAg^{III}_2Me_8]^-$ and its fragment ions produced upon collision-induced dissociation at $E_{LAB} = 7.5 \text{ eV}$; a: $[LiAg^{I/III}_2Me_6]^-$.



Fig. S42 Mass spectrum of mass-selected $[LiRAg^{III}_{2}Me_{7}]^{-}$ (R = allyl) and its fragment ions produced upon collision-induced dissociation at $E_{LAB} = 7.5 \text{ eV}$; a: $[RAg^{III}Me_{3}]^{-}$, b: $[Ag^{I}_{2}Me_{3}]^{-}$, c: $[LiAg^{I}_{2}Me_{4}]^{-}$, d: $[LiRAg^{I/III}_{2}Me_{5}]^{-}$.



Fig. S43 Mass spectrum of mass-selected $[\text{LiR}_2\text{Ag}^{III}_2\text{Me}_6]^-$ (R = allyl) and its fragment ions produced upon collision-induced dissociation at $E_{\text{LAB}} = 5.0 \text{ eV}$; a: $[\text{Ag}^{III}\text{Me}_4]^-$, b: $[\text{Ag}^I_2\text{Me}_3]^-$, c: $[\text{LiAg}^I_2\text{Me}_4]^-$.

7) Comparison of measured and theoretical m/z ratios

Table S1 Measured and theoretical m/z ratios of the main ions observed upon ESI-MS of organoargentate solutions in THF. For each ion, only the most abundant isotopologue is considered, unless noted otherwise.

ion	<i>m/z</i> (measured)	<i>m/z</i> (theoretical)			
[Ag ^l Me ₂] ⁻	136.954	136.953			
[Ag ^{III} Me ₄] ⁻	167.002	167.000			
[LiAg ^I Me(CN) ₂] ⁻	180.954	180.951			
[RAg ^{III} Me ₃] ⁻ , R = allyl	193.019	193.015			
[Ag ^l Mel] ⁻	248.837	248.834			
[Ag ^l ₂Me₃] [−]	260.881	260.881			
[Ag ^l ₂Me₂(CN)] [−]	271.864	271.860			
[LiAg ^I Me(CN)I] ⁻	281.857	281.853			
[LiAg ¹ ₂ Me ₃ (CN)] ⁻	290.905 ^a	290.899			
[LiAg ₂ Me ₂ (OH)(CN)] ⁻	297.883 ^b	297.879			
$[LiAg_{2}^{I}Me_{2}(CN)_{2}]^{-}$	304.885	304.880			
[LiAg ^{1/III} 2Me ₆]	309.965 ^c	309.967			
[LiAg ^{1/III} 2Me ₅ (OH)] ⁻	316.943 ^d	316.946			
[LiAg ^{1/III} 2Me ₅ (CN)]	323.952	323.947			
$[\text{Li}_2\text{Ag}^{\text{I}}_2\text{Me}_2(\text{OH})(\text{CN})_2]^{-1}$	328.903	328.898			
$[\text{Li}_2\text{Ag}^{\text{I}}_2\text{Me}_2(\text{CN})_3]^{-1}$	337.901	337.899			
[LiAg ^{III} 2Me8]	343.020	343.014			
$[LiRAg^{I/III}_2Me_4(CN)]^-$, R = allyl	349.964	349.962			
$[Li_2Ag^l_2Me_2(CN)_3]^-$	337.901	337.899			
[LiAg ^{III} ₂ Me ₇ (CN)] ⁻	353.999	353.994			
[LiRAg ^{III} ₂ Me ₇] ⁻	369.032	369.030			
[Ag ^l ₃ Me ₄] ⁻	382.809	382.809			
[LiR ₂ Ag ^{III} ₂ Me ₆]	395.047	395.046			
[Li ₂ Ag ^I ₃ Me ₆] ⁻	426.889	426.888			
$[Li_2Ag_2^{I}Me_2(CN)_2I]^{-1}$	438.805	438.800			
$[Li_2Ag_3^{l}Me_3(OH)(CN)_2]^{-1}$	450.829	450.827			
$[\text{Li}_2\text{Ag}^{\text{I}}_3\text{Me}_3(\text{CN})_3]^{-1}$	459.832	459.827			
[Ag ^l ₄Me₅] [¯]	506.736	506.738			
[Li₅Ag ^l ₆ Me ₈ (OH)₄] [−]	870.703	870.709			

^a Due to overlapping signals of $[\text{LiAg}_{2}^{I}\text{Me}_{3}(\text{CN})]^{-}$ and $[\text{LiAg}_{2}\text{Me}_{2}(\text{OH})(\text{CN})]^{-}$, the peak centered at m/z 290.9 (corresponding to the isotopologue $[{}^{6}\text{Li}{}^{107}\text{Ag}_{2}({}^{12}\text{C}^{1}\text{H}_{3})_{3}({}^{12}\text{C}{}^{14}\text{N})]^{-}$) is considered in this case (Figure S13).

^b Due to overlapping signals of $[\text{LiAg}_2^{l}\text{Me}_3(\text{CN})]^-$ and $[\text{LiAg}_2^{2}\text{Me}_2(\text{OH})(\text{CN})]^-$, the peak centered at m/z 297.9 (corresponding mainly to the isotopologue $[^7\text{Li}^{109}\text{Ag}_2(^{12}\text{C}^{1}\text{H}_3)_2(^{16}\text{O}^{1}\text{H})(^{12}\text{C}^{14}\text{N})]^-$) is considered in this case (Figure S13). ^c Due to overlapping signals of $[\text{LiAg}_2^{l/\text{III}}_2\text{Me}_6]^-$ and $[\text{LiAg}_2^{l/\text{III}}_2\text{Me}_5(\text{OH})]^-$, the peak centered at m/z 310.0 (corresponding to the isotopologue $[^6\text{Li}^{107}\text{Ag}_2(^{12}\text{C}^{1}\text{H}_3)_6]^-$) is considered in this case (Figure S34).

^{*d*} Due to overlapping signals of [LiAg^{VIII}₂Me₆]⁻ and [LiAg^{VIII}₂Me₅(OH)]⁻, the peak centered at m/z 316.9 (corresponding mainly to the isotopologue [⁷Li¹⁰⁹Ag₂(¹²C¹H₃)₅(¹⁶O¹H)]⁻) is considered in this case (Figure S34).

8) Additional energy diagrams



Fig. S44 Energy diagram for the gas-phase dissociation of $[LiAg_2Me_8]^-$ and the reductive elimination of ethane from $[LiAg_2Me_8]^-$ obtained from DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3BJ/cc-pVDZ calculations. The values in brackets correspond to $-T \Delta S^{298}$ in kJ mol⁻¹.



Fig. S45 Energy diagram for the reductive elimination of ethane from: free ions $[AgMe_4]^- + [Li(THF)_4]^+$ (black); solvent separated ion pair (blue); contact-ion pair (red); neutral $[AgMe_3]$ (green) in THF. Gas-phase energies were obtained from DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3BJ/cc-pVDZ calculations. The C-PCM approach was used for calculating the corresponding PBE0-D3BJ/cc-pVDZ solvation energies. The PBE0-D3BJ/cc-pVDZ structures of the silver-containing species involved in these reactions are shown below the energy diagram. H atoms are omitted for clarity.



Fig. S46 Energy diagram for the reductive elimination of ethane from: free ions $[AgMe_4]^- + [Li(THF)_4]^+$ (black); neutral $[AgMe_3]$ including the formation of 0.25 equiv. of $[Li_4Me_4(THF)_4]$ (green); neutral $[AgMe_3]$ including the formation of $[LiMe(THF)_3]$ (olive); neutral $[AgMe_3(THF)]$ including the formation of 0.25 equiv. of $[Li_4Me_4(THF)_4]$ (lime green) in THF. Gas-phase energies were obtained from DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3BJ/cc-pVDZ calculations. The C-PCM approach was used for calculating the corresponding PBE0-D3BJ/cc-pVDZ solvation energies.



Fig. S47 Energy diagram for the reductive elimination of ethane from: free ions $[AgMe_4]^- + [Li(THF)_4]^+$ (black); solvent separated ion pair (blue); contact-ion pair (red); neutral $[AgMe_3]$ (green) in THF. Gas-phase energies were obtained from DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3BJ/cc-pVDZ calculations. The SMD approach was used for calculating the corresponding PBE0-D3BJ/cc-pVDZ solvation energies.

9) List of calculated ΔG^{298} values and overview of the individual contributions

Table S2 ΔG^{298} values (in kJ mol⁻¹) for the reductive elimination of ethane from Ag(III) ate complexes and neutral Ag(III) complexes in THF relative to $[AgMe_4]^- + [Li(THF)_4]^+$. Gas-phase energies H^0 (in kJ mol⁻¹) were obtained from DLPNO-CCSD(T)/cc-pVTZ//PBE0-D3BJ/cc-pVDZ calculations. The applied $T \cdot S^{298}$ values (in kJ mol⁻¹) refer to the respective standard state in solution. The C-PCM as well as the SMD approach were used for calculating the corresponding PBE0-D3BJ/cc-pVDZ solvation energies ΔG_{solv} (in kJ mol⁻¹). The values in brackets correspond to the energies relative to the respective reactant.

	$\Delta G^{298}(\text{C-PCM})$		$\Delta G^{298}(SMD)$		ΔH^0		$-T \cdot \Delta S^{298}$		$\Delta\Delta G_{solv}(C-PCM)$		$\Delta\Delta G_{solv}(SMD)$	
[AgMe₄] [−] + [Li(THF)₄] ⁺	0		0		0		0		0		0	
$\left[AgMe_4\right]^{-\ddagger} + \left[Li(THF)_4\right]^{+}$	146		143		166		-4		-17		-20	
$[AgMe_2]^- + Me_2 + [Li(THF)_4]^+$	-212		-214		-153		-34		-24		-27	
[AgMe₄]⁻[Li(THF)₄]⁺	15	(0)	22	(0)	-298	(0)	58	(0)	257	(0)	264	(0)
[AgMe ₄] ⁻ [Li(THF) ₄] ^{+‡}	160	(145)	170	(148)	-186	(112)	59	(1)	289	(32)	298	(34)
$[AgMe_2]^{-}[Li(THF)_4]^{+} + Me_2$	-186	(-201)	-178	(-200)	-480	(-182)	18	(-40)	277	(20)	282	(18)
[(THF) ₂ LiAgMe ₄] + 2 THF	5	(0)	15	(0)	-234	(0)	-21	(0)	264	(0)	274	(0)
$[(THF)_2 LiAgMe_4]^{\ddagger} + 2 THF$	118	(113)	129	(114)	-129	(105)	-19	(2)	271	(7)	282	(8)
[(THF) ₂ LiAgMe ₂] + Me ₂ + 2 THF	-195	(-200)	-169	(-184)	-390	(-156)	-58	(-37)	257	(-7)	283	(9)
[AgMe ₃] + ¼ [Li ₄ Me ₄ (THF) ₄] + 3 THF	132	(0)	146	(0)	-54	(0)	-73	(0)	262	(0)	276	(0)
[AgMe ₃] [‡] + ¼ [Li ₄ Me ₄ (THF) ₄] + 3 THF	134	(2)	148	(2)	-50	(4)	-67	(6)	257	(-5)	270	(-6)
[AgMe] + Me ₂ + ¼ [Li ₄ Me ₄ (THF) ₄] + 3 THF	-77	(-209)	-64	(-210)	-236	(-182)	-96	(-23)	260	(-2)	273	(-3)
[AgMe ₃] + [LiMe(THF) ₃] + THF	166	(0)	176	(0)	-64	(0)	-40	(0)	270	(0)	281	(0)
$[AgMe_3]^{\ddagger}$ + [LiMe(THF) ₃] + THF	168	(2)	178	(2)	-60	(4)	-35	(5)	265	(-5)	275	(-6)
[AgMe] + Me ₂ + [LiMe(THF) ₃] + THF	-43	(-209)	-34	(-210)	-246	(-182)	-64	(-24)	268	(-2)	278	(-3)
[AgMe ₃ (THF)] + ¼ [Li ₄ Me ₄ (THF) ₄] + 2 THF	96	(0)	107	(0)	-131	(0)	-35	(0)	265	(0)	276	(0)
[AgMe ₃ (THF)] [‡] + ¼ [Li ₄ Me ₄ (THF) ₄] + 2 THF	148	(52)	160	(53)	-78	(53)	-35	(0)	265	(0)	276	(0)
[AgMe(THF)] + Me ₂ + ¼ [Li ₄ Me ₄ (THF) ₄] + 2 THF	-123	(-219)	-113	(-220)	-307	(-176)	-72	(-37)	259	(-6)	269	(-7)

10) References

- (a) S. H. Bertz, S. Cope, M. Murphy, C. A. Ogle and B. J. Taylor, *J. Am. Chem. Soc.*, 2007, **129**, 7208; (b) S. H. Bertz, S. Cope, D. Dorton, M. Murphy and C. A. Ogle, *Angew. Chem.*, *Int. Ed.*, 2007, **46**, 7082; (c) E. R. Bartholomew, S. H. Bertz, S. Cope, M. Murphy and C. A. Ogle, *J. Am. Chem. Soc.*, 2008, **130**, 11244; (d) E. R. Bartholomew, S. H. Bertz, S. K. Cope, M. D. Murphy, C. A. Ogle and A. A. Thomas, *Chem. Commun.*, 2010, **46**, 1253.
- 2 C. A. Ogle, B. K. Huckabee, H. C. Johnson IV, P. F. Sims, S. D. Winslow and A. A. Pinkerton, *Organometallics*, 1993, **12**, 1960.
- 3 CRC Handbook of Chemistry and Physics, ed. D. R. Lide, CRC Press, Boca Raton, 88th edn, 2008.
- 4 K. Watanabe, N. Yamagiwa, Y. Torisawa, Org. Process Res. Dev., 2007, 11, 251.
- 5 A. E. Reed, R. B. Weinstock and F. Weinhold, J. Chem. Phys., 1985, 83, 735.
- 6 (a) F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73; (b) F. Neese, *WIREs Comput. Mol. Sci.*, 2018, DOI: 10.1002/wcms.1327; (c) F. Neese, F. Wennmohs, D. Aravena, M. Atanasov, U. Becker, D. Bykov, V. G. Chilkuri, D. Datta, A. Kumar Dutta, D. Ganyushin, Y. Guo, A. Hansen, L. Huntington, R. Izsák, C. Kollmar, S. Kossmann, M. Krupička, D. Lenk, D. G. Liakos, D. Manganas, D. A. Pantazis, T. Petrenko, P. Pinski, C. Reimann, M. Retegan, C. Riplinger, T. Risthaus, M. Roemelt, M. Saitow, B. Sandhöfer, I. Schapiro, K. Sivalingam, G. Stoychev and B. Wezisla, with contributions from M. Kállay, S. Grimme, E. Valeev, G. Chan, J. Pittner and M. Brehm, ORCA (Version 4.0), Max Planck Institute for Chemical Energy Conversion, Mülheim a. d. Ruhr, Germany, 2017.
- 7 C. Adamo and V. Barone, J. Chem. Phys., 1999, 110, 6158.
- 8 (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
- 9 (a) T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007; (b) B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning Jr., A. K. Wilson, *Theor. Chem. Acc.*, 2011, **128**, 69.
- 10 (a) D. Figgen, G. Rauhut, M. Dolg and H. Stoll, *Chem. Phys.*, 2005, **311**, 227; (b) K. A. Peterson and C. Puzzarini, *Theor. Chem. Acc.*, 2005, **114**, 283.
- (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Revision D.01), Gaussian Inc., Wallingford, CT, 2013; (b) E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, NBO (Version 3.1), University of Wisconsin, Madison, WI, 1995.
- 12 (a) C. Riplinger and F. Neese, J. Chem. Phys., 2013, **138**, 034106; (b) C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, J. Chem. Phys., 2013, **139**, 134101; (c) C. Riplinger, P. Pinski, U. Becker, E. F. Valeev and F. Neese, J. Chem. Phys., 2016, **144**, 024109.
- 13 R. A. Kendall, T. H. Dunning Jr. and R. J. Harrison, J. Chem. Phys., 1992, 96, 6796.
- 14 (a) F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175; (b) C. Hättig, *Phys. Chem. Chem. Phys.*, 2005, **7**, 59.
- 15 C. Hättig, aug-cc-pVTZ-PP-RI basis set for silver taken from the EMSL Basis Exchange: (a) D. Feller, J. Comput. Chem., 1996, 17, 1571; (b) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, J. Chem. Inf. Model., 2007, 47, 1045.
- 16 S. Grimme, Chem. Eur. J., 2012, 18, 9955.
- 17 (a) V. Barone and M. Cossi, J. Phys. Chem., A 1998, 102, 1995; (b) J. L. Pascual-Ahuir and E. Silla, J. Comput. Chem., 1990, 11, 1047; (c) E. Silla, I. Tuñón and J. L. Pascual-Ahuir, J. Comput. Chem., 1991, 12, 1077; (d) J. L. Pascual-Ahuir, E. Silla and I. Tuñón, J. Comput. Chem., 1994, 15, 1127.

- 18 (a) A. Klamt and G. Schüürmann, J. Chem. Soc., Perkin Trans. 2, 1993, 799; (b) M. Cossi, N. Rega, G. Scalmani and V. Barone, J. Comput. Chem., 2003, 24, 669.
- 19 (a) J. Ho, A. Klamt and M. L. Coote, *J. Phys. Chem. A*, 2010, **114**, 13442; (b) R. F. Ribeiro, A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2011, **115**, 14556.
- 20 R. E. Plata and D. A. Singleton, J. Am. Chem. Soc., 2015, 137, 3811.
- 21 A. V. Marenich, C. J. Cramer and D. G. Truhlar, J. Phys. Chem. B, 2009, 113, 6378.