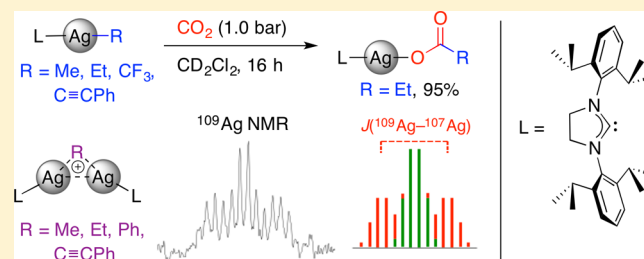


Stable Mono- and Dinuclear Organosilver Complexes

Brandon K. Tate,^{†,§} Abraham J. Jordan,[†] John Bacsa,[‡] and Joseph P. Sadighi^{*,†,§}[†]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States[‡]X-ray Crystallography Center, Emory University, Atlanta, Georgia 30322, United States

Supporting Information

ABSTRACT: A series of mononuclear and dinuclear complexes of silver(I), supported by an N-heterocyclic carbene and bound to sp³-, sp²-, and sp-hybridized carbanions, has been synthesized. Synthetic routes include transmetalation from organozinc, organomagnesium, and organosilicon reagents, as well as the deprotonation of a terminal alkyne. These complexes exhibit greater thermal stability than typical organosilver reagents, permitting spectroscopic and structural characterization. The carbanion-bridged disilver cations feature three-center, two-electron bonding with short Ag...Ag distances. A mononuclear vinylsilver complex releases organic homocoupling products upon thermal decomposition, while mononuclear alkylsilver complexes exhibit nucleophilic behavior, for example, inserting CO₂ to form silver carboxylates.



INTRODUCTION

The organometallic chemistry of silver has been less explored than that of its congeners, copper and gold. The study of organosilver chemistry has been limited in many cases by thermal instability and photosensitivity. For example, phosphine-supported alkylsilver complexes decompose quickly at room temperature, giving primarily the coupling products of organic radicals, elemental silver, and free phosphine. Many organosilver compounds that are stable at room temperature, such as alkynylsilver compounds and phenylsilver, form coordination polymers, and low solubility limits their utility. Under the right conditions, however, organosilver compounds have been effectively used as sources of carbon-based radicals or carbanions.¹ They are probable intermediates in both stoichiometric² and catalytic³ silver-mediated C–C coupling processes, and have been identified in studies of C–C coupling reactions in the gas phase.⁴

Early studies of alkylsilver complexes focused on the detection of thermal decomposition products. Semerano and Riccoboni⁵ first inferred the intermediacy of alkylsilver compounds in the reaction of tetraalkyllead reagents with silver nitrate, which produces alkyl dimers and elemental silver.⁶ Further studies followed, demonstrating silver-mediated C–C coupling of organomagnesium and organolithium reagents.^{2d–h} Whitesides and co-workers carried out mechanistic studies⁷ of the reaction of Grignard reagents with (phosphine)silver halides. The results suggested that the observed disproportionation to elemental silver and alkyl homocoupling products sometimes involves homolysis of Ag–C bonds, with release of free alkyl radicals, but in other cases proceeds through a concerted bimolecular process. These studies led to the development of methods for the silver-mediated synthesis of cycloalkanes,^{2a} and to a variety of silver-catalyzed C–C coupling processes.^{1,3} Alkylsilver complexes produced via the

decarboxylation of silver carboxylates have also been studied in the gas phase.⁸

Complexes of silver with sp²-hybridized carbanions were among the earlier known organosilver species. Krause and Schmitz prepared phenylsilver by transmetalation from tin, lead, or magnesium, isolated it as a complex with AgNO₃, and reported its violent decomposition upon evaporation of solvent.⁹ The reaction of phenylmagnesium bromide with AgBr was likewise reported to form an explosive product.¹⁰ Later synthetic routes provided pure, isolable phenylsilver. Despite its low solubility, this complex reacts with acyl halides to form a mixture of nucleophilic substitution products and biphenyl.¹¹ Mesitylsilver¹² and 2,4,6-triethylphenylsilver¹³ are stable at room temperature in the dark, are soluble in solvents such as toluene and THF, and have been characterized crystallographically as tetramers with symmetrically bridging aryl ligands. The more sterically encumbered 2,4,6-(triphenyl)phenylsilver is also stable at room temperature but crystallizes as a monomer.¹⁴ Diarylargentate ions, isolated as lithium salts, decompose slowly at room temperature.¹⁵ Vinylsilver^{7c,d,16} and allenylsilver¹⁷ compounds have also been studied.

Alkynylsilver complexes are among the oldest known organometallic species, and have found relatively widespread synthetic applications.¹⁸ The reaction of silver nitrate with acetylene in basic media, first described by Berthelot in 1866,¹⁹ results in the precipitation of silver acetylide, a primary explosive.²⁰ Complexation of silver acetylide with various combinations of Ag⁺, other anions, and ancillary donors results in a broad array of supramolecular architectures.²¹ Substituted acetylides may be prepared under similar conditions²² or from alkynylmagnesium halides,²³ and are generally stable at room

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temperature in the dark. Although they typically exhibit low solubility in common solvents, alkynylsilver compounds have served as mildly nucleophilic acetylide sources in the substitution of acyl halides,²⁴ other activated carbonyls,²⁵ and alkyl halides.²⁶ Alkynylsilver compounds are also likely intermediates in catalytic C–C and C–N coupling processes²⁷ as well as in the carboxylation of terminal alkynes.²⁸

Complexes of silver with carbanions bearing electron-withdrawing groups are relatively stable, and their reaction chemistry has been more widely investigated. The addition of silver(I) fluoride to perfluoroolefins, for example, gives rise to perfluoroalkylsilver compounds,²⁹ which can undergo sequential carboxylation/alkylation³⁰ or reductive C–C homocoupling.³¹ Perfluoroalkyl and pentafluorophenyl complexes of silver, which are generally stable at room temperature, can also be conveniently prepared by treatment of AgF with the corresponding trimethylsilyl reagent.^{32,33} Synthetic applications of perfluoroorganosilver complexes include substitution reactions with acyl halides,^{34,35} chlorosilanes,³⁵ benzyl bromide,³⁵ and alkyl and aryl iodides,³⁵ and the oxidative transfer of the perfluoroorganic group to elemental copper or to a wide variety of elements in groups 12–16.^{33,35} Other halogens, alkoxy, amino, and trifluoromethyl substituents enhance the stability of arylsilver compounds, allowing further investigation of their structures and reactivity.³⁶ Recently Shen and co-workers³⁷ have prepared N-heterocyclic carbene (NHC)-supported (difluoromethyl)silver complexes via metathesis of alkoxysilver precursors with (difluoromethyl)trimethylsilane, demonstrated silver-mediated difluoromethylation and difluorothiomethylation of a range of electrophiles, and developed a method for palladium/silver-catalyzed difluoromethylation of aryl halides. Silyl-substituted alkyl complexes of silver have also been structurally characterized.³⁸

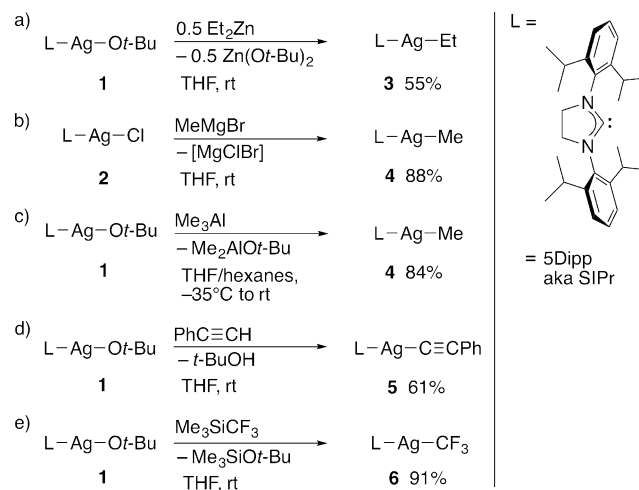
Here we report the preparation of a series of stable mononuclear and dinuclear complexes of silver with carbanion ligands featuring sp^3 -, sp^2 -, and sp -hybridization, supported by the NHC ligand 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (SDipp). We have characterized these complexes using X-ray crystallography and ^{109}Ag NMR spectroscopy; the dinuclear complexes exhibit significant and varied intermetallic interactions. Two of these complexes proved amenable to mass spectrometric characterization. The mononuclear alkylsilver compounds react as carbon nucleophiles toward CO_2 , forming carboxylates.

RESULTS AND DISCUSSION

Terminal Organosilver Complexes. Various synthetic approaches were employed, including transmetalation from organozinc and organoaluminum compounds, Grignard reagents, and a trimethylsilyl derivative, using known silver precursors (SDipp)Ag(O-*t*-Bu) (**1**) and (SDipp)AgCl (**2**) (Scheme 1). The C–H bond of phenylacetylene proved sufficiently acidic to protonolyze a silver *tert*-butoxide. Collectively, these approaches permit the synthesis of a range of organosilver complexes.

The preparation of (SDipp)AgEt (**3**) via ligand exchange between **1** and 0.5 equiv of diethylzinc proceeds rapidly and quantitatively in C_6D_6 or THF- d_8 solution at ambient temperature (Scheme 1a), as judged by ^1H NMR spectroscopy. Complex **3** can be separated from the hydrocarbon-soluble bis(*tert*-butoxy)zinc byproduct by precipitation from THF with the addition of hexanes, allowing its isolation in 55% yield. The addition of excess diethylzinc does not impede the reaction or

Scheme 1. Synthesis of Neutral Organosilver Complexes



the separation of byproducts. The ethyl ligand exhibits ^1H NMR resonances with defined ^1H – ^{107}Ag and ^1H – ^{109}Ag nuclear dipole coupling for both the α and β protons, resulting in two doublets of triplets centered at δ 0.89 ppm for the methyl protons (Figure 1a), and two doublets of quartets at δ –0.25

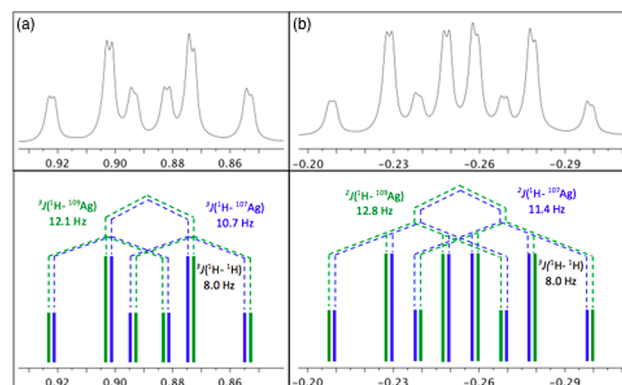


Figure 1. ^1H NMR (400 MHz, THF- d_8) resonances of the (a) CH_3 and (b) CH_2 protons of the ethyl ligand of **3**. Corresponding splitting diagrams are shown underneath.

ppm for the methylene protons (Figure 1b). Because the two-bond and three-bond ^1H – ^{109}Ag coupling constants are similar [$^2J(^1\text{H}$ – $^{109}\text{Ag}) = 12.8$ Hz, $^3J(^1\text{H}$ – $^{109}\text{Ag}) = 12.1$ Hz], the ^{109}Ag NMR signal resolves as an apparent sextet (Figure 2a).

Rather than using the expensive dimethylzinc, we chose to prepare (SDipp)AgMe (**4**) from methylmagnesium bromide, which reacts smoothly with **2** in C_6D_6 or THF solution (Scheme 1b). The magnesium halide byproducts were precipitated as 1,4-dioxane adducts, allowing the isolation of

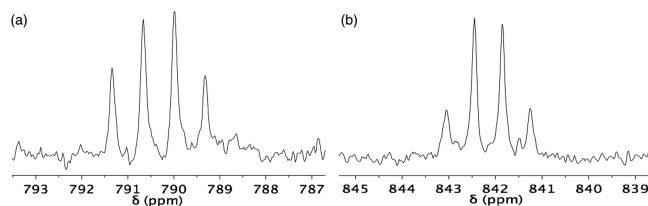


Figure 2. ^{109}Ag NMR (18.6 MHz) resonances for (a) (SDipp)AgEt (**3**) and (b) (SDipp)AgMe (**4**).

4 in 85% yield. We subsequently found³⁹ that the reaction between a trimethylaluminum solution and **1** affords **4** cleanly (Scheme 1c), and that the hydrocarbon-soluble byproduct Me₂AlOt-Bu is somewhat more conveniently removed. The ¹H NMR spectrum of **4** in CD₂Cl₂ solution exhibits a doublet signal for the methyl protons at δ −1.38 ppm. Because coupling to the ¹⁰⁷Ag and ¹⁰⁹Ag nuclei is not resolved, the observed coupling constant of 10 Hz is presumed an average for the coupling of ¹H to the two silver isotopes. Indeed, a slightly greater coupling constant of 11 Hz is observed for the quartet resonance in the ¹⁰⁹Ag NMR spectrum of **4** (Figure 2b), consistent with the 15% greater gyromagnetic ratio of ¹⁰⁹Ag relative to ¹⁰⁷Ag.⁴⁰ Complex **4** crystallizes as a monomer with linear coordination about silver (C–Ag–C = 180.0°) (Figure 3).

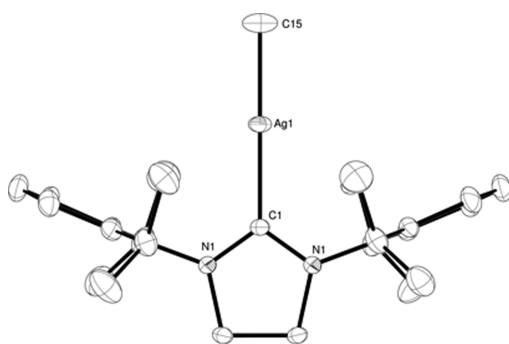


Figure 3. Solid-state structure of **4**, shown as 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1–C1, 2.114(3); Ag1–C15, 2.076(3); C1–Ag1–C15, 180.0; N1–C1–N1, 108.7(3).

Treatment of a suspension of (SDipp)AgCl in C₆D₆ with vinylmagnesium bromide resulted in a clear solution within seconds, indicating rapid consumption of the sparingly soluble starting complex. A ¹H NMR spectrum recorded 15 min after the addition of vinylmagnesium bromide exhibited broad signals at δ 6.59, 5.78, and 5.74 ppm, assigned to the vinylsilver complex. Traces of 1,3-butadiene, the vinyl homocoupling product, were also detected, and the deposition of elemental silver soon became visibly apparent. After 24 h, the integration of ¹H NMR signals against an internal standard suggested nearly complete conversion to free SDipp (>95%), with 1,3-butadiene formed in at least 80% yield⁴¹ (Scheme 2). Because of its thermal instability, this vinylsilver complex was not isolated.

Scheme 2. Decomposition of Inferred Vinylsilver Complex

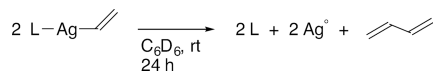


Table 1. ¹³C NMR Data for Donor Carbons of Monosilver Complexes (SDipp)AgR

compd	R	δ(¹³ C _{NHC}), ppm	¹ J(¹³ C _{NHC} – ^{107/109} Ag), Hz	δ(¹³ C _R), ppm	¹ J(¹³ C _R – ^{107/109} Ag), Hz
3	Et	214.6	100/115	1.4	129/149
4	Me	213.4	111/129	−15.7	120/138
5	CCPh	210.1	156/181	122.3	194/224
6	CF ₃	209.6	152/175	154.0	272/314

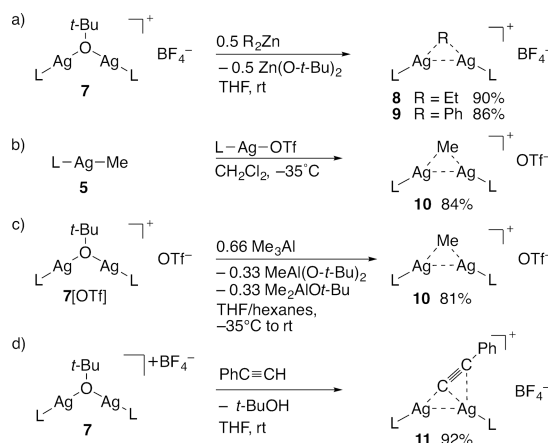
Deprotonation of phenylacetylene by **1** affords (SDipp)-AgCCPh (**5**) (Scheme 1d). This reaction proceeds rapidly and quantitatively in C₆D₆ or THF-*d*₈, as judged by ¹H NMR spectroscopy. Addition of hexanes to a THF solution of **5** causes its precipitation in 61% yield. Excess phenylacetylene may be used without adverse consequences.

A silver trifluoromethyl complex, (SDipp)AgCF₃ (**6**), was prepared by reaction of **1** with (trifluoromethyl)trimethylsilane in THF (Scheme 1e). Precipitation of the product by addition of hexanes allowed its isolation in 91% yield. The ¹⁹F NMR spectrum of **6** exhibits distinct ¹⁹F–¹⁰⁷Ag and ¹⁹F–¹⁰⁹Ag nuclear dipole coupling, giving rise to a pair of doublets at δ −291.9 ppm with ²J(¹⁹F–¹⁰⁷Ag) = 92 Hz and ²J(¹⁹F–¹⁰⁹Ag) = 106 Hz. The ¹⁰⁹Ag NMR spectrum displays a quartet resonance, again with a silver–fluorine coupling constant of 106 Hz.

The silver-bound carbon nuclei of the terminal organosilver complexes exhibit ¹³C NMR signals as pairs of doublets due to well-resolved coupling to ¹⁰⁷Ag and ¹⁰⁹Ag, as shown in Table 1. The ¹³C NMR signals of the Ag-bound carbons of **6** are further split into quartets, due to coupling to ¹⁹F (³J(¹³C_{NHC}–¹⁹F) = 5 Hz, ¹J(¹³C_R–¹⁹F) = 368 Hz).

Carbanion-Bridged Disilver Cations. Disilver complexes were prepared either by treatment of the alkoxide-bridged precursor {[(SDipp)Ag]₂(μ-O-*t*-Bu)}⁺ with a carbanion source or by the combination of a neutral organosilver species with equimolar (SDipp)AgOTf (OTf = trifluoromethanesulfonate), which serves as a ready source of [(SDipp)Ag]⁺ (Scheme 3).

Scheme 3. Synthesis of Carbanion-Bridged Disilver Cations



Both methyl-bridged⁴² and alkynyl-bridged⁴³ disilver cations have been generated in the gas phase by collision-induced dissociation of the corresponding carboxylate-bridged precursors; alkynyl-bridged cations can also be generated from neutral alkynylsilver(I) complexes by electrospray impact.⁴³ The reactions of these complexes with allyl iodide to form new C–C bonds have been studied using both mass spectrometry and density functional theory. Analogous complexes of gold(I)

with bridging carbanions have been studied extensively,⁴⁴ and are likely intermediates in gold-catalyzed processes.⁴⁵

The disilver cations feature three-center, two-electron bonding, characterized by short Ag–Ag distances, nonlinear geometry about each silver center, and ¹⁰⁹Ag–¹⁰⁷Ag nuclear dipolar coupling (see Table 2). This structural motif was

Table 2. ¹⁰⁹Ag NMR Data for [(LAg)₂R]⁺ Complexes

compd	R	δ (¹⁰⁹ Ag), ppm ^a	J(¹⁰⁹ Ag– ¹⁰⁷ Ag), Hz
8	Et	681.2	55
9	Ph	728.4	76
10	Me	no signal detected	
11	CCPh	673.9	18

^aChemical shift relative to 4.00 M AgNO₃ in D₂O.

previously observed in the hydride-bridged disilver complex {[(SDipp)Ag]₂(μ-H)}⁺,⁴⁶ and has been postulated in studies of hydrido-, alkyl- and arylsilver cations in the gas phase.^{8f,h}

The ethyl-bridged {[(SDipp)Ag]₂(μ-Et)}⁺BF₄[−] (**8**) was prepared by ligand exchange of **7** and 0.5 equiv of diethylzinc in THF (Scheme 3a). Precipitation of **8** by the addition of hexanes results in a 90% yield. The (SDipp)Ag fragments of **8** are equivalent in solution on the NMR time scale. Although coupling to silver is observed for both the α and β protons of the bridging ethyl ligand, the two isotopes of silver do not give rise to well-resolved couplings in the ¹H NMR spectrum. The two-bond and three-bond ¹H–¹⁰⁹Ag couplings in **8** are of approximately equal magnitude, and coincidentally roughly equal to the vicinal ¹H–¹H coupling (²J(¹H–^{107/109}Ag) ≈ ³J(¹H–^{107/109}Ag) ≈ ³J(¹H–¹H) ≈ 7 Hz), resulting in ¹H NMR signals resembling a sextet for the ethyl α protons at δ 0.64 ppm and a quintet for the β protons at δ 0.17 ppm. The ¹⁰⁹Ag NMR spectrum of **8** features an apparent triplet of sextets (Figure 4a), reflecting the roughly 7 Hz ¹H–Ag coupling observed in the ¹H NMR spectrum as well as substantial ¹⁰⁹Ag–¹⁰⁷Ag coupling (J(¹⁰⁹Ag–¹⁰⁷Ag) = 56 Hz). ¹H-decoupling reduces the ¹⁰⁹Ag NMR signal of **8** to an apparent triplet (Figure 4b). This signal is more properly described as a singlet arising from the homonuclear ¹⁰⁹Ag₂ isotopologue, and a superimposed doublet arising from the heteronuclear ¹⁰⁹Ag¹⁰⁷Ag isotopologue. Complex **8** crystallizes with a triangular Ag–C–Ag structure featuring a Ag⋯Ag distance of 2.7091(8) Å, considerably shorter than twice the van der Waals radius for silver of 1.72 Å (Figure 5a),⁴⁷ and similar to the distances found in silver amidinate dimers.⁴⁸

The phenyl-bridged disilver complex {[(SDipp)Ag]₂(μ-Ph)}⁺BF₄[−] (**9**) was prepared by treatment of **7** with diphenylzinc in THF (Scheme 3a) and precipitated in 86% yield by the addition of hexanes. As for **8**, the (SDipp)Ag fragments of **9** are equivalent according to NMR spectroscopy, and its solid-state structure (Figure 5b) likewise features a triangular Ag–C–Ag core. Interestingly the Ag⋯Ag distance of 2.8168(4) Å in **9** is somewhat longer than in **8**, yet the ¹⁰⁹Ag–¹⁰⁷Ag coupling is greater (J(¹⁰⁹Ag–¹⁰⁷Ag) = 76 Hz). The Ag–C distances in turn are somewhat shorter than in **8**. In principle, a weak donation from the phenyl π-system to a vacant Ag–Ag σ* orbital (Figure S21) would weaken the direct metal–metal interaction slightly, while strengthening the Ag–C interactions and a through-bond component of the ¹⁰⁹Ag–¹⁰⁷Ag coupling. This explanation is speculative, however, and other factors likely play a role.

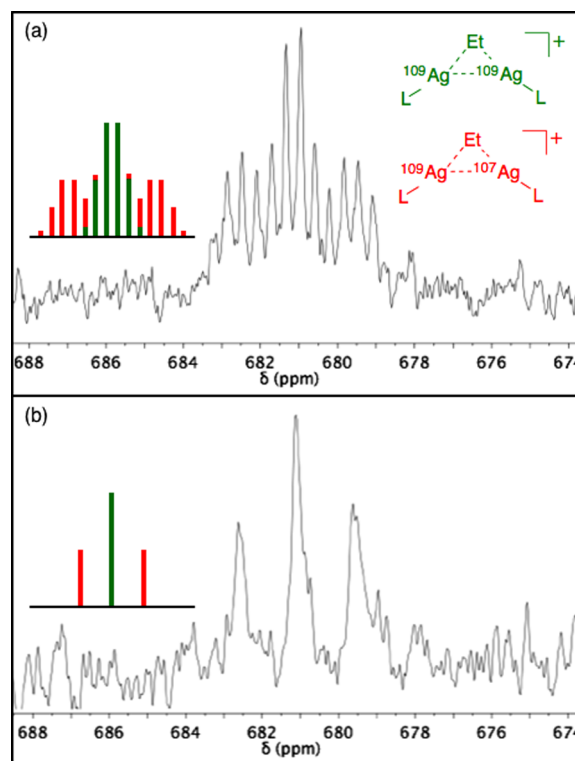


Figure 4. (a) ¹⁰⁹Ag and (b) ¹⁰⁹Ag{¹H} NMR spectra (18.6 MHz, CD₂Cl₂) of **8**. ²J(¹⁰⁹Ag–¹H) ≈ ³J(¹⁰⁹Ag–¹H) ≈ 7 Hz; J(¹⁰⁹Ag–¹⁰⁷Ag) = 57 Hz. Insets show rationalization of the pattern as the coincident signals arising from the two ¹⁰⁹Ag-containing isotopologues.

We synthesized the methyl-bridged complex {[(SDipp)Ag]₂(μ-Me)}⁺OTf[−] (**10**) by treatment of the terminal analogue **4** with 1 molar equivalent of (SDipp)AgOTf in CH₂Cl₂ at −35 °C (Scheme 3b). The complex may also be prepared³⁹ by treatment of **7**[OTf] with less than 1 equiv of trimethylaluminum at −35 °C (Scheme 3c); the very soluble byproducts Me₂AlOt-Bu and MeAl(Ot-Bu)₂ are easily separated from **10**. Although cold reaction conditions are required in both routes to prevent the formation of [(SDipp)₂Ag]⁺ and Ag⁰, the dinuclear complex **10** is stable at ambient temperature. The methyl ligand exhibits a singlet in the ¹H NMR spectrum of **10**, lacking the ¹H–^{107/109}Ag coupling observed for **4** as well as the ethyl-bridged analogue **8**. We were unable to detect a ¹⁰⁹Ag NMR signal for **10**. However, the triangular structural motif was confirmed by crystallography (Figure 5c). The Ag⋯Ag distance of 2.7061(16) Å is nearly the same as in ethyl-bridged complex **8**.

The disilver phenylethynyl complex {[(SDipp)Ag]₂(μ-CCPh)}⁺BF₄[−] (**11**) was synthesized via the deprotonation of phenylacetylene by **7** in THF (Scheme 3d). The single set of NHC resonances observed in its ¹H NMR spectrum suggests a symmetrically bridging phenylethynyl ligand, but the solid-state structure displays an asymmetric σ,π-bound arrangement. An analogous gold complex, bearing the supporting ligand IDipp [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, also denoted IPr], exhibits a similar solid-state structure.

Its ¹H NMR spectrum likewise featured resonances for equivalent NHC ligands, consistent with an averaged structure on the NMR timescale.^{45g} Recently Bertrand and co-workers reported a phenylacetylide-bridged dicopper cation, supported by a cyclic alkylaminocarbene (CAAC) ligand. This complex likewise exhibits equivalent carbene resonances in solution but

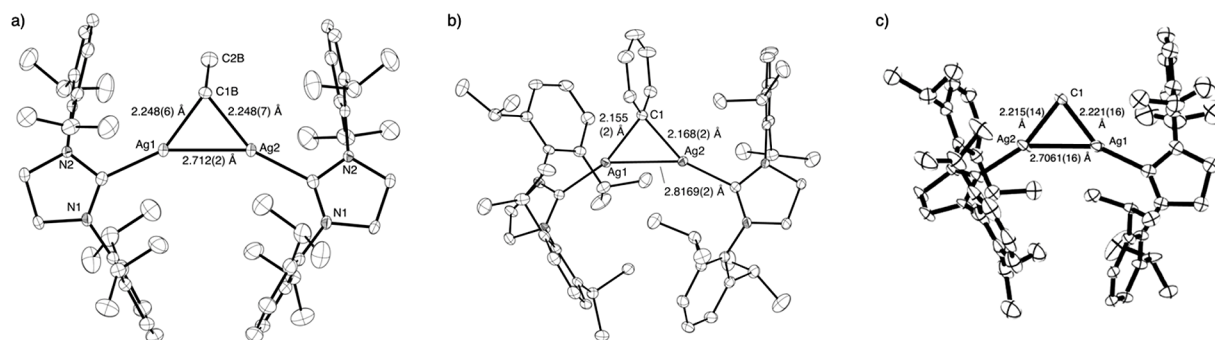


Figure 5. Solid-state structures of **8**, **9**, and **10**, shown as 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

distinctly asymmetric σ,π -binding to the two copper centers in the solid-state structure.⁴⁹

Two crystallographically distinct molecules, one of which is shown in **Figure 6**, are present in the asymmetric unit of **11**. In

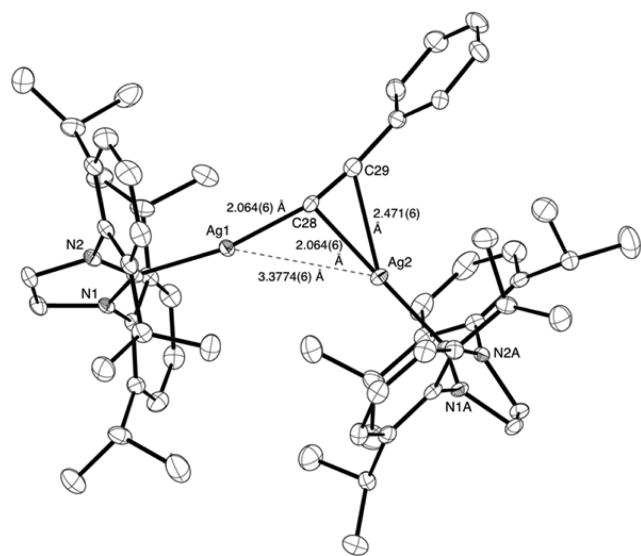


Figure 6. One of the two crystallographically distinct molecules of **11** in the asymmetric unit, shown as 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1–Ag2, 3.3707(7); Ag1–C28, 2.061(5); Ag2–C28, 2.177(5); Ag2–C29, 2.468(5); Ag1–C1, 2.092(5); Ag2–C1A, 2.094(5); C28–C29, 1.223(8); Ag1–C28–Ag2, 105.3(2).

contrast to the gold and copper analogues described above, the intermetallic distances in **11** (3.3774(6) and 3.2894(6) Å) are shorter than two van der Waals radii of the metal, albeit only slightly: A recent review sets ca. 3.44 Å as the distance within which an argentophilic interaction should be considered present.⁵⁰ In fact, the π -bound silver center is not equidistant from the two alkynyl carbon atoms but lies distinctly closer to the terminal carbon, resulting in a T-shaped binding mode. The η^2 -binding of organic alkynes and of metal alkynyls to copper(I) and silver(I) fragments has been reviewed.⁵¹ For side-bound acetylides bound to silver(I), differences in Ag–C distances on the order of 0.1 Å have been calculated when the donor ligand is a gold acetylide,⁵² and observed crystallographically for some,⁵³ but not all,⁵⁴ complexes bearing bis(alkynyl)titanocenes as ligands. A more pronounced difference, and an arrangement qualitatively similar to that in **11**, occurs in the solid-state structure of $[(\text{Me}_3\text{P})_2\text{Ag}]^+[\text{Ag}(\text{CCPh})_2]^-$: Each silver cation binds to two silver-bound

alkynyls, with distances of 2.552(14) Å to the carbanionic carbon and 3.040(12) Å to the phenyl-substituted carbon. The intermetallic distances are 3.033 Å.⁵⁵

Complex **11** exhibits an apparent triplet in its ¹⁰⁹Ag NMR spectrum, again actually a singlet and coincident doublet. At 18 Hz, the ¹⁰⁹Ag–¹⁰⁷Ag dipolar coupling of **11** is considerably smaller than that of **8** (55 Hz) and **9** (76 Hz). Although differences in solvent and ligation should be borne in mind, the chemical shift of 673.9 ppm is intermediate between the values reported for the $[(\eta^2\text{-1-hexyne})]\text{silver(I)}$ cation (990 ppm) and the corresponding σ -(1-hexynyl)silver(I) (416 ppm) in a weakly donating solvent.⁵⁶

In light of the importance of mass spectrometry to early studies of carbanion-bridged disilver cations,^{42,43} we sought to obtain electrospray ionization (ESI) mass spectra of complexes **8**–**11**. To date, we have been unable to obtain satisfactory mass spectra of ethyl-bridged **8** and methyl-bridged **10**, possibly because of their sensitivity in solution to oxidation and hydrolysis. The more robust phenyl- and phenylacetylide-bridged cations **9** and **11**, however, gave rise to intense parent ion peaks consistent with the calculated patterns, as shown in **Figure 7**.

Reactivity of Alkylsilver Complexes with CO₂. The insertion of CO₂ into Ag–C bonds is inferred from several silver-catalyzed carboxylations^{28,57} but has been difficult to study in isolation due to the transient nature of the organosilver intermediates in these processes. Because of their generally greater thermal stability, the reactivity of Cu–C³⁵ and Au–C³⁶ bonds toward CO₂ has been more thoroughly studied. Anticipating nucleophilic behavior, we investigated the reactivity of the NHC-supported organosilver compounds toward CO₂. Complex **3** reacts cleanly with CO₂ (1.0 bar) in CD₂Cl₂ solution, undergoing complete conversion to (SDipp)AgO₂CET (**12**) within 16 h at ambient temperature (**Scheme 4**). Evaporation of volatiles allows isolation of **12** in analytical purity. Complex **4** reacts more slowly with CO₂. After 92 h under CO₂ (1.0 bar) in THF-*d*₈, 79% conversion to the known complex (SDipp)AgO₂CMe⁵⁸ is observed, while 12% of **4** is unreacted and two unidentified new species represent 9% of the observed $[(\text{SDipp})\text{Ag}]$ resonances, as quantified by integration of ¹H NMR signals against an internal standard.

The alkynyl complex **5**, the trifluoromethyl complex **6**, and the bridging complexes **8**–**11** exhibited no reactivity toward carbon dioxide in solution at ambient temperature. Because the reactivity of metal–carbon bonds with CO₂ tends to correlate with their Lewis basicity,⁵⁹ we speculate that ethyl complex **3** reacts more readily than methyl complex **4** simply because of the inductive effect of the –CH₃ substituent on the silver-bound carbon. In this view the less basic alkynyl or

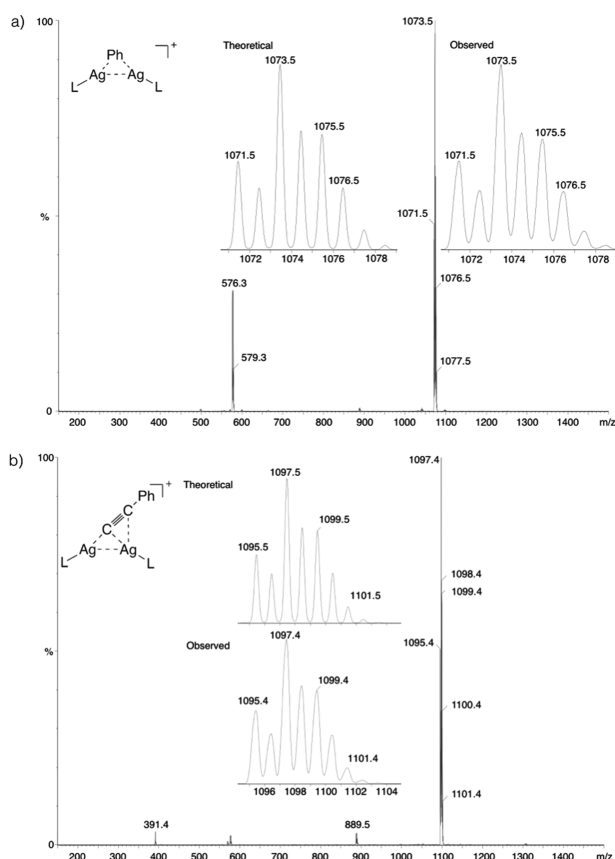
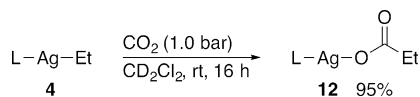


Figure 7. ESI mass spectra of complexes **9** (a) and **11** (b) in THF solution, positive ion mode. Insets are expanded to show the theoretical and observed patterns for the parent ion peaks.

Scheme 4. Reaction of **4** with CO₂



trifluoromethyl groups, or the bridging carbanions in [Ag₂R]⁺ cores, are kinetically deactivated toward CO₂ insertion. This lack of reactivity is somewhat surprising, however, in light of processes reported earlier in which the insertion of CO₂ into analogous silver–carbon bonds seems necessary.^{28,30} Further investigation will be needed to establish the reactive species in such processes, and to broaden the scope of this reactivity.

CONCLUSION

A bulky N-heterocyclic carbene ligand supports a series of terminal carbanion-bound silver complexes, as well as a series of carbanion-bridged disilver cations (Scheme 3). These series include donor carbons featuring sp³, sp²- and sp-hybridization. Most of these complexes, notably including simple neutral alkyls, proved stable at ordinary temperatures. This stability probably reflects the rather inert silver–carbene bonding. The silver vinyl complex, which decomposes readily to silver(0) and 1,3-butadiene at ordinary temperatures, represents a key exception to this stability. The dinuclear cations include several examples of three-center, two-electron systems featuring Ag–Ag interactions, as well as an alkynyl-bridged disilver complex with a T-shaped coordination mode. Insertion of CO₂ into a

terminal alkyl complex results in the clean formation of a silver carboxylate.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise indicated, manipulations were performed in an MBraun glovebox under an inert atmosphere of purified nitrogen (NexAir), or in sealable glassware on a Schlenk line under an atmosphere of argon (NexAir). Glassware and magnetic stir bars were dried in a ventilated oven at 160 °C and were allowed to cool under vacuum.

Dichloromethane (BDH), diethyl ether (EMD Millipore Omnisolv), hexanes (EMD Millipore Omnisolv), and THF (EMD Millipore Omnisolv) were sparged with argon for 30 min prior to first use and dried over 3 Å molecular sieves (1/16 in., Alfa-Aesar). Anhydrous benzene (EMD Millipore Drisolv) and anhydrous pentane (EMD Millipore Drisolv) were stored over 3 Å molecular sieves. Dichloromethane-*d*₂ (Cambridge Isotope Labs) was dried over calcium hydride overnight, vacuum-transferred to an oven-dried sealable flask, and degassed by successive freeze–pump–thaw cycles. Tetrahydrofuran-*d*₈ (Cambridge Isotope Labs) and benzene-*d*₆ (Cambridge Isotope Labs) were dried over sodium benzophenone ketyl, vacuum-transferred to an oven-dried sealable flask, and degassed by successive freeze–pump–thaw cycles. Deuterium oxide (Cambridge Isotope Labs) was used as received.

Carbon dioxide (NexAir) was passed through phosphorus pentoxide (Sigma-Aldrich) to ensure dryness. Phenylacetylene (Sigma-Aldrich) and (trifluoromethyl)trimethylsilane (Sigma-Aldrich) were dried by passing through activated alumina. Diethylzinc (Acros, 1 M in hexanes), 4,4'-dimethylbiphenyl (Sigma-Aldrich), diphenylzinc (Strem), methylmagnesium bromide (Strem, 3 M in diethyl ether), and vinylmagnesium bromide (Sigma-Aldrich, 0.70 M in THF) were used as received. Compounds **1**,⁴⁶ **2**,⁶⁰ **7**,⁴⁶ **7**[OTf],⁴⁶ and (SDipp)-AgOTf⁶⁰ were prepared according to published procedures.

¹H, ¹³C, ¹⁹F, and ¹⁰⁹Ag NMR spectra were obtained at the Georgia Institute of Technology NMR Center using a Bruker DSX 400 MHz spectrometer or a Varian Vx 400 MHz spectrometer. ¹H and ¹³C NMR chemical shifts were referenced with respect to solvent signals and are reported relative to tetramethylsilane. ¹⁰⁹Ag NMR chemical shifts were referenced with respect to an external solution of 4.00 M silver nitrate (Alfa-Aesar) in deuterium oxide (defined as δ 0 ppm). ¹⁹F NMR chemical shifts were referenced to external neat hexafluorobenzene (Alfa-Aesar, δ –164.90 ppm) and are reported with respect to trichlorofluoromethane.

Infrared spectra were collected using microcrystalline samples on a Bruker Alpha-P infrared spectrometer equipped with an attenuated total reflection (ATR) attachment. Samples were exposed to air as briefly as possible prior to data collection.

Mass spectra were obtained from THF solutions of the complexes using a Micromass (Waters) Quattro LC triple quadrupole mass spectrometer, scanning from *m/z* = 150 to 1500 Da in positive ion mode.

Elemental analyses were performed by Atlantic Microlab in Norcross, Georgia.

(SDipp)AgEt (3). A solution of diethylzinc (1.0 M in hexanes, 0.21 mL, 0.21 mmol) was added dropwise to a solution of **1** (0.200 g, 0.350 mmol) in THF (2 mL). The solution was stirred for 10 min, and then hexanes (15 mL) was added, causing the product to slowly crystallize. The crystals were allowed to grow for 3 days at –35 °C. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexanes (3 × 2 mL), and dried *in vacuo* for 30 min, affording **3** as a white powder (0.111 g, 0.194 mmol, 55%). Compound **3** hydrolyzes readily in the presence of atmospheric moisture. ¹H NMR (400 MHz, THF-*d*₈): δ (ppm) 7.34 (mult, 2H, *para*-CH), 7.24 (mult, 4H, *meta*-CH), 3.99 (s, 4H, NCH₂), 3.19 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.38 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.32 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 0.89 (approximate dtd, ³*J*(¹H–¹⁰⁹Ag) = 12.1 Hz, ³*J*(¹H–¹⁰⁷Ag) = 10.7 Hz, ³*J*(¹H–H) = 8.0 Hz, 3H, CH₂CH₃), –0.25 (approximate dqd, ²*J*(¹H–¹⁰⁹Ag) = 12.8 Hz, ²*J*(¹H–¹⁰⁷Ag) = 11.4 Hz, ³*J*(¹H–H) = 8.0 Hz, 2H, CH₂CH₃). ¹³C{¹H} NMR (100 MHz,

THF- d_8): δ (ppm) 214.6 (approximate dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 115$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 100$ Hz, NCAg), 147.5 (*ortho-C*), 136.5 (*ipso-C*), 129.7 (*para-C*), 124.6 (*meta-C*), 54.4 (d, $J(^{13}\text{C}-^{107/109}\text{Ag}) = 4$ Hz, NCH₂), 29.4 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.0 (CH(CH₃)₂), 16.9 (d, $J(^{13}\text{C}-\text{Ag}) = 4$ Hz, CH₂CH₃), 1.4 (approximate dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 149$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 129$ Hz, CH₂CH₃). ¹⁰⁹Ag NMR (18.6 MHz, THF- d_8): δ (ppm) 790.3 (sextet, $J(^{109}\text{Ag}-^1\text{H}) = 12.5$ Hz). IR: ν (cm⁻¹) 2961, 2931, 2837, 1490, 1463, 1275, 1099, 1049 (s), 804, 758. Anal. Calcd for C₂₉H₄₃N₂Ag: C, 66.03; H, 8.05; N, 5.31. Found: C, 65.85; H, 8.21; N, 5.17.

(5Dipp)AgMe (4). Method A: A solution of methylmagnesium bromide (3.0 M in THF, 0.30 mL, 0.90 mmol) was added to a suspension of **2** (0.400 g, 0.75 mmol) in THF (2 mL). The mixture was stirred until it became clear, less than 5 min. Dioxane (18 mL) was added and the mixture was stirred for 16 h, inducing precipitation of a magnesium halides as a white powder, which was removed by filtration through Celite. Volatiles were removed from the filtrate *in vacuo*, and the product was extracted from the residue with CH₂Cl₂. The extract was filtered through Celite, the solvent was removed *in vacuo*, and the residue was dried *in vacuo* for 2 h, affording **4** as a white powder (0.341 g, 0.66 mmol, 88%). Diffraction quality crystals were grown by diffusion of pentane vapor into a solution of **4** in CH₂Cl₂ at -35 °C over a period of 3 days. Compound **4** hydrolyzes readily in the presence of atmospheric moisture. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.45 (t, $J = 7.8$ Hz, 2H, *para-CH*), 7.29 (d, $J = 7.8$ Hz, 4H, *meta-CH*), 3.99 (s, 4H, NCH₂), 3.13 (sept, $J = 6.9$ Hz, 4H, CH(CH₃)₂), 1.37 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂), 1.35 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂), -1.38 (d, $J(^1\text{H}-\text{Ag}) = 10$ Hz, 3H, AgCH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 213.4 (approximate dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 129$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 111$ Hz, NCAg), 147.4 (*ortho-C*), 135.7 (*ipso-C*), 129.6, (*para-C*), 124.6 (*meta-C*), 54.1 (d, $J(^{13}\text{C}-^{107/109}\text{Ag}) = 5$ Hz, NCH₂), 29.2 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 24.1 (CH(CH₃)₂), -15.7 (approximate dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 138$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 120$ Hz, AgCH₃). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 842.1 (q, $J(^{109}\text{Ag}-^1\text{H}) = 11.2$ Hz). IR: ν (cm⁻¹) 2962, 2926, 2870, 1481, 1467, 1457, 1328, 1265, 1258, 809, 763. Anal. Calcd for C₂₈H₄₁N₂Ag: C, 65.49; H, 8.05; N, 5.46. Found: C, 65.73; H, 7.89; N, 5.59.

Method B: A solution of **1** (0.069 g, 0.12 mmol) in THF (1.5 mL) and a solution of trimethylaluminum (3 M in hexanes, 0.027 mL, 0.081 mmol) were chilled to -35 °C. The solution of **1** was added to the solution of trimethylaluminum, and the resulting mixture allowed to warm to room temperature with stirring. After 15 min, addition of pentane (6 mL) caused the formation of a white precipitate, which was collected on a fritted glass filter by vacuum filtration. The solid was redissolved in THF (1 mL), layered with pentane (5 mL) and placed in the freezer at -35 °C for 8 h. The supernatant was decanted by pipet, and the resulting crystals were dried *in vacuo* for 1 h to afford the title complex (0.052 g, 84%). The ¹H NMR spectrum of the product matched that of a sample prepared by Method A.

(5Dipp)AgCCPh (5). Phenylacetylene (0.047 mL, 0.42 mmol) was added to a solution of **1** (0.200 g, 0.350 mmol) in THF (2 mL). The solution was stirred for 10 min, and then hexanes (15 mL) was added, causing the product to slowly crystallize. The crystals were allowed to grow for 3 days at -35 °C. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexanes (3 × 2 mL), and dried *in vacuo* for 30 min, affording **5** as a white powder (0.128 g, 0.214 mmol, 61%). Compound **5** is air- and moisture-stable in the solid state and in solution. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.50 (t, $J = 7.8$ Hz, 2H, Dipp-*para-CH*), 7.33 (d, $J = 7.8$ Hz, 4H, Dipp-*meta-CH*), 7.19 (d, $J = 7$ Hz, 2H, CCPh-*ortho-CH*), 7.11 (t, $J = 7$ Hz, 2H; CCPh-*meta-CH*), 7.19 (t, $J = 7$ Hz, 1H, CCPh-*para-CH*), 4.05 (s, 4H, NCH₂), 3.11 (sept, $J = 6.9$ Hz, 4H, CH(CH₃)₂), 1.39 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂), 1.38 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 210.1 (approximate dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 181$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 156$ Hz, NCAg), 147.2 (Dipp-*ortho-C*), 135.2 (Dipp-*ipso-C*), 131.7 (CCPh-*ortho-C*), 130.1, (Dipp-*para-C*), 128.0 (CCPh-*meta-C*), 127.4 (CCPh-*para-C*), 125.7 (CCPh-*ipso-C*), 124.9 (Dipp-*meta-C*), 122.3 (approximate dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 224$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 194$ Hz, CCPh)

106.5 ($J(^{13}\text{C}-^{107/109}\text{Ag}) = 54$ Hz, CCPh), 54.3 (d, $J(^{13}\text{C}-^{107/109}\text{Ag}) = 6$ Hz, NCH₂), 29.2 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 24.1 (CH(CH₃)₂). IR: ν (cm⁻¹) 3076, 2963, 2929, 2871, 2093 (C≡C), 1597, 1486, 1464, 1270, 1059, 806, 758, 697, 622, 548, 528, 445. Anal. Calcd for C₃₅H₄₃N₂Ag: C, 70.11; H, 7.23; N, 4.67. Found: C, 69.88; H, 7.24; N, 4.70.

(5Dipp)AgCF₃ (6). (Trifluoromethyl)trimethylsilane (0.155 mL, 1.05 mmol) was added to a solution of **1** (0.500 g, 0.875 mmol) in THF (4 mL). The mixture was stirred for 30 min, and then hexanes (15 mL) was added, causing the product to precipitate. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexanes (3 × 2 mL), and dried *in vacuo* for 30 min, affording **6** as a white powder (0.451 g, 0.795 mmol, 91%). Compound **6** hydrolyzes readily in the presence of atmospheric moisture. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.46 (t, $J = 7.8$ Hz, 2H, *para-CH*), 7.30 (d, $J = 7.8$ Hz, 4H, *meta-CH*), 4.06 (s, 4H, NCH₂), 3.08 (sept, $J = 6.9$ Hz, 4H, CH(CH₃)₂), 1.35 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂), 1.33 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 209.6 (approximate ddq, $J(^{13}\text{C}-^{109}\text{Ag}) = 175$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 152$ Hz, $J(^{13}\text{C}-^{19}\text{F}) = 5$ Hz, NCAg), 154.0 (approximate qdd, $J(^{13}\text{C}-^{19}\text{F}) = 368$ Hz, $J(^{13}\text{C}-^{109}\text{Ag}) = 314$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 272$ Hz, CF₃), 147.2 (Dipp-*ortho-C*), 134.9 (Dipp-*ipso-C*), 130.2, (Dipp-*para-C*), 124.9 (Dipp-*meta-C*), 54.4 (d, $J(^{13}\text{C}-^{107/109}\text{Ag}) = 5$ Hz, NCH₂), 29.2 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 24.1 (CH(CH₃)₂). ¹⁹F NMR (376 MHz, CD₂Cl₂): δ (ppm) 251.3 (approximate dd, $J(^{109}\text{Ag}-^{19}\text{F}) = 92$ Hz, $J(^{109}\text{Ag}-^{19}\text{F}) = 106$ Hz). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 601.3 (q, $J(^{109}\text{Ag}-^{19}\text{F}) = 106$ Hz). IR: ν (cm⁻¹) 2964, 2926, 2869, 1488, 1469, 1272, 1110, 938 (s), 807, 762, 446. Anal. Calcd for C₂₈H₃₈N₂AgF₃: C, 59.26; H, 6.75; N, 4.94. Found: C, 59.11; H, 6.78; N, 5.00.

{(5Dipp)Ag}₂(μ -Et)}⁺BF₄⁻ (8). A solution of diethylzinc (1.0 M in hexanes, 0.10 mL, 0.10 mmol) was added dropwise to a solution of **7** (0.200 g, 0.173 mmol) in THF (2 mL). The solution was stirred for 10 min, and then hexanes (15 mL) was added with stirring, causing the formation of a white precipitate. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexanes (3 × 2 mL), and dried *in vacuo* for 30 min, affording **8** as a white powder (0.171 g, 0.154 mmol, 90%). Diffraction-quality crystals were grown by diffusion of Et₂O vapor into a solution of **8** in CH₂Cl₂ at -35 °C for 48 h. Compound **8** hydrolyzes readily in the presence of atmospheric moisture. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.40 (t, $J = 7.8$ Hz, 4H, *para-CH*), 7.18 (d, $J = 7.8$ Hz, 8H, *meta-CH*), 4.02 (s, 8H, NCH₂), 2.92 (sept, $J = 6.9$ Hz, 8H, CH(CH₃)₂), 1.28 (d, $J = 6.9$ Hz, 24H, CH(CH₃)₂), 1.01 (d, $J = 6.9$ Hz, 24H, CH(CH₃)₂), 0.64 (approximate sextet, $^2J(^1\text{H}-^{109}\text{Ag}) \approx ^2J(^1\text{H}-^{107}\text{Ag}) \approx ^3J(^1\text{H}-^1\text{H}) \approx 7$ Hz, 2H, CH₂CH₃), 0.17 (approximate quint, $^3J(^1\text{H}-^{109}\text{Ag}) \approx ^3J(^1\text{H}-^{107}\text{Ag}) \approx ^3J(^1\text{H}-^1\text{H}) \approx 7$ Hz, 3H, CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 208.8 (mult, NCAg), 146.9 (*ortho-C*), 135.0 (*ipso-C*), 130.0 (*para-C*), 124.8 (*meta-C*), 54.4 (approximate 1:1:1 t, $J(^{13}\text{C}-^{107/109}\text{Ag}) = 6$ Hz, NCH₂), 28.9 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 13.4 (t, $J(^{13}\text{C}-\text{Ag}) = 2$ Hz, CH₂CH₃), -1.9 (approximate tt, $J(^{13}\text{C}-^{109}\text{Ag}) = 74$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 64$ Hz, CH₂CH₃). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 681.2 (approximate t of sextets, $^3J(^1\text{H}-^{109}\text{Ag}) \approx ^2J(^1\text{H}-^{109}\text{Ag}) \approx 7$ Hz, $J(^{109}\text{Ag}-^{107}\text{Ag}) = 55$ Hz). ¹⁰⁹Ag{¹H} NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 681.2 (approximate t, $J(^{109}\text{Ag}-^{107}\text{Ag}) = 55$ Hz). IR: ν (cm⁻¹) 2957, 2929, 2871, 1490, 1462, 1275, 1099, 1056 (s), 803, 756. Anal. Calcd for C₅₆H₈₁N₄Ag₂BF₄: C, 60.44; H, 7.34; N, 5.03. Found: C, 60.47; H, 7.33; N, 4.91.

{(5Dipp)Ag}₂(μ -Ph)}⁺BF₄⁻ (9). Diphenylzinc (0.023 g, 0.10 mmol) was added to a solution of **7** (0.200 g, 0.173 mmol) in THF (2 mL). The solution was stirred for 10 min, and then hexanes (15 mL) was added with stirring, causing the formation of a white precipitate. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexanes (3 × 2 mL), and dried *in vacuo* for 30 min, affording **9** as a white powder (0.173 g, 0.149 mmol, 86%). Diffraction-quality crystals were grown by diffusion of pentane vapor into a solution of **9** in THF at -35 °C for 48 h. Compound **9** hydrolyzes readily in the presence of atmospheric moisture. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.38 (t, $J = 7.8$ Hz, 4H, Dipp-*para-*

Table 3. X-ray Crystallographic Parameters and Refinement Data

	(SDipp)AgMe	{[(SDipp)Ag] ₂ (μ-Et)} ⁺ [BF ₄] ⁻	{[(SDipp)Ag] ₂ (μ-Ph)} ⁺ [BF ₄] ⁻	{[(SDipp)Ag] ₂ (μ-Me)} ⁺ [O ₃ SCF ₃] ⁻	{[(SDipp)Ag] ₂ (μ-CCPh)} ⁺ [BF ₄] ⁻
empirical formula	C ₂₈ H ₄₁ AgN ₂	C ₁₁₂ H ₁₆₂ Ag ₄ B ₂ F ₈ N ₈	C ₆₈ H ₉₇ Ag ₂ BF ₄ N ₄ O ₂	C ₅₆ H ₇₉ Ag ₂ F ₃ N ₄ O ₃ S	C ₇₀ H ₉₇ Ag ₂ BF ₄ N ₄ O ₂
CCDC number ^{a†}	1519157	1519158	1519159	1519160	1519161
formula weight	513.50	2225.59	1305.04	1161.03	1329.06
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>Pccn</i>	<i>C2</i>	<i>P</i> $\bar{1}$	<i>P2₁/n</i>	<i>P2₁</i>
crystal size (mm)	0.386 × 0.219 × 0.145	0.81 × 0.62 × 0.37	0.42 × 0.42 × 0.26	0.22 × 0.12 × 0.10	0.512 × 0.196 × 0.126
<i>a</i> (Å)	10.9650(4)	24.156(7)	10.22449(11)	11.9647(15)	12.50202(20)
<i>b</i> (Å)	12.6078(3)	12.240(4)	16.3504(2)	16.135(2)	31.8127(5)
<i>c</i> (Å)	19.5211(6)	29.519(9)	20.3736(3)	33.041(4)	17.2528(3)
α (Å)	90	90	86.8617(10)	90	90
β (Å)	90	104.219(4)	79.8545(10)	91.299(2)	99.2266(17)
γ (Å)	90	90	88.8799(9)	90	90
<i>V</i> (Å ³)	2698.69(13)	8460(5)	3347.50(7)	6377.1(14)	6773.0(2)
<i>Z</i>	4	3	2	4	4
absorption coefficient (mm ⁻¹)	0.763	0.745	0.640	0.695	0.637
<i>D</i> _{calc} (g/cm ³)	1.264	1.310	1.295	1.209	1.308
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)	100(2)
θ (deg)	2.087–29.567	1.710–29.572	2.024–29.574	1.405–24.713	1.50–29.575
reflections collected	32 554	57 223	68 935	35 281	86 841
independent reflections (<i>R</i> _{int})	3796 (0.0638)	23570 (0.0283)	18720 (0.0476)	10863 (0.137)	37836 (0.0474)
data/restraints/parameter	3796/0/147	23570/81/980	18720/91/779	10863/811/699	37836/287/1569
final <i>R</i> ₁ indices [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0468 <i>wR</i> ₂ = 0.1019	<i>R</i> ₁ = 0.0394 <i>wR</i> ₂ = 0.0948	<i>R</i> ₁ = 0.0438 <i>wR</i> ₂ = 0.1065	<i>R</i> ₁ = 0.1350 <i>wR</i> ₂ = 0.2673	<i>R</i> ₁ = 0.0510 <i>wR</i> ₂ = 0.1058
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0629 <i>wR</i> ₂ = 0.1091	<i>R</i> ₁ = 0.0433 <i>wR</i> ₂ = 0.0991	<i>R</i> ₁ = 0.0567 <i>wR</i> ₂ = 0.1127	<i>R</i> ₁ = 0.1965 <i>wR</i> ₂ = 0.2834	<i>R</i> ₁ = 0.0638 <i>wR</i> ₂ = 0.1117
largest difference peak/hole (e Å ⁻³)	1.60/−0.28	1.37/−0.70	1.56/−0.66	1.46/−1.92	1.08/−0.60
goodness of fit	1.087	1.047	1.047	1.157	1.031

^{a†}Crystallographic information files have also been deposited with the Cambridge Crystallographic Database, and are available via the Internet at <http://www.ccdc.cam.ac.uk/>

CH), 7.12 (d, *J* = 7.8 Hz, 8H, Dipp-*meta*-CH), 6.99 (t, *J* = 7.5 Hz, 1H, μ -Ph-*para*-CH), 6.69 (t, *J* = 7.5 Hz, 2H, μ -Ph-*meta*-CH), 6.14 (mult, 2H, μ -Ph-*ortho*-CH), 3.96 (s, 8H, NCH₂), 2.82 (sept, *J* = 6.9 Hz, 8H, CH(CH₃)₂), 1.22 (d, *J* = 6.9 Hz, 24H, CH(CH₃)₂), 0.84 (d, *J* = 6.9 Hz, 24H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 208.9 (mult, NCAg), 146.9 (Dipp-*ortho*-C), 144.74 (t, *J*(¹³C-Ag) = 3 Hz, μ -Ph-C) 136.0 (approximate tt, *J*(¹³C-¹⁰⁹Ag) = 94 Hz, *J*(¹³C-¹⁰⁷Ag) = 81 Hz, μ -Ph-*ipso*-C), 134.7 (Dipp-*ipso*-C), 131.5 (μ -Ph-*para*-C), 130.0, (Dipp-*para*-C), 127.7 (t, *J*(¹³C-Ag) = 3 Hz, μ -Ph-C), 124.8 (Dipp-*meta*-C), 54.3 (approximate 1:1:1 t, *J*(¹³C-^{107/109}Ag) = 3 Hz, NCH₂), 28.9 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 24.0 (CH(CH₃)₂). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 728.4 (approximate t, *J*(¹⁰⁹Ag-¹⁰⁷Ag) = 76 Hz). IR: ν (cm⁻¹) 2956, 2929, 2872, 1490, 1460, 1273, 1098, 1051 (s), 804, 769, 758. Anal. Calcd for C₃₁H₄₇N₂AgO: C, 62.08; H, 7.03; N, 4.83. Found: C, 62.03; H, 6.91; N, 4.81.

{[(SDipp)Ag]₂(μ-Me)}⁺[OTf]⁻ (10). Method A: A solution of **5** (0.050 g, 0.097 mmol) in THF (2 mL) and a solution of (SDipp)Ag(OTf) (0.063 g, 0.097 mmol) in THF (2 mL) were chilled to -35 °C. The (SDipp)Ag(OTf) solution was added to the solution of **5** dropwise with stirring. The mixture was allowed to warm to room temperature. After 15 min, the mixture was filtered to remove traces of a barely perceptible gray precipitate. Diethyl ether (15 mL) was added to the filtrate, causing the formation of a white precipitate, which was collected on a fritted glass filter by vacuum filtration, washed with diethyl ether (3 × 2 mL), and dried *in vacuo* for 2 h, affording the product as a white powder (0.094 mg, 0.081 mmol, 84%). Diffraction-quality crystals were grown by the diffusion of a layer of Et₂O into a CH₂Cl₂ solution of **10** at -35 °C over a period of 3 days. Compound **10** hydrolyzes readily in the presence of atmospheric moisture. ¹H

NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.40 (t, *J* = 7.8 Hz, 4H, *para*-CH), 7.18 (d, *J* = 7.8 Hz, 8H, *meta*-CH), 3.98 (s, 8H, NCH₂), 2.89 (sept, *J* = 6.9 Hz, 8H, CH(CH₃)₂), 1.27 (d, *J* = 6.9 Hz, 24H, CH(CH₃)₂), 0.98 (d, *J* = 6.9 Hz, 24H, CH(CH₃)₂), -0.87 (s, 3H, AgCH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 208.4 (approximate dd, *J*(¹³C-¹⁰⁹Ag) = 216 Hz, *J*(¹³C-¹⁰⁷Ag) = 186 Hz, NCAg), 146.9 (*ortho*-C), 134.8 (*ipso*-C), 130.1, (*para*-C), 124.9 (*meta*-C), 121.4 (q, *J*(¹³C-¹⁹F) = 319 Hz, O₃SCF₃), 54.4 (NCH₂), 28.9 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), -15.7 (dd, *J*(¹³C-¹⁰⁹Ag) = 138 Hz, *J*(¹³C-¹⁰⁷Ag) = 120 Hz, AgCH₃), Ag₂CH₃ not detected. ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): Signal not detected. IR: ν (cm⁻¹) 2961, 2927, 2872, 1488, 1457, 1267 (s), 1149, 1031, 804, 759, 637 (s). Anal. Calcd for C₅₆H₇₉N₄Ag₂F₃O₃S: C, 57.93; H, 6.86; N, 4.83. Found: C, 58.14; H, 6.80; N, 4.89.

Method B: A solution of **7**[OTf] (0.089 g, 0.072 mmol) in THF (1.5 mL) and a solution of trimethylaluminum (3 M in hexanes, 0.016 mL, 0.048 mmol) were chilled to -35 °C. The solution of **7** was added to the solution of trimethylaluminum, and the resulting mixture allowed to warm to room temperature with stirring. After 15 min, addition of pentane (6 mL) caused the formation of a white precipitate, which was collected on a fritted glass filter by vacuum filtration. The collected solid was redissolved in THF (1.5 mL), layered with pentane (4 mL) and placed in the freezer at -35 °C for 6 h. The supernatant was decanted by pipet, and the resulting crystals were dried *in vacuo* for 1 h to afford the title complex (0.067 g, 81%). The ¹H NMR spectrum of the product matched that of a sample prepared by Method A.

{[(SDipp)Ag]₂(μ-CCPh)}⁺BF₄⁻ (11). Phenylacetylene (0.023 mL, 0.21 mmol) was added to a solution of **7** (0.200 g, 0.173 mmol) in THF (2 mL). The solution was stirred for 10 min, and then hexanes

(15 mL) was added with stirring, causing the formation of a white precipitate. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexanes (3 × 2 mL), and dried *in vacuo* for 30 min, affording the product as a white powder (0.188 g, 0.159 mmol, 92%). Diffraction-quality crystals were grown by diffusion of pentane vapor into a solution of **11** in THF at −35 °C for 48 h. Compound **11** is air- and moisture-stable in the solid state and in solution. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.40 (t, *J* = 7.8 Hz, 4H, Dipp-*para*-CH), 7.25 (t, *J* = 8 Hz, 1H, CCPh-*para*-CH), 7.19 (d, *J* = 8 Hz, 8H, Dipp-*meta*-CH), 7.12 (t, *J* = 7.2 Hz, 8 Hz; 2H; CCPh-*meta*-CH), 6.65 (d, *J* = 6.9 Hz, 2H, CCPh-*ortho*-CH), 4.03 (s, 8H, NCH₂), 2.96 (sept, *J* = 6.9 Hz, 8H, CH(CH₃)₂), 1.29 (d, *J* = 6.9 Hz, 24H, CH(CH₃)₂), 1.05 (d, *J* = 6.9 Hz, 24H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 207.3 (approximate dd, *J*(¹³C–¹⁰⁹Ag) = 233 Hz, *J*(¹³C–¹⁰⁷Ag) = 201 Hz, NCAg), 147.0 (Dipp-*ortho*-C), 134.7 (Dipp-*ipso*-C), 132.9 (CCPh-*ortho*-C), 130.2, (Dipp-*para*-C), 129.3 (CCPh-*para*-C), 128.4 (CCPh-*meta*-C), 125.0 (CCPh-*ipso*-C) 124.8 (Dipp-*meta*-C), 121.3 (mult, CCPh), 98.5 (mult, CCPh) 54.4 (approximate 1:1:1 t, *J*(¹³C–^{107/109}Ag) = 4 Hz, NCH₂), 29.0 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.0 (CH(CH₃)₂). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 673.9 (approximate t, *J*(¹⁰⁹Ag–¹⁰⁷Ag) = 18 Hz). IR: ν (cm^{−1}) 2961, 2930, 2871, 1487, 1459, 1272, 1048 (s), 804, 756, 443. Anal. Calcd for C₆₂H₈₁N₄Ag₂BF₄: C, 62.85; H, 6.89; N, 4.75. Found: C, 62.85; H, 6.96; N, 5.76.

(5Dipp)Ag(O₂CET) (12). A solution of (5Dipp)AgEt (0.120 g, 0.227 mmol) in CD₂Cl₂ (1.0 mL) in a J. Young NMR tube was degassed by two freeze–pump–thaw cycles, and the tube was backfilled with carbon dioxide (1.0 bar). After 16 h, the ¹H and ¹³C NMR spectra of the product were recorded. The tube was opened to air, and no more effort was made to maintain an inert atmosphere. The solution was transferred to a vial, and the volatiles were removed *in vacuo*. The residue was dried for 4 h at 40 °C, affording **12** as a white powder (0.123 mg, 0.216 mmol, 95%). Compound **12** is air- and moisture-stable in the solid state and in solution. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.46 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.30 (d, *J* = 7.8 Hz, 4H, *meta*-CH), 4.08 (s, 4H, NCH₂), 3.09 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.95 (q, *J* = 7.6 Hz, 2H, CH₂CH₃), 1.36 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.35 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 0.87 (t, *J* = 7.6 Hz, 3H, CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 207.8 (approximate dd, *J*(¹³C–¹⁰⁹Ag) = 247 Hz, *J*(¹³C–¹⁰⁷Ag) = 205 Hz, NCAg), 180.6 (O₂C) 147.2 (Dipp-*ortho*-C), 135.2 (Dipp-*ipso*-C), 130.1, (Dipp-*para*-C), 124.9 (Dipp-*meta*-C), 54.5 (d, *J*(¹³C–^{107/109}Ag) = 9 Hz, NCH₂), 29.4 (CH₂CH₃), 29.2 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.1 (CH(CH₃)₂) 11.1 (CH₂CH₃). IR: ν (cm^{−1}) 2965, 2920, 2868, 2850, 1727 (C=O), 1588, 1488, 1461, 1385, 1275, 1058, 805, 760. Anal. Calcd for C₃₀H₄₃N₂AgO₂: C, 63.04; H, 7.58; N, 4.90. Found: C, 62.77; H, 7.64; N, 4.86.

Reaction of Vinylmagnesium Bromide with (5Dipp)AgCl. A solution of vinylmagnesium bromide (0.70 M in THF) was added to a suspension of (5Dipp)AgCl (0.030 g, 0.056 mmol) in C₆D₆, resulting instantly in a transiently clear solution from which elemental silver gradually precipitated. The ¹H NMR spectrum was recorded after 15 min (see Figure S19 in the Supporting Information). The reaction was repeated with the addition of an internal standard of 4,4'-dimethylbiphenyl (0.010 g, 0.056 mmol) in a sealed NMR tube, and the ¹H NMR spectrum was recorded after 24 h.

Reaction of (5Dipp)AgMe (4) with CO₂. Several crystals of 4,4'-dimethylbiphenyl (internal standard) were added to a solution of **4** (0.040 g, 0.076 mmol) in THF-*d*₈ (1.0 mL) in a J. Young NMR tube. A preliminary ¹H NMR spectrum was recorded to quantify the amount of internal standard relative to **4**. The solution was degassed by two freeze–pump–thaw cycles, and the tube was backfilled with carbon dioxide (1.0 bar). After 92 h, the ¹H NMR spectrum was again recorded (see Figure S20 in the Supporting Information), and the products quantified by integration of NMR signals.

X-ray Diffraction Studies. For each structurally characterized complex, diffraction-quality crystals were grown as described in the individual entry. A suitable crystal was selected, fixed on a loop using paratone oil, and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100(2) K during data collection (see Table 3

for more information). Using Olex2,⁶¹ the structure was solved with the XT⁶² or XS⁶³ structure solution program using direct methods and refined with the XL⁶³ refinement package using least-squares minimization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00771.

X-ray crystallographic data for (5Dipp)AgMe, {[(5Dipp)Ag]₂(μ-Et)⁺[BF₄][−]}, {[(5Dipp)Ag]₂(μ-Ph)⁺[BF₄][−]}, {[(5Dipp)Ag]₂(μ-Me)⁺[O₃SCF₃][−]}, and {[(5Dipp)Ag]₂(μ-CCPh)⁺[BF₄][−] (CIF)

NMR spectra of isolated compounds and key reaction mixtures (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: joseph.sadighi@chemistry.gatech.edu.

ORCID

Joseph P. Sadighi: 0000-0003-1304-1170

Present Address

[§]B.K.T.: Department of Chemistry, University of Illinois at Urbana–Champaign.

Notes

The authors declare no competing financial interest.

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