

A dinuclear silver hydride and an umpolung reaction of CO₂

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For crystallographic data in CIF format see DOI: 10.1039/b000000x/

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General Considerations

Unless otherwise indicated, manipulations were performed in an MBraun glovebox under an inert atmosphere of nitrogen, or in sealable glassware on a Schlenk line under an atmosphere of argon. Glassware and magnetic stir bars were dried in a ventilated oven at 160°C and were allowed to cool under vacuum. Compounds of silver were stored in the dark as a precaution against photodegradation, and glassware was covered with aluminum foil during manipulations to minimize exposure to light.

Dichloromethane (BDH), diethyl ether (EMD Millipore Omnisolv), hexane (EMD Millipore Omnisolv), tetrahydrofuran (THF, EMD Millipore Omnisolv), and toluene (EMD Millipore Omnisolv) were sparged with ultra high purity argon (NexAir) for 30 minutes prior to first use, dried using an MBraun solvent purification system, transferred to Straus flasks, degassed using three freeze-pump-thaw cycles, and stored under nitrogen or argon. Anhydrous benzene (EMD Millipore Drisolv) and anhydrous pentane (EMD Millipore Drisolv), both sealed under a nitrogen atmosphere, were used as received and stored in a glovebox. Tap water was purified in a Barnstead International automated still prior to use.

Dichloromethane- d_2 (Cambridge Isotope Labs) and acetonitrile- d_3 (Cambridge Isotope Labs) were dried over excess 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) was 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), chloroform- d (Cambridge Isotope Labs), and methanol- d_1 (Cambridge Isotope Labs) were used as received.

Sodium *tert*-butoxide (TCI America), potassium *tert*-butoxide (Alfa-Aesar), silver trifluoromethanesulfonate (Alfa-Aesar), silver nitrate (Alfa-Aesar), triphenylcarbenium tetrafluoroborate (Alfa-Aesar), sodium trimethylsilylanolate (Sigma-Aldrich), tetrafluoroboric acid (50% w/w aqueous solution, Sigma-Aldrich), 1,3-diisopropylimidazolium chloride (Sigma-Aldrich), 1,3-diisopropylimidazolium tetrafluoroborate (Sigma-Aldrich), trichlorophenylsilane (Sigma-Aldrich), lithium aluminum deuteride (Sigma-Aldrich), magnesium sulfate (Alfa-Aesar), sodium metal (Alfa-Aesar), benzophenone (Alfa-Aesar), calcium hydride (Alfa-Aesar), $^{13}\text{C}_2$ (Cambridge Isotope Labs), potassium bromide (anhydrous, spectroscopic grade, Sigma-Aldrich), nitrogen (NexAir), and argon (both industrial and ultra high purity grades, NexAir) were used as received. Phenylsilane (Sigma-Aldrich) was degassed using three freeze-pump-thaw cycles prior to use. $\text{SIDipp}\cdot\text{HCl}\cdot(\text{EtO})_3\text{CH}^1$ and $(\text{SIDipp})\text{AgCl}^2$ were prepared according to literature protocols and were characterized by ^1H NMR spectroscopy. Phenylsilane- d_3 was prepared by the reaction of trichlorophenylsilane with lithium aluminum deuteride in analogy to a published protocol for the preparation of alkylsilanes.³ *N,N*-Dimethylanilinium tetrafluoroborate was prepared according to a published procedure.⁴

Spectroscopic Measurements

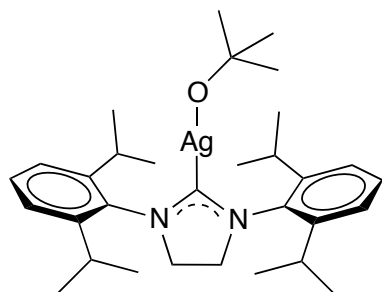
^1H , ^2H , ^{13}C , and ^{109}Ag NMR spectra were obtained using a Bruker DSX 400 MHz spectrometer, and ^{19}F NMR spectra were obtained using a Varian Vx 400 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are referenced with respect to solvent signals⁵ and are reported relative to tetramethylsilane. ^2H NMR chemical shifts are referenced to solvent signals, with the assumption that the ^2H chemical shifts of deuterated solvents are identical to the ^1H chemical shifts of their protiated isotopologues. ^{109}Ag 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). ^{19}F NMR chemical shifts were referenced to external neat hexafluorobenzene (Alfa-Aesar, δ -164.90 ppm) and are reported with respect to trichlorofluoromethane.

Samples for infrared spectroscopy were prepared as pellets in potassium bromide, using a pellet die which was dried in a ventilated oven at 160°C and cooled under vacuum prior to use. The pellets were prepared in the glovebox under an atmosphere of dry nitrogen, and were exposed to air as briefly as possible prior

to data collection. Spectra were recorded using a Perkin Elmer Spectrum 1000 infrared spectrometer.

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

Experimental Procedures



(SIDipp)Ag(Ot-Bu). (SIDipp)Ag(Ot-Bu) was prepared by a modification of the reported procedure.⁶ Sodium *tert*-butoxide (0.360 g, 3.74 mmol) was added to a suspension of (SIDipp)AgCl (2.000 g, 3.746 mmol) in THF (10 mL) with stirring. The reaction flask was covered with foil to exclude light. After stirring for 2 hours, the reaction mixture was filtered through Celite, and the filter pad was washed with two portions of THF (5 mL each). The solvent was removed from the filtrate under vacuum, and the residue was dried in the dark for 16 hours at 40°C under vacuum, affording the product as a white powder (2.283 g, 3.47 mmol, 93%). In anhydrous CH₂Cl₂, (SIDipp)Ag(Ot-Bu) rapidly decomposes to (SIDipp)AgCl and *tert*-butanol. The product hydrolyses readily in the presence of atmospheric moisture. ¹H NMR (400 MHz, THF-*d*₈): δ (ppm) 7.35 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.26 (d, *J* = 7.8 Hz, 4H, *meta*-CH), 4.06 (s, 4H, NCH₂), 3.15 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.35 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.31 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 0.66 (s, 9H, OC(CH₃)₃). ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ (ppm) 209.0 (pseudo-dd, *J*(¹³C-¹⁰⁹Ag) = 218 Hz, *J*(¹³C-¹⁰⁷Ag) = 190 Hz, NCAg), 147.5 (*ortho*-C), 136.4 (*ipso*-C), 129.9 (*para*-C), 124.9 (*meta*-C), 68.5 (OC(CH₃)₃), 54.5 (d, *J*(¹³C-Ag) = 7 Hz, NCH₂), 37.13 (OC(CH₃)₃), 29.3 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.2 (CH(CH₃)₂). ¹⁰⁹Ag NMR (18.6 MHz, THF-*d*₈): δ (ppm) 677.2 (s). IR: ν (cm⁻¹) 3071 (w), 2981 (s), 2930, 2870, 1941 (w), 1871 (w), 1800 (w), 1706 (w), 1655 (w), 1489 (s), 1467 (s), 1459 (s), 1384, 1388, 1342, 1327, 1274 (s), 1249, 1216, 1190 (s), 1180, 1116, 1103, 1060, 1017, 961 (s), 935, 913, 878, 804 (s), 757 (s), 711, 620, 563, 547, 516, 445. Anal. Calcd. for C₃₁H₄₇N₂AgO: C, 65.14; H, 8.29; N, 4.90. Found: C, 64.54; H, 8.13; N, 4.59. Note: Attempts to purify this complex further, via filtration or recrystallization, have failed to result in satisfactory carbon analyses. Both complexes prepared directly from this one, **1**[OTf] and **1**[BF₄], were nonetheless isolated in analytically pure form. The purity of the (SIDipp)Ag(Ot-Bu) reported here is unsatisfying, but sufficient for practical purposes.

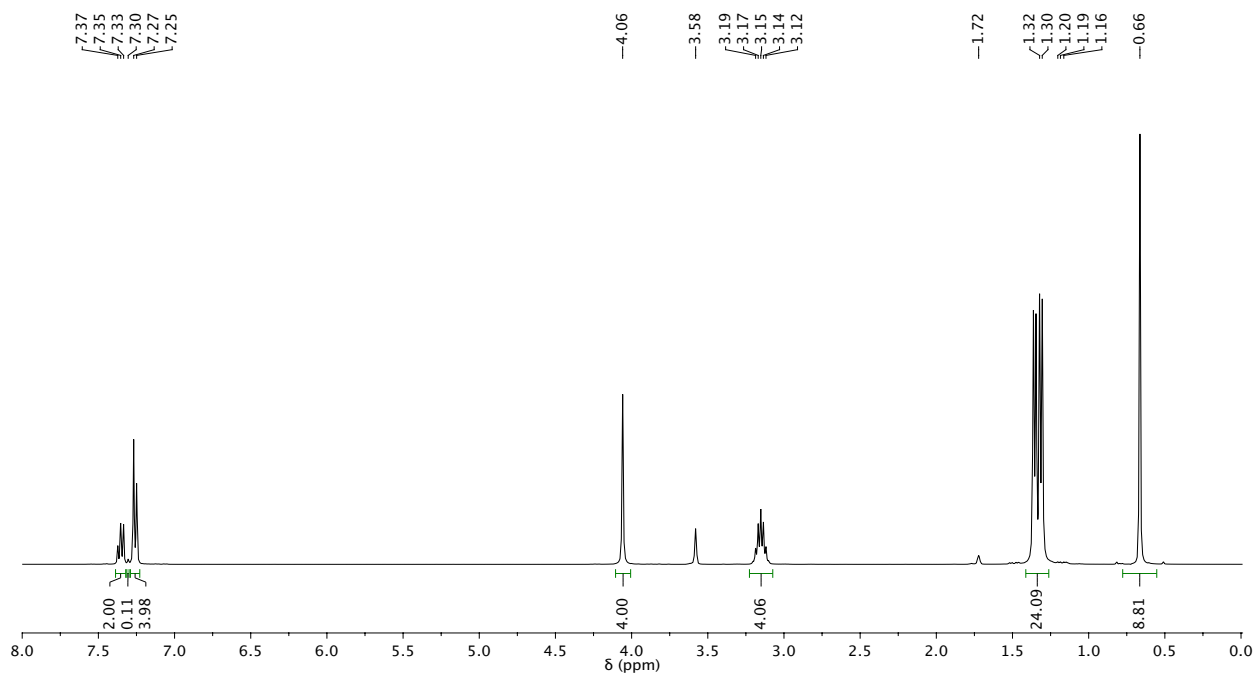


Figure S1. ^1H NMR (400 MHz, $\text{THF-}d_8$) spectrum of $(\text{SIDipp})\text{Ag}(\text{Ot-Bu})$. A trace of benzene (δ 7.30 ppm)⁵ is present as the result of benzophenone ketyl decomposition.

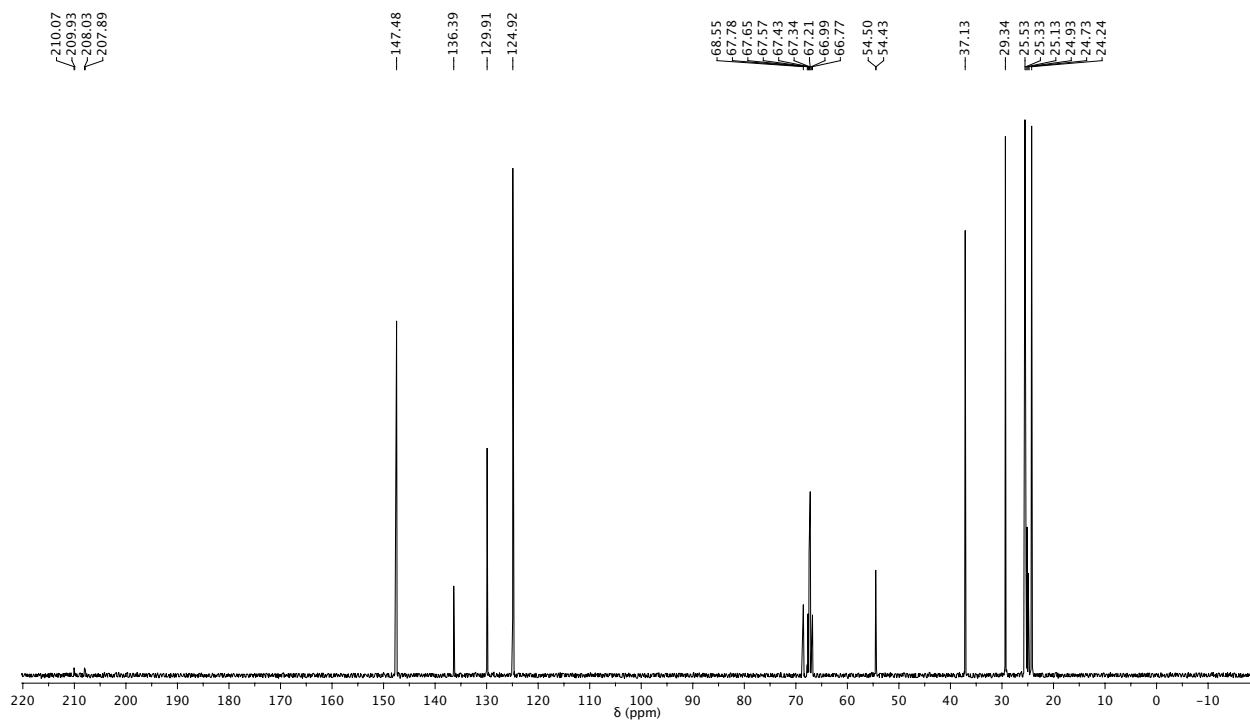
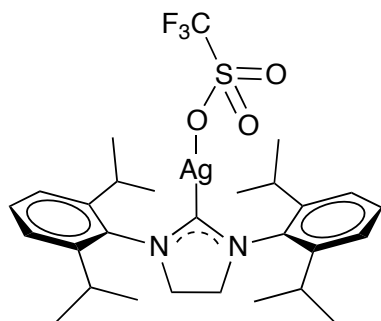
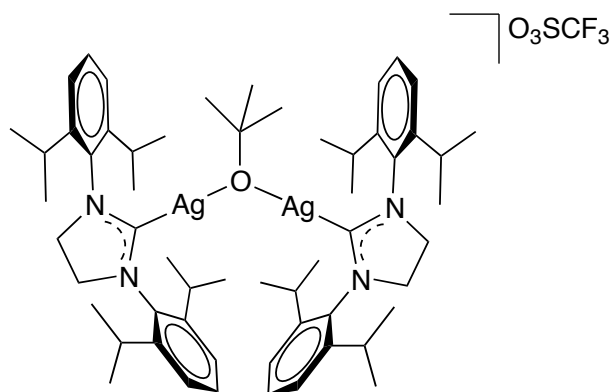


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{THF-}d_8$) spectrum of $(\text{SIDipp})\text{Ag}(\text{Ot-Bu})$.



(SIDipp)AgOTf. (SIDipp)AgOTf was prepared by a procedure analogous to that reported for [1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene]gold(I) trifluoromethanesulfonate.⁷ A solution of silver trifluoromethanesulfonate (0.962 g, 3.74 mmol) in THF (2 mL) was added to a suspension of (SIDipp)AgCl (2.000 g, 3.746 mmol) in THF (15 mL). The reaction flask was covered with foil to exclude light, and the mixture was stirred at room temperature for 1 hour, producing a white silver chloride precipitate. The precipitate was removed by filtration through Celite, and the filter pad was rinsed with two portions of THF (5 mL each). The solvent was removed from the filtrate under vacuum, and the residue was dried in the dark at 40°C for 4 hours under vacuum, affording the product as a white powder (2.164 g, 3.342 mmol, 89%). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.45 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.28 (d, *J* = 7.8 Hz, 4H, *meta*-CH), 4.11 (s, 4H, NCH₂), 3.02 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.34 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.25 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 205.3 (pseudo-dd, *J*(¹³C-¹⁰⁹Ag) = 304 Hz, *J*(¹³C-¹⁰⁷Ag) = 264 Hz, NCAg), 147.1 (*ortho*-C), 134.7 (*ipso*-C), 130.4 (*para*-C), 125.1 (*meta*-C), 120.4 (q, *J*(¹³C-¹⁹F) = 320 Hz, O₃SCF₃), 54.5 (d, *J*(¹³C-Ag) = 10 Hz, NCH₂), 29.1 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.2 (CH(CH₃)₂). ¹⁹F NMR (400 MHz, CD₂Cl₂): δ (ppm) -76.9 (s). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 386.7 (s). IR: ν (cm⁻¹) 3071 (w), 2981 (s), 2930, 2870, 1590, 1491 (s), 1467 (s), 1460 (s), 1384, 1364, 1342, 1327, 1274 (s), 1233 (s), 1205 (s), 1170 (s), 1061, 1018 (s), 936, 915, 808 (s), 760 (s), 709, 637 (s), 620, 580, 569, 548, 515, 447. Anal. Calcd. for C₂₈H₃₈N₂AgF₃O₃S: C, 51.93; H, 5.91; N, 4.33. Found: C, 51.73; H, 5.91; N, 4.27.



{[(SIDipp)Ag]₂(μ-Ot-Bu)}[OTf] (1[OTf]). A solution of (SIDipp)AgOTf (0.650 g, 1.00 mmol, 1.00 equiv) in 3 mL THF and a solution of (SIDipp)Ag(Ot-Bu) (0.600 g, 1.05 mmol, 1.05 equiv) in THF (3 mL) were cooled to -35°C. The (SIDipp)Ag(Ot-Bu) solution was added via pipette to the (SIDipp)AgOTf solution with stirring, and the reaction flask was covered with foil to exclude light. The reaction mixture was allowed to warm to room temperature. After 20 minutes, a layer of toluene (19 mL) was carefully added above the THF solution. The THF and toluene layers were allowed to mix by diffusion at -35°C for 10 hours, resulting in the formation of colourless crystals. The mother liquor was decanted. Two portions of toluene (5 mL each) were successively added to the residue and decanted. The residue was

dissolved in THF (3 mL) and the product was precipitated by the addition of pentane (15 mL). The precipitate was collected on a fritted glass filter and was washed with three portions of pentane (5 mL each). The filtrand was dried in the dark under vacuum at 40°C for 16 hours, affording the product as a white powder (0.971 g, 0.796 mmol, 80%). The product hydrolyses readily in the presence of atmospheric moisture. ^1H NMR (400 MHz, THF- d_8): δ (ppm) 7.39 (t, $J = 7.8$ Hz, 4H, *para-CH*), 7.23 (d, $J = 7.8$ Hz, 8H, *meta-CH*), 4.15 (s, 8H, NCH_2), 3.08 (sept, $J = 6.9$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, $J = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, $J = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 0.31 (s, 9H, $\text{O}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_8): δ (ppm) 205.3 (pseudo-dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 265$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 229$ Hz, NCAg), 147.5 (*ortho-C*), 136.1 (*ipso-C*), 130.2 (*para-C*), 125.1 (*meta-C*), 122.4 (q, $J(^{13}\text{C}-^{19}\text{F}) = 321.4$ Hz, O_3SCF_3), 72.2 ($\text{OC}(\text{CH}_3)_3$), 55.0 (d, $J(^{13}\text{C}-\text{Ag}) = 9$ Hz, NCH_2), 29.1 ($\text{CH}(\text{CH}_3)_2$), 25.6 ($\text{CH}(\text{CH}_3)_2$), 24.0 ($\text{CH}(\text{CH}_3)_2$). ^{19}F NMR (400 MHz, THF- d_8): δ (ppm) -77.6 (s). ^{109}Ag NMR (18.6 MHz, THF- d_8): δ (ppm) 541.4 (s). IR: ν (cm^{-1}): 3071 (w) 2964 (s), 2926, 2870, 1591 (w), 1492 (s), 1460 (s), 1384, 1363, 1327, 1272 (s), 1220, 1176, 1148, 1101, 1056, 1032, 931, 805, 757, 706, 637 (s), 572, 548, 513, 447. Anal. Calcd. for $\text{C}_{59}\text{H}_{85}\text{N}_4\text{Ag}_2\text{F}_3\text{O}_4\text{S}$: C, 58.13; H, 7.03; N, 4.60. Found: C, 58.11; H, 6.91; N, 4.49.

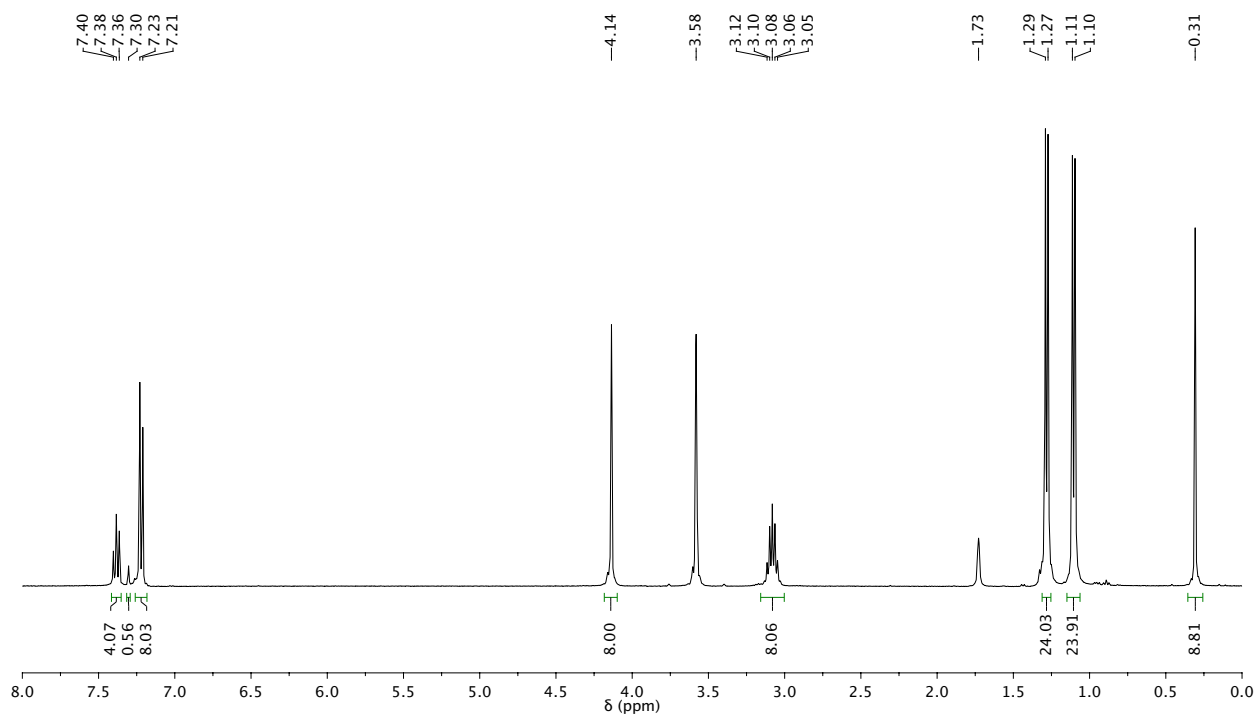
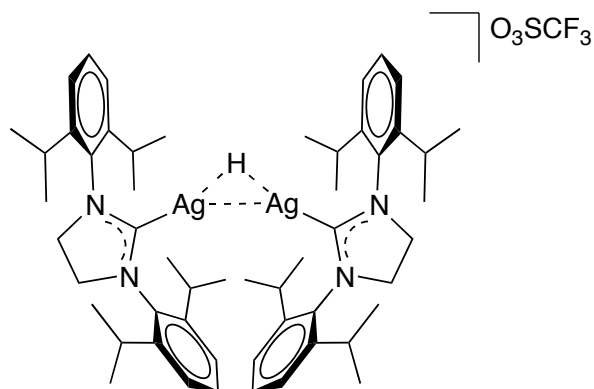


Figure S3. ^1H NMR (400 MHz, THF- d_8) spectrum of **1**[OTf]. Benzene (δ 7.30 ppm)⁵ is present as the result of benzophenone ketyl decomposition.



{[(SIDipp)Ag]₂(μ-H)}[OTf] (2[OTf]). A solution of {[(SIDipp)Ag]₂(μ-*Ot*-Bu)}[OTf] (0.600 g, 0.492 mmol) in THF (2 mL) and a solution of phenylsilane (0.061 mL, 0.053 g, 0.49 mmol) in THF (2 mL) were cooled to -35°C . The phenylsilane solution was added dropwise via pipette to the {[(SIDipp)Ag]₂(μ-*Ot*-Bu)}[OTf] solution with stirring, and the resultant mixture was stored in the dark at -35°C for 2 hours. A layer of pentane (12 mL) was carefully added over the THF solution, and the layers were allowed to mix by diffusion at -35°C for 16 hours, resulting in the formation of colourless crystals. The mother liquor was decanted, and the crystals were collected on a fritted glass filter. The crystals were triturated, then washed with three portions of pentane (2 mL each) and dried in the dark under vacuum at 40°C for 16 hours, affording the product as a white powder (0.490 g, 0.427 mmol, 87%). The product is stable toward brief exposure to air and moisture. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.41 (t, $J = 7.8$ Hz, 2H, *para*-CH), 7.19 (d, $J = 7.8$ Hz, 4H, *meta*-CH), 4.02 (s, 4H, NCH_2), 2.92 (sept, $J = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.03 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), -1.18 (pseudo-tt, 1H, $J(^1\text{H}-^{109}\text{Ag}) = 134$ Hz, $J(^1\text{H}-^{107}\text{Ag}) = 116$ Hz, AgHAg). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ (ppm) 208.3 (m, NCAg), 147.0 (*ortho*-C), 134.5 (*ipso*-C), 130.3 (*para*-C), 124.9 (*meta*-C), 121.5 (q, $J(^{13}\text{C}-^{19}\text{F}) = 319.4$ Hz, O_3SCF_3), 54.5 (m, NCH_2), 29.0 ($\text{CH}(\text{CH}_3)_2$), 25.7 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$). ^{19}F NMR (400 MHz, CD_2Cl_2): δ (ppm) -77.6 (s). ^{109}Ag NMR (18.6 MHz, CD_2Cl_2): δ (ppm) 519.3 (pseudo-dt, $J(^{109}\text{Ag}-^1\text{H}) = 134$ Hz, $J(^{109}\text{Ag}-^{107}\text{Ag}) = 113$ Hz). IR: ν (cm^{-1}) 3068 (w), 3049 (w), 2963 (s), 2924, 2869, 1591, 1486 (s), 1461 (s) 1383, 1362, 1327, 1272 (s), 1223, 1181, 1147, 1105, 1059, 1032 (s), 938, 907, 806, 754, 709, 637 (s), 619, 572, 545, 514, 449, 420. Anal. Calcd. for $\text{C}_{55}\text{H}_{77}\text{N}_4\text{Ag}_2\text{F}_3\text{O}_3\text{S}$: C, 57.59; H, 6.77; N, 4.88. Found: C, 57.41; H 6.79; N, 4.95.

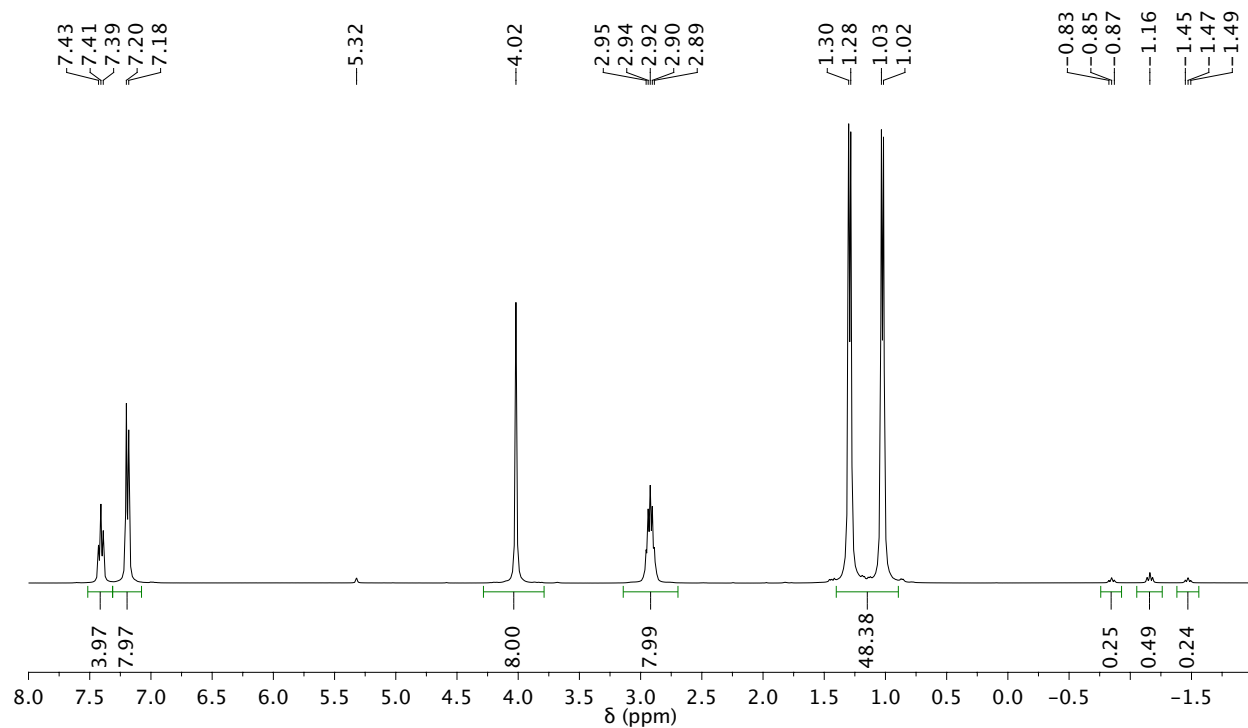


Figure S4a. ^1H NMR (400 MHz, CD_2Cl_2) spectrum of $2[\text{OTf}]$.

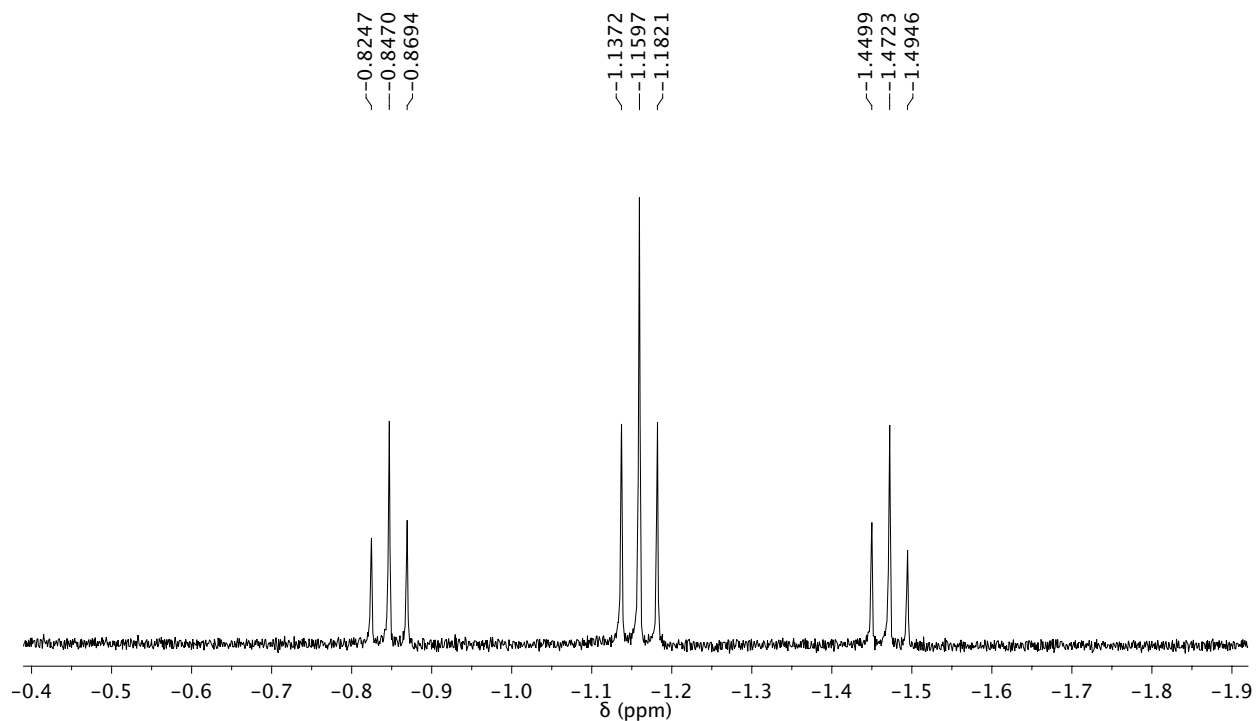


Figure S4b. Detail of the hydride resonance in the ^1H NMR (400 MHz, CD_2Cl_2) spectrum of $2[\text{OTf}]$. The splitting pattern, which appears to be a triplet of triplets, is more accurately described as three coincident resonances for each of three isotopologues of the complex: $^{107}\text{Ag}-^{107}\text{Ag}$ (triplet, 27% abundance), $^{109}\text{Ag}-^{109}\text{Ag}$ (triplet, 24% abundance), and $^{107}\text{Ag}-^{109}\text{Ag}$ (doublet of doublets, 50% abundance), where $J(^1\text{H}-^{107}\text{Ag}) = 116$ Hz and $J(^1\text{H}-^{109}\text{Ag}) = 134$ Hz.

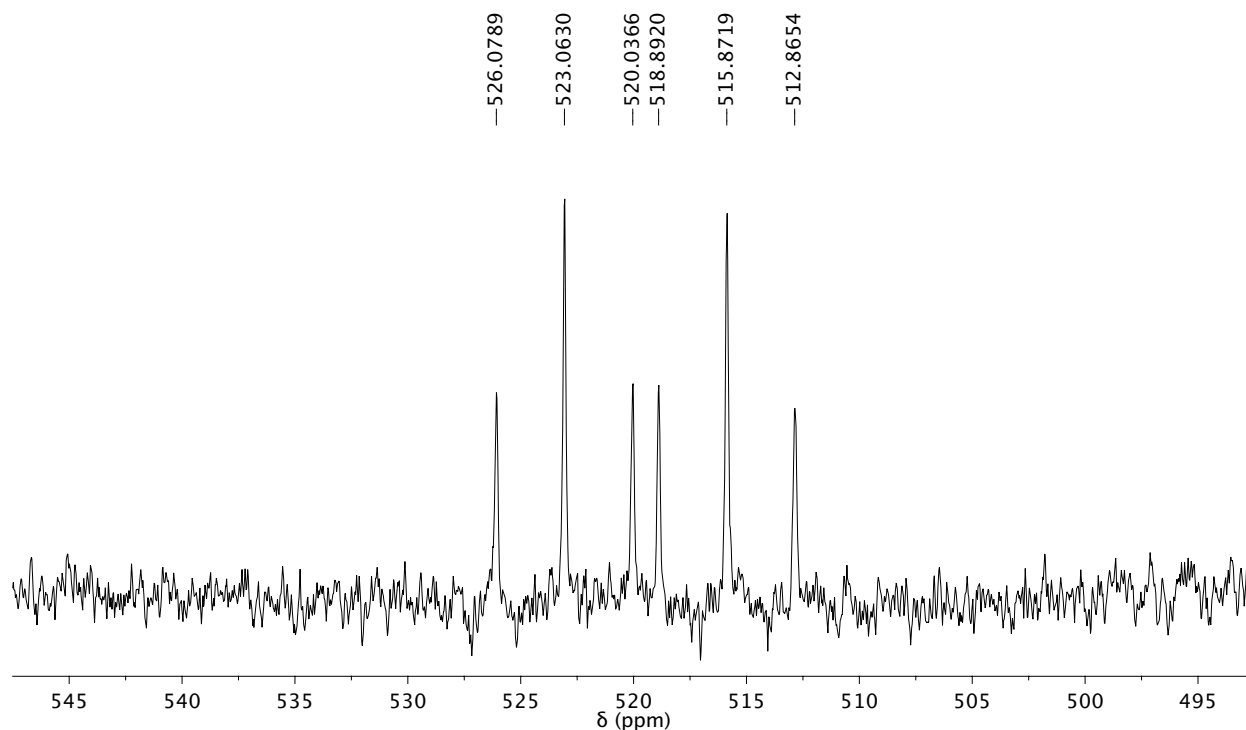
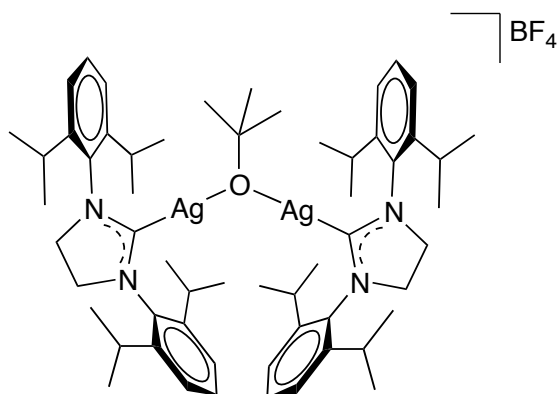
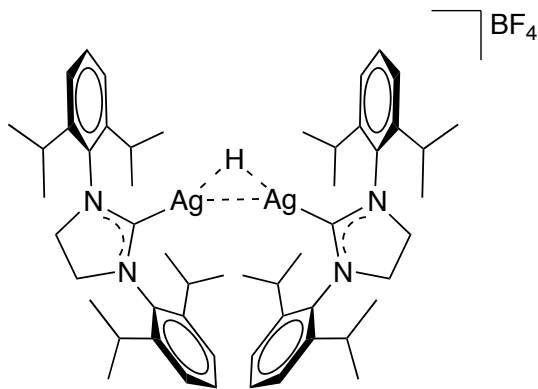


Figure S5. ^{109}Ag NMR (18.6 MHz, CD_2Cl_2) spectrum of $2[\text{OTf}]$. The splitting pattern, which appears to be a doublet of triplets, is more accurately described as two coincident resonances for each of two ^{109}Ag -containing isotopologues of the complex: ^{109}Ag - ^{109}Ag (doublet, 24% abundance), and ^{107}Ag - ^{109}Ag (doublet of doublets, 50% abundance), where $J(^{109}\text{Ag}\text{-}^1\text{H}) = 134$ Hz and $J(^{109}\text{H}\text{-}^{107}\text{Ag}) = 113$ Hz.

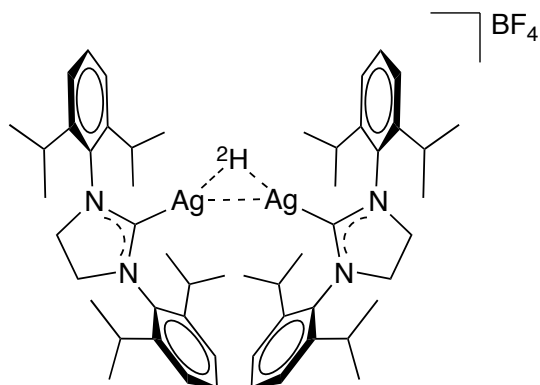


$\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-Ot-Bu})\}[\text{BF}_4]$ ($1[\text{BF}_4]$). Triphenylcarbenium tetrafluoroborate (0.200 g, 0.606 mmol) was added to a solution of $(\text{SIDipp})\text{Ag}(\text{Ot-Bu})$ (0.700 g, 1.22 mmol) in THF (4 mL). The reaction flask was covered with foil to exclude light, and the mixture was stirred for 4 hours. A layer of toluene (12 mL) was carefully added over the THF solution. The layers were allowed to mix by diffusion at -35°C for 16 hours, resulting in the formation of colourless crystals from which the mother liquor was decanted. Two portions of toluene (10 mL) were successively added and decanted. The crystals were collected on a fritted glass filter and were washed with pentane (5 mL). The crystals were dissolved in THF (2 mL) and were precipitated by the addition of pentane (12 mL). The precipitate was collected on a fritted glass filter and was washed with three portions of pentane (5 mL each). Residual solvents were removed in the dark under vacuum at 40°C for 16 hours, affording the product as a white powder (0.603 g, 93%). The product hydrolyses readily in the presence of atmospheric moisture. ^1H NMR (400 MHz, $\text{THF}-d_8$): δ (ppm) 7.38

(t, $J = 7.8$ Hz, 2H, *para-CH*), 7.22 (d, $J = 7.8$ Hz, 4H, *meta-CH*), 4.14 (s, 4H, NCH_2), 3.08 (sept, $J = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.28 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.10 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.31 (s, 9H, $\text{O}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF- d_8): δ (ppm) 205.3 (pseudo-dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 265$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 229$ Hz, NCAg), 147.5 (*ortho-C*), 136.1 (*ipso-C*), 130.2 (*para-C*), 125.1 (*meta-C*), 72.2 ($\text{OC}(\text{CH}_3)_3$), 55.0 (d, $J(^{13}\text{C}-\text{Ag}) = 9$ Hz, NCH_2), 29.1 ($\text{CH}(\text{CH}_3)_2$), 25.6 ($\text{CH}(\text{CH}_3)_2$), 24.0 ($\text{CH}(\text{CH}_3)_2$). ^{19}F NMR (400 MHz, THF- d_8): δ (ppm) -152.30 (s, $^{10}\text{BF}_4^-$), -152.35 (s, $^{11}\text{BF}_4^-$). IR: ν (cm^{-1}) 3071 (w), 2981 (s), 2930, 2870, 1590, 1488 (s), 1459 (s), 1384, 1364, 1327, 1274 (s), 1180, 1099, 1064 (s), 1017, 932, 913, 809, 763, 625, 550, 522, 450. Anal. Calcd. for $\text{C}_{58}\text{H}_{85}\text{N}_4\text{Ag}_2\text{BF}_4\text{O}$: C, 60.22; H, 7.41; N, 4.84. Found: C, 60.35; H, 7.50; N, 4.83.



$\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-H})\}[\text{BF}_4] \cdot 2[\text{BF}_4]$. A solution of $\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-}i\text{-Bu})\}[\text{BF}_4]$ (0.800 g, 0.692 mmol) in THF (2 mL) and a solution of phenylsilane (0.085 mL, 0.075 g, 0.693 mmol) in THF (2 mL) were cooled to -35°C . The phenylsilane solution was added dropwise via pipette to the $\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-}i\text{-Bu})\}[\text{OTf}]$ solution with stirring, and the resultant mixture was stored in the dark at -35°C for 2 hours. A layer of pentane (12 mL) was carefully added over the THF solution, and the layers were allowed to mix by diffusion at -35°C for 16 hours, resulting in the formation of colourless crystals. The mother liquor was decanted, and the crystals were collected on a fritted glass filter. The crystals were ground to a powder and were washed with three portions of pentane (2 mL each). Residual solvents were removed in the dark under vacuum at 40°C for 16 hours, affording the product as a white powder (0.600 g, 0.553 mmol, 92%). The product is stable toward brief exposure to air and moisture. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.42 (t, $J = 7.8$ Hz, 2H, *para-CH*), 7.19 (d, $J = 7.8$ Hz, 4H, *meta-CH*), 4.02 (s, 4H, NCH_2), 2.92 (sept, $J = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.03 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), -1.18 (pseudo-tt, 1H, $J(^1\text{H}-^{109}\text{Ag}) = 134$ Hz, $J(^1\text{H}-^{107}\text{Ag}) = 116$ Hz, AgHAg). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ (ppm) 208.3 (m, NCAg), 147.0 (*ortho-C*), 134.5 (*ipso-C*), 130.3 (*para-C*), 124.9 (*meta-C*), 54.5 (m, NCH_2), 29.0 ($\text{CH}(\text{CH}_3)_2$), 25.7 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$). ^{19}F NMR (400 MHz, CD_2Cl_2): δ (ppm) -152.30 (s, $^{10}\text{BF}_4^-$), -152.35 (s, $^{11}\text{BF}_4^-$). IR: ν (cm^{-1}) 3071 (w), 2981 (s), 2930, 2870, 1941 (w), 1871 (w), 1800 (w), 1706 (w), 1655 (w), 1489 (s), 1467 (s), 1459 (s), 1384, 1388, 1342, 1327, 1274 (s), 1249, 1216, 1190 (s), 1180, 1116, 1103, 1060, 1017, 961 (s), 935, 913, 878, 804 (s), 757 (s), 711, 620, 563, 547, 516, 445. Anal. Calcd. for $\text{C}_{54}\text{H}_{77}\text{N}_4\text{Ag}_2\text{B}_1\text{F}_4$: C, 59.79; H, 7.15; N, 5.16. Found: C, 59.53; H, 7.22; N, 5.09.



{[(SIDipp)Ag]₂(μ-²H)}[BF₄] (2-d[BF₄]). The deuteride complex was prepared by analogy to the hydride, using phenylsilane-*d*₃ as the deuteride source. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.42 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.20 (d, *J* = 7.8 Hz, 4H, *meta*-CH), 4.03 (s, 4H, NCH₂), 2.93 (sept., *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.30 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.03 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 208.3 (m, NCAg), 147.0 (*ortho*-C), 134.5 (*ipso*-C), 130.3 (*para*-C), 124.9 (*meta*-C), 54.5 (m, NCH₂), 29.0 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 23.9 (CH(CH₃)₂). ¹⁹F NMR (400 MHz, CD₂Cl₂): δ (ppm) -152.30 (s, ¹⁰BF₄⁻), -152.35 (s, ¹¹BF₄⁻). ²H NMR (30.0 MHz, CD₂Cl₂): δ (ppm) -1.12 (t, *J*(²H-^{107/109}Ag) = 18.7 Hz) ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 522.2 (pseudo-tt, 1:1:1:2:2:2:1:1:1, *J*(¹⁰⁹Ag-¹⁰⁷Ag) = 114 Hz), *J*(¹⁰⁹Ag-²H) = 20.5 Hz). IR: ν (cm⁻¹) 3071 (w), 2981 (s), 2930, 2870, 1941 (w), 1871 (w), 1800 (w), 1706 (w), 1655 (w), 1489 (s), 1467 (s), 1459 (s), 1384, 1388, 1342, 1327, 1274 (s), 1249, 1216, 1190 (s), 1180, 1116, 1103, 1060, 1017, 961 (s), 935, 913, 878, 804 (s), 757 (s), 711, 620, 563, 547, 516, 445.

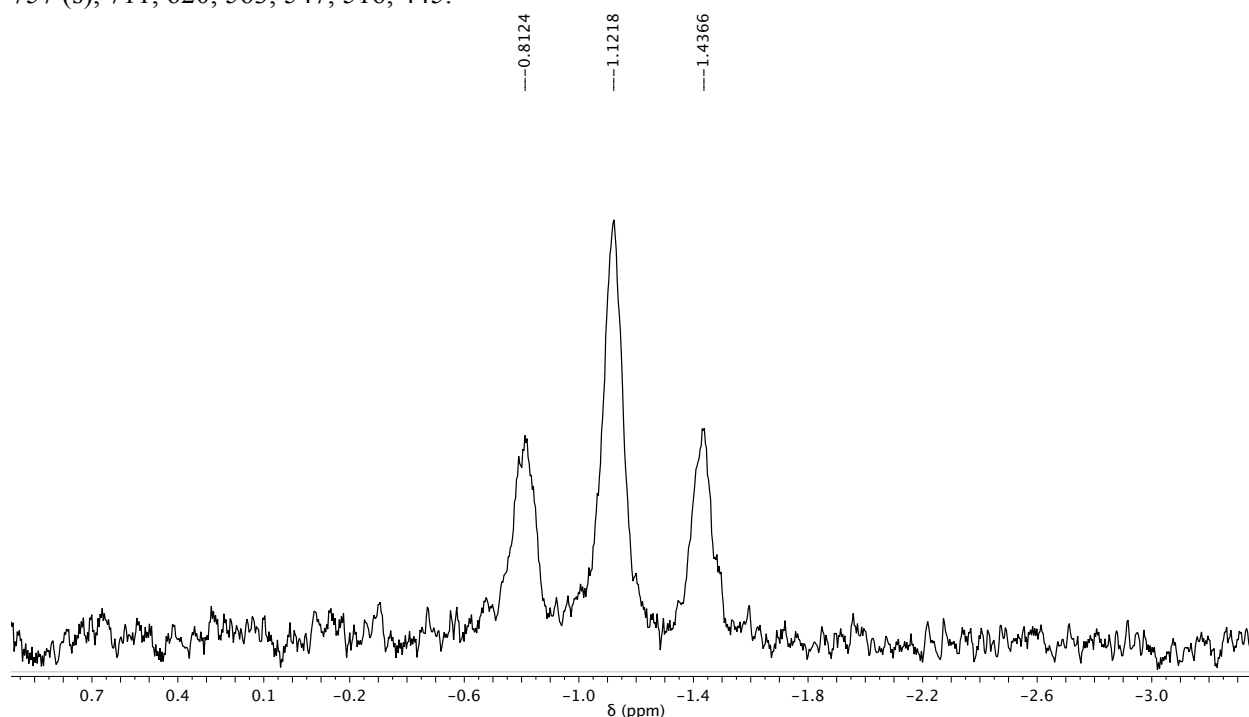


Figure S6. ²H NMR (30.0 MHz, CD₂Cl₂) spectrum of **2-d[BF₄]**.

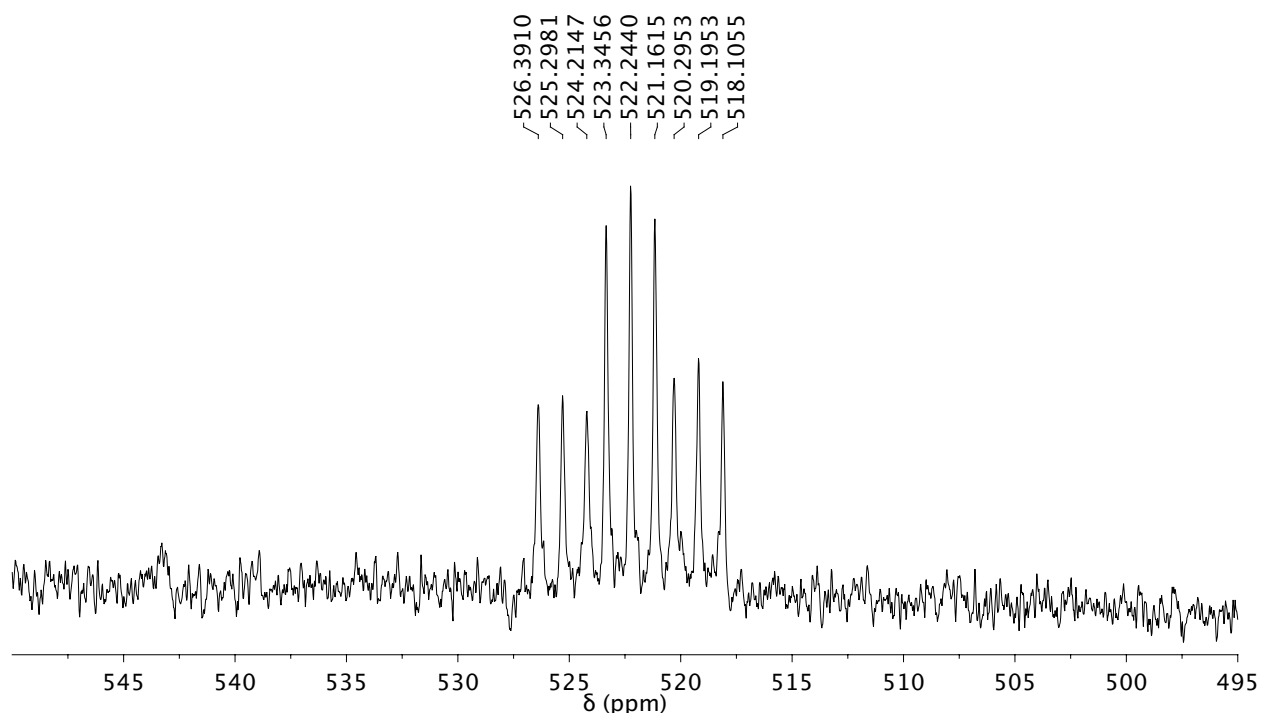


Figure S7. ^{109}Ag NMR (18.6 MHz, CD_2Cl_2) spectrum of $2\text{-}d[\text{BF}_4]$. The multiplet, which has the appearance of a 1:2:1 triplet of 1:1:1 triplets, is attributable to coincident signals from each of the two ^{109}Ag -containing isotopologues of the complex: $^{109}\text{Ag}\text{-}^{109}\text{Ag}$ (1:1:1 triplet, 23% abundance) and $^{107}\text{Ag}\text{-}^{109}\text{Ag}$ (1:1 doublet of 1:1:1 triplets, 50% abundance), where $J(^{109}\text{Ag}\text{-}^{107}\text{Ag}) = 114$ Hz and $J(^{109}\text{Ag}\text{-}^2\text{H}) = 20.5$ Hz.

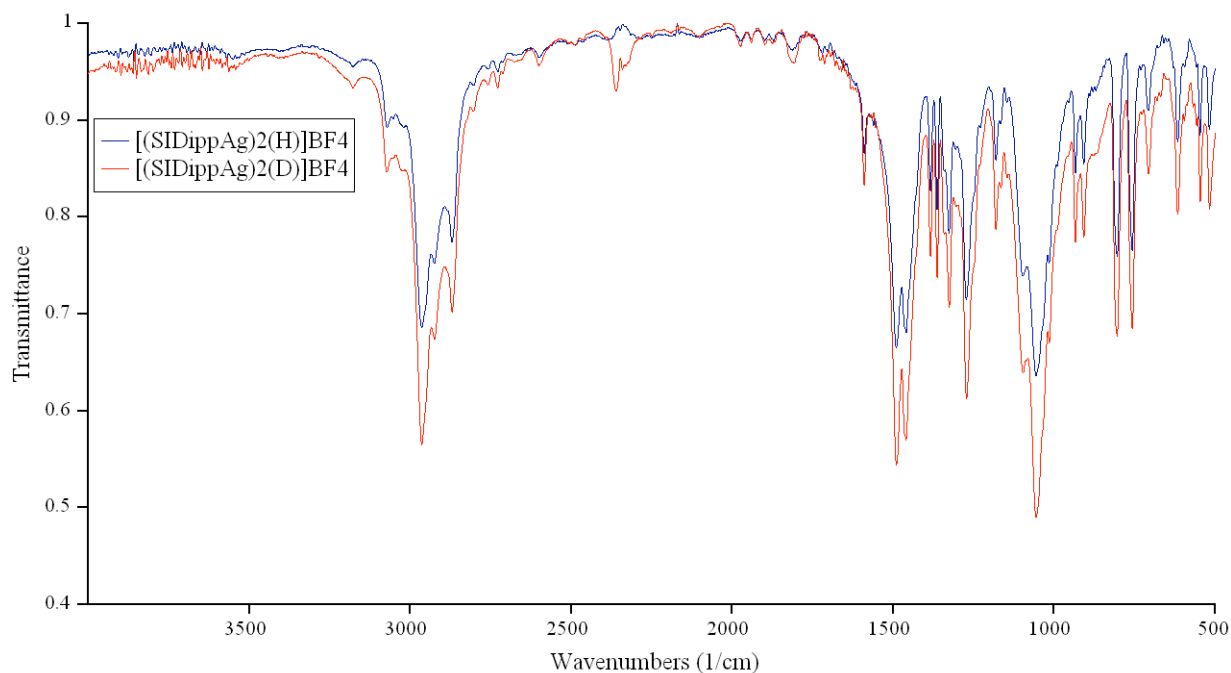
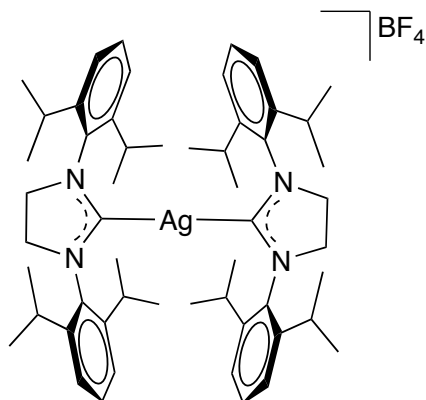
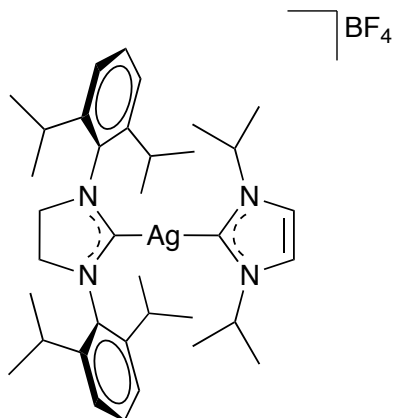


Figure S8. Overlay of the infrared absorption spectra of the hydride $2[\text{BF}_4]$ (blue spectrum) and deuteride $2\text{-}d[\text{BF}_4]$ (red spectrum). No discernible hydride or deuteride stretching resonances are observed. The

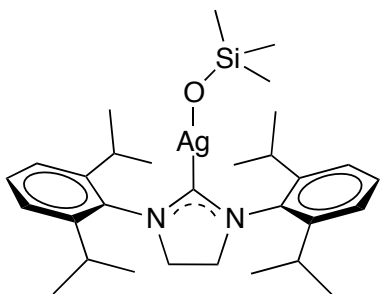
feature at $\nu = 2360 \text{ cm}^{-1}$ is attributable to fluctuations in CO_2 concentration in the sample chamber of the spectrometer.



[(SIDipp)₂Ag]BF₄. A solution of (SIDipp)Ag(OSiMe₃) (0.150 g, 0.255 mmol) in CH₂Cl₂ (1.5 mL) was prepared in a Schlenk flask equipped with a stir bar, and the flask was sealed with a rubber septum. A solution of SIDipp·HBF₄ (0.122 g, 0.255 mmol) in CH₂Cl₂ (1.5 mL) was added dropwise via syringe through the septum, with stirring. The reaction flask was covered with foil to exclude light. After stirring for 30 minutes, the flask was opened to air and no further attempt was made to maintain anhydrous conditions. The diffusion of a layer of hexane into the solution at -20°C for 24 hours resulted in the formation of colourless crystals. The mother liquor was decanted, and residual solvent was removed under vacuum in the dark at 50°C for 6 hours, affording the product as a white solid (0.160 g, 0.164 mmol, 64%). The product is stable in the presence of air and moisture. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.38 (t, $J = 7.8$ Hz, 2H, *para*-CH), 7.08 (d, $J = 7.8$ Hz, 4H, *meta*-CH), 3.80 (s, 4H, NCH₂), 2.75 (sept., $J = 6.9$ Hz, 4H, CH(CH₃)₂), 1.17 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂), 0.77 (d, $J = 6.9$ Hz, 12H, CH(CH₃)₂). ¹³C {¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 205.8 (d, $J(^{13}\text{C}-^{109}\text{Ag}) = 178$ Hz, NCAg), 146.6 (*ortho*-C), 134.9 (*ipso*-C), 130.3 (*para*-C), 124.8 (*meta*-C), 54.5 (m, NCH₂), 28.8 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.1 (CH(CH₃)₂). ¹⁹F NMR (400 MHz, CD₂Cl₂): δ (ppm) -152.30 (s, ¹⁰BF₄⁻), -152.35 (s, ¹¹BF₄⁻). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 386.7 (s). IR: ν (cm⁻¹) 3072 (w), 2966 (s), 2926, 2870, 1591, 1479 (s), 1459 (s), 1381, 1365, 1324, 1271 (s), 1246, 1184, 1094, 1054 (s), 938, 903, 806 (s), 762 (s), 735, 711, 618, 548, 517, 445, 419. Anal. Calcd. for C₅₄H₇₆N₄AgBF₄: C, 66.46; H, 7.85; N, 5.74. Found: C, 66.33; H, 7.84; N, 5.72.

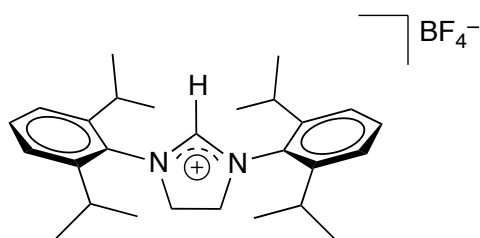


[(SIDipp)Ag(IiPr)]BF₄. A solution of (SIDipp)Ag(OSiMe₃) (0.150 g, 0.255 mmol) in CH₂Cl₂ (2 mL) was prepared in a Schlenk flask equipped with a stir bar, and the flask was sealed with a rubber septum. A solution of IiPr·HBF₄ (0.050 g, 0.25 mmol) in CH₂Cl₂ (2 mL) was added dropwise via syringe with stirring. The reaction flask was covered with foil to exclude light. After stirring for 30 minutes, the reaction mixture was dried in the dark under vacuum at 80°C for 16 hours to remove the water and hexamethyldisiloxane byproducts. The residue was dissolved in CH₂Cl₂ (2 mL) and was filtered through Celite. A layer of diethyl ether (10 mL) was added over the filtrate. The layers were allowed to mix by diffusion at -35°C for 16 hours, resulting in the formation of colourless crystals. The crystals were collected on a fritted glass filter, were washed with diethyl ether (2 mL), and were ground to a fine powder. Residual solvents were removed in the dark under vacuum at 40°C for 16 hours, affording the product as a white powder (0.109 g, 0.148 mmol, 59%). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.48 (t, *J* = 7.6 Hz, 2H, *para*-CH), 7.31 (d, *J* = 7.6 Hz, 4H, *meta*-CH), 6.90 (d, *J*(¹H-Ag) = 1.8 Hz, 2H, NCHCHN), 4.24 (s, 4H, NCH₂), 3.50 (sept, *J* = 6.7 Hz, 2H, IiPr CH(CH₃)₂), 3.13 (sept., *J* = 6.7 Hz, 4H, SIDipp CH(CH₃)₂), 1.38 (d, *J* = 6.7 Hz, 12H, SIDipp CH(CH₃)₂), 1.29 (d, *J* = 6.7 Hz, 12H, CH(CH₃)₂), 1.02 (d, *J* = 6.7 Hz, 12H, IiPr CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 208.6 (pseudo-dd, *J*(¹³C-¹⁰⁹Ag) = 218 Hz, *J*(¹³C-¹⁰⁷Ag) = 194 Hz, SIDipp NCAg), 175.3 (pseudo-dd, *J*(¹³C-¹⁰⁹Ag) = 209 Hz, *J*(¹³C-¹⁰⁷Ag) = 180 Hz, IiPr NCAg), 147.6 (*ortho*-C), 135.0 (*ipso*-C), 130.3 (*para*-C), 125.0 (*meta*-C), 118.6 (d, *J*(¹³C-Ag) = 6 Hz, NCH), 54.4 (d, *J*(¹³C-Ag) = 5 Hz, NCH₂), 29.2 (SIDipp CH(CH₃)₂), 25.6 (SIDipp CH(CH₃)₂), 24.2 (SIDipp CH(CH₃)₂) 23.7 (IiPr CH(CH₃)₂). ¹⁹F NMR (400 MHz, CD₂Cl₂): δ (ppm) -152.30 (s, ¹⁰BF₄⁻), -152.35 (s, ¹¹BF₄⁻). ¹⁰⁹Ag NMR (18.6 MHz, CD₂Cl₂): δ (ppm) 684.0 (s). IR: ν (cm⁻¹) 3168, 3139, 3072 (w), 2966 (s), 2926, 2870, 1591 (w), 1558 (w), 1491, 1466, 1460, 1397, 1381, 1365, 1324, 1271 (s), 1216 (s), 1184, 1109, 1064 (s), 935, 916, 811 (s), 764, 744, 681, 606, 621, 548, 522, 444. Anal. Calcd. for C₃₆H₅₄N₄AgBF₄: C, 58.63 ; H, 7.38; N, 7.60. Found: C, 58.66; H, 7.25; N, 7.50.

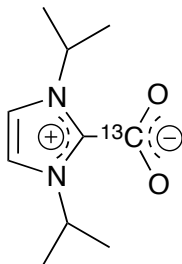


(SIDipp)Ag(OSiMe₃). Sodium trimethylsilylanolate (0.210 g, 1.87 mmol) was added to a suspension of (SIDipp)AgCl (1.000 g, 1.873 mmol) in THF (2 mL) with stirring. The reaction flask was covered with

foil to exclude light. After stirring for 2 hours, the reaction mixture was filtered through Celite into a Schlenk flask. The solvent was removed from the filtrate under vacuum. The residue was dissolved in 10 mL toluene and was filtered once more through Celite into a Schlenk flask. The solvent was again removed from the filtrate under vacuum. The residue was dissolved in 2 mL CH_2Cl_2 , and a layer of 18 mL diethyl ether was added. The layers were allowed to mix in the dark at -35°C for 72 hours, resulting in the formation of colourless crystals. The crystals were collected on a fritted glass filter and were ground to a fine powder. The product was washed with diethyl ether (2 mL). Residual solvents were removed in the dark for 16 hours at 40°C under vacuum, affording the product as a white powder (0.531 g, 0.605 mmol, 48%). The product hydrolyses readily in the presence of atmospheric moisture. ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.43 (t, $J = 7.8$ Hz, 2H, *para-CH*), 7.28 (d, $J = 7.8$ Hz, 4H, *meta-CH*), 4.07 (s, 4H, NCH_2), 3.09 (sept, $J = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.37 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.35 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), -0.44 (s, 9H, $\text{OSi}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ (ppm) 207.8 (pseudo-dd, $J(^{13}\text{C}-^{109}\text{Ag}) = 241$ Hz, $J(^{13}\text{C}-^{107}\text{Ag}) = 208$ Hz, NCAg), 147.2 (*ortho-C*), 135.4 (*ipso-C*), 130.0 (*para-C*), 124.8 (*meta-C*), 54.2 (d, $J(^{13}\text{C}-\text{Ag}) = 8$ Hz, NCH_2), 29.2 ($\text{CH}(\text{CH}_3)_2$), 25.5 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$), 4.3 ($\text{OSi}(\text{CH}_3)_3$). ^{109}Ag NMR (18.6 MHz, CD_2Cl_2): δ (ppm) 645.3 (s). IR: ν (cm^{-1}) 3071 (w), 2981 (s), 2930, 2870, 1590, 1488 (s), 1459 (s), 1384, 1367, 1327, 1274 (s), 1245, 1230 (s) 1180, 1103, 1060, 1017, 984 (s) 935, 824 (s), 808 (s), 763, 736, 663, 620, 550, 439. Anal. Calcd. for $\text{C}_{30}\text{H}_{47}\text{N}_2\text{AgSiO}$: C, 61.31; H, 8.06; N, 4.77. Found: C, 61.07; H, 8.13; N, 4.74.



SIDipp·HBF₄. 1,3-Bis(2,6-diisopropylphenyl)imidazolium tetrafluoroborate was prepared in analogy with the literature protocol for the synthesis of 1,3-diarylimidazolium tetrafluoroborate salts.⁸ The procedure was conducted in air with solvents and reagents which were neither dried nor degassed, and in glassware which was not oven-dried. A 50% w/w aqueous solution of tetrafluoroboric acid (0.047 mL, 0.382 mmol HBF₄) was added in stoichiometric excess to a solution of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (added as the triethylorthoformate adduct SIDipp·HCl·(EtO)₃CH, 0.200g, 0.348 mmol) in water (10 mL). The reaction mixture was stirred for 30 minutes, and the product was extracted with three portions of CH_2Cl_2 (5 mL each). The extract was dried over excess magnesium sulfate and filtered through Celite, and the filtrate was concentrated under vacuum to a volume of 2 mL. The diffusion of a layer of diethyl ether (18 mL) at -20°C for 16 hours resulted in the precipitation of colourless crystals, which were collected in a fritted glass funnel. The crystals were triturated and washed with diethyl ether (5 mL), affording the product as a white solid (0.130 g, 0.781 mmol, 78%). The product was characterized by ^1H NMR spectroscopy. Spectral data were in agreement with those reported in the literature.⁹ ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.58 (s, 1H, $\text{N}(\text{CH})\text{N}$), 7.52 (t, $J = 7.8$ Hz, 2H, *para-CH*), 7.32 (d, $J = 7.8$ Hz, 4H, *meta-CH*), 4.54 (s, 4H, NCH_2), 2.98 (sept, $J = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.38 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$).



LiPr·¹³CO₂. Isotopically labeled 1,3-diisopropylimidazolium ¹³C-carboxylate (LiPr·¹³CO₂) was prepared by an adaptation of a literature protocol for the preparation 1,3-di-*tert*-butylimidazolium-2-carboxylate.¹⁰ Potassium *tert*-butoxide (0.240 g, 2.14 mmol, 1.35 equiv) was added to a suspension of LiPr·HCl (0.300 g, 1.58 mmol, 1.00 equiv) in THF (3 mL) to generate free 1,3-diisopropylimidazol-2-ylidene in solution. After stirring for 2 hours, the reaction mixture was filtered through Celite into a Schlenk flask equipped with a magnetic stir bar. The filtrate was degassed by three freeze-pump-thaw cycles, and the flask was pressurized with 160 kPa ¹³C-carbon dioxide. The product began to precipitate as a white solid. After stirring for 16 hours under ¹³CO₂, the precipitate was collected on a fritted glass filter and was washed with diethyl ether (2 mL), affording the product as a white solid (0.260 g, 1.32 mmol, 83%). The product was characterized by ¹H NMR spectroscopy. Spectral data were in agreement with the literature.¹¹ ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.11 (d, *J*(H-¹³C) = 0.3 Hz, 2H, NCHCHN), 5.56 (sept, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 1.48 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂).

Hydride Delivery to LiPr·CO₂. A solution of {[SIDipp)Ag]₂(μ-H)}[BF₄] (**2**[BF₄], 0.030 g, 0.028 mmol, 1.0 equiv) and 4,4'-dimethylbiphenyl (internal standard; 0.010 g, 0.055 mmol) in CD₂Cl₂ was prepared in a sealable NMR tube and was chilled to -35°C. Isotopically labeled 1,3-diisopropylimidazolium-2-¹³C-carboxylate (LiPr·¹³CO₂, 0.011 g, 0.056 mmol, 2.0 equiv) was added. The reaction tube was quickly capped, and its contents were thoroughly mixed by inversion. Gas evolution was observed immediately and subsided over the course of approximately 60 seconds. The solution was allowed to warm to room temperature en route to the NMR facility. ¹H and ¹³C NMR spectra were promptly recorded, and a second ¹³C NMR spectrum was recorded after cooling the NMR tube at -78°C for 2 hours to increase ¹³CO₂ solubility. The components of the product solution were identified as [(SIDipp)Ag(LiPr)]⁺ (0.95 equiv), free ¹³C-formate ion (0.66 equiv), and ¹³CO₂ (not quantified). [(SIDipp)Ag(LiPr)]⁺ and ¹³C-formate were quantified by integration of peak areas with respect to those of 4,4'-dimethylbiphenyl in the ¹H NMR spectrum. No unexpected signals were observed in the ¹⁹F NMR spectrum of the product solution, confirming the BF₄⁻ anion remained unchanged.

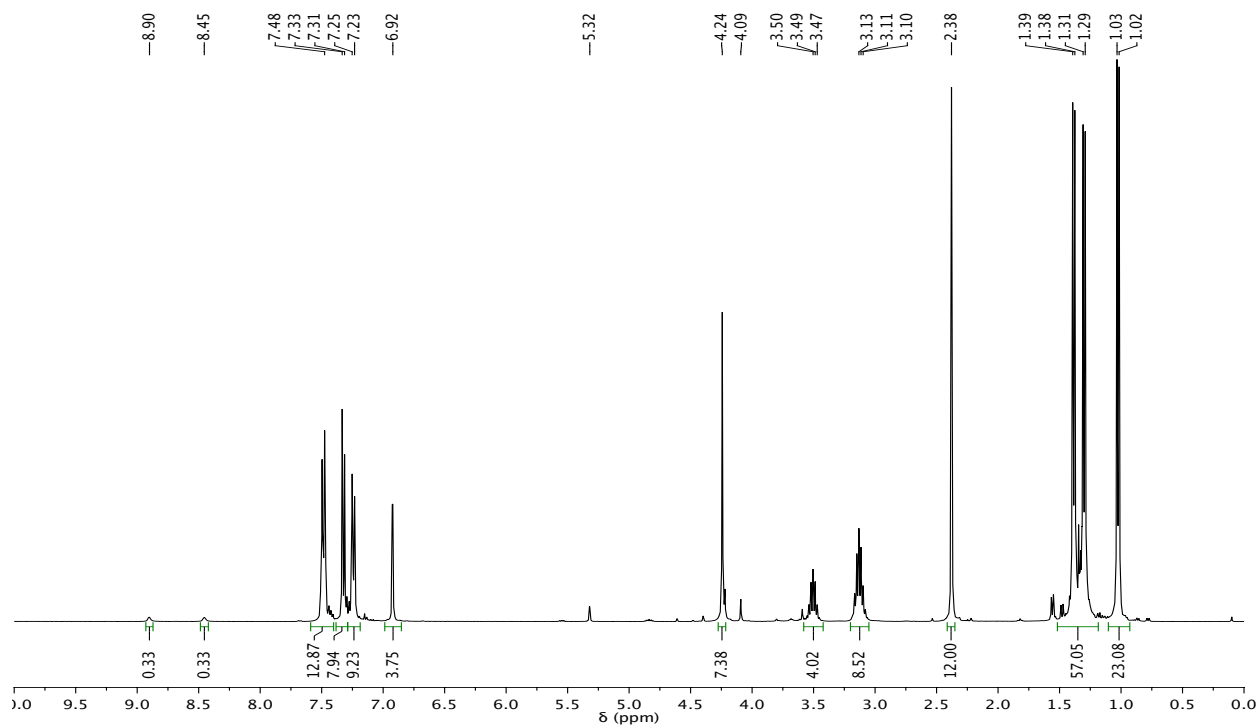


Figure S10. ^1H NMR (400 MHz, CD_2Cl_2) spectrum of the reaction of $2[\text{BF}_4]$ with two equivalents of $\text{LiPr}\cdot^{13}\text{CO}_2$ after 5 minutes. Two equivalents of 4,4'-dimethylbiphenyl [δ (ppm) 7.49 (d, 4H, $J = 7.8$ Hz), 7.24 (d, 4H, $J = 7.8$ Hz), 2.38 (s, 6H)] are present as an internal standard.

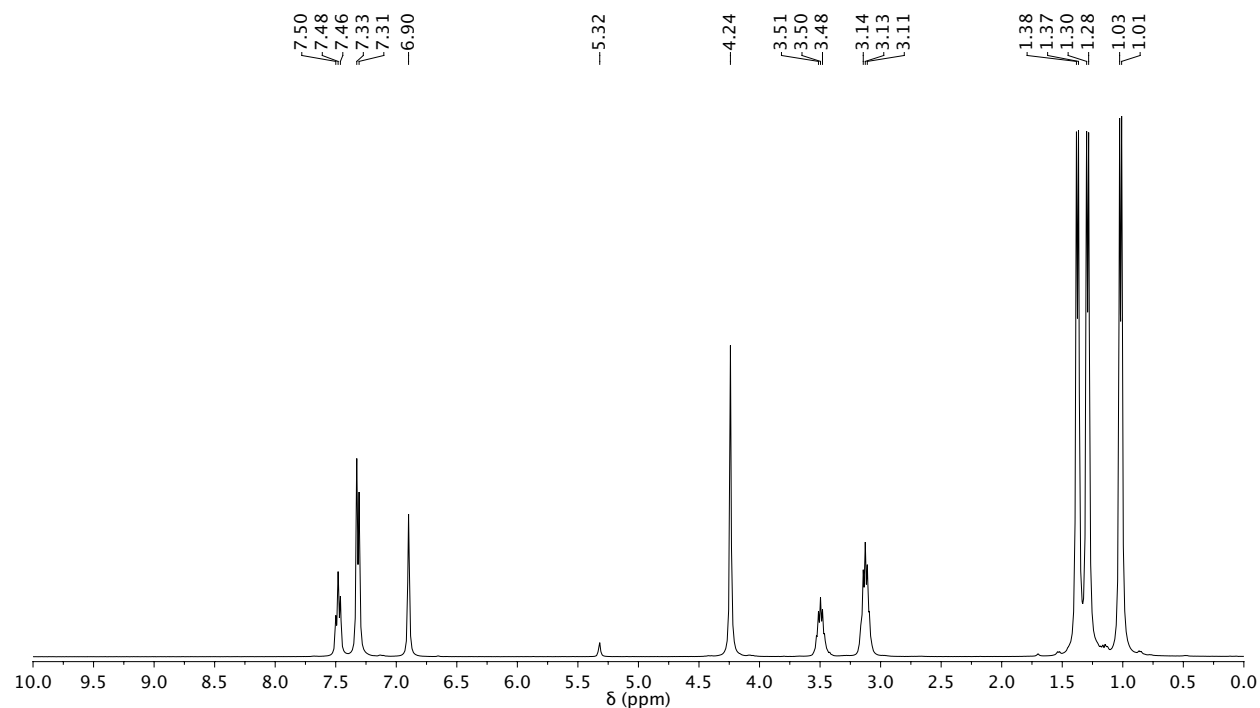


Figure S11. ^1H NMR (400 MHz, CD_2Cl_2) spectrum of $[(\text{SIDipp})\text{Ag}(\text{LiPr})]\text{BF}_4$, prepared independently by the treatment of $(\text{SIDipp})\text{Ag}(\text{OSiMe}_3)$ with $\text{LiPr}\cdot\text{HBF}_4$.

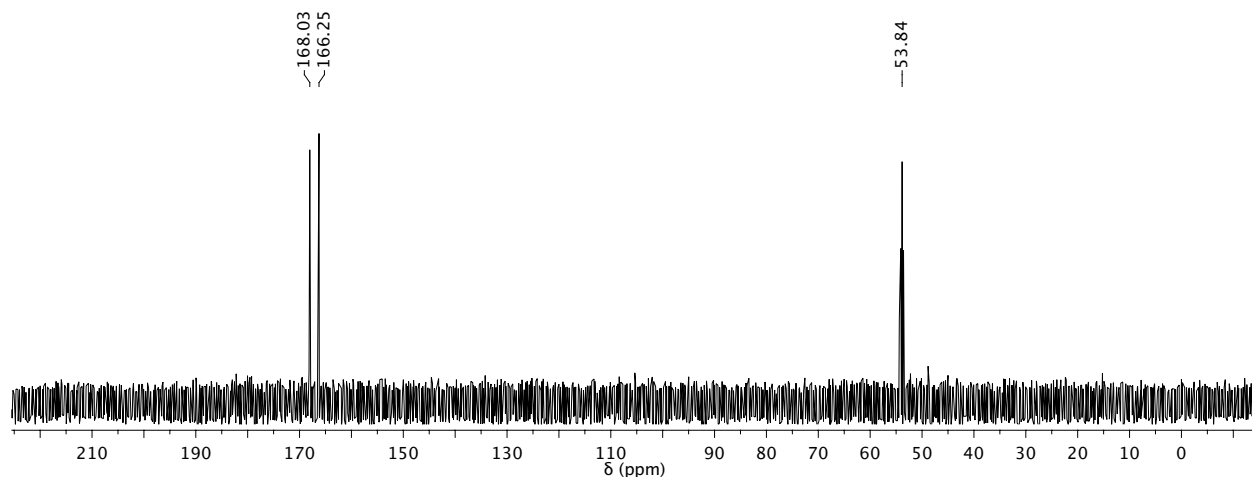


Figure S12. ^{13}C NMR (100 MHz, CD_2Cl_2 , ^1H -nondecoupled) spectrum of the reaction of $2[\text{BF}_4]$ with two equivalents of $\text{LiPr-}^{13}\text{CO}_2$ after 7 minutes, showing the production of ^{13}C -formate.

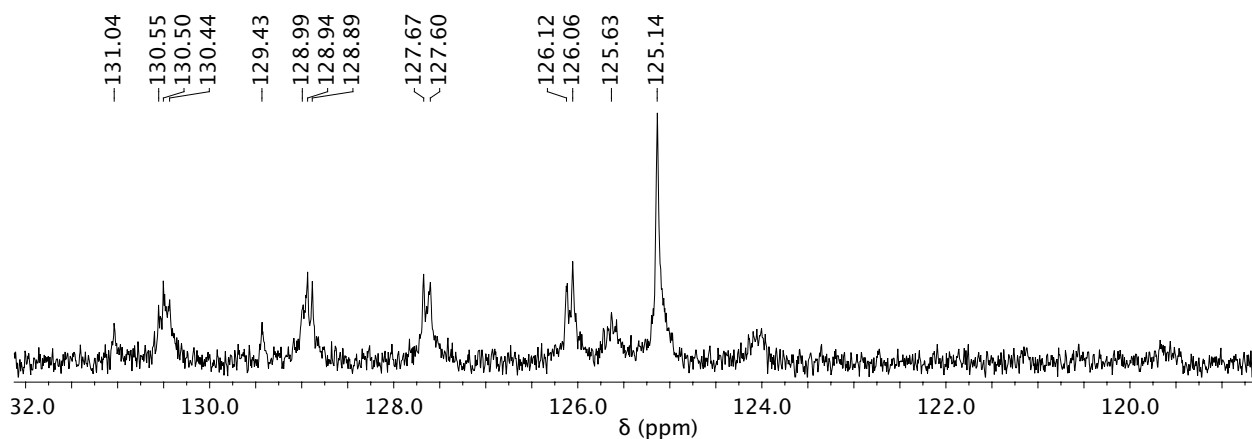


Figure S13. Detail of the $^{13}\text{CO}_2$ resonance (δ 125.14 ppm) in the ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2 , ^1H -nondecoupled, after cooling to -78°C) of the reaction of $2[\text{BF}_4]$ with two equivalents of $\text{LiPr-}^{13}\text{CO}_2$. Resonances arising from the aryl groups of SIDipp and 4,4'-dimethylbiphenyl are also visible.

Reaction of $\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-H})\}^+$ with free CO_2 . A solution of $\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-H})\}[\text{BF}_4]$ ($2[\text{BF}_4]$, 0.020 g) in CD_2Cl_2 (0.7 mL) in a NMR tube equipped with a J. Young valve was degassed by three freeze-pump-thaw cycles and, at room temperature, was pressurized with $^{13}\text{CO}_2$ (ca. 160 kPa). The tube was wrapped in foil and was agitated continuously to ensure mixing. The reaction was monitored by ^1H and ^{13}C NMR spectroscopy at intervals over four days. Over time, the tube became opaque as the result of silver(0) deposition on the interior walls. Slow hydride delivery to $^{13}\text{CO}_2$ was observed by NMR (less than 5% conversion of hydride in four days). The decomposition of $2[\text{BF}_4]$ to $[(\text{SIDipp})_2\text{Ag}]^+$ and SIDippH^+ occurred more rapidly than the formation of ^{13}C -formate.

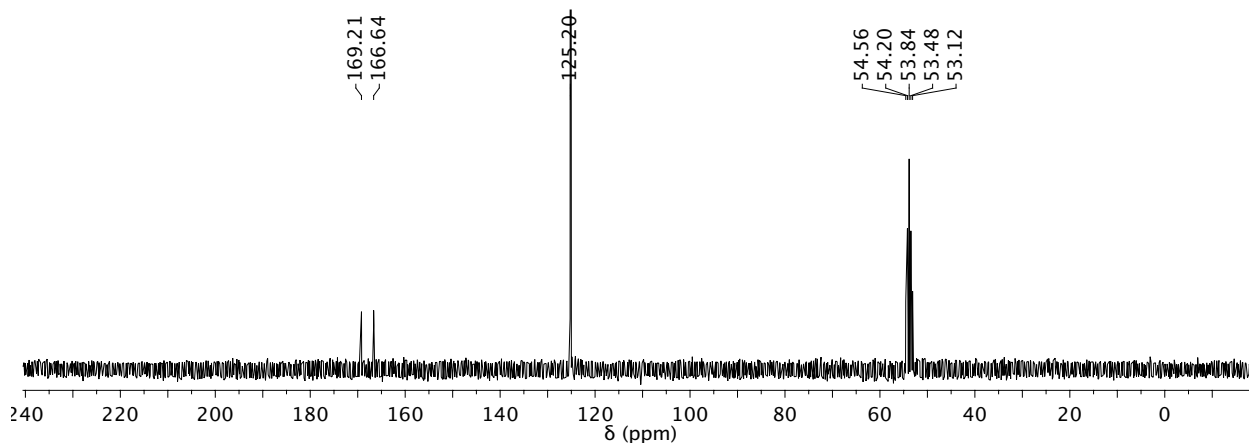


Figure S14. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2 , ^1H -nondecoupled) of the reaction of $2[\text{BF}_4]$ with 160 kPa $^{13}\text{CO}_2$ after 4 days. The doublet at δ 167.9 ppm ($J(^{13}\text{C}\text{-}^1\text{H}) = 194$ Hz) is believed to indicate ^{13}C -formate complexed with silver. The intense singlet at δ 125.2 ppm corresponds to $^{13}\text{CO}_2$.⁵

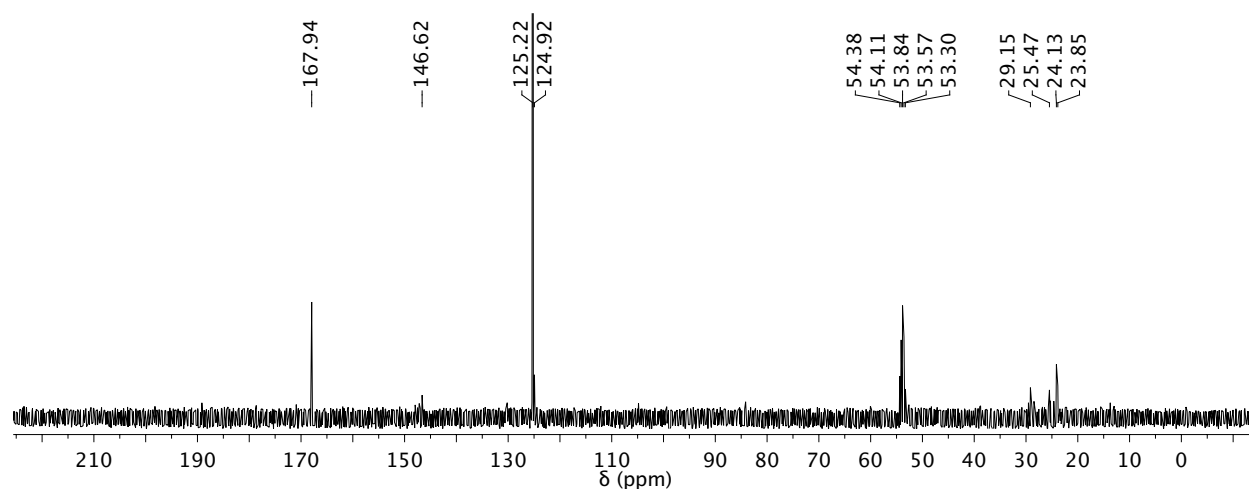


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75.5 MHz, CD_2Cl_2) of the reaction of $2[\text{BF}_4]$ with 160 kPa $^{13}\text{CO}_2$ after 4 days. ^1H decoupling reduces the ^{13}C -formate signal at δ 167.9 ppm to a singlet. The intense singlet at δ 125.2 ppm corresponds to $^{13}\text{CO}_2$.⁵ ^1H decoupling also enhances unlabeled SIDipp-derived resonances, which are observed at δ 146.6 ppm and 124.9 ppm and in the range of 29.2–23.9 ppm.

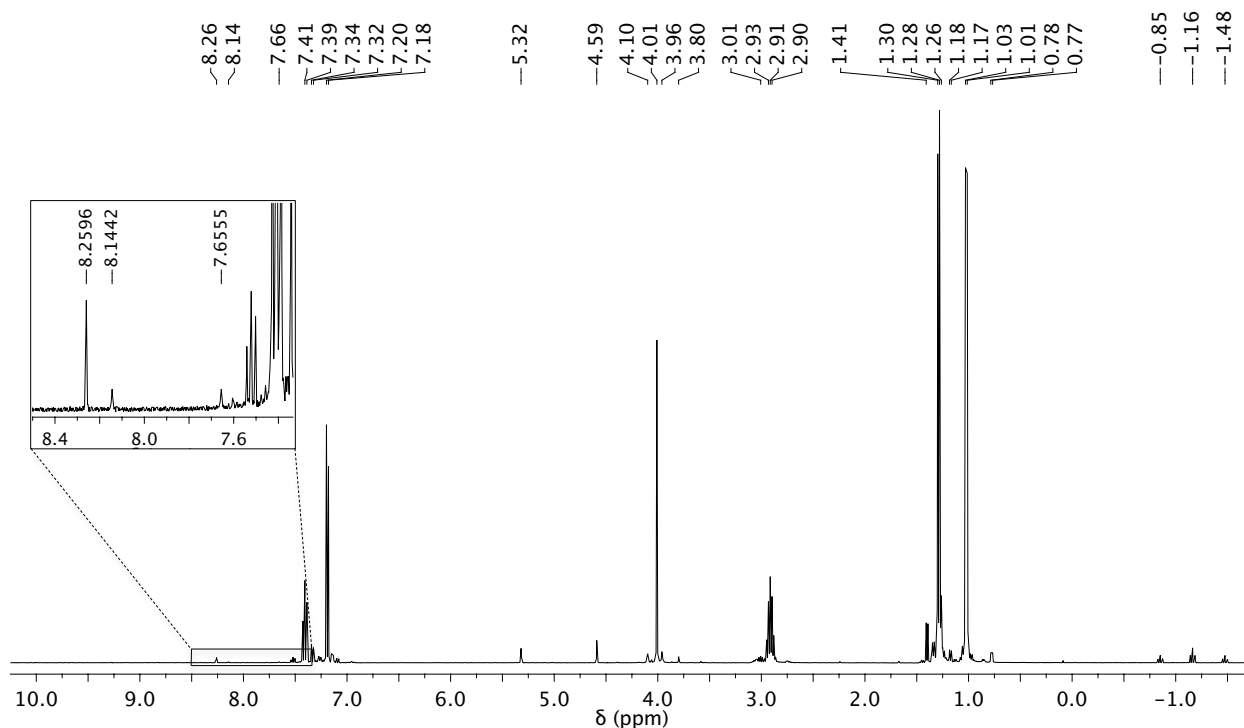


Figure S16. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , ^{13}C -nondecoupled) of the reaction of $2[\text{BF}_4]$ with 160 kPa ^{13}C - CO_2 after 4 days. In addition to ^{13}C -formate, indicated by a doublet ($J(^1\text{H}-^{13}\text{C}) = 195$ Hz) at δ 7.90 ppm, decomposition products including $[(\text{SIDipp})_2\text{Ag}]^+$ and SIDippH^+ are also observed.

Acidolysis of $\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-H})\}^+$

No attempt to maintain anhydrous or air-free conditions was made in the investigation of the reactivity of **2** with potential proton donors.

The treatment of $2[\text{BF}_4]$ with either methanol- d_1 , 2,4,6-trimethylphenol, or *N,N*-dimethylanilinium tetrafluoroborate in CDCl_3 solution resulted in no reaction as discerned by ^1H NMR spectroscopy.

Treatment of $2[\text{BF}_4]$ (0.025 g, 0.023 mmol) with benzoic acid (0.003 g, 0.02 mmol) in CD_2Cl_2 resulted in the evolution of hydrogen gas (δ 4.61 ppm),⁵ the deposition of silver(0), and a mixture of unreacted **2** (accounting for 39% of the SIDipp derivatives in solution, quantified by the integration of ^1H NMR peak area), SIDippH^+ (31%), an unidentified SIDipp derivative (28%), and $[(\text{SIDipp})_2\text{Ag}]^+$ (2%).

X-ray Diffraction Studies

$\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-Ot-Bu})\}[\text{OTf}]$ (**1**[OTf]). Diffraction-quality crystals were grown by the diffusion of hexane vapour into a solution of **1**[OTf] in THF at -35°C .

A suitable crystal was selected from the sample and mounted quickly onto a nylon fibre with paratone oil and placed under a cold stream at -100°C . Single crystal X-ray data were collected on a Bruker APEX2 diffractometer with 1.6 kW graphite monochromated Mo radiation. The detector-to-crystal distance was 5.1 cm. The data collection was performed using a combination of sets of ω scans yielding data in the θ range 1.81° to 32.10° with an average completeness of 97.7%. The frames were integrated with the SAINT v7.68a.¹² A multi-scan absorption correction was carried out using the program SADABS V2008-1.¹³ The structure was solved with JANA2006¹⁴ and refined with Olex2¹⁵ and SHELX.¹⁶

The crystal structure contains a $\{[(\text{SIDipp})\text{Ag}]_2(\mu\text{-Ot-Bu})\}^+$ complex, a triflate anion and two THF molecules of crystallisation. One THF molecule is badly disordered, and was modelled using two components each with similarity restraints in SHELX. However, the disorder of this molecule is severe and the electron density ill-defines such that the locations of the O atoms cannot be identified with certainty (these too are probably disordered).

Table S1. Crystallographic details for (**1**[OTf]).

$\text{C}_{63}\text{H}_{101}\text{Ag}_2\text{F}_3\text{N}_4\text{O}_6\text{S}$

$M = 1363.33$

colourless prism

$0.678 \times 0.264 \times 0.173 \text{ mm}^3$

triclinic, space group $P-1$

$a = 10.5882(11) \text{ \AA}$

$b = 16.8592(17) \text{ \AA}$

$c = 20.800(2) \text{ \AA}$

$\alpha = 74.8830(10)^\circ$

$\beta = 79.9550(10)^\circ$

$\gamma = 76.1030(10)^\circ$

$V = 3454.7(6) \text{ \AA}^3$

$Z = 2$

$D_c = 1.311 \text{ g/cm}^3$

MoK α radiation, $\lambda = 0.71073 \text{ \AA}$

$T = 173\text{K}$

$2\theta_{\text{max}} = 64.2^\circ$

53022 reflections collected, 23653 unique

Numerical absorption correction

$R_{\text{int}} = 0.0377$

Final $\text{Goof} = 1.022$

$RI = 0.0514$

$wR2 = 0.1206$

807 parameters, 102 restraints

$m = 0.655 \text{ mm}^{-1}$

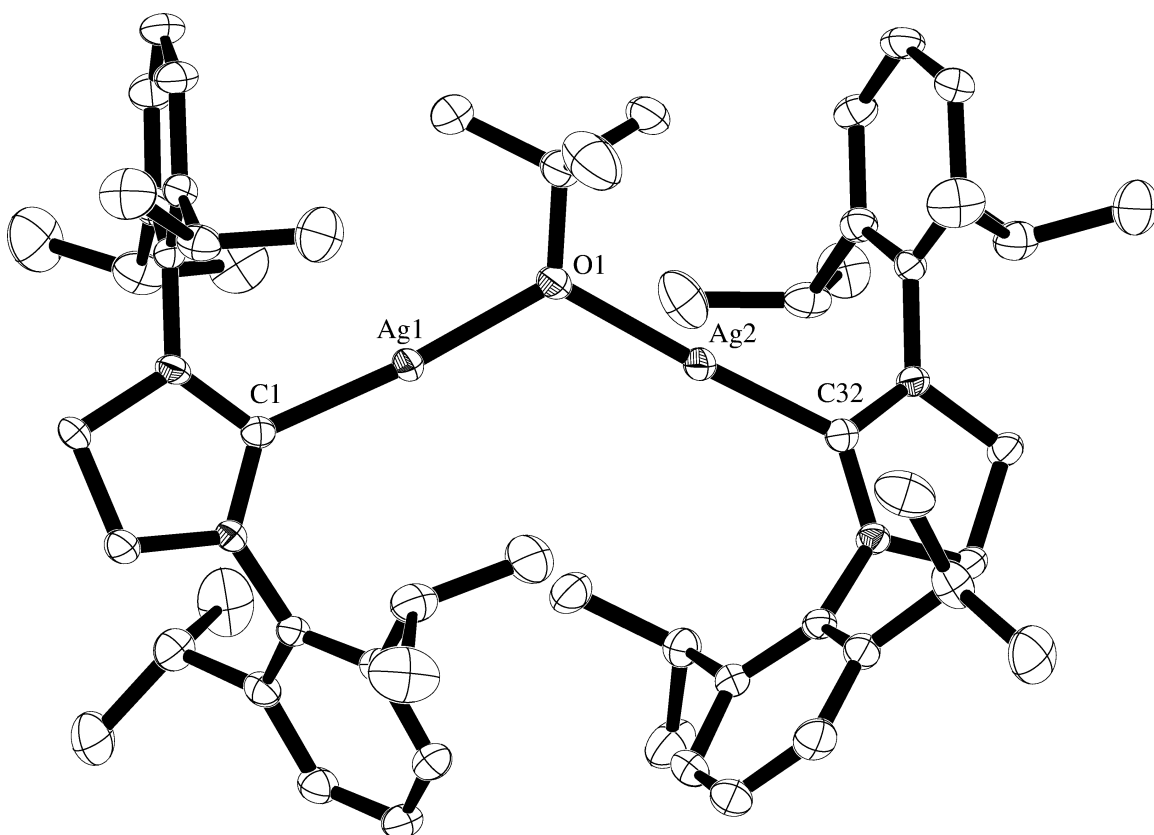


Figure S17. Crystal structure of 1[OTf], showing 50% probability ellipsoids. Anion and solvent are omitted for clarity.

{{(SIDipp)Ag}₂(μ-H)}{OTf} (2[OTf]). Diffraction-quality crystals were grown by the diffusion of pentane vapour into a solution of 2[OTf] in THF at -35°C .

A suitable crystal was selected from the sample and mounted quickly onto a nylon fibre with paratone oil and placed under a cold stream at -100°C . Single crystal X-ray data were collected on a Bruker APEX2 diffractometer with 1.6 kW graphite monochromated Mo radiation. The detector-to-crystal distance was 5.1 cm. The data collection was performed using a combination of sets of ω scans yielding data in the θ range 1.39° to 29.61° with an average completeness of 99.6%. The frames were integrated with the SAINT v7.68a.¹² A multi-scan absorption correction was carried out using the program SADABS V2008-1.¹³ The structure was solved with JANA2006¹⁴ and refined with Olex2¹⁵ and SHELX.¹⁶

The crystal structure contains a **{{(SIDipp)Ag}₂(μ-H)}**⁺ complex, a triflate anion and two THF molecules of crystallisation. Both solvent molecules are disordered, and were modelled using two components each with similarity restraints in SHELX.

Table S2. Crystallographic details for (2[OTf]).

$\text{C}_{63}\text{H}_{93}\text{Ag}_2\text{F}_3\text{N}_4\text{O}_5\text{S}$

$M = 1291.21$

colourless prism

$0.453 \times 0.24 \times 0.193 \text{ mm}^3$

monoclinic, space group $P2_1/c$

$a = 14.8245(14) \text{ \AA}$

$b = 23.508(2) \text{ \AA}$
 $c = 19.9054(19) \text{ \AA}$
 $\beta = 110.1180(10)^\circ$
 $V = 6513.8(11) \text{ \AA}^3$
 $Z = 4$
 $D_c = 1.317 \text{ g/cm}^3$
MoK α radiation, $\lambda = 0.71073 \text{ \AA}$
 $T = 173\text{K}$,
 $2\theta_{\text{max}} = 59.2^\circ$
70399 reflections collected, 18272 unique
Multi-scan
 $R_{\text{int}} = 0.0593$
Final $Goof = 1.025$
 $RI = 0.0502$
 $wR2 = 0.1214$
704 parameters, 20 restraints
 $\mu = 0.690 \text{ mm}^{-1}$

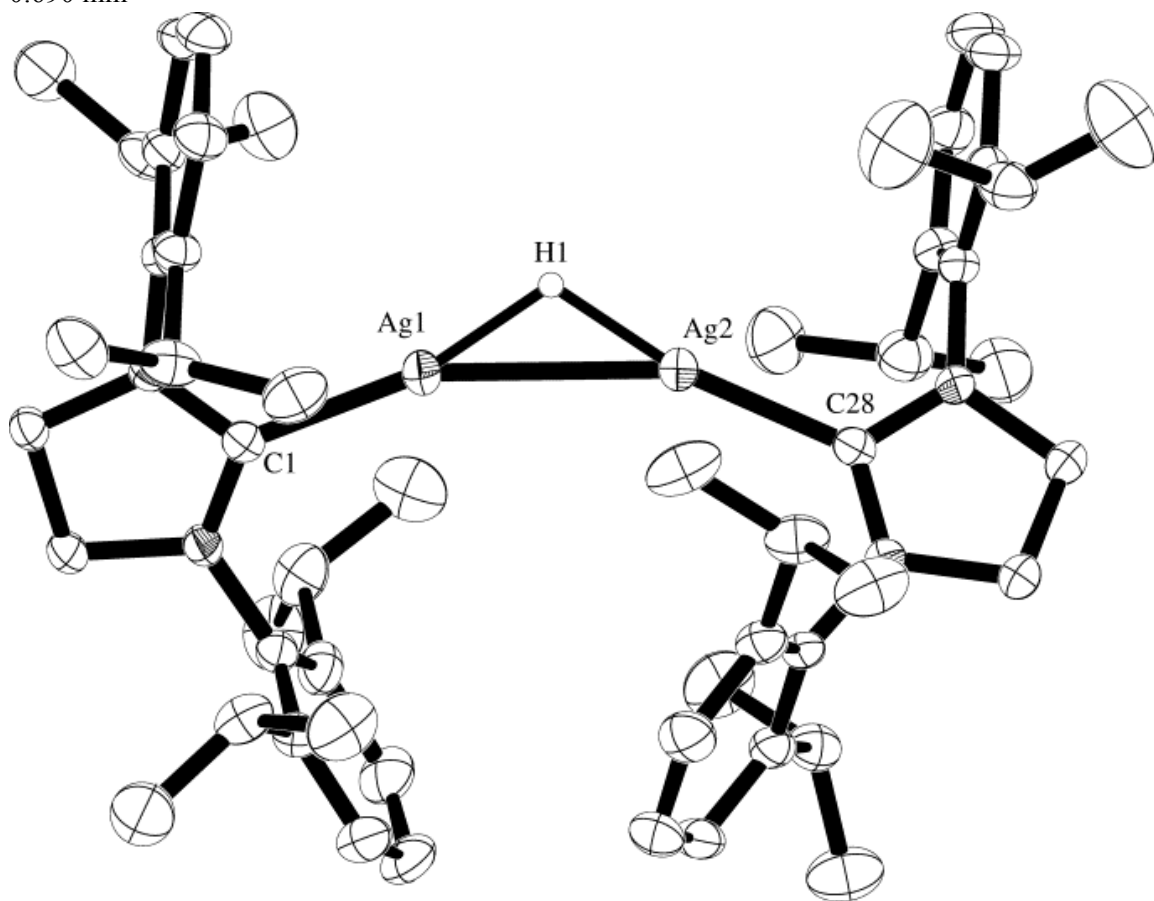


Figure S18. Crystal structure of 2[OTf], showing 50% probability ellipsoids. Anion and solvent are omitted for clarity.

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