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Homoleptic Carbene–Silver(I) and Carbene–Copper(I) Complexes

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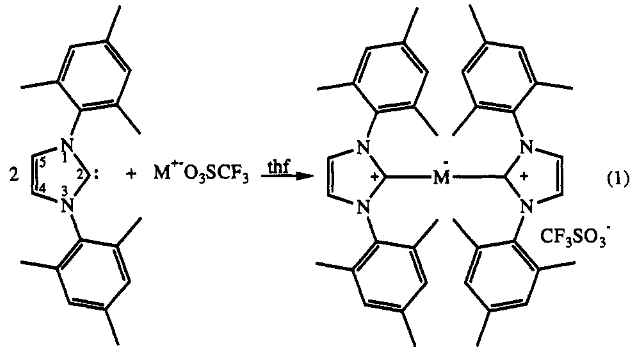
The syntheses and characterizations of homoleptic bis(carbene) adducts of Ag(I) and Cu(I) are described. These carbene adducts are available directly from the reaction of the stable nucleophilic carbene 1,3-dimesitylimidazol-2-ylidene and the corresponding metal triflate. NMR data are consistent with the bis(carbene)metal structures and suggest a level of delocalization in the imidazole ring that is intermediate between those of the free carbene and imidazolium ions. The X-ray crystal structure of the silver–carbene adduct is reported: $[C_{42}H_{48}N_4Ag]CF_3SO_3$, monoclinic, space group $P2_1/c$ (No. 14), a = 1167.5(1) pm, b = 1472.9(2) pm, c = 2479.8(2) pm, β = 95.31(1)°; T = −70 °C, Z = 4. The silver is essentially linearly coordinated with the imidazole rings twisted 39.7° relative to one another. The solid-state structure of the silver–carbene adduct is compared with those of related gold–carbene adducts.

Introduction

Gold–carbene complexes appear to be quite stable and have been widely studied.[1-26] Although the other transition group I metals, copper and silver, have very common usage as catalysts for reactions in which carbenes are believed to be intermediates, no stable carbene complexes have been reported with these metals.[27] We have previously reported the syntheses, characterizations, and isolation of stable nucleophilic carbenes.[28,29] These imidazol-2-ylidenes have singlet ground states[30] and offer a convenient opportunity to observe the direct reactivity of carbenes with various reagents[31,32] without byproducts from carbene generation. These new stable imidazol-2-ylidenes should be good candidates for the exploration of the unobserved silver and copper carbene complexes.

Results and Discussion

The reactions of copper(I) triflate or silver(I) triflate with 2 equiv of carbene 1 in tetrahydrofuran (thf)



(1)

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2a M = Cu
2b M = Ag

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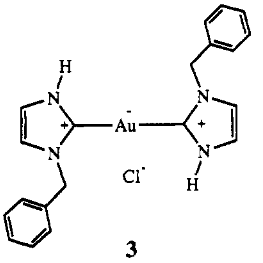
Table I. Selected NMR Chemical Shifts (δ) in 1–3[a]

nucleus	**1**[b]	**2a**[b]	**2b**[c]	**3**[d]
$^{13}C_2$	219.7	178.2	183.6 ($^1J_{^{107}AgC}$ = 188.0 Hz, $^1J_{^{109}AgC}$ = 208.6 Hz)	180.3
$^{13}C_{4(5)}$	121.3	124.2	124.2 ($^3J_{AgC}$ = 5.4 Hz)	119.5, 121.5
$^1H_{4(5)}$	7.04	7.33	7.45[b] ($^4J_{AgH}$ = 1.5 Hz)	7.47, 7.65
$^{15}N_{1(3)}$	−178.9	−180.8	−179.1 ($^2J_{^{107}AgN}$ = 6.3 Hz, $^2J_{^{109}AgN}$ = 7.2 Hz)	
^{109}Ag			642.4 ($^4J_{AgH}$ = 1.7 Hz)	

[a] The numbering scheme for all compounds is as indicated for **1**. References are tetramethylsilane, $NH_4^{+15}NO_3^-$, and 5 M $AgNO_3$. [b] In thf-d_8 solution. [c] In pyridine-d_5 solution. [d] In $CDCl_3$ solution. See ref 2.

proceeded smoothly to give the carbene adducts **2a,b** in good yield (eq 1). The related homoleptic gold complexes **3** and **4** have been reported previously from indirect synthetic routes and serve as interesting comparisons.[2,26]



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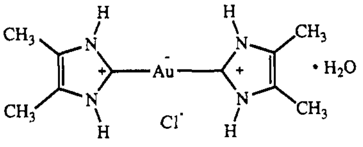

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Both the copper and silver adducts, **2a,b**, are high-melting crystalline solids. The ^{13}C resonances for the former carbene centers shift upfield from δ 219.7 for **1** to δ 178.2 and 183.6 for **2a,b**, respectively (Table I). The gold complex **3** shows a similar chemical shift of δ 180.3 for the analogous carbon. These upfield shifts for C_2 in the metal adducts relative to the free carbenes were also observed for magnesium,[33] zinc,[33] aluminum,[32] germanium,[34] and iodine[31] adducts. The imidazolium ion precursors of the stable imidazol-2-ylidenes bear a proton on C_2 and also show resonances for C_2 that are upfield of the carbenes.[28,29] The ^{15}N resonances for $N_{1(3)}$ in adducts **2a,b** are very slightly upfield from the resonances of the free carbene. Both the resonances for $C_{4(5)}$ and the protons ($H_{4(5)}$) at these positions are downfield from those of the same nuclei in the free carbene. As we have noted previously, the $H_{4(5)}$ resonances are particularly sensitive indicators of positive charge and delocalization in the imidazole ring.[28,35,36] The substantial downfield shift for the imidazole ring protons in **2a,b** suggests a higher degree of delocalization in the imidazole ring compared to the free carbene. The $H_{4(5)}$ resonances reported for the gold complex **3** are similar to the copper and silver structures **2a,b**. The silver center in **2b** resonates at δ 642.4 downfield of 5 M aqueous silver nitrate. Figure 1 illustrates the observed proton-coupled ^{109}Ag NMR spectrum of **2b**, in which a quintet reflects the couplings to the four equivalent imidazole protons. Couplings from the silver nuclei are observed throughout the imidazole ring (Table I). For C_2 and $N_{1(3)}$ the couplings from ^{107}Ag and ^{109}Ag are resolved and the observed coupling constants reflect the ratio of the magnetogyric ratios for these nuclei. Observation of these silver couplings, which is uncommon for many silver complexes,[37] suggests that the structure of **2b** does not experience rapid ligand exchange, at least on the NMR time scale. A dicarbonylsilver(I) complex, $[Ag(CO)_2]^+[B(OTeF_5)_4]^-$, has recently been reported.[38] The solution spectra of this carbonyl adduct show evidence for ligand exchange that is typical for many silver(I) complexes. The solid-state ^{13}C NMR spectra for such 2-coordinate silver carbonyls typically show $^1J_{^{109}AgC}$ values of about 183 Hz.[38] The $^1J_{^{109}AgC}$ value for **2b** is a little larger at 208.6 Hz.

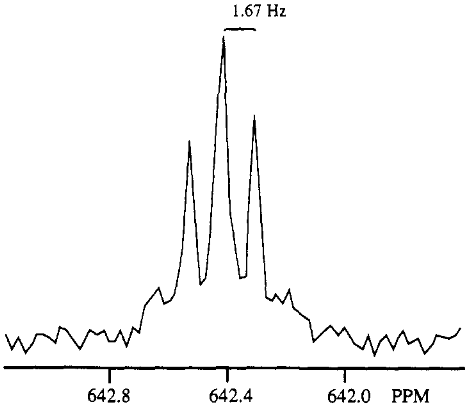

Figure 1. ^{109}Ag (^1H coupled) NMR spectrum of **2b**.

The silver–carbene adduct **2b** was crystallized from thf to afford crystals suitable for X-ray diffraction studies. Selected bond distances and angles are given in Table II along with comparisons for some reference compounds. The ring internal angles at the former carbene centers are 103.6 and 104.8° for the two bound carbene centers. This value is slightly larger than that in the corresponding carbene but not as large as those in 2*H*-imidazolium ions which show a more relaxed angle of ~109°.[39] The gold adducts **3** and **4** show ring internal angles at C_2 very similar to those of **2b**. The diethylzinc complex derived from **1** similarly also shows a 104.2° ring internal angles at the former carbene center.[33] The C–N bond distances (r_{av} = 135.6 pm) at the former carbene center are shorter than those in the free carbene, which seems to be typical of derivatives of these nucleophilic carbenes. The C–Ag distances are 206.7 and 207.8 pm, which are actually slightly longer than the C–Au distances in **3** and **4** (r_{av} = 201.8 pm). A survey of the structures in the Cambridge Crystallographic Database that contain Au–C or Ag–C bonds indicates that both types of bonds range from about 200 to 220 pm and are quite similar in related structures with C–Ag bonds occasionally longer than their gold counterparts.[40] The Ag–C distance in $[Ag(CO)_2]^+$ is 214

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Table II. Selected Bond Lengths (pm) and Angles (deg) in 2 and Related Structures[a]

property	1	2b	3[b]	4[c]	1,3-diphenylimidazolium ion[d]
$r(C_2–N_{1(3)})$	136.5(4), 137.1(4)	135.6(6), 136.0(6) 135.2(6), 135.5(6)	134.8, 135.5	132.8(7), 135.3(9) 132.2(8), 133.1(8)	133.6
$r(C_4–C_5)$	133.1(5)	133.0(7), 132.9(7)	138.0	134.7(9), 131.0(10)	133.9
$r(N_{1(3)}–C_{5(4)})$	138.1(4), 137.8(4)	139.6(6), 139.8(6) 139.9(6), 139.0(6)	135.3, 135.8	140.0(8), 138.1(8) 139.0(9), 139.8(8)	138.0
$r(N_{1(3)}$–mesityl)	144.1(4), 144.2(4)	143.7(6), 144.5(7) 143.4(6), 143.9(6)			143.2 (phenyl)
$r(C_2–M)$		206.7(4), 207.8(4)	202.6	201.2(6), 201.6(6)	
$\theta(N_1–C_2–N_3)$	101.4(2)	103.6(4), 104.8(4)	104.4	104.2(5), 104.0(5)	109.2
$\theta(C_{5(4)}–N_{1(3)}–C_2)$	112.8(3), 112.8(3)	111.1(4), 111.8(4) 110.6(4), 110.6(4)	111.2, 111.4	111.9(5), 111.7(5) 112.4(6), 111.0(6)	108.0
$\theta(N_{1(3)}–C_{5(4)}–C_{4(5)})$	106.5(3), 106.5(3)	107.6(4), 105.9(5) 106.7(4), 107.3(4)	107.0, 106.0	105.7(5), 106.4(6) 105.8(6), 106.8(6)	106.5
$\theta(C_2–N_{1(3)}$–mesityl)	121.8(2), 122.6(2)	125.4(4), 124.3(4) 126.3(4), 124.6(4)			126.6 (phenyl)
$\theta(M–C_2–N_{1(3)})$		132.5(3), 123.7(3) 131.8(4), 123.4(3)	129.2, 125.5	129.6(5), 126.1(4) 128.0(5), 128.1(4)	
$\theta(C_2–M–C_2)$		176.3(2)	175.9	175.8(2)	

[a] The numbering scheme for all compounds is as indicated for **1**. [b] See ref 2. Average values for two crystallographically unique molecules. Large errors were reported in the determination of this structure. [c] See ref 26. [d] See ref 38c.

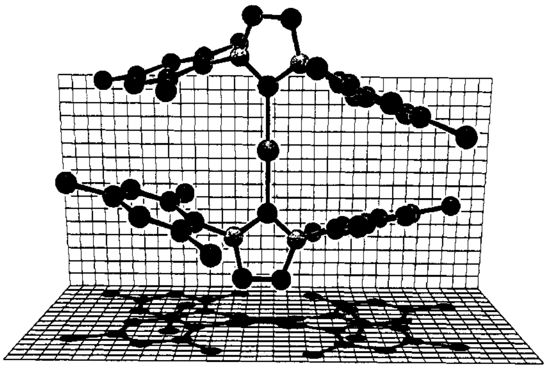

Figure 2. KANVAS[41] drawing of the **2b** cation.

pm, somewhat longer than that for **2b**.[38] This suggests that the C–Ag–C geometry in **2b** is not substantially strained by the steric bulk of the carbene ligands (although there is a possible orientation effect; *vide infra*). The mesityl substituents of the imidazole rings are twisted an average of 76.5° with respect to the central rings, similar to their orientation in **1**. The silver atom of **2b** is essentially linearly coordinated with a valence angle of 176.3°. The planes of the two imidazole rings are twisted 39.7° from coplanarity. This orientation of the imidazole rings, which is depicted clearly in the shadow of Figure 2, is likely the result of steric effects between the mesityl substituents on the nitrogens. The imidazole rings in **3** and **4** are twisted by 50 and 0°, respectively. These various twist angles suggest that there is little electronic preference for the orientation of the two imidazole rings and that steric interactions and crystal packing forces play important roles.

An attempt was made to characterize copper complex **2a** by means of X-ray crystallography. The diffraction data were collected for a unit cell of dimensions $a = 1088.8$ pm, $b = 1222.0$ pm, $c = 3287.8$ pm, $\alpha = 94.97°$, $\beta = 99.28°$, and $\gamma = 93.12°$. Structure refinement would not proceed past 10% residual values. The gross structural features for the copper complex were similar to those of the silver complex although the poor quality of the structure precluded examination of structural details. The chemically equivalent imidazole ring features showed considerable asymmetry, as did the C–Cu distances (~189 and 173 pm). A close inspection of the data, axial photographs, and additional crystals revealed that the *c* axis was actually 6576 pm. The asymmetry observed in the refinement is likely to be due to the absence of the *c*-odd layers. Because of the large unit cell, no attempt to recollect the data was made.

Conclusion

The first homoleptic carbene–copper and carbene–silver complexes have been isolated. The NMR spectra of these compounds indicate that the imidazole moieties experience a degree of delocalization that is intermediate between those of the parent carbene (imidazol-2-ylidene) precursor and related carbenium (imidazolium) ions. The silver–carbene complex exhibits coupling of the silver nucleus throughout the imidazole ring. Unlike many silver complexes, the homoleptic carbene–silver complex does not undergo a rapid ligand exchange. There was no evidence of exchange even with the nucleophilic solvent pyridine. The X-ray crystallographic structure of the silver–carbene adducts shows a nearly linear geometry for the silver center and imidazole ring structural parameters that are intermediate between those of carbene and carbenium ion structures. The C–Ag distances are remarkably similar to C–Au distances in related structures.

Experimental Section

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Solvents were dried (using standard procedures),[42] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. The carbene **1** was prepared as previously described.[29] The copper and silver triflates were purchased from Alfa Inorganics and used without further purification. The ^1H (300.75 MHz), ^{13}C (75.629 MHz), ^{19}F (282.987 MHz), ^{109}Ag (13.994 MHz), and ^{15}N (30.484 MHz) NMR spectra were recorded on a GE Omega 300WB spectrometer. NMR

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(41) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE), to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

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Table III. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters

atom	*x*	*y*	*z*	*B*(iso) (Å^2)
Ag(1)	4303.2(3)	1345.5(3)	1979.4(2)	2.6(1)
N(1)	6973(3)	1252(3)	2296(2)	3.2(1)
N(1′)	1658(3)	1140(3)	1627(2)	2.8(1)
N(3)	6019(3)	1512(3)	2974(2)	3.3(1)
N(3′)	2563(3)	1829(3)	1034(2)	2.9(1)
C(2)	5881(4)	1345(4)	2432(2)	2.9(1)
C(2′)	2715(4)	1438(4)	1530(2)	2.4(1)
C(4)	7180(4)	1516(4)	3172(2)	4.3(2)
C(4′)	1414(5)	1790(4)	831(2)	3.7(2)
C(5)	7768(4)	1353(5)	2748(2)	4.0(2)
C(5′)	848(4)	1361(4)	1196(2)	3.7(2)
C(11)	7290(4)	1013(4)	1768(2)	3.0(2)
C(11′)	1375(4)	650(4)	2096(2)	2.7(1)
C(12)	7310(4)	1677(4)	1370(2)	3.0(2)
C(12′)	1199(4)	−272(4)	2059(2)	3.3(2)
C(13)	7670(4)	1430(4)	872(2)	3.5(2)
C(13′)	884(5)	−729(4)	2513(3)	4.3(2)
C(14)	7993(4)	553(5)	762(2)	3.8(2)
C(14′)	714(5)	−278(5)	2984(3)	4.3(2)
C(15)	7958(5)	−93(4)	1167(3)	4.6(2)
C(15′)	897(4)	646(5)	3008(2)	3.8(2)
C(16)	7599(4)	126(4)	1675(2)	3.6(2)
C(16′)	1240(4)	1133(3)	2573(2)	3.1(2)
C(17)	6947(5)	2641(4)	1476(2)	4.3(2)
C(17′)	1326(6)	−777(4)	1538(3)	5.5(2)
C(18)	8423(5)	316(5)	222(3)	5.9(2)
C(18′)	341(6)	−771(6)	3472(3)	7.5(3)
C(19)	7567(6)	−593(5)	2105(3)	5.9(2)
C(19′)	1432(5)	2128(4)	2617(2)	4.8(2)
C(21)	5083(5)	1656(4)	3307(2)	3.6(2)
C(21′)	3445(4)	2302(4)	778(2)	3.0(2)
C(22)	4923(5)	2530(5)	3497(2)	4.8(2)
C(22′)	3469(5)	3240(4)	803(2)	3.6(2)
C(23)	4041(6)	2657(6)	3832(3)	6.5(3)
C(23′)	4295(5)	3689(4)	542(2)	4.4(2)
C(24)	3360(6)	1948(8)	3970(3)	6.7(3)
C(24′)	5080(5)	3223(5)	254(2)	4.6(2)
C(25)	3525(5)	1104(6)	3762(3)	6.4(3)
C(25′)	5039(5)	2294(5)	253(2)	4.3(2)
C(26)	4408(5)	934(5)	3425(2)	4.8(2)
C(26′)	4242(5)	1808(5)	510(2)	3.7(2)
C(27)	5659(6)	3311(5)	3365(3)	7.1(3)
C(27′)	2624(5)	3763(4)	1107(3)	5.4(2)
C(28)	2398(6)	2095(8)	4339(3)	11.1(4)
C(28′)	5948(5)	3738(6)	−45(3)	6.8(2)
C(29)	4558(6)	−8(6)	3200(3)	7.0(3)
C(29′)	4243(6)	782(5)	505(3)	6.0(2)
S(1)	9173(1)	2330(1)	4389(1)	3.2(1)
F(11)	8954(4)	1485(4)	5294(2)	10.2(2)
F(12)	10328(3)	993(3)	4865(2)	9.2(2)
F(13)	8580(4)	670(3)	4596(2)	8.0(2)
O(11)	7983(3)	2578(3)	4382(1)	4.4(1)
O(12)	9526(3)	2019(3)	3882(1)	4.4(1)
O(13)	9968(3)	2938(3)	4680(2)	4.8(1)
C(1S)	9274(6)	1314(6)	4805(3)	5.6(2)

references are $(CH_3)_4Si$ (^1H, ^{13}C), $CFCl_3$ (^{19}F), $NH_4^+NO_3^-$ (^{15}N), and $Ag^+NO_3^-(H_2O)$ (^{109}Ag). The ^{15}N DEPT experiments were run using the standard DEPT sequence[43] assuming $J_{HN} \approx 7$ Hz with a θ pulse of 45°. The ^{109}Ag DEPT experiments were run using the standard DEPT sequence[43] assuming $J_{^{109}AgH} \approx 1.6$ Hz with a θ pulse of 36° with a delay of 60 s between pulses to avoid rf heating. Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Bis(1,3-dimesitylimidazol-2-ylidene)copper(I) Triflate (2a). Copper(I) triflate benzene solvate $[CuCF_3SO_3\cdot{}^1/_2C_6H_6]$ (0.330 g, 1.31 mmol) and 1 (0.400 g, 1.31 mol) were mixed, and thf (50 mL) was added at room temperature. A cream-colored solution was obtained. This was stirred for 5 min, and second portions of 1 (0.400 g, 1.31 mmol) and thf (20 mL) were added at room temperature. Immediately after the second addition of carbene, a white precipitant was formed. This suspension was stirred for 30 min, warmed to obtain a clear solution, and filtered over Celite. The filtrate was concentrated (5 mL), hexane was added, and the solution was concentrated to 15 mL and cooled at −25 °C to give 0.865 g (92%) of **2a** as colorless crystals, mp 312.5–314 °C. ^1H NMR (thf-d_8): δ 1.71 (s, 12 H, *o*-CH_3), 2.42 (s, 6 H, *p*-CH_3), 6.99 (s, 4 H, *m*-H), 7.33 (s, 2 H, NCH). ^{13}C NMR (thf-d_8): δ 17.27 (s, *o*-CH_3), 21.16 (s, *p*-CH_3), 124.16 (s, NCH), 129.97 (s, Mes C-3,5), 135.44 (s, Mes C-2,6), 135.94 (s, Mes C-1), 140.15 (s, Mes C-4), 178.24 (s, NCN). ^{19}F NMR (thf-d_8): δ −78.2. ^{15}N NMR (py-d_5): δ −180.84. Anal. Calcd for $C_{43}H_{48}N_4O_3F_3SCu$: C, 62.87; H, 5.89; N, 6.82. Found: C, 62.60; H, 5.88; N, 6.78.

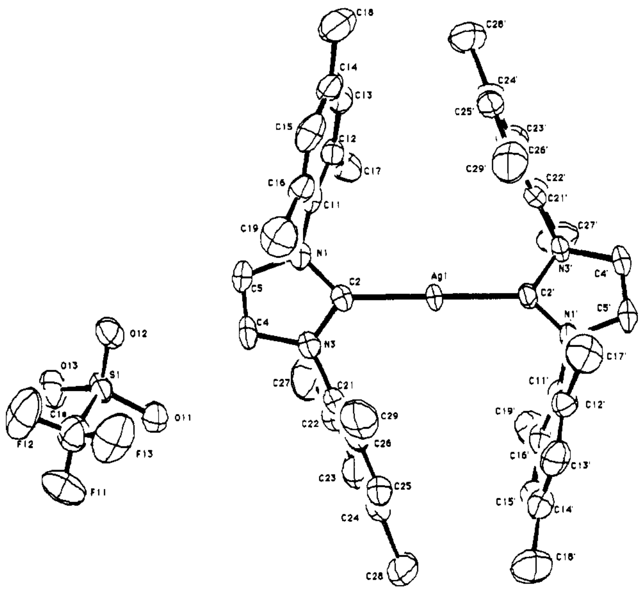

Figure 3. ORTEP view and atom-numbering scheme of **2b**.

Bis(1,3-dimesitylimidazol-2-ylidene)silver(I) Triflate (2b). Silver triflate (0.220 g, 0.856 mmol) and 1 (0.522 g, 1.71 mmol) were mixed in thf (25 mL) and stirred for 30 min. The resulting cloudy mixture was warmed and filtered, and the filtrate was then cooled at −25 °C to obtain 0.590 g (80%) of **2b** as colorless crystals, mp 274–275 °C. ^1H NMR (thf-d_8): δ 1.75 (s, 12 H, *o*-CH_3), 2.43 (s, 6 H, *p*-CH_3), 6.99 (s, 4 H, *m*-H), 7.45 (d, $^4J_{HAg} = 1.43$ Hz, 2 H, NCH). ^{13}C NMR (py-d_5): δ 17.59 (s, *o*-CH_3), 21.52 (s, *p*-CH_3), 124.17 (d, $^3J_{CAg} = 5.39$ Hz, NCH), 130.01 (s, Mes C-3,5), 135.26 (s, Mes C-2,6), 136.04 (s, Mes C-1), 139.93 (s, Mes C-4), 183.6 (dd, $^1J_{C^{109}Ag} = 208.57$ Hz, $^1J_{C^{107}Ag} = 187.95$ Hz, NCN). ^{15}N NMR (py-d_5): δ −179.11 (dd, $^2J_{N^{109}Ag} = 7.24$ Hz, $^2J_{N^{107}Ag} = 6.30$ Hz). ^{109}Ag NMR (py-d_5): δ 642.41 (quin, $^4J_{AgH} = 1.67$ Hz). ^{19}F NMR (thf-d_8): δ −79.4. Anal. Calcd for $C_{43}H_{48}N_4O_3F_3SAg$: C, 59.65; H, 5.59; N, 6.47. Found: C, 59.84; H, 5.54; N, 6.49.

X-ray Crystal Structure of Bis(1,3-dimesitylimidazol-2-ylidene)silver(I) Triflate (2b). Crystal data: $[C_{42}H_{48}N_4Ag]$-CF_3SO_3, monoclinic, space group $P2_1/c$ (No. 14), $a = 1167.5(1)$ pm, $b = 1472.9(2)$ pm, $c = 2479.8(2)$ pm, $\beta = 95.31(1)°$; $T = -70$ °C, $Z = 4$, fw = 865.82, $D_c = 1.354$ g/cm^3, μ(Mo) = 5.69 cm^{-1}. Crystal description: colorless, parallelepiped (0.40 × 0.24 × 0.49 mm) grown from a saturated thf solution of **2b**. A total of 7120 reflections were collected; $1.7° \le 2\theta \le 48.0°$; data octants + + +, − + +; ω-scan method, scan width = 1.2–1.50° ω, scan speed 1.50–5.00 °/min; Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm); typical half-height peak width = 0.15° ω, 2 standards collected 50 times, 3% fluctuation, 4.0% variation in azimuthal scan, no absorption correction, 176 duplicates, 1.5% *R* merge. With 4075 unique reflections of intensity greater than 3.0σ, the structure was solved by automated Patterson analysis (PHASE) and standard difference Fourier techniques. Anomalous terms for silver and sulfur were included, biweight $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$. The asymmetric unit consisted of one ion pair in general positions. Hydrogen

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[43] Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* 1982, *48*, 323.

atoms idealized with $r_{\mathrm{C-H}} = 0.95$ Å. There were 496 parameters (data/parameter ratio = 8.22) with all non-hydrogen atoms anisotropic and all hydrogens in fixed positions. The final R factors were $R = 0.039$, $R_w = 0.040$. The error of fit was 1.40, max $\Delta/\sigma = 0.05$. The final difference Fourier map showed the largest residual density to be 0.34 e/Å^3 near a hydrogen on a *p*-methyl. The final atomic coordinates are given in Table III with the numbering scheme illustrated by the ORTEP drawing in Figure 3. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

Acknowledgment is made for the excellent technical assistance of H. A. Craig and W. F. Marshall.

Supplementary Material Available: A complete description of the X-ray crystallographic determination of **2b**, tables of hydrogen fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles, and ORTEP drawings (8 pages). Ordering information is given on any current masthead page.

OM930168B