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Phosphine- and Carbene-Ligated Silver Acetate: Easily-Accessed Synthons for Reactions with Silylated Nucleophiles

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The useful synthon tricyclohexylphosphinesilver(I) acetate is easily prepared on gram scale by the reaction of silver(I) acetate and tricyclohexylphosphine in a 1:1 ratio in toluene. $(PCy_3)Ag(OAc)$ (**1**) reacts with a wide range of silylated nucleophiles (Me_3Si-X; product with X = N_3, **2**; Cl, **3**; SCN, **4**; 1,2,4-triazol-1-yl, **5**; trifluoromethanesulfonate (OTf), **6**; SPh, **8**; Br, **9**) to effect room temperature Ag−X bond formation at the expense of the Ag−OAc bond. All new products were characterized by multinuclear NMR spectroscopies, IR spectroscopy, microanalysis, and X-ray crystallography. X-ray crystallography indicated a variety of coordination geometries at silver(I) are accessible, as di- and tetranuclear complexes were observed in all cases except **1**, which forms a three-coordinate, mononuclear complex. In the case of **8**, NMR and mass spectrometric data suggest fluxional species of variable nuclearity (but with empirical formula $[(PCy_3)Au(SPh)]_n$) exist in solution. To provide more definitive evidence of Ag−S bond formation, the ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) was used to synthesize a new starting material, (IPr)AgOAc (**10**), the Ag−OAc bond of which is amenable to silylation by Me_3Si-X (complex with X = N_3, **11**; Cl, **12**; SPh, **14**). Complex **14** was characterized crystallographically, and provided definitive evidence for Ag−S bond formation via silylation with PhS-$SiMe_3$. Me_3SiBr and Me_3SiI are also competent in the silylation of **10** to yield **13** and **15**, but these compounds were more cleanly synthesized by the reaction of **12** and KBr/KI in a biphasic CH_2Cl_2/H_2O mixture. In a preliminary exploration of reactivity, it was determined that azidosilver(I) complexes **2** and **11** react rapidly and quantitatively with $(NO)(SbF_6)$ (as was previously demonstrated in a related azidogold(I) system) to yield cationic silver(I) species (detected by mass spectrometry). In acetonitrile solution, ligand rearrangements of these cationic silver(I) species yield cationic bis(phosphine) or bis(carbene) complexes, the identities of which were authenticated by X-ray crystallography.

Introduction

In recent years, complexes of silver(I) have received considerable attention in catalytic applications,[1] as antimicrobial agents,[2] and in coordination polymers.[3] Because of its preference for a coordination number higher than two, trigonal planar and tetrahedral binding geometries are more frequently observed for complexes of silver(I) relative to complexes of gold(I), although these modes of binding are known for gold(I).[4] In many of the investigations of recent years, silver(I) halides or pseudohalides form the building blocks or are precursors to the catalysts, antimicrobial agents, or coordination polymers of interest. Silver(I) complexes of the halides or pseudohalides (e.g., SCN^-, N_3^-) are most commonly synthesized by two methods. The first method is to treat a silver(I) halide or pseudohalide with the ligand of interest (e.g., a phosphine, but can be other neutral donor such as an isonitrile), leading to formation of $(PR_3)AgX$ which may then oligomerize to silver complexes of various nuclearities, depending on the cone angle of the phosphine.[5] The advantage of this method is that there is a rich variety of AgX salts and phosphines that could be used to synthesize $(PR_3)AgX$. However, the disadvantages are that not all AgX salts (where X is a coordinating anion) are commercially or readily available, and anything more complex than a simple halide or pseudohalide cannot be directly made using this method. The second method involves the use of imidazolium

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pro-ligands with an acidic proton, in which the pro-ligand reacts with a basic silver salt (e.g., Ag_2O or AgOAc) in an acid−base reaction to generate a silver(I)-carbene complex and a protic byproduct (such as water).[6] This method is easily performed in air, but one is limited to certain X by this route (usually halide).

Recently, Gray and co-workers have developed a method of making gold(I) azide complexes from the corresponding gold(I) acetate and azidotrimethylsilane.[7] As part of that investigation, it was discovered that this methodology is also suitable to the synthesis of both phosphine- and carbene-ligated silver(I) azide complexes. However, the synthetic methodology was never extended beyond azidotrimethylsilane. In an effort to ascertain the scope of this useful methodology, we have demonstrated the utility of the reaction of two silver(I) complexes LAg(OAc) (L = tricyclohexylphosphine (PCy_3) or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr)) for a larger cross-section of silanes (Me_3Si-X). The products have been characterized by multinuclear NMR spectroscopies, IR spectroscopy, X-ray crystallography, mass spectrometry, and microanalysis. Furthermore, a preliminary investigation of the reactivity of some of the products is described. Overall, the methodology described herein provides the foundation for the development of silver(I) complexes of higher complexity and utility, and should be broadly applicable to the synthesis of other late transition metal complexes, especially gold(I).

Experimental Section

All solvents and reagents were used as received except toluene, which was purified by an MBraun Solvent Purification System.[8] Silver acetate was purchased from Acros, and all silylated reagents were purchased from Alfa Aesar. Microanalyses (C, H, and N) were performed by Quantitative Technologies Inc. (Madison, NJ). All NMR spectra (^{1}H, ^{13}C, ^{19}F, and $^{31}P\{^{1}H\}$) were recorded in $CDCl_3$ (unless otherwise stated) on a Varian AS-400 spectrometer operating at 399.7, 100.5, 376.1, and 161.8 MHz, respectively. Chemical shifts for ^{1}H NMR spectra were determined relative to the residual solvent signals, and for $^{31}P\{^{1}H\}$ NMR spectra, relative to H_3PO_4. For ^{19}F NMR spectra, chemical shifts were determined relative to an internal standard ($CFCl_3$ in $CDCl_3$). Melting points were measured in flame-sealed glass capillary tubes under nitrogen on a Thomas-Hoover Capillary Melting Point Apparatus.

Caution! *Metal azide complexes are potentially explosive, and appropriate precautions should be taken. Although we have not experienced incidents with the present compounds, metal azides should be protected from heat and percussion. Reaction with acids may release toxic hydrazoic acid. Protective eyewear and protective clothing are essential.*

[(PCy_3)AgOAc] (1). In 5 mL of toluene (in a glovebox) silver(I) acetate (342 mg, 2.05 mmol) was suspended, and a 20 mL toluene solution of tricyclohexylphosphine (1.03 equiv, 592 mg, 2.11 mmol) was added dropwise. The suspension was stirred for 8 h and became a solution over this period of time. The solution was filtered through Celite, and the filtrate volume reduced via rotary evaporation until a residue remained. Pentane was added, and the residue was mixed with this solvent until a colorless solid separated. This solid, which was analytically pure, was collected and dried. Yield: 914 mg (99%). This procedure could be scaled up to multigram quantities with little decrease in yield and no decrease in purity. ^{1}H NMR: δ 2.06 (s, 3H, O_2CCH_3), 1.18−1.95 (m, 33H, $P(C_6H_{11})_3$) ppm. $^{31}P\{^{1}H\}$ NMR: δ 43.3 (dd, $^{1}J(^{107}Ag-P)$ = 651 Hz, $^{1}J(^{109}Ag-P)$ = 747 Hz) ppm. Anal. Calcd for $C_{20}H_{36}AgO_2P$: C, 53.70; H, 8.11. Found: C, 53.57; H, 8.19.

[(PCy_3)Ag(μ_3-N_3)]$_4$ (2). In a round-bottom flask, **1** (203 mg, 0.45 mmol) was dissolved in 5 mL of toluene, and the flask was fit with a rubber septum. Azidotrimethylsilane (2 equiv, 0.13 mL, 0.97 mmol) was added via syringe, and the solution was stirred for 7 h. The toluene was removed by rotary evaporation, and the remaining residue was triturated with pentane. The white solid that separated was collected and dried. Yield: 161 mg (82%). ^{1}H NMR: δ 1.20−2.00 (m, 33H, $P(C_6H_{11})_3$) ppm. $^{31}P\{^{1}H\}$ NMR: δ 43.4 (dd, $^{1}J(^{107}Ag-P)$ = 610 Hz, $^{1}J(^{109}Ag-P)$ = 703 Hz) ppm. IR (KBr, cm^{-1}): 2019 (ν_{as} N=N=N, vs), 1308 (ν_{s} N=N=N, m) cm^{-1}. Anal. Calcd for $C_{72}H_{132}Ag_4N_{12}P_4$: C, 50.24; H, 7.73; N; 9.76. Found: C, 50.19; H, 8.01; N; 9.71.

[(PCy_3)Ag(μ-Cl)]$_2$ (3). This compound has been prepared previously,[9] but using different methodology. In 4 mL of toluene, **1** (85 mg, 0.19 mmol) was dissolved and under an inert atmosphere, ∼1.4 equiv of chlorotrimethylsilane (29 mg, 0.27 mmol) in 2 mL of toluene was added dropwise. After 6 h, the toluene was removed by rotary evaporation, the white solid washed with pentane, and the solid collected and dried. The solution phase chemical shifts and $^{1}J(^{107/109}Ag-P)$ coupling constants for $^{31}P\{^{1}H\}$ NMR spectra of **3** matched the values in ref 9. Yield: 70 mg (87%). Anal. Calcd for $C_{36}H_{66}Ag_2Cl_2P_2$: C, 51.02; H, 7.85. Found: C, 50.90; H, 7.60.

[(PCy_3)Ag(μ-SCN)]$_2$ (4). In 4 mL of toluene, **1** (103 mg, 0.23 mmol) was dissolved and trimethylsilylisothiocyanate (49 mg, 0.37 mmol) was added. The solution became slightly cloudy and was stirred 6 h. The toluene was removed by rotary evaporation, and the residue triturated with pentane. The resultant white solid was collected and dried. Yield: 89 mg (87%). ^{1}H NMR: δ 1.18−1.92 (m, 33H, $P(C_6H_{11})_3$) ppm. $^{31}P\{^{1}H\}$ NMR: δ 39.1 (dd,

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$^{1}J(^{107}\mathrm{Ag-P}) = 571$ Hz, $^{1}J(^{109}\mathrm{Ag-P}) = 662$ Hz) ppm. IR (KBr, cm^{-1}): 2105 (ν S=C=N, vs) cm^{-1}. Melting Point: 197−198 °C. Anal. Calcd for $C_{38}H_{66}Ag_2N_2P_2S_2$: C, 51.12; H, 7.45; N; 3.14. Found: C, 50.85; H, 7.48; N; 3.10.

[(PCy$_3$)Ag(μ-(1,2,4-triazol-1-yl)]$_2$ (5). In 5 mL of toluene, **1** (118 mg, 0.26 mmol) was dissolved and under an inert atmosphere, ~1.05 equiv of 1-trimethylsilyl(1,2,4-triazole) (0.04 mL, 0.28 mmol) was added via syringe. After 6 h, cesium carbonate (201 mg, 0.62 mmol) was added, and the suspension stirred for 1 h. The suspension was filtered through potassium carbonate, and the filtrate collected. The toluene was removed by rotary evaporation, the residue triturated with pentane, the white solid collected, washed with ether, and dried. Yield: 107 mg (89%). ^{1}H NMR: δ 8.07 (s, 4H, $C_2N_3H_2$), 1.18−2.05 (m, 66H, $P(C_6H_{11})_3$) ppm. $^{31}P\{^{1}H\}$ NMR: δ 38.4 (dd, $^{1}J(^{107}\mathrm{Ag-P}) = 558$ Hz, $^{1}J(^{109}\mathrm{Ag-P}) = 645$ Hz) ppm. Melting Point: 165−167 °C. Anal. Calcd for $C_{40}H_{70}Ag_2N_6P_2$: C, 52.62; H, 7.73; N, 9.20. Found: C, 52.38; H, 7.49; N, 9.32.

[(PCy$_3$)Ag(μ-OTf)]$_2$ (6). In 4 mL of toluene, **1** (97 mg, 0.22 mmol) was dissolved and (in a glovebox freezer) cooled to −20 °C. Separately, ~1.2 equiv of trimethylsilyltrifluoromethanesulfonate (58 mg, 0.26 mmol) in 2 mL of toluene was cooled in a glovebox freezer to the same temperature. The two solutions were removed from the freezer, and the trimethylsilyltrifluoromethanesulfonate solution was added dropwise to the solution of **1**. After 1.5 h, the product solution was taken to dryness via rotary evaporation, and the residue triturated with pentane. The dry, crude solid was dissolved in a minimum of benzene, and pentane vapor was diffused into the saturated benzene solution, causing separation of a colorless, crystalline solid that was dried and collected. Yield: 85 mg (73%). ^{1}H NMR: δ 1.17−1.96 (m, 66H, $P(C_6H_{11})_3$) ppm. ^{19}F NMR: δ −77.58 ppm. $^{31}P\{^{1}H\}$ NMR: δ 47.1 (br d) ppm. IR (KBr, cm^{-1}): 1321, 1188, 994 (vs) cm^{-1}. Melting Point: 171−172 °C. Anal. Calcd for $C_{38}H_{66}Ag_2F_6O_6P_2S_2$: C, 42.47; H, 6.19. Found: C, 42.43; H, 5.92.

[(PCy$_3$)Ag(pyr)](OTf) (7). Compound **6** (63 mg, 0.059 mmol) was dissolved in a minimum of pyridine (low-water content, Acros) and pentane vapor was diffused into the saturated pyridine solution, causing separation of colorless crystals which were analytically pure upon drying. Yield: 55 mg (76%). ^{1}H NMR: δ 8.66−8.70 (2H, m, C_5H_5N), 7.82 (tt, 1H, *para*-C_5H_5N, J = 1.6, 8.0 Hz), 7.41−7.46 (m, 2H, C_5H_5N), 1.02−2.02 (m, 33H, $P(C_6H_{11})_3$) ppm. ^{19}F NMR: δ −78.43 ppm. $^{31}P\{^{1}H\}$ NMR: δ 42.9 (dd, $^{1}J(^{107}\mathrm{Ag-P}) = 599$ Hz, $^{1}J(^{109}\mathrm{Ag-P}) = 692$ Hz) ppm. IR (KBr, cm^{-1}): 1281, 1251, 1027 (vs) cm^{-1}. Anal. Calcd for $C_{24}H_{38}AgF_3NO_3PS$: C, 46.76; H, 6.21; N, 2.27. Found: C, 46.51; H, 6.02; N, 2.24.

[(PCy$_3$)Ag(SPh)]$_n$ (8). In 4 mL of toluene, **1** (95 mg, 0.21 mmol) was dissolved. Under an inert atmosphere, (phenylthio)trimethylsilane (47 mg, 0.26 mmol) was added, and the solution was stirred for 6 h. The toluene was removed via rotary evaporation, and pentane was added. The pentane was removed by rotary evaporation, and methanol was added to cause separation of a sticky white (pentane soluble) precipitate which was collected and dried under vacuum. A foamy white solid was collected. Yield: 65 mg (62%). ^{1}H NMR: δ 7.51 (2H, d, *ortho*-C_6H_5S, J = 7.2 Hz), 6.97 (t, 2H, *meta*-C_6H_5S, J = 7.6 Hz), 6.86 (t, 1H, *para*-C_6H_5S, J = 7.2 Hz), 1.05−1.98 (m, 33H, $P(C_6H_{11})_3$) ppm. ^{13}C NMR: δ 144.76 (s), 133.22 (s), 127.45 (s), 122.00 (s), 32.00 (d, $^{1}J_{C-P}$ = 12.3 Hz), 30.82 (d, J_{C-P} = 4.6 Hz), 27.25 (d, J_{C-P} = 11.4 Hz), 25.93 (s) ppm. $^{31}P\{^{1}H\}$ NMR (243 K, only one doublet resolved): δ 35.5 (d) ppm. Anal. Calcd for $C_{24}H_{38}AgPS$: C, 57.94; H, 7.70. Found: C, 57.88; H, 7.49.

[(PCy$_3$)Ag(μ-Br)]$_2$ (9). This compound has been prepared previously,[9] but using different methodology. In 4 mL of toluene, **1** (90 mg, 0.20 mmol) was dissolved and under an inert atmosphere, 1 equiv of bromotrimethylsilane (31 mg, 0.20 mmol) in 2 mL of toluene was added dropwise. After 6 h, the toluene was removed by rotary evaporation, the white solid washed with pentane, and the solid collected and dried. The solution phase chemical shifts and $^{1}J(^{107/109}\mathrm{Ag-P})$ coupling constants for $^{31}P\{^{1}H\}$ NMR spectra of **9** matched the values in reference 9. Yield: 87 mg (92%). Anal. Calcd for $C_{36}H_{66}Ag_2Br_2P_2$: C, 46.18; H, 7.10. Found: C, 46.27; H, 6.89.

[(IPr)Ag(OAc)] (10). In 5 mL of dichloromethane, **12** (prepared in large scale from reference 6d, 332 mg, 0.62 mmol) was dissolved. Silver(I) acetate (1.06 equiv, 110 mg, 0.66 mmol) was added, and the flask covered with aluminum foil. Under argon, the suspension was stirred for 2 h, filtered through Celite (in air), and the solvent removed by rotary evaporation. The residue was triturated with pentane and dried, extracted into toluene, and filtered through Celite. The toluene was removed by rotary evaporation, and the colorless solid triturated with pentane. The resultant colorless solid was collected and dried. Yield: 300 mg (86%). ^{1}H NMR: δ 7.50 (t, 2H, *para*-$C_6H_3(CH(CH_3)_2)_2$, J = 7.6 Hz), 7.30 (d, 4H, *meta*-$C_6H_3(CH(CH_3)_2)_2$, J = 7.6 Hz), 7.23 (s, 2H, vinyl CH), 2.56 (sep, 4H, $C_6H_3(CH(CH_3)_2)_2$, J = 6.8 Hz), 1.85 (s, 3H, O_2CCH_3), 1.30 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, J = 6.8 Hz), 1.23 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, J = 6.8 Hz) ppm. ^{13}C NMR: δ 184.32 (dd, C_{carbene}, $J(^{107/109}\mathrm{Ag}/^{13}\mathrm{C})$ = 249, 286 Hz), 178.05 (s, O_2CCH_3), 145.53 (s), 134.60 (s), 130.51 (s), 124.17 (s), 123.42 (d, vinyl carbon, J = 8.3 Hz), 28.62 (s), 24.59 (s), 23.92 (s), 22.58 (s) ppm. Melting Point: 200 °C (dec.). Anal. Calcd for $C_{29}H_{39}AgN_2O_2$: C, 62.50; H, 7.08; N, 5.04. Found: C, 62.70; H, 7.11; N, 4.99.

[(IPr)Ag(N$_3$)] (11). In 5 mL of toluene, **10** (80 mg, 0.14 mmol) was dissolved in a round-bottom flask (fitted with a rubber septum), and trimethylsilylazide (2 equiv, 0.04 mL, 0.30 mmol) was added via syringe. The solution became cloudy and was stirred for 6 h. The toluene was removed by rotary evaporation, and the solid was triturated with pentane. The spectroscopically and analytically pure white solid was collected and dried. Yield: 74 mg (95%). ^{1}H NMR: δ 7.52 (t, 2H, *para*-$C_6H_3(CH(CH_3)_2)_2$, J = 8.0 Hz), 7.31 (d, 4H, *meta*-$C_6H_3(CH(CH_3)_2)_2$, J = 7.6 Hz), 7.24 (s, 2H, vinyl CH), 2.52 (sep, 4H, $C_6H_3(CH(CH_3)_2)_2$, J = 6.8 Hz), 1.26 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, J = 6.8 Hz), 1.23 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, J = 6.8 Hz) ppm. ^{13}C NMR: δ 183.04 (dd, C_{carbene}, $J(^{107/109}\mathrm{Ag}/^{13}\mathrm{C})$ = 237, 273 Hz), 145.36 (s), 134.28 (s), 130.69 (s), 124.26 (s), 123.65 (d, vinyl carbon, J = 7.5 Hz), 28.56 (s), 24.53 (s), 23.88 (s) ppm. IR (KBr, cm^{-1}): 2038 (ν_{as} N=N=N, vs), 1326 (ν_{s} N=N=N, m) cm^{-1}. Anal. Calcd for $C_{27}H_{36}AgN_5$: C, 60.22; H, 6.74; N; 13.01. Found: C, 60.24; H, 6.90; N; 12.91.

[(IPr)AgCl] (12). This compound has been prepared previously, but using different methodology.[6d] In a glovebox, in 3 mL of toluene, **10** (52 mg, 0.094 mmol) was dissolved. A solution of chlorotrimethylsilane (1.2 equiv, 12 mg, 0.11 mmol) in 1 mL of toluene was added dropwise, and the solution stirred for 6 h. Toluene was removed by rotary evaporation, and the colorless solid was triturated with pentane. The resultant solid was collected and dried. Yield: 48 mg (96%). Anal. Calcd for $C_{27}H_{36}AgClN_2$: C, 60.97; H, 6.82; N; 5.27. Found: C, 60.73; H, 6.74; N; 5.00.

[(IPr)AgBr] (13). In 10 mL of dichloromethane, **12** (70 mg, 0.13 mmol) was dissolved. A 10 mL aqueous solution of KBr (5.5 equiv, 86 mg, 0.72 mmol) was added, and the resultant biphasic mixture was vigorously stirred for 4 h. The organic phase was segregated, and the aqueous phase was washed once with 10 mL of dichloromethane. The organic phases were combined and washed twice with 10 mL of distilled water, dried with $MgSO_4$, and filtered through Celite. The filtrate was reduced to dryness via rotary evaporation, and the resultant residue was triturated with pentane to cause separation of a colorless solid, which was collected and dried. Yield: 54 mg (71%). ^{1}H NMR: δ 7.48 (t, 2H, *para*-$C_6H_3(CH(CH_3)_2)_2$, J = 7.6 Hz), 7.28 (d, 4H, *meta*-$C_6H_3(CH(CH_3)_2)_2$, J = 7.6 Hz), 7.21 (d, 2H, vinyl CH, J = 1.6 Hz), 2.53 (sep, 4H, $C_6H_3(CH(CH_3)_2)_2$,

$J = 6.8$ Hz), 1.26 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, $J = 6.8$ Hz), 1.21 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, $J = 6.8$ Hz) ppm. ^{13}C NMR: δ 185.63 (dd, $C_{carbene}$, $J(^{107/109}Ag/^{13}C) = 233, 272$ Hz), 145.42 (s), 134.36 (s), 130.61 (s), 124.19 (s), 123.51 (d, vinyl carbon, $J = 7.6$ Hz), 28.55 (s), 24.65 (s), 23.91 (s) ppm. Melting Point: > 250 °C. Anal. Calcd for $C_{27}H_{36}AgBrN_2$: C, 56.26; H, 6.30; N; 4.86. Found: C, 56.42; H, 5.73; N; 4.83.

[(IPr)Ag(SPh)] (14). In a glovebox, **10** (82 mg, 0.14 mmol) was dissolved in toluene (4 mL). A solution of (phenylthio)-trimethylsilane (41 mg, 0.22 mmol) in 2 mL of toluene was added dropwise, and the solution was stirred for 6 h, after which a white solid had precipitated. The toluene was removed in vacuo, and the residue was washed with pentane in the glovebox and dried. The dry solid was extracted into a minimum of tetrahydrofuran (THF) and filtered through Celite in the glovebox. Pentane vapor was diffused into the saturated solution, causing separation of a colorless, crystalline solid and an amorphous, gooey solid. Care was taken to manually separate the crystals from the amorphous solid; the crystals were collected and dried. Yield: 25 mg (28%). The solubility of **14** is too low in C_6D_6 to record a ^{13}C NMR spectrum, but **14** partially decomposes in chlorinated solvents (e.g., $CDCl_3$) and THF. ^1H NMR (C_6D_6): δ 7.32−7.35 (m, 2H, C_6H_5S), 7.21 (t, 2H, *para*-$C_6H_3(CH(CH_3)_2)_2$, $J = 8.0$ Hz), 7.02 (d, 4H, *meta*-$C_6H_3(CH(CH_3)_2)_2$, $J = 7.6$ Hz), 6.88−6.91 (m, 3H, C_6H_5S), 6.27 (d, 2H, vinyl C*H*, $J = 1.2$ Hz), 2.48 (4H, sep, $C_6H_3(CH(CH_3)_2)_2$, $J = 7.2$ Hz), 1.24 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, $J = 7.2$ Hz), 1.01 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, $J = 7.2$ Hz) ppm. Anal. Calcd for $C_{33}H_{41}AgN_2S$: C, 65.44; H, 6.82; N; 4.63. Found: C, 65.16; H, 6.58; N; 4.45.

[(IPr)AgI] (15). In 15 mL of dichloromethane, **12** (172 mg, 0.32 mmol) was dissolved. A 20 mL aqueous solution of KI (5.5 equiv, 295 mg, 2.5 mmol) was added, and the resultant biphasic mixture was vigorously stirred for 4 h. The organic phase was segregated, and the aqueous phase was washed once with 10 mL of dichloromethane. The organic phases were combined and washed twice with 10 mL of distilled water, dried with $MgSO_4$, and filtered through Celite. The filtrate was reduced to dryness via rotary evaporation, and the resultant residue was triturated with pentane to cause separation of a colorless solid, which was extracted into benzene/THF and filtered through Celite. The solvent was again removed by rotary evaporation and the residue triturated with pentane. The white solid that remained was collected and dried. Yield: 120 mg (60%). In the ^1H NMR spectrum of **15** in $CDCl_3$, a small amount of $[(carbene)_2Ag]^+$ appeared (by comparison to ^1H NMR signals for **17**), presumably in equilibrium with **15**. ^1H NMR: δ 7.47 (t, 2H, *para*-$C_6H_3(CH(CH_3)_2)_2$, $J = 8.0$ Hz), 7.27 (d, 4H, *meta*-$C_6H_3(CH(CH_3)_2)_2$, $J = 8.0$ Hz), 7.21 (d, 2H, vinyl C*H*, $J = 1.2$ Hz), 2.52 (sep, 4H, $C_6H_3(CH(CH_3)_2)_2$, $J = 6.8$ Hz), 1.25 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, $J = 6.8$ Hz), 1.20 (d, 12H, $C_6H_3(CH(CH_3)_2)_2$, $J = 6.8$ Hz) ppm. ^{13}C NMR: δ 185.63 (dd, $C_{carbene}$, $J(^{107/109}Ag/^{13}C) = 221, 254$ Hz), 145.39 (s), 134.26 (s), 130.51 (s), 124.09 (s), 123.44 (d, vinyl carbon, $J = 6.7$ Hz), 28.48 (s), 24.63 (s), 23.90 (s) ppm. Melting Point: > 250 °C. Anal. Calcd for $C_{27}H_{36}AgIN_2$: C, 52.02; H, 5.82; N; 4.50. Found: C, 51.40; H, 5.75; N; 4.31.

X-ray Structure Determination. Crystals of **1** were grown by mixing pentane with a saturated toluene residue of **1** and placing the resultant solution in a −20 °C freezer. Crystals of **2**, **13**, **14**, and **15** were grown by diffusion of pentane vapor into saturated THF solutions. Crystals of **4** and **6** were grown by diffusion of pentane vapor into a saturated benzene solution. Crystals of **5** were grown by diffusion of pentane vapor into a saturated chloroform solution. Crystals of **11** were grown by diffusion of pentane into a saturated $CDCl_3$ solution. Single crystal X-ray data were collected at 100(2) K (except for **17**, which was collected at 296(2) K) on a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo Kα radiation with omega scan technique. The unit cell was determined using SMART and SAINT+. All structures were solved by direct methods and refined by full matrix least-squares against F^2 with all reflections using SHELXTL (Tables 1 and 2). Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were placed in standard calculated positions, and all hydrogen atoms were refined with an isotropic displacement parameter 1.5 (CH_3) or 1.2 (all others) times that of the adjacent carbon or nitrogen atom.

Results and Discussion

Synthesis. Preparation of tricyclohexylphosphine-ligated silver(I) complexes begins with the synthesis of $(PCy_3)Ag(OAc)$ (**1**) by the reaction of silver(I) acetate with tricyclohexylphosphine in toluene (reaction 1).

$$PCy_3 + AgOAc \rightarrow (PCy_3)Ag(OAc) \qquad (1)$$

This methodology has precedence in the syntheses of complexes of the type $(PCy_3)AgX$ (X = Cl, Br, I) from the reaction of AgX with PCy_3 in pyridine.[9] Complex **1** is a highly soluble synthon (readily soluble in benzene, toluene, THF, chlorinated solvents) that reacts rapidly at room temperature with silylated nucleophiles Me_3Si-X to yield products of the type $(PCy_3)AgX$ (**2**−**6**, **8**, **9**) in moderate to excellent yields (62−92%). In each case the crude material was spectroscopically and analytically pure, did not require recrystallization for purification, and could be handled and stored in air without decomposition. It should be noted that as control reactions, the chloro complexes **3** (and **12**) were both treated with an excess of trimethylsilylthiocyanate (in toluene, 24 h) and azidotrimethylsilane (in THF, 8 h) to determine if the silver acetate complexes **1** (and **10**) were necessary for successful formation of products. In each case, no evidence for product formation was discerned spectroscopically, underscoring the utility of synthons **1** and **10**. Scheme 1 illustrates the sequence of reactions and products isolated from **1**.

The reaction of Me_3Si-SPh with **1** is slightly problematic. Although ^1H NMR spectroscopy and microanalysis indicated the product (**8**) has the empirical formulation $[(PCy_3)Ag(SPh)]_n$, and $^{31}P\{^1H\}$ NMR spectroscopy indicated the presence of Ag−P bonding in solution, it was unclear what the precise value of n was. Mass spectrometric analysis suggested that species for which $n = 1$ and $n = 2$ (and probably higher values of n as well) were present in an acetonitrile solution (in Scheme 1, the dinuclear complex in which $n = 2$ is depicted). In addition, **8** was unexpectedly soluble in most solvents (with the exception of methanol), and was even soluble in pentane at −20 °C. Therefore, X-ray quality crystals were not forthcoming.

It has been demonstrated that *N*-heterocyclic carbene ligands are highly effective at stabilizing reactive inorganic fragments.[10] Furthermore, our own experience has

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Table 1. Crystallographic Data for Phosphine-Ligated Complexes **1**, **2**, **4**–**6**, and **16**

	1	**2**·2THF	**4**	**5**	**6**	**16**
formula	$C_{20}H_{36}$-AgO_2P	$C_{72}H_{132}Ag_4N_{12}$-$P_4 \cdot 2C_4H_8O$	$C_{19}H_{33}$-AgNPS	$C_{40}H_{70}$-$Ag_2N_6P_2$	$C_{38}H_{66}Ag_2$-$F_6O_6P_2S_2$	$C_{37}H_{66}Ag$-$F_3O_3P_2S$
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	17.1303(12)	27.025(4)	8.6533(6)	8.2098(8)	15.8931(18)	25.606(3)
b, Å	7.7764(5)	14.5163(16)	24.8159(17)	9.9738(1)	10.9553(13)	11.7936(15)
c, Å	16.9212(12)	23.243(3)	9.5044(7)	15.2288(15)	26.347(3)	26.490(3)
α, deg	90	90	90	101.132(1)	90	90
β, deg	118.100(1)	108.477(2)	98.468(1)	98.343(1)	102.302(1)	93.142(2)
γ, deg	90	90	90	96.050(1)	90	90
cell volume, Å^3	1988.4(2)	8648.1(18)	2018.7(2)	1199.1(2)	4482.1(9)	7987.8(17)
Z	4	4	4	1	4	8
θ_{min}, θ_{max}, deg	2.70, 26.98	1.61, 27.50	1.64, 27.50	1.38, 27.50	1.38, 27.50	1.08, 27.50
no. of reflns collected	21301	51053	23534	14186	52365	90094
no. of indep reflns	4088	8874	4196	4993	9465	15380
no. of refined params	218	460	209	227	505	847
Goodness-of-fit on F^{2a}	1.131	1.083	1.238	1.225	1.189	1.043
final R indices^b [$I > 2\sigma(I)$] R_1	0.0211	0.0304	0.0298	0.0281	0.0498	0.0319
wR_2	0.0590	0.0823	0.0887	0.0860	0.0536	0.0411
R indices (all data) R_1	0.0221	0.0358	0.0341	0.0301	0.1276	0.0840
wR_2	0.0595	0.0908	0.0977	0.0872	0.1358	0.0927

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$; n = number of reflections, p = number of parameters refined. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 2. Crystallographic Data for Carbene-Ligated Complexes **11**, **13**–**15**, and **17**

	11	**13**	**14**	**15**	**17**
formula	$C_{27}H_{36}AgN_5$	$C_{27}H_{36}AgBrN_2$	$C_{33}H_{41}AgN_2S$	$C_{27}H_{36}AgIN_2$	$C_{54}H_{72}AgF_6N_4Sb$
cryst syst	triclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)	$C2/c$ (No. 15)	$Pna2_1$ (No. 33)	$Fddd$ (No. 70)
a, Å	9.7306(9)	20.0737(11)	21.321(4)	20.608(4)	21.4951(14)
b, Å	11.3549(10)	10.6655(6)	14.465(4)	10.826(2)	25.6925(14)
c, Å	12.2261(11)	12.5882(7)	20.057(4)	12.542(3)	37.072(3)
α, deg	85.732(1)	90	90	90	90
β, deg	85.596(1)	90	99.832(3)	90	90
γ, deg	85.463(1)	90	90	90	90
cell volume, Å^3	1339.5(2)	2695.1(3)	6095(2)	2798.3(10)	20474(2)
Z	2	4	8	4	16
θ_{min}, θ_{max}, deg	1.67, 27.50	2.03, 27.49	1.71, 27.50	1.98, 27.05	1.35, 27.50
no. of reflns collected	15772	31227	34520	29695	59775
no. of indep reflns	5843	5633	6285	5920	5424
no. of refined params	306	288	342	288	311
goodness-of-fit on F^{2a}	0.840	1.024	1.245	1.101	1.043
final R indices^b [$I > 2\sigma(I)$] R_1	0.0210	0.0257	0.0469	0.0263	0.0182
wR_2	0.0220	0.0300	0.0532	0.0272	0.0207
R indices (all data) R_1	0.0871	0.0550	0.1136	0.0791	0.0467
wR_2	0.0912	0.0569	0.1193	0.0800	0.0491

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$; n = number of reflections, p = number of parameters refined. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

shown that NHC-carbene ligated complexes are less soluble than their PCy_3 analogues and readily yield X-ray quality crystals.[7,11] Therefore, the ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) was used to prepare (IPr)Ag(OAc) (**10**) from the known chloride precursor (reaction 2).

$$\text{(IPr)AgCl} + \text{AgOAc} \xrightarrow[\text{AgCl}]{} \text{(IPr)Ag(OAc)} \qquad (2)$$

Similar to **1**, **10** is also a useful synthon, reacting with silylated nucleophiles (Me_3Si-X) to yield products of the type (IPr)Ag-X. As test cases, **10** was found to react smoothly with Me_3SiN_3 and Me_3SiCl to yield azidylated derivative **11** and to regenerate chlorinated derivative **12** in excellent yields (95% and 96% respectively, reaction 3).

$$\text{(IPr)Ag(OAc)} + \text{Me}_3\text{Si-X} \xrightarrow[\text{Me}_3\text{Si(OAc)}]{} \text{(IPr)Ag-X} \qquad (3)$$

$$\text{X} = \text{N}_3\ (\mathbf{11}),\ \text{Cl}\ (\mathbf{12})$$

Although NMR spectroscopy indicated that the analogous reactions using bromotrimethylsilane and iodotrimethylsilane did yield **13** and **15**, the product was contaminated in each case with a small amount of byproducts, even when performed at low temperature in a glovebox. However, a biphasic reaction (CH_2Cl_2/H_2O,

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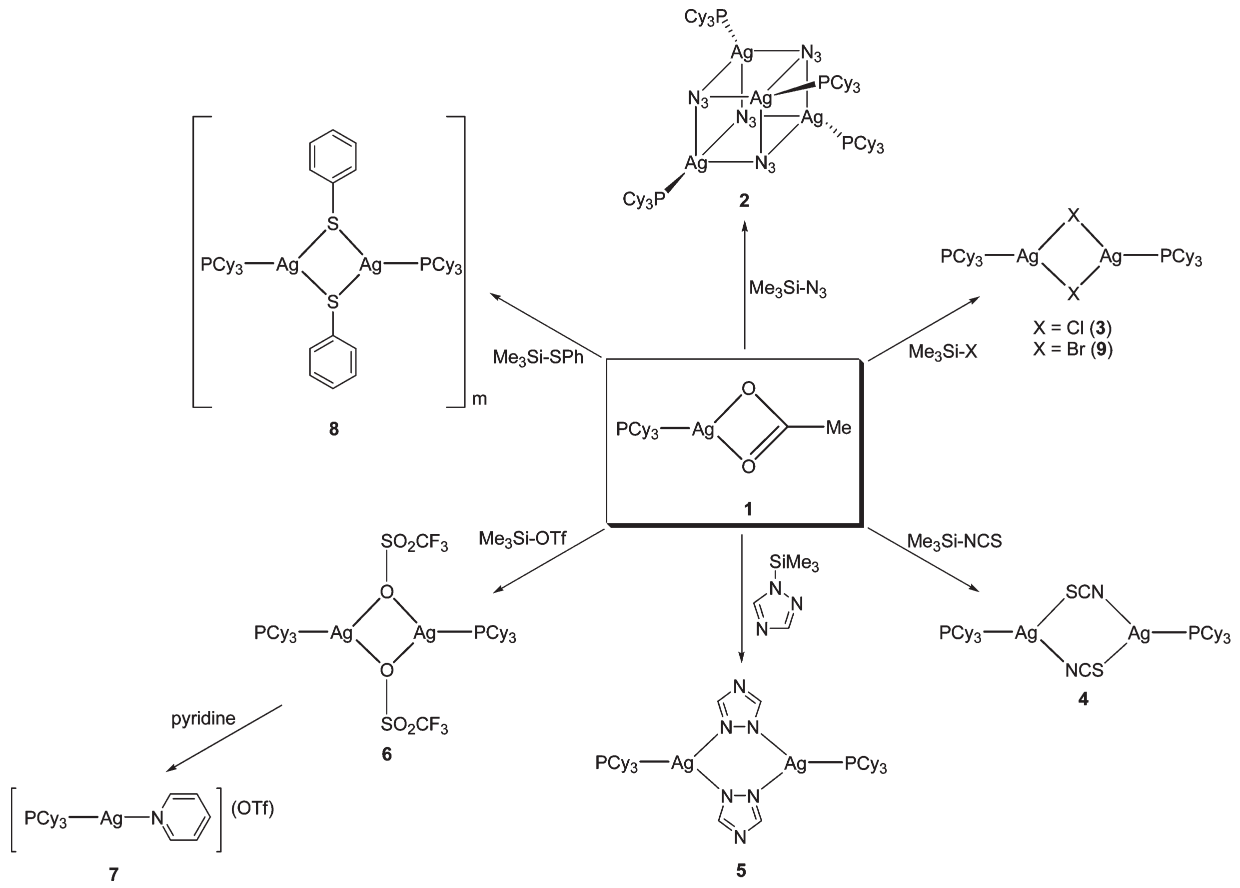
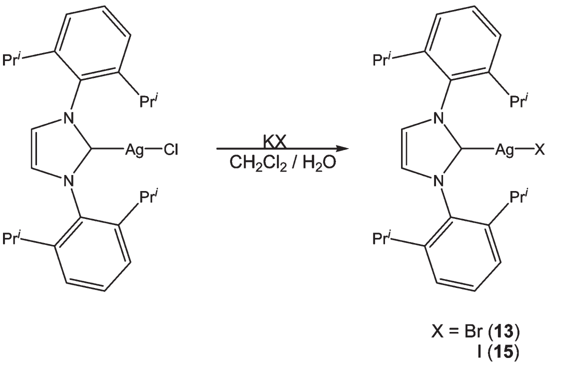
(11) Partyka, D. V.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2007**, *26*, 3279.

Scheme 1. Reactions Series for **1**



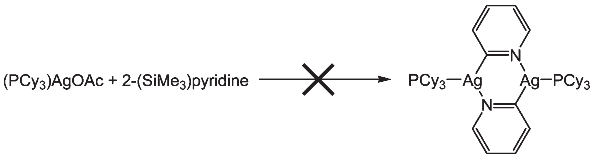
reaction 4) of **11** with excess KBr or KI (which has been utilized in several investigations successfully for analogous gold(I) systems[12]) yielded **13** and **15**, respectively.



(4)

Thus, reactions to synthesize **11**−**13** and **15** clearly indicated that the Ag−OAc bond of **10** could be cleaved by reagents Me_3Si-X to form complexes of the type IPrAg-X. Therefore, in an attempt to unequivocally demonstrate the cleavage of the Ag−OAc bond with concomitant formation of the Ag−SPh bond (as in the synthesis of $[(PCy_3)Ag(SPh)]_n$), **10** was treated with Me_3Si-SPh in toluene. It was unambiguously demonstrated (by NMR spectroscopy, X-ray crystallography, and microanalysis; vide infra) that formation of **14** was indeed effected by treatment of **10** with Me_3Si-SPh; therefore, it is concluded that the product of **1** (containing a much less sterically demanding PCy_3 ligand) and Me_3Si-SPh is **8**. The three-coordinate formulation is depicted as the empirical building block in Scheme 1, as all products **1**−**7** and **9** have been unequivocally shown to have coordination numbers of 3 or 4.

An attempt was also made to activate C−Si and Si−Si bonds by treating **1** (separately) with 2-(trimethylsilyl)-pyridine and hexamethyldisilane, both at room temperature and by heating in toluene (reactions 5 and 6). However, in both cases, only unreacted **1** was recovered and detected by NMR spectroscopy.



(5)

$$(PCy_3)AgOAc + Me_3Si\text{-}SiMe_3 \xrightarrow{\times} PCy_3{-}Ag{-}SiMe_3 \qquad (6)$$

To obtain more information on why reactions 5 and 6 did not proceed, even with heating, **1** was treated with a very bulky chlorosilane to determine if **3** would still be obtained in high yield at room temperature (reaction 7). In fact, reaction 7 proceeded at room temperature to

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[12] (a) Schneider, D.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2004**, 1995. (b) Partyka, D. V.; Robilotto, T. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2008**, *27*, 28. (c) Teets, T. S.; Nocera, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 7411.

Table 3. Coupling Constant Data for Compounds **1**−**5**, **7**, **9**−**15**[a,b]

compound	$^{1}J(^{31}\mathrm{P}\text{-}^{107,109}\mathrm{Ag})$	$^{1}J(^{109}\mathrm{Ag})/^{1}J(^{107}\mathrm{Ag})$ for $^{31}\mathrm{P}$	$^{1}J(^{13}\mathrm{C}\text{-}^{107,109}\mathrm{Ag})$	$^{1}J(^{109}\mathrm{Ag})/^{1}J(^{107}\mathrm{Ag})$ for $^{13}\mathrm{C}$
1	651, 747	1.15		
2	610, 703	1.15		
3[c]	595, 690	1.16		
4	571, 662	1.16		
5	558, 645	1.16		
7	599, 692	1.16		
9[c]	584, 670	1.15		
$[(\mathrm{PCy_3})\mathrm{AgI}]_4$[c]	505, 582	1.15		
10			249, 286	1.15
11			237, 273	1.15
12[d]			235, 271	1.15
13			233, 272	1.17
14[e]			186, 216	1.16
15			221, 254	1.15

[a] Spectra recorded in $CDCl_3$ unless otherwise noted. [b] Compounds **6** and **8** are not included since broad $^{31}P\{^1H\}$ signals do not resolve at room temperature (and still not at 0 or −25 °C for **6** and **8** respectively) on a 600 MHz NMR spectrometer. [c] Values from ref 9; spectra recorded in CH_2Cl_2/CD_2Cl_2 (9:1 v:v). [d] Values from ref 6d. [e] For solubility reasons, spectrum recorded in THF-d_8; partial decomposition occurs in this solvent to **14** (76%) and an imidazolium species (24%) (by ^1H NMR analysis). Only one carbene signal is observed in the ^{13}C NMR spectrum, presumably from the 76% component (**14**), as supported by the multiplicity of the signal.

produce **3** in high yield (93%) over the course of 6 h.

$$(\mathrm{PCy_3})\mathrm{AgOAc} + \mathrm{Bu}^t\mathrm{Ph_2SiCl} \rightarrow (\mathrm{PCy_3})\mathrm{AgCl} \qquad (7)$$

Therefore, it is unlikely that steric bulk precludes the success of reactions 5 and 6. Considering that the only material isolated from the reaction of **1** with 2-trimethylsilylpyridine (1.05 equiv) in pyridine (60 °C for 10 h) was unreacted **1**, this is significant when considering the rate accelerating effect of pyridine and other nitrogenous bases on silylation reactions.

NMR Spectroscopy. All new products were characterized by multinuclear NMR spectroscopies (^1H, ^{13}C, ^{19}F, or ^{31}P, depending on whether the product was carbene- or phosphine-ligated). For the phosphine complexes **1**−**9** (PCy_3AgX, where X is a ligand bound to Ag), ^1H NMR spectra were all characterized by a high-field multiplet typical of the PCy_3 ligand. For complexes **1**, **5**, **7**, and **8**, ^1H NMR integration helped determine the PCy_3 to X empirical ratio, but X-ray crystallography or mass spectrometry was necessary to unequivocally determine the identity of the product (since the coordination of silver(I) complexes can typically vary from two to four, silver(I) complexes could therefore be mononuclear or oligonuclear with the same phosphine to ligand stoichiometry). In the case of **7**, binding of 1 equiv of pyridine ligand to silver was unequivocally determined by integration and the downfield shift of the pyridine resonances relative to free pyridine (in $CDCl_3$). Furthermore, ^{19}F NMR data suggests that the pyridine ligand in fact displaces the triflate ligand of **6** from the coordination sphere of silver(I) to form **7** (consistent with the IR data, vide infra), as the ^{19}F NMR shift observed for **7** (−78.4 ppm relative to $CFCl_3$ in $CDCl_3$) is practically identical to that observed for triflate in $(Bu_4N)(SO_3CF_3)$[13] (−78.7 ppm relative to $CFCl_3$ in $CDCl_3$; for mass spectrometric data vide infra). These data contrast with the ^{19}F NMR data observed for **6**, which suggests a coordinated triflate ligand (as supported by IR spectroscopy and unequivocally ascertained by X-ray crystallography, vide infra).

For complexes **1**−**9**, the $^{31}P\{^1H\}$ was especially useful in determining the $^1J_{\mathrm{Ag-P}}$ coupling constants (silver is a ~48:52 mixture of ^{109}Ag and ^{107}Ag, both of which are spin $^1/_2$). Table 3 lists the calculated coupling constants (including known complexes **3**, **9**, and $[(PCy_3)AgI]_4$ for comparative purposes); the $^{109}Ag/^{107}Ag$ gyromagnetic ratio is approximately 1.15 in each case, as expected.[14] The observed chemical shifts are sensitive to the identity of the ligand X, but (qualitatively) not as sensitive as what is observed for the analogous two coordinate complexes of gold, PCy_3AuX. This is perhaps to be expected in comparing two- coordinate d^{10} complexes (i.e., gold) to three- and four-coordinate d^{10} complexes (i.e., silver). The doublets observed in the $^{31}P\{^1H\}$ spectrum of complex **4** were slightly broadened but the coupling was resolvable, whereas for **6**, the doublets were broadened further and could not be resolved down to 273 K. Both data are suggestive of fluxionality; the latter is consistent with the NMR data for a PPh_3 analogue (a triflate-bridged trinuclear complex).[15] These data stand in contrast to the $^{31}P\{^1H\}$ resonances observed for **2**, which are noticeably sharper than those of **4** and **6** and do not appear to be broadened. This suggests that whatever dynamic processes account for the fluxionality in these complexes proceeded at a much slower rate at room temperature for **2**, if it proceeded at all.

Although the ^1H NMR spectrum of **8** is clearly indicative of a monothiolate complex in which the tricyclohexyl proton resonances and thiophenol proton resonances integrate in the expected 33:5 ratio, the $^{31}P\{^1H\}$ NMR spectrum possesses only one broad singlet, in contrast to the expected set of two doublets. However, fluxional silver(I) phosphine complexes in which only one of the expected ^{31}P resonances is observed are known in the literature (the other doublet is presumably broadened to the point where it is unobservable).[16] In this case, not even

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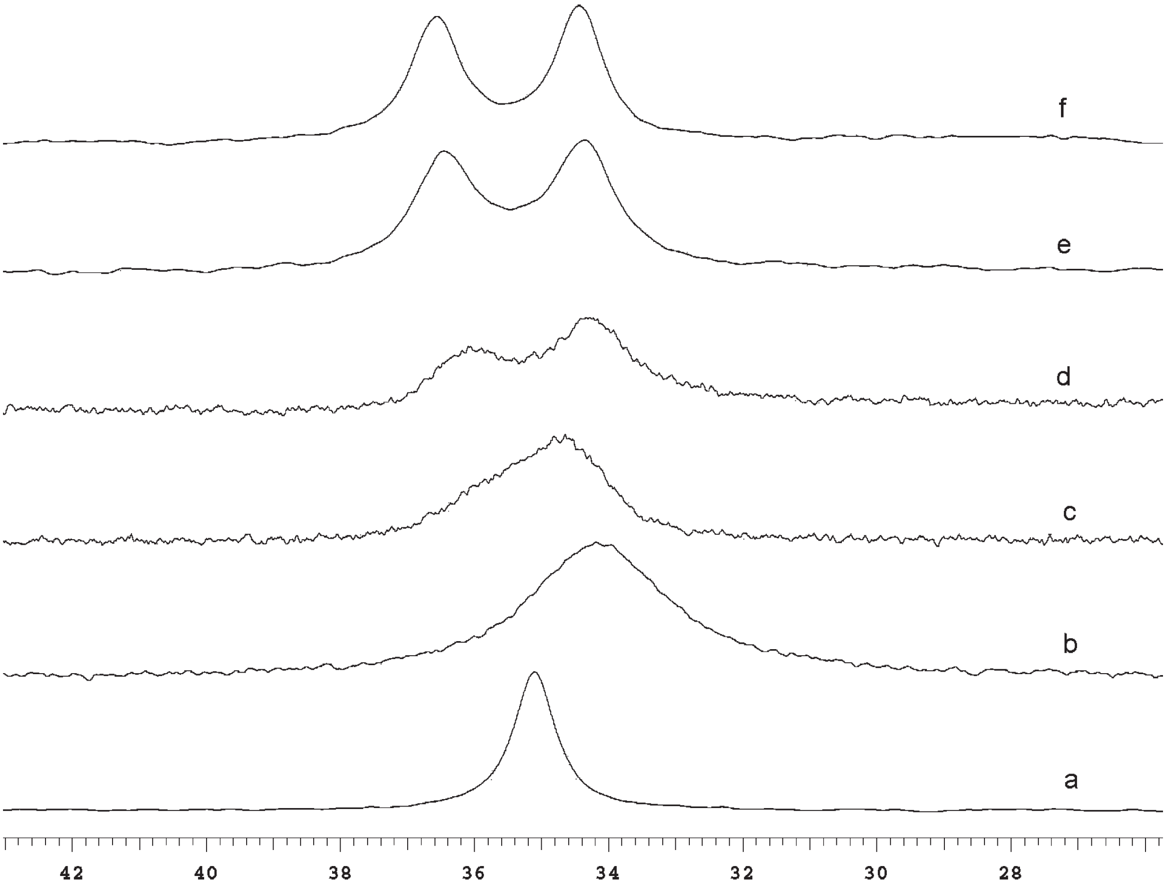

Figure 1. Effect of temperature on the $^{31}P\{^{1}H\}$ NMR signal observed for **8**. (a) 298 K, (b) 288 K, (c) 278 K, (d) 268 K, (e) 258 K, (f) 248 K.

one doublet is observed at room temperature. However, by gradually lowering the temperature of the $CDCl_3$ solution down to −25 °C, one doublet was resolved (Figure 1), indicating that silver−phosphorus coupling is indeed present in **8** and lending further credence to the identity of **8** as $[(PCy_3)Ag(SPh)]_n$, a presumably oligomeric species (as further supported by mass spectrometry) with the empirical formula $(PCy_3)Ag(SPh)$.

For the carbene-ligated complexes **10**−**15**, ^{1}H NMR spectra were typical for diamagnetic d^{10} complexes such that none of the bis(2,6-diisopropylphenyl)imidazol-2-ylidene resonances were sensitive to the identity of the ligand *trans* to the carbene. For **14**, ^{1}H NMR does not suggest that rotation about the Ag−S bond is hindered, as the thiophenolate resonances appear sharp and well-defined. In contrast to the ^{1}H NMR data, the ^{13}C NMR data is sensitive to the identity of the ligand *trans* to the carbene, as suggested by the chemical shift data and the values of the $^{1}J_{Ag-C}$ coupling constants (see Table 3). Sensitivity of the carbene chemical shift to the ligand *trans* to the carbene was also observed in the isoelectronic gold complexes of a similar *N*-heterocyclic carbene.[17]

IR Spectroscopy. Several of the products possess functional groups which exhibit intense, diagnostic bands in the infrared region. IR spectra of complexes **2** and **11** unequivocally demonstrate the presence of the azide functionality, with a high intensity band observed near 2000 cm^{-1} (asymmetric azide stretch) and a moderate intensity band observed near 1300 cm^{-1} (symmetric stretch); these are the frequencies commonly observed in metal azide complexes.[7,18]Isothiocyanate complex **4** has a high intensity band at 2105 cm^{-1}, which is assigned to the isothiocyanate stretch. These bands offer additional characterization data for these complexes, which are already well-characterized by a combination of X-ray crystallography and NMR spectroscopy. However, IR spectroscopy was very useful in distinguishing between metal-bound and free (ionic) triflate observed in complexes **6** and **7**. In the case of **6**, X-ray crystallography (vide infra) unequivocally determined the identity of **6** to be a bis-(μ-κ^1-OTf) dinuclear silver(I) complex, and the IR spectrum of **6** was characterized by diagnostic bands typical of ligated triflate ligands (but at energies lower than those observed for monodentate triflate complexes).[19] In contrast, **7** possesses intense band in the triflate region that are characteristic of ionic triflate, indicating that triflate is not bonded to silver in **7**.

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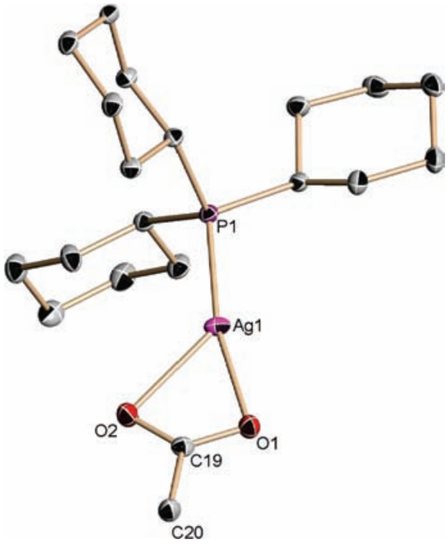

Figure 2. ORTEP representation of one crystallographically independent molecule of **1** showing 50% probability ellipsoids and partial atom-labeling scheme; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ag1−P1, 2.3263(4); Ag1−O1, 2.2255(12); Ag1−O2, 2.4276(13). P1−Ag1−O1, 168.46(3); P1−Ag1−O2, 134.92(3); O1−Ag1−O2, 56.28(4); O1−C19−O2, 122.40(16).

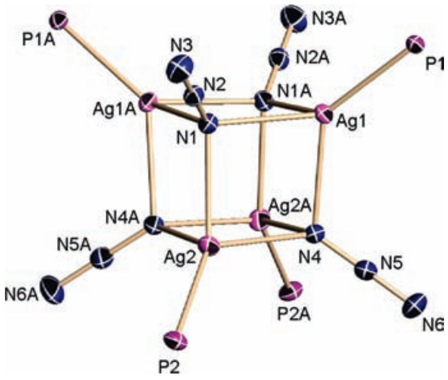

Figure 3. ORTEP representation of one crystallographically independent molecule of **2** showing 50% probability ellipsoids and partial atom-labeling scheme; hydrogen atoms, cyclohexyl groups, and THF molecules of co-crystallization have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ag1−P1, 2.3642(6); Ag2−P2, 2.3676(7); Ag1−N1, 2.394(2); Ag1−N1A, 2.467(2); Ag1−N4, 2.350(2); Ag2−N1, 2.334(2); Ag2−N4, 2.424(2); Ag2−N4A, 2.461(2); N1−N2, 1.214(3); N2−N3, 1.152(3); N4−N5, 1.206(3); N5−N6, 1.155(3). N1−Ag1−N1A; 84.91(7); N1−Ag1−N4, 86.54(7); N1A−Ag1−N4, 82.36(7); N1−Ag1−P1, 126.08(5); N1A−Ag1−P1, 127.57(5); N4−Ag1−P1, 133.19(5); N1−Ag2−N4; 86.20(7); N1−Ag2−N4A, 82.82(7); N4−Ag2−N4A, 81.55(8); N1−Ag2−P2, 137.65(6); N4−Ag2−P2, 128.01(5); N4A−Ag2-P2, 121.80(5); N1−N2−N3, 179.2(3); N4−N5−N6; 179.2(4).

X-ray Crystallography. The solid state structures of several of the silver complexes of both the PCy$_3$ and IPr ligands were ascertained by X-ray crystallography (Tables 1 and 2; vide supra). Beginning with the PCy$_3$-ligated complexes, **1** was determined to be a three-coordinate, mononuclear species, as shown in Figure 2. Although the acetate ligand clearly chelates the metal center with a small bite angle (~56.3°), the coordination sphere of silver may be best described as pseudo three-coordinate, because one of the Ag−O bonds is relatively long (2.4276(13) Å) and the P1−Ag1−O1 bond angle is only slightly deflected from linearity (168.46(3)°). It is remarkable that **1** is mononuclear because the trifluoroacetate analogue of **1** is a dinuclear complex reinforced by argentophilic interactions.[20]

Complex **1** is a valuable starting material in the synthesis of other PCy$_3$AgX derivatives. One of the derivatives is **2**, a material that is readily recrystallized from THF and pentane. An Oak Ridge thermal ellipsoid plot (ORTEP) representation of **2** is shown as Figure 3. In complex **2**, each four-coordinate silver atom is in a pseudotetrahedral environment in which the set of N−Ag−N′ angles (all of which form vertices on faces of the cubane) is acute (82−87°) relative to the set of N−Ag−P angles (these angles range from 126 to 138°). These angles are not unexpected, since the N−Ag−P angles would need to be large relative to the N−Ag−N′ angles for four-coordinate silver to accommodate the sterically encumbered PCy$_3$ ligand. Tetrameric (PR$_3$AgX)$_4$ complexes which assume a cubane geometry are known, for example, with PCy$_3$ (X = I)[9] and PPh$_3$ (X = Cl, Br, I).[21] However, this geometry has not previously been assumed by LAgX tetramers when X = N$_3$. Interestingly, the bond lengths between nitrogen atoms of the bridging azide ligand suggest a bonding geometry that has some (N−N≡N) character. This is expected since the terminal (singly bonded) nitrogen atom of the azido ligand would be more nucleophilic in this arrangement and would therefore render azide a better bridging ligand, though it should be noted that this pattern of N−N bond lengths in the azido ligand is observed for **11** and for SIPrAgN$_3$.[7]

Less-hindered ligands incapable of chelation formed three-coordinate, dinuclear complexes. ORTEP representations of two of these (**4** and **5**) are shown in Figure 4.

Complexes **4** and **5** differ in the bridging ligand (SCN$^-$ and 1,2,4-triazol-1-yl respectively), but both are described as three-coordinate complexes of silver(I) with two silver-ligand bonds of unexceptional length and a third, conspicuously longer silver-ligand interaction. In the case of **4**, the Ag−P and Ag−N distances are unexceptional but the Ag−S bond is more than 0.3 Å longer than the Ag−S bond length in **14** (vide infra). Similarly, the Ag−P and one Ag−N bond are unexceptional in **5** but one Ag−N bond is conspicuously longer (~0.05 Å longer). A similar set of properties describes the geometry of **6** (see Supporting Information, Figure S1), which is best described as a bis-(μ-κ^1-OTf) dinuclear silver(I) analogue of **3** and **9** (halide-bridged dinuclear complexes which feature three-coordinate silver atoms). Analogues of **6** which feature other phosphine ligands and empirical formula LAg(OTf) have been structurally characterized and determined to exist as triflate-bridged dimers (L = P-(NPr$^i{}_2$)$_2$(O$_2$CCF$_3$)),[22] trimers (L = PPh$_3$),[15] or cubane tetramers (L = PPh$_2$Me)[15] in the solid state. The cone angle of the phosphine clearly correlates with the nuclearity of the silver complex in the solid state.

Several of the IPr-ligated complexes synthesized in this investigation have also been characterized by X-ray crystallography. Complex **10** was easily crystallized, but

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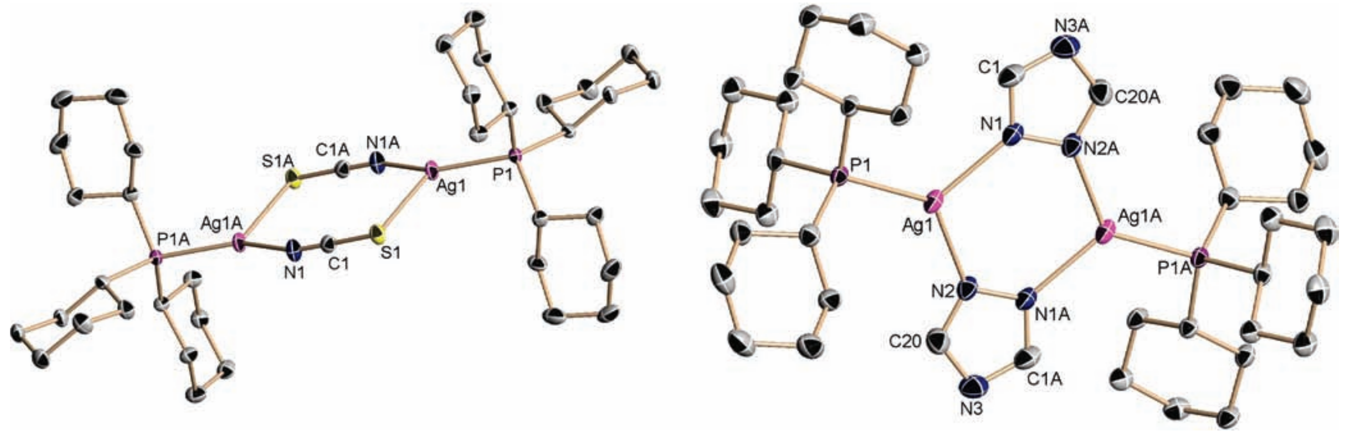

Figure 4. ORTEP representation of one crystallographically independent molecule of **4** (left) and **5** showing 50% probability ellipsoids and partial atom-labeling scheme; hydrogen atoms (for **4** and **5**) have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): (**4**) Ag1−N1, 2.131(3); Ag1−P1, 2.3588(7); Ag1−S1, 2.6720(8); C1−N1, 1.151(4). N1−Ag1−P1, 151.84(7); N1−Ag1−S1, 101.36(7); P1−Ag1−S1, 106.71(2); N1−C1−S1, 179.5(3). (**5**) Ag1−N1, 2.2594(19); Ag1−N2, 2.2093(18), Ag1−P1, 2.3654(5). N1−Ag1−N2, 107.01(7); N1−Ag1−P1, 120.71(5); N2−Ag1−P1, 132.07(5).

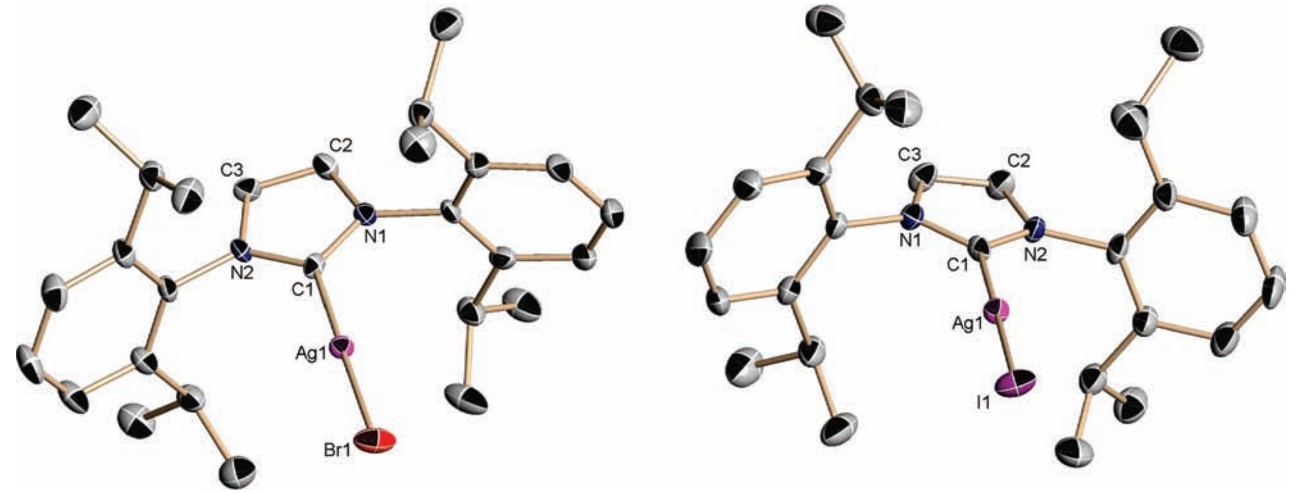

Figure 5. ORTEP representation of one crystallographically independent molecule of **13** (left) and **15** showing 50% probability ellipsoids and partial atom-labeling scheme; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (deg) for **13**: Ag1−C1, 2.063(2); Ag1−Br1, 2.4118(3); C1−Ag1−Br1, 178.89(16). Selected bond distances (Å) and bond angles (deg) for **15**: Ag1−C1, 2.068(3); Ag1−I1, 2.5473(6); C1−Ag1−I1, 178.02(9).

unfortunately a variety of solvent combinations and temperatures did not produce X-ray quality crystals. However, a series of much less bulky NHC carbene complexes of Ag(OAc) have been crystallized previously,[6c] and in each case the silver complexes were two-coordinate, featuring a κ^1-OAc ligand. It is likely that this is the case here; this is supported by IR spectroscopy. As a test case, X-ray quality crystals of **11** were prepared, and as expected, the bonding parameters are very similar to those observed for the known azidosilver(I) complex SIPrAgN_3[7] (see Supporting Information, Figure S2 for an ORTEP representation of **11**). Thus, **11** is a two-coordinate silver(I) complex with a nearly linear $C_{carbene}$−Ag−N_{azide} angle, as expected. In similar fashion, X-ray quality single crystals of **13** and **15** were prepared, and an ORTEP representation of each is shown in Figure 5.

Bonding parameters for **13** and **15** are nearly identical, with the most obvious difference being the Ag−X bond length, as expected. In each case, the $C_{1(carbene)}$−Ag−X bond angle is very nearly linear, and the C_1−Ag bond lengths are nearly identical. These parameters are very similar to those observed for **12**, a complex previously prepared (using a different route) by Nolan and co-workers.[6d]

The enforcement of two-coordination (even in the iodo complex **15**) and the ease of crystallization of the IPr-ligated derivatives were encouraging signs that the structure of **14** would reveal a two-coordinate silver thiolate that would unequivocally demonstrate Ag−S bond formation via Me_3Si-SPh. Indeed this was the case, as shown in Figure 6.

Complex **14** is another two-coordinate silver complex in which the C_1−Ag−X bond (here X = S) is nearly linear. The Ag−C and Ag−S bond lengths are unexceptional except for the slightly increased Ag−C bond length for **14** relative to the halide analogues **12**, **13**, and **15**. These data are suggestive of a slightly enhanced *trans* influence of the thiolate ligand relative to the halide ligand (the Ag−C distance for **14** is approximately $\geq$0.04 Å longer than the Ag−C distances of the IPrAg(halide) complexes). The trend also holds for IPrAgN_3

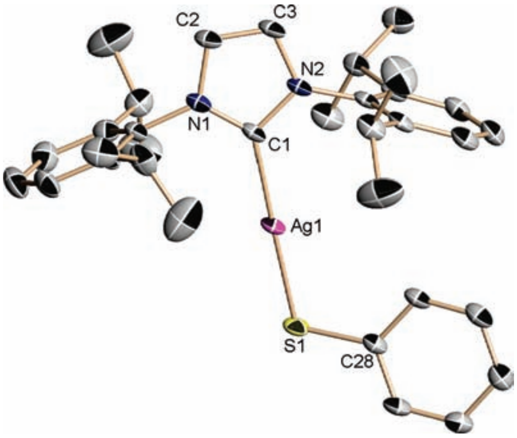

Figure 6. ORTEP representation of one crystallographically independent molecule of **14** showing 50% probability ellipsoids and partial atom-labeling scheme; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ag1−C1, 2.106(3); Ag1−S1, 2.3475(10); C1−Ag1−S1, 176.60(9); C28−S1−Ag1, 106.25(11).

(**11**), in which the Ag−C distance is 2.0591(17) Å, more than 0.4 Å shorter than the corresponding distance for **14**.

Reactivity. A preliminary survey of some of the modes of reactivity of some of the complexes described here was necessary to determine future research directions. We focused on azidylated complexes **2** and **11**, as a reaction of a gold(I) azide and (NO)(SbF_6) has previously yielded a fruitful result for one of us.[23] Treating a suspension of **2** in dry acetonitrile with an acetonitrile solution of (NO)(SbF_6) immediately resulted in gas evolution. A mass spectrum of a fresh solution revealed two dominant species, one of the solvate $[(PCy_3)Ag(NCMe)]^+$ and the other of the known cation $[(PCy_3)_2Ag]^+$ (**16**).[24] However, concentration of the solution to dryness yielded a colorless solid that was beset by a slight amount of impurities (by ^{1}H NMR). Similar to **2**, a suspension of **11** in dry acetonitrile was treated with an acetonitrile solution of (NO)(SbF_6), immediately causing gas evolution. An electrospray mass spectrum (low resolution) of a fresh solution again revealed two dominant species, one of the solvate $[(IPr)Ag(NCMe)]^+$ and the other of the unknown cation $[(IPr)_2Ag]^+$ (**17**). Unfortunately, **17** was too unstable upon concentration of solution to isolate in analytical purity under the reaction conditions, despite repeated efforts. However, in both cases, the cations could be crystallized to authenticate their identities.

In the case of **17**, X-ray quality crystals (as the SbF_6^- salt) could be grown by vapor diffusion of diethylether into a saturated acetonitrile solution of the solid isolated from the reaction of **11** with (NO)(SbF_6) (Figure 7). In the case of **16**, another method needed to be developed. It was discovered that the dinuclear triflate complex **6**, when recrystallized from pyridine and pentane, yielded the pyridine adduct **7** (in analogy with the use of pyridine to break up the tetrameric complex $[(PCy_3)Ag(\mu_3\text{-}I)]_4$).[9] The formulation of **7** as $[(PCy_3)Ag(pyr)](OTf)$ (vide supra) was further supported by electrospray mass spectrometry in acetonitrile (low resolution, see Supporting Information, Figure S3). The mass spectrum suggests that once **7**

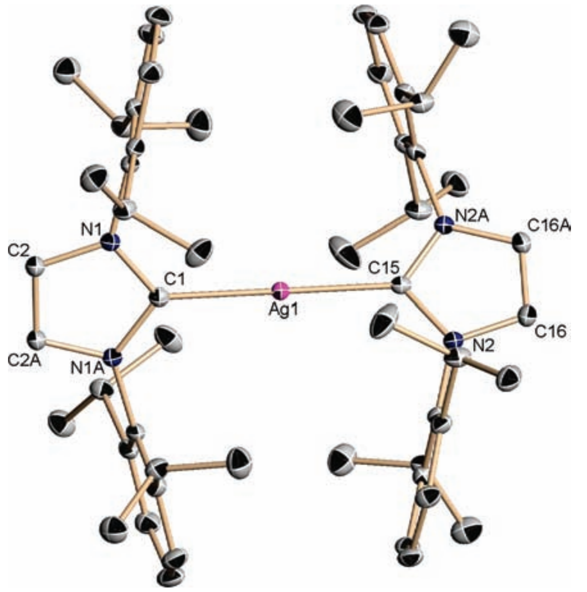

Figure 7. ORTEP representation of one crystallographically independent cation of **17** showing 50% probability ellipsoids and partial atom-labeling scheme; hydrogen atoms and SbF_6^- counterion have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ag1−C1, 2.1295(18); Ag1−C15, 2.1278(18); C1−Ag1−C15, 180.00(1).

is dissolved in acetonitrile, an equilibrium mixture of $[(PCy_3)Ag(NCMe)]^+$ and $[(PCy_3)Ag(pyr)]^+$ forms.[25] In addition, **16** and some higher mass peaks are present, so motivated by this data, X-ray quality crystals of [**16**](OTf) were grown by recrystallization of **7** in benzene/pentane (the ORTEP representation of **16** is included in the Supporting Information as Figure S4).

Discussion

The Ag−OAc bonds of **1** and **10** are stable enough to be able to store both complexes indefinitely at room temperature in air, but reactive enough to be easily cleaved at room temperature in the presence of reagents Me_3Si-X. Furthermore, chloro derivatives **3** and **12** did not show any sign of reacting with silyl reagents trimethylsilylthiocyanate or azidotrimethylsilane (respectively), underscoring the utility of **1** and **10**. This methodology has been previously used to synthesize azido complexes of both silver(I) and gold(I) carbene and phosphine complexes,[7] but it was unclear to what extent this methodology was general. This investigation clearly demonstrated the versatility of the LAgOAc/Me_3SiX system in the synthesis of complexes LAgX, but the limitations of this methodology were demonstrated by a lack of reactivity with 2-trimethylsilylpyridine and hexamethyldisilane. However, since **3** could still be formed at room temperature (in high yield) from the reaction of **1** and the hindered silane Bu^tPh_2SiCl without increasing the reaction time, these data suggest that the silver-bound OAc ligand is not nucleophilic enough to cleave the Si−C and Si−Si bonds of 2-trimethylsilylpyridine and hexamethyldisilane, in

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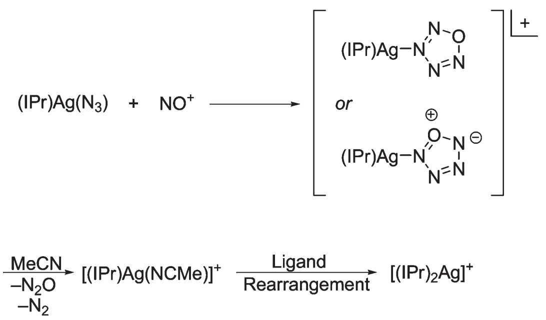
[25] Mass spectrometric characterization data for an analytically pure sample of **7**: Low resolution ESI (positive ion mode in acetonitrile), (observed m/e = 430.88; calculated m/e = 430.16) for $[(PCy_3)Ag(NCMe)]^+$ and (observed m/e = 468.49; calculated m/e = 468.18) for $[(PCy_3)Ag(pyr)]^+$

contrast to the nucleophiles (e.g., methoxide) that are potent enough to cleave these bonds.[26]

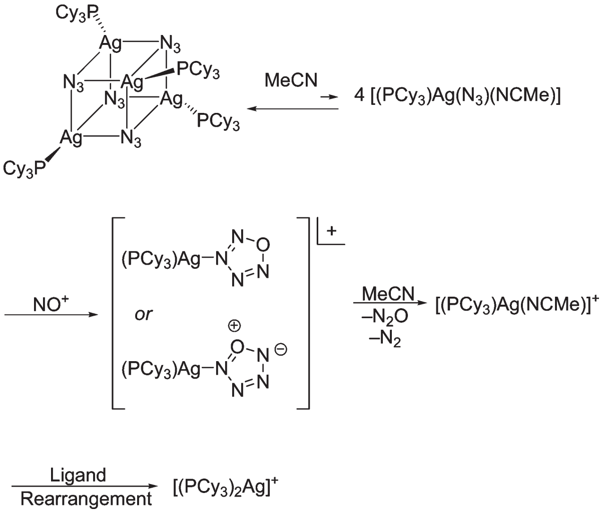
In the solid state, coordination numbers from two to four were observed with linear, trigonal, and tetrahedral bonding modes observed at silver. In general, the primary coordination spheres for all complexes which feature three- and four-coordinate silver are best described by one Ag–P bond length of unexceptional distance, one or two Ag–X bond distances of unexceptional distance, and one relatively long Ag–X′ distance. The crystallographic data suggests that ligand steric bulk (cone angle when considering only phosphines) correlates most intuitively with the observed bonding geometry at silver. For example, when X = Cl or Br, complexes of the type LAgX are mononuclear for L = IPr (X = Cl, reference 6d; X = Br, this work) and P(2,4,6-(MeO)$_3$-C$_6$H$_2$)$_3$,[27] dinuclear (halide-bridged) for L = PCy$_3$,[9] and tetranuclear (halide-bridged and overall cubane geometry) for L = PPh$_3$.[21b,28] Other examples include **2** (L = PCy$_3$, tetranuclear cubane complex) versus **11** (L = IPr, mononuclear) or SIPrAgN$_3$ (L = SIPr[7]), and **6** (L = PCy$_3$, dinuclear complex bridged by triflate) versus [(PPh$_2$Me)-Ag(μ_3-OTf)]$_4$ (cubane geometry).[15] Interestingly, use of an exceptionally bulky phosphanylidene changes the OTf bridging mode from (μ-κ^1-OTf) in **6** to (μ-κ^2-OTf) in the phosphanylidene-σ^4-phosphorane complex {(DmpP=PMe$_3$)-[Ag(OTf)]}$_2$ (Dmp = 2,6-dimesitylphenyl).[16] However, it appears that steric effects are not the only factor that dictate observed coordination geometries. For example, in the solid state the shortest Ag–X distances in [(PCy$_3$)Ag(μ-X)]$_2$ (X = Cl, Br) are approximately 2.45 Å and 2.58 Å respectively,[9] whereas in **2** (X = N$_3$) the two shortest Ag–X distances (per silver atom) are on average ~0.09 Å shorter, yet **2** forms the more sterically congested [(PCy$_3$)Ag(μ_3-X)]$_4$ complex (cubane). This may be a case where the Ag–N binding energy is greater than the energy due to increased steric strain.

In solution, there is evidence for fluxionality and ligand lability. The most obvious example of ligand lability is observed with the triflate complex **6**, in which simple recrystallization from pyridine and pentane (at room temperature over ~2 days) cleaves the Ag–OTf bond and yields the ion pair [(PCy$_3$)Ag(pyr)](OTf) (**7**) (as indicated by ^{1}H NMR, ^{19}F NMR and IR spectroscopies and elemental analysis). In solution, mass spectrometry (in acetonitrile) suggests that both the pyridine and phosphine ligands are fluxional, as strong signal intensity is observed for both [(PCy$_3$)Ag(pyr)]$^+$, [(PCy$_3$)Ag(NCMe)]$^+$, and [(PCy$_3$)$_2$Ag]$^+$ (**16**). Furthermore, X-ray quality crystals of **16**·OTf were obtained from recrystallization of **7** from benzene and pentane (no additional pyridine added, which means that both Ag–PCy$_3$ and Ag–pyridine bonds would need to break). Even in a noncoordinating solvent such as CDCl$_3$, the ^{31}P{^{1}H} resonances for **6** are broad at room temperature down to 0 °C, suggestive of fluxionality. In contrast, ^{31}P{^{1}H} and ^{1}H NMR spectra of recrystallized (pyridine/pentane) samples of **2**–**5** and **9** are indistinguishable from samples that were never in contact with pyridine, indicating that other ligands bind to silver more strongly than pyridine. However, the ^{31}P{^{1}H} NMR resonances of **4** are broadened relative to **1**, and at room temperature, the same resonance for **8** is a broad singlet in which only one doublet is well-resolved (a precedented phenomenon for a silver(I)-phosphine complex at room temperature; see references 9 and 16) at −25 °C (Figure 1, vide supra). For **8**, fluxionality probably describes a fast process occurring in solution on the ^{1}H NMR time scale, as only one set (three separate signals in 1:2:2 ratio) of sharp thiophenolate resonances is observed at room temperature in the ^{1}H NMR spectrum. The identity of the ligand (X) is clearly important, as noted by White and co-workers[9] and as suggested by the $^{107/109}$Ag–^{31}P and $^{107/109}$Ag–^{13}C coupling constant data (Table 3, vide supra), both of which suggest the same relative order of magnitude of coupling to silver given X (OAc > N$_3$ > Cl ~ > Br > I).

Scheme 2. Proposed Sequence of Reactions When **11** Is Treated with (NO)(SbF$_6$)



Scheme 3. One Possible Sequence of Reactions When **2** Is Treated with (NO)(SbF$_6$)



In addition to the synthesis of **7** from **6**, which demonstrates the lability of the triflate ligand, the reaction of azidosilver(I) complexes **2** and **11** with (NO)(SbF$_6$) generated the acetonitrile solvated cations [(IPr)Ag(NCMe)]$^+$ and [(PCy$_3$)Ag(NCMe)]$^+$, respectively, in solution (as determined by mass spectrometry). The latter cation, in particular, is strictly analogous to the solvated gold cation observed in CD$_3$CN (i.e., [(PCy$_3$)Au(NCCD$_3$)]$^+$) when (PCy$_3$)AuN$_3$ is treated with (NO)(SbF$_6$).[23] Considering

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[26] (a) Clark, W. *J. Org. Chem.* **1976**, *41*, 3063. (b) Shippey, M. A.; Dervan, P. B. *J. Org. Chem.* **1977**, *42*, 2654.

[27] Baker, L.-J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Steigelmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656.

[28] Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.

the rough similarity of chemical reactivity patterns between gold(I) and silver(I), this is not an unexpected result. Furthermore, the reaction which occurs initially (Scheme 2, shown with **11**) is likely analogous to that proposed for the analogous azidogold(I) complex (see reference 23).

It is assumed that the reaction of **2** with (NO)(SbF_6) is similar, but may initially require cluster dissociation in a coordinating solvent to produce reactive monomeric units, as in Scheme 3. For both Schemes 2 and 3, it should be noted that the "ligand rearrangement" product was not only observed by mass spectrometry, but characterized by X-ray crystallography (Figure 7 and Supporting Information, Figure S3). In addition, the proposed equilibrium step in Scheme 3 likely favors **2**, as it was noted above that the recrystallization of **2** in pyridine (vapor diffusion of pentane) showed no trace of a pyridine adduct in the product mixture (by NMR spectroscopy). However, the addition of NO^+ in both Schemes 2 and 3 are likely irreversible steps, as gas evolution and slight solution warming was noted for both **2** and **11**.

Clearly, now that the generation of stable d^{10} metal cations has been demonstrated for both Ag and Au, this methodology may be extended to other elements in the periodic table. Similarly, the formation of complexes LM-X from the corresponding metal acetates via Me_3Si-X has been demonstrated to be a viable methodology for both silver and gold. Clearly, more work needs to be done to ascertain the full scope and utility of these transformations. Future work will address these topics.

Conclusions

Facile synthetic routes to complexes of the type LAgX (L = PCy_3 or IPr; X = halide, pseudohalide, triazolyl, or thiolate) have been developed. The starting materials, LAgOAc, are easily accessed in nearly one-half or one gram scale, are not sensitive to oxygen or atmospheric moisture, and can be stored (in the absence of light) indefinitely at room temperature. In addition, the complexes $LAgN_3$ and $[(PCy_3)Ag(\mu\text{-OTf})]_2$ are convenient, air- and light-stable sources of $[LAg]^+$ by the treatment of (NO)(SbF_6) (on contact in acetonitrile) and pyridine, respectively. Clearly, the reactions described above have potential uses in catalysis and offer new routes to exciting and useful silver-containing materials, which will be the subject of future work.

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Supporting Information Available: Crystallographic information files (CIF) for all new complexes (except **8**), detailed crystallographic tables, mass spectrum of **7** in acetonitrile, and ORTEP representations of **6**, **11**, and **16** (cation). This material is available free of charge via the Internet at http://pubs.acs.org.