Synthesis and Characterization of Water-Soluble Silver and Palladium Imidazol-2-ylidene Complexes with Noncoordinating Anionic Substituents

Lucas R. Moore,[†] Sheritta M. Cooks,[†] Matthew S. Anderson,[‡] Hans-Jörg Schanz,*[,‡]
Scott T. Griffin,[†] Robin D. Rogers,[†] Marion C. Kirk,[§] and Kevin H. Shaughnessy*[,†]

*Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa,
Alabama 35487-0336, Department of Chemistry and Biochemistry, The University of Southern Mississippi,
118 College Drive, Hattiesburg, Mississippi 39406-5043, and Comprehensive Cancer Center Mass
Spectrometry Shared Facility, University of Alabama at Birmingham, Birmingham, Alabama 35294*

Zwitterionic imidazolium salts have been synthesized bearing alkylsulfonate and alkylcarboxylate substituents and used as precursors to water-soluble metal−carbene complexes. Reaction of the zwitterionic imidazolium compounds with Ag$_2$O gave bis(imidazol-2-ylidene)silver complexes. These compounds have been characterized spectroscopically and by electrospray mass spectrometry. A DMSO solvate of bis[1-(2,6-diisopropylphenyl)-3-(3-sulfonatopropyl)imidazol-2-ylidene]silver sodium salt has been structurally characterized. In the solid state, this complex exists as a coordination polymer in which the sodium ions bridge the sulfonate groups from two bis(imidazol-2-ylidene)silver moieties. Diiodobis[1-mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene]palladium disodium salt has also been prepared in low yield and characterized by NMR spectroscopy and electrospray mass spectrometry.

Introduction

Since Arduengo's report of stable imidazol-2-ylidenes,[1,2] there has been growing interest in the use of these *N*-heterocyclic carbene (NHC) species as supporting ligands in organometallic chemistry.[3,4] NHC ligands act as σ-donor ligands with minimal π-accepting ability. In this way, NHC ligands are similar to commonly used alkylphosphine ligands. The σ-donating ability of NHC ligands is significantly stronger than electron-rich phosphines, such as tri-*tert*-butylphosphine.[5] NHC ligands generally give stronger M−L bonds than trialkylphosphines, such as tricyclohexylphosphine, unless the NHC ligand is very sterically demanding.[6,7] As a result, NHC ligands can give more stable organometallic structures than phosphines in many cases.

The strong electron-donating ability of NHC ligands combined with their easily varied steric demand have made them attractive ligands in a variety of metal-catalyzed processes. The strong M−L bonds typical of NHC ligands provide more stable active catalyst species than phosphines, resulting in longer catalyst lifetimes. NHC ligands have proven to be particularly useful in olefin metathesis and palladium-catalyzed cross-coupling reactions. Imidazol-2-ylidene and imidazolin-2-ylidene-based ruthenium alkylidenes are more active and thermally

stable than the original tricyclohexylphosphine-based systems developed by Grubbs.[8−12] NHC ligands give highly active and stable catalysts for a wide range of palladium-catalyzed cross-coupling reactions.[13−16]

Water is an attractive solvent for organic reactions due to its low toxicity, nonflammability, low cost, and good heat transfer properties.[17,18] By using hydrophilic catalyst systems, it is possible to simply separate the homogeneous catalyst from the organic product stream. This strategy requires that the metal remain bound to the water-soluble ligands in order to eliminate loss of the metal to the organic phase or through decomposition. Given the success of NHC−metal complexes in a wide variety of catalytic reactions coupled with the potentially improved stability of these catalysts compared to metal−phosphine species, hydrophilic NHC ligands would be expected to give efficient aqueous-phase catalyst systems.

Until recently, there were few examples of hydrophilic metal−NHC complexes in the literature. The free carbene cannot exist in water, as it has a pK_a of approximately 20,[19] but metal−carbene complexes are generally stable to protic solvents.

* To whom correspondence should be addressed. E-mail: kshaughn@bama.ua.edu; hans.schanz@usm.edu.

† The University of Alabama.

‡ The University of Southern Mississippi.

§ University of Alabama at Birmingham.

(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(2) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913−921.

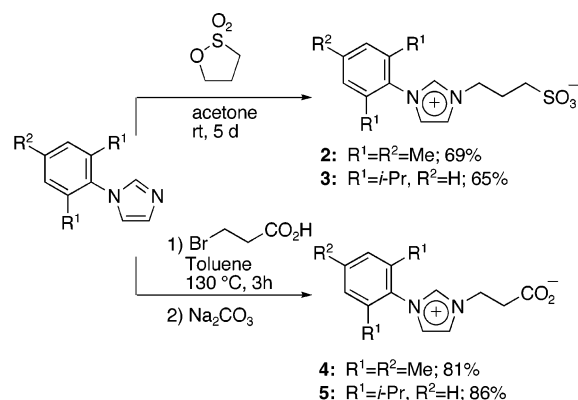(3) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

(4) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815−1828.

(5) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461−2468.

(6) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370−2375.

(7) Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878−2882.

(8) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375−5380.

(9) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

(10) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236−3253.

(11) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.

(12) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117−7140.

(13) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363−1365.

(14) Jørgensen, M.; Lee, S.; Liu, X.; Wolkowski, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 12557−12565.

(15) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101−4111.

(16) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A., III; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685−692.

(17) Li, C.-J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68−82.

(18) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095−3165.

Scheme 1. Synthesis of Zwitterionic Imidazolium Ligand Precursors

2: R^1=R^2=Me; 69%
3: R^1=*i*-Pr, R^2=H; 65%

4: R^1=R^2=Me; 81%
5: R^1=*i*-Pr, R^2=H; 86%

Özdemir[20] was the first to report a hydrophilic imidazol-2-ylidene complex and apply it catalytically. Water-soluble silver complexes of caffeine and alcohol-substituted imidazol-2-ylidenes have been reported, although not applied catalytically.[21,22] Recently, Grubbs[23,24] reported water-soluble olefin metathesis catalysts based on poly(ethylene glycol)-substituted NHC−Ru alkylidene complexes. In addition, there are several examples of the use of hydrophobic metal−NHC complexes to catalyze reactions in aqueous solvent systems.[25−28]

To date, there have been no examples of incorporation of anionic substituents, such as carboxylate, sulfonate, or phosphonate, in NHC ligands, although these moieties are widely used in hydrophilic phosphine ligands. Imidazolium salts with alkylsulfonate substituents have been prepared, such as 1-butyl-3-(3-propanesulfonic acid)imidazolium salts, as Brønsted acid-modified ionic liquids.[29−31] In this contribution, we report the synthesis of *N*-aryl zwitterionic imidazolium compounds with sulfonate and carboxylate substituents that can serve as precursors to water-soluble imidazol-2-ylidene ligands. These zwitterions have been complexed with silver to give water-soluble bis(imidazol-2-ylidene)silver complexes, one of which has been structurally characterized. A bis(imidazol-2-ylidene)palladium diiodide complex has also been prepared and characterized.

Results and Discussion

Synthesis and Structural Characterization of Zwitterionic Imidazolium Precursors. 1-Butyl-3-(ethyl-2-sodiumsulfonate)-imidazolium bromide (**1**) was prepared from 1-butylimidazole

(19) Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366−4374.
(20) Özdemir, I.; Yigit, B.; Çetinkaya, B.; Ülkü, D.; Tahir, M. N.; Arici, C. *J. Organomet. Chem.* **2001**, *633*, 27−32.
(21) Kascatan-Nebioglu, A.; Panzner, M. J.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2004**, *23*, 1928−1931.
(22) Melaiye, A.; Simons, R. S.; Milsted, A.; Pingitore, F.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *J. Med. Chem.* **2004**, *47*, 973−977.
(23) Gallivan, J. P.; Jordan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **2005**, *46*, 2577−2580.
(24) Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508−3509.
(25) Özdemir, I.; Gürbüz, N.; Gök, Y.; Çetinkaya, E.; Çetinkaya, B. *Synlett* **2005**, 2394−2396.
(26) Özdemir, I.; Demir, S.; Yasar, S.; Çetinkaya, B. *Appl. Org. Chem.* **2005**, *19*, 55−58.
(27) Fürstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343−350.
(28) Zhao, Y.; Zhou, Y.; Ma, D.; Liu, J.; Li, L.; Zhang, T. Y.; Zhang, H. *Org. Biomol. Chem.* **2003**, *1*, 1643−1646.
(29) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. M., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 5962−5963.
(30) Yoshizawa, M.; Hirao, M.; Ito-Akita, K.; Ohno, H. *J. Mater. Chem.* **2001**, *11*, 1057−1062.
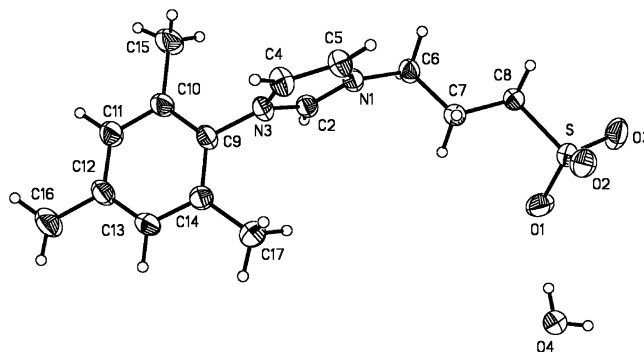(31) Yoshizawa, M.; Ohno, H. *Chem. Commun.* **2004**, 1828−1829.

Figure 1. Thermal ellipsoid plot of the molecular structure of **2·**H$_2$O. Ellipsoids are drawn at the 50% probability level. Selected bond angles (deg): N1−C2−N3 108.12(14), C2−N1−C6−C7 −102.60(18), N1−C6−C7−C8 −169.85(14), C6−C7−C8−S −170.75(11).

and 2-bromoethylsulfonate sodium salt as previously described.[32] The aryl-substituted zwitterions were prepared by reacting 1-arylimidazoles[33] with 1,3-propane sultone[30] or 3-bromopropionic acid to give the salt-free zwitterions **2**−**5** in good yields (Scheme 1). X-ray-quality crystals of zwitterions **2** and **3** were obtained as hydrates by recrystallization from methanol/ether and 2-propanol, respectively.

The monohydrate of zwitterion **2** (Figure 1) crystallizes as a hydrogen-bonded dimer. The alkylsulfonate chain of **2** adopts an all *s-trans* conformation (N1−C6−C7−C8 = 169.9°; C6−C7−C8−S = 170.8°). The dihedral angle between the alkylsulfonate chain and the imidazolium ring (C2−N1−C6−C7) is 102.6°. Two molecules of water bridge between the sulfonate groups of two molecules of the zwitterion **2** (Figure 2).[34] In addition, the oxygen of water accepts a hydrogen bond from the C2 proton of the imidazolium ring. A bifurcated hydrogen-bonding interaction is also seen between the C5 proton of the imidazolium ring with two oxygen atoms of the sulfonate group of a neighboring dimer.

In the solid state, zwitterion **3** crystallizes as a hemihydrate (Figure 3). The alkylsulfonate chain adopts an all-*gauche* conformation in this structure (N1−C6−C7−C8 = −55.2°; C6−C7−C8−S = −66.6°). This conformation places O3 2.358 Å from the C2 proton, although the angle (131.3°) is severe for a hydrogen-bonding interaction. The water molecule has four hydrogen-bonding interactions (Figure 4).[34] Each hydrogen of water is hydrogen bonded to a sulfonate oxygen. In addition, the oxygen of water accepts hydrogen bonds from the C5 protons of two imidazolium rings. The C4 proton hydrogen bonds to the sulfonate oxygen of a neighboring zwitterion.

Synthesis of Imidazol-2-ylidene Metal Complexes. Zwitterion **1** was stirred with Ag$_2$O in water at room temperature for 2.5 h. Sodium chloride was then added to precipitate uncomplexed silver ions. Recrystallization of the crude products from 2-propanol/methanol gave air-stable silver complex **6** in 56% yield (eq 1). Complex **6** slowly decomposes with deposition

(1)
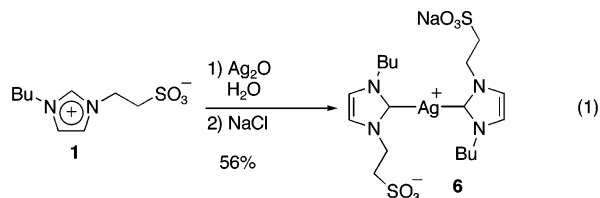
of silver metal when dissolved in protic solvents. Exposure to light appears to accelerate this process. The resulting product was sufficiently stable to be characterized by ^{1}H and ^{13}C NMR
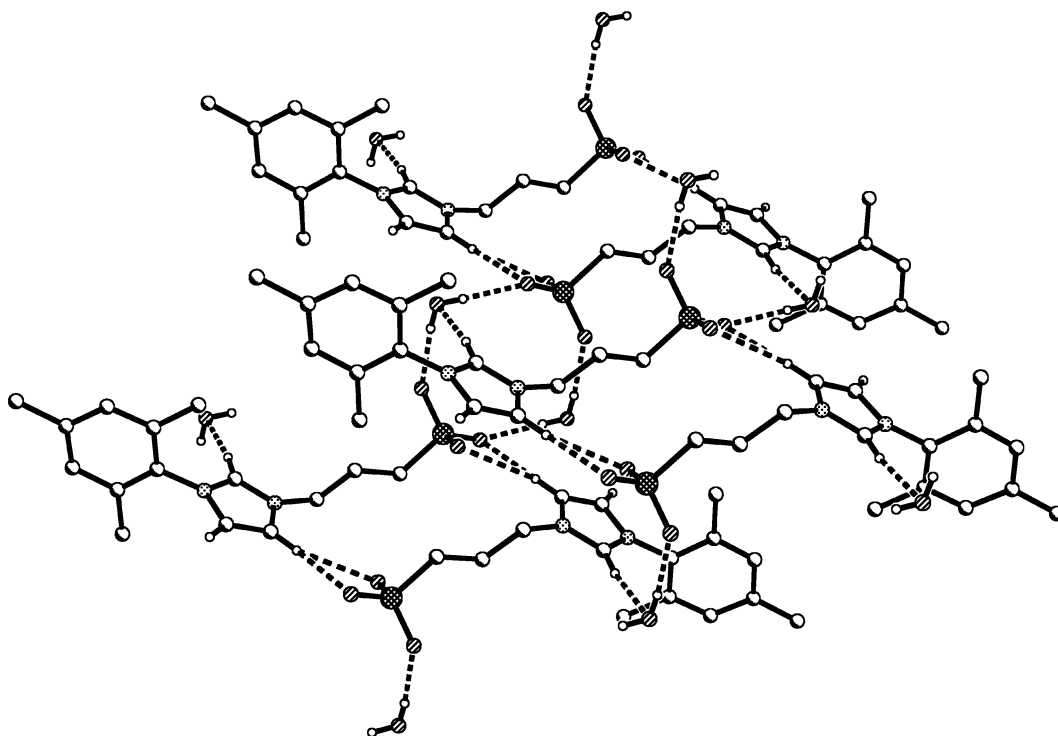
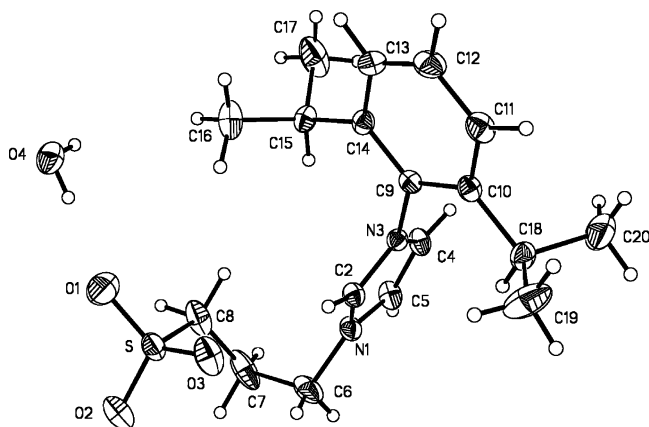**Figure 2.** Hydrogen-bonding interactions in the crystal structure of **2·**H_2O.

Figure 3. Thermal ellipsoid plot of the molecular structure of **3·** 0.5H_2O showing the 50% probability level. Selected bond angles (deg): N1−C2−N3 108.36(14), C2−N1−C6−C7 98.1(2), N1− C6−C7−C8 −55.2(2), C6−C7−C8−S −66.6(2).

spectroscopy. The ^{1}H NMR spectrum did not show a resonance for the C2 proton of the starting imidazolium salt. Formation of a silver−carbene complex was confirmed by the presence of the C2 resonance at 182 ppm in the ^{13}C NMR spectrum of **6**, which is similar to the chemical shift seen in other silver imidazolylidene complexes.[35] No coupling was observed between C2 and the silver, however. The lack of coupling may be due to reversible coordination of the carbene to the silver center in solution. The reversible coordination may account for the low stability of this complex in protic solvents, which would be expected to protonate the free carbene. Attempts to obtain

(32) Herrmann, W.; Elison, M.; Fischer, J.; Köcher, C.; Öfele, K. Ger. Offen., 4447066, 1996; *Chem. Abstr.* **125**:143019.

(33) Arduengo, A. J., III; Gentry, F. P., Jr.; Taverkere, P. K.; Simmons, H. E., III. U.S. Patent 6,177,575, 2001; *Chem. Abstr.* **134**:115958.

(34) Drawings of crystal-packing diagrams for **2·**H_2O, **3·**0.5H_2O, and **8·**4DMSO can be found in the Supporting Information.

(35) Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405−3409.
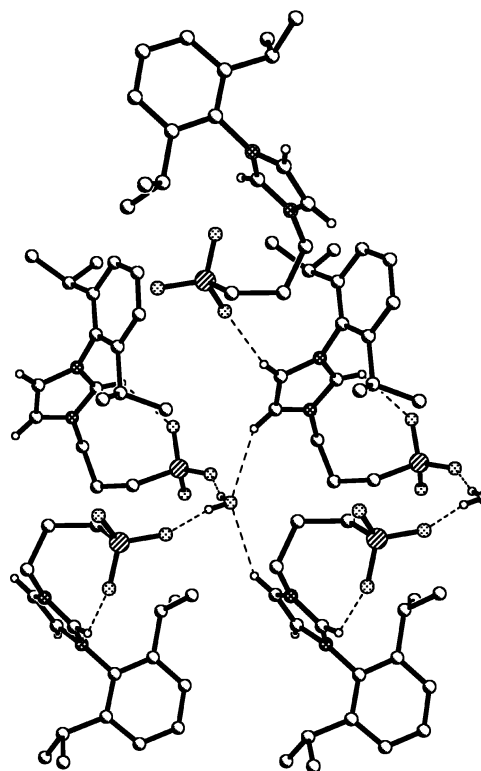

Figure 4. Hydrogen-bonding interactions of **3·**0.5H_2O.

negative ion mode electrospray mass spectra (ESI-MS) of complex **6** were unsuccessful, presumably due to the poor stability of this complex under the ESI conditions (50% aqueous acetonitrile, 0.1% HCO_2H). The major species seen in the negative ion mass spectrum was the free imidazol-2-ylidene [**1** − H]$^−$ at *m/z* 231. Complex **6** was tentatively assigned a bis-(imidazol-2-ylidene)silver structure in analogy with the more fully characterized structures of silver complexes derived from zwitterions **2−5**. Other silver−carbene structures, such as
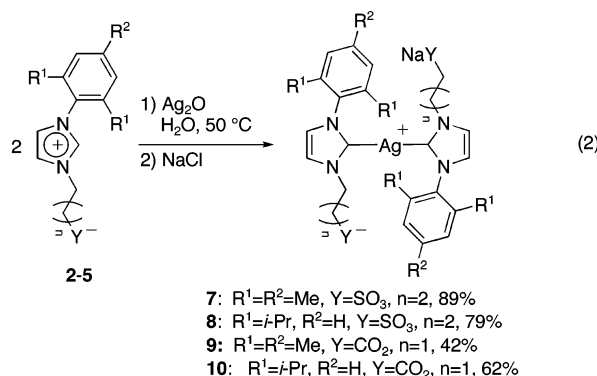
**Table 1. Characterization Data for
Bis(imidazol-2-ylidene)silver Complexes**

	δ_{C2} (ppm)	$^1J(^{107}Ag-^{13}C)$ (Hz)	$^1J(^{109}Ag-^{13}C)$ (Hz)	ESI-MS (m/z)
6	182.0	*a*	*a*	*b*
7	180.6	180.3	207.6	721, 723
8	182.5	193.9*c*		805, 807
9	180.8	181.6	209.5	621, 623
10	180.7	182.4	210.8	705, 707

a No coupling was observed between the silver and C2. *b* This complex was not stable under the ESI-MS conditions. *c* The individual coupling of the silver isotope was not resolved in this complex.

[(**1**)AgCl]⁻Na⁺, cannot be ruled out on the basis of the spectroscopic data, however.

Silver complexes derived from zwitterions **2**−**5** were prepared by stirring the zwitterion with Ag_2O in water at 50 °C under nitrogen in the dark overnight to give **7**−**10** in yields ranging from 42 to 89% (eq 2). The sulfonate complexes were obtained

(2)

2-5

7: R¹=R²=Me, Y=SO₃, n=2, 89%
8: R¹=*i*-Pr, R²=H, Y=SO₃, n=2, 79%
9: R¹=R²=Me, Y=CO₂, n=1, 42%
10: R¹=*i*-Pr, R²=H, Y=CO₂, n=1, 62%

in higher yield than the carboxylate analogues. The formation of a carbene complex was confirmed in each case by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of complexes **7**−**10** showed an upfield shift of the C4 and C5 protons compared to the zwitterions **2**−**5**. In each case, no resonance was observed above 8 ppm, which is consistent with formation of the imidazol-2-ylidene. The formation of a silver carbene complex was confirmed by the appearance of the C2 resonance of the imidazol-2-ylidene for complexes **7**, **9**, and **10** as two doublets in the ^{13}C NMR spectra due to coupling of C2 with the two spin 1/2 isotopes of silver (Table 1). For example, the C2 resonance of complex **7** appeared at 180.6 ppm as a pair of doublets ($^1J(^{107}Ag-^{13}C) = 180.3$ Hz, $^1J(^{109}Ag-^{13}C) = 207.6$ Hz). Complexes **9** and **10** gave very similar C2 resonances. The chemical shift and coupling constant values for the carbene carbons are similar to those reported for bis(1,3-dimesitylimidazol-2-ylidene)Ag⁺.[35] The coupling constants suggest a bis-(imidazol-2-ylidene)silver structure, as the coupling constants for (1,3-di(2,6-diisopropylphenyl)imidazol-2-ylidene)AgCl are much higher (237 and 273 Hz).[36,37] In the ^{13}C NMR spectrum of complex **8** the C2 resonance appeared as a doublet at 182.5 ppm with $^1J(^{107/109}Ag-^{13}C) = 193.9$ Hz. The individual coupling to the two isotopes of silver was not resolved in this spectrum, although the observed coupling constant was in the range of the average values for the resolved ^{107}Ag and ^{109}Ag coupling constants found in complexes **7**, **9**, and **10**.

The bis(imidazol-2-ylidene)silver structures of complexes **7**−**10** were confirmed on the basis of their negative ion mode

(36) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301−6309.
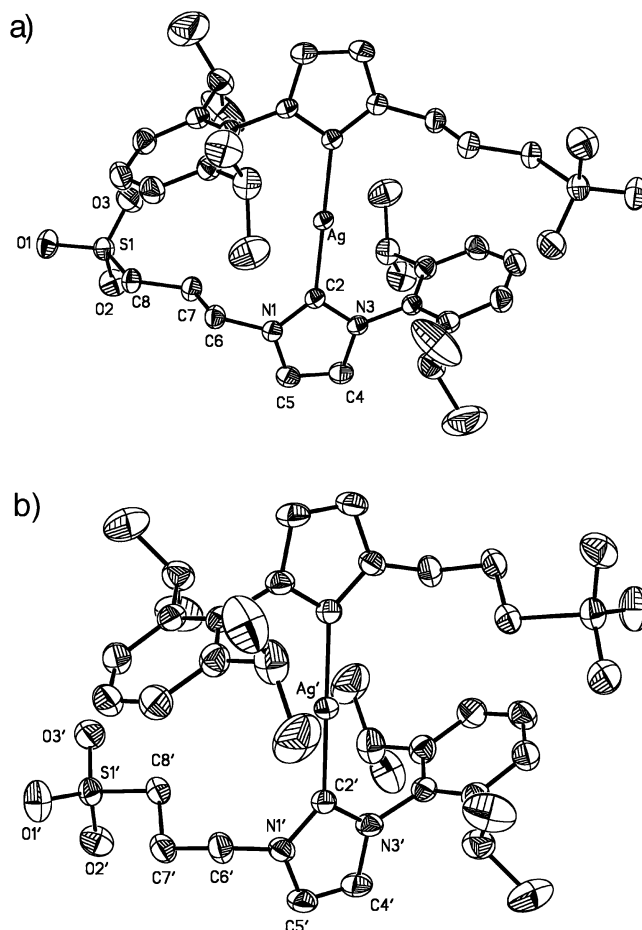(37) Yu, X.-Y.; Patrick, B. O.; James, B. R. *Organometallics* **2006**, *25*, 2359−2363.

Figure 5. Thermal ellipsoid plots (50% probability level) of the two [(**3**)₂Ag]⁻ molecular moieties in **8**·4DMSO. Selected bond lengths (Å) and angles (deg): (a) Ag−C2 2.069(3); N1−C2−N3 104.2(2), N1−C2−Ag 133.47(19), N3−C2−Ag 122.24(19), C2−N1−C6−C7 90.5(3), N1−C6−C7−C8 173.1(2), C6−C7−C8−S1 178.7(2); (b) Ag′−C2′ 2.074(3); N1′−C2′−N3′ 104.6(2), N1′−C2′−Ag′ 134.1(2), N3′−C2′−Ag′ 121.34(19), C2′−N1′−C6′−C7′ 112.9(3), N1′−C6′−C7′−C8′ −66.7(4), C6′−C7′−C8′−S1′ −173.8(2).

electrospray ionization mass spectra (ESI-MS). Complex **7** gave a single cluster of peaks with major peaks at m/z 721 and 723 with roughly equal intensity. These values were consistent with the ^{107}Ag and ^{109}Ag isotopomers of [(**2**)₂Ag]⁻, confirming the coordination of two carbene ligands to each silver ion. No fragment ions were observed, showing that the complex was stable under the conditions of the electrospray ionization and detection. Complex **8** also gave a cluster of ions with major peaks at m/z 805 and 807. Again these masses were consistent with the two silver isotopomers of [(**3**)₂Ag]⁻. A minor set of peaks (ca. 2% rel int) was observed centered at m/z 493 corresponding to [(**3**)AgCl], which may be formed as a minor impurity in the synthesis of **8**. Complexes **9** and **10** gave mass spectra that were consistent with [(**4**)₂Ag] (m/z 621 and 623) and [(**5**)₂Ag] (m/z 705 and 707).

X-ray-quality crystals of complex **8**·4DMSO were obtained by diffusion of ether into a solution of **8** in DMSO. The structure further confirms that complex **8** is a bis(imidazol-2-ylidene)silver complex (Figure 5). There are two unique bis(imidazol-2-ylidene)silver moieties in the solid state. The major difference between these two structures is the conformation of the propylsulfonate group. In the first (a, Figure 5), the propylsulfonate groups both have an all *s-trans* conformation (N1−C6−C7−C8 = 173.1°, C6−C7−C8−S1 = 178.7°), in which the
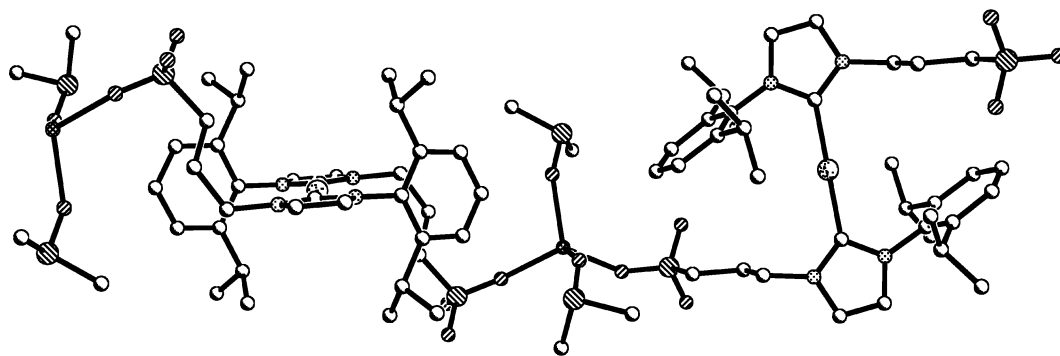
Figure 6. Polymeric structure of **8**·4DMSO showing one repeat unit. Unbound DMSO molecules and the hydrogen atoms are not shown. The left bis(carbene)silver unit (perpendicular to page) corresponds to Ag′ (b, Figure 5) and the right bis(carbene)silver complex is Ag (a, Figure 5).

plane of the C and S atoms is perpendicular to the imidazol-2-ylidene ring (C2−N1−C6−C7 = 90.5°). In the second moiety (b, Figure 5), there is a *gauche* relationship between C8′ and the imidazol-2-ylidene ring (N1′−C6′−C7′−C8′ = −66.7°). The propylsulfonate chain retained the *s-trans* conformation, however (C6′−C7′−C8′−S1′ = −173.8°).

The Ag−C2 bond lengths are 2.069(3) and 2.074(3) Å, which are typical for other reported silver−carbene bond lengths.[38] The two imidazol-2-ylidene ligands coordinated to each silver are symmetry related, resulting in perfectly linear C2−Ag−C2 bond angles. The N−C−N angles of the imidazol-2-ylidene rings are approximately 104°, which are typical for metal−imidazol-2-ylidene complexes and smaller than that of zwitterion **3** (108.6°).[35] The imidazol-2-ylidene ligands adopt an *anti*-relationship in which the sterically demanding 2,6-diisopropylphenyl groups point in opposite directions. Due to the difference in steric demand between the two imidazol-2-ylidene substituents, the ring is skewed relative to the Ag−C2 bond (N1−C2−Ag = 133°, N3−C2−Ag = 122°; N1′−C2′−Ag′ = 134°, N3′−C2′−Ag′ = 121°).

The solid-state structure of **8**·4DMSO is a linear polymer, in which the bis(carbene)silver units are bridged by sodium ions (Figure 6).[34] The sodium ions coordinate to two sulfonate groups from different bis(carbene)silver units as well as to two molecules of DMSO in a distorted tetrahedral arrangement. In addition there are two unbound molecules of DMSO (one of which was disordered) for each [(**3**)$_2$Ag][Na(DMSO)$_2$]$^+$ repeat unit. The Ag and Ag′ moieties alternate in this solid-state polymer and are roughly perpendicular to each other. The dihedral angle between the C2−Ag−C2 and C2′−Ag′−C2′ axes is 88.5°.

Treatment of **2** with Pd(OAc)$_2$, potassium *tert*-butoxide, and sodium iodide in DMSO for 3 h at 50 °C gave a crude product that was consistent with a Pd−carbene complex (eq 3). The
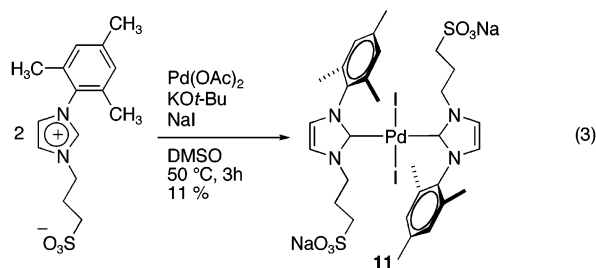
at 166.7 ppm in the ^{13}C NMR spectrum, which is similar to reported bis(diarylimidazol-2-ylidene)palladium(II) complexes.[39−41] After repeated cycles of dissolving in cold methanol and precipitation with acetonitrile, complex **11** was isolated in reasonably pure form, although in low yield (11%). The low yield was largely due to difficulty in separating complex **11** from uncharacterized side products, which are believed to be carbene- or imidazolium-derived decomposition products. The negative ion mode ESI-MS of complex **7** showed clusters of peaks at *m/z* 997 and 975 with the expected pattern of peak intensities for a palladium-containing complex. These ions were consistent with the sodium ion and proton adducts of [(**2**)$_2$PdI$_2$]$^{2−}$. In addition, the free dianion was observed at *m/z* 487. The presence of two iodine atoms in the structure suggests that the palladium charge is balanced by coordinated iodide ions and that the sulfonate groups are not coordinated to palladium.

Conclusion

In conclusion, zwitterionic imidazolium precursors have been used to prepare silver and palladium imidazol-2-ylidene complexes containing alkylsulfonate and alkylcarboxylate substituents. Starting from arylimidazolium precursors, imidazol-2-ylidene silver and palladium complexes were prepared and characterized. The 1-aryl-3-(3-sulfonatopropyl)imidazolium precursors all gave bis(carbene) complexes with silver and palladium as determined by electrospray mass spectrometry and X-ray crystallography. In each case, the anionic substituent does not to coordinate to the metal center. To our knowledge, these complexes represent the first examples of imidazol-2-ylidene type ligands with noncoordinating anionic substituents. Ligands of this type may prove useful in the synthesis of hydrophilic metal complexes for aqueous-phase catalysis and other applications.

Experimental Section

General Procedures. 1-Butyl-3-(ethyl-2-sodiumsulfate)imidazolium bromide,[32] 1-mesitylimidazole,[33] and 2,6-diisopropylimidazole[33] were prepared according to previously reported procedures. All other reagents were obtained commercially and used as received. Solvents used in the synthesis of the metal complexes were deoxygenated by sparging with N$_2$ prior to use. All syntheses of silver complexes were carried out so as to limit exposure to light.

(3)

C2 proton of **2** was no longer present in the ^{1}H NMR spectrum of the crude product. In addition, the C2 carbon was observed

(38) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978−4008.

(39) Tulloch, A. A. D.; Winston, S.; Danopoulos, A. A.; Eastham, G. R.; Hursthouse, M. B. *Dalton Trans.* **2003**, 699−708.
(40) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046−5047.
(41) Campeau, L.-C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857−1860.

1-Mesityl-3-(3-sulfonatopropyl)imidazolium (2). Compound **2** was prepared by a modification of Ohno's[30] procedure. A solution of 1,3-propane sultone (3.758 g, 30.77 mmol) and acetone (60 mL) was slowly added to a round-bottom flask containing 1-mesityl-imidazole (3.009 g, 16.15 mmol) and acetone (60 mL) while at 0 °C. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 5 days. Filtration gave a white solid that was recrystallized from 2-propanol/methanol to give zwitterion **2** (3.42 g, 69%). ^{1}H NMR (360 MHz, DMSO-d_6): δ 9.38 (s, 1H), 8.11 (s, 1H), 7.92 (s, 1H) 7.14 (s, 2H), 4.42 (t, J = 6.9 Hz, 2H), 2.44 (t, J = 6.9 Hz, 2H), 2.33 (s, 3H), 2.20 (quint, J = 6.9 Hz, 2H), 2.02 (s, 6H). ^{13}C NMR (90.5 MHz, DMSO-d_6): δ 140.1, 137.5, 134.3, 131.1, 129.1, 123.8, 123.1, 48.3, 47.3, 25.9, 20.5, 16.8. MS (FAB): 309 m/z [M + H].

1-(2,6-Diisopropylphenyl)-3-(3-sulfonatopropyl)imidazolium (3). The preparation was the same as that described for **2** from 1,3-propane sultone (3.764 g, 31.5 mmol), 1-(2,6-diisopropylphenyl)imidazole (3.642 g, 16.12 mmol), and acetone (60 mL) to give **3** (3.637 g, 65%) as a colorless crystalline material. ^{1}H NMR (360 MHz, DMSO-d_6): δ 9.08 (s, 1H), 8.15 (s, 1H), 8.08 (s, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 4.44 (t, J = 6.9 Hz, 2H), 2.44 (t, J = 6.9 Hz, 2H), 2.23 (m, 4H), 1.14 (m, 12H). ^{13}C NMR (90.5 MHz, D$_2$O w/MeOH spike): δ 145.8, 137.0, 131.9, 125.7, 124.6, 123.1, 48.3, 47.1, 28.4, 25.2, 23.8, 23.4, 23.1.

1-Mesityl-3-(2-carboxyethyl)imidazolium bromide (12). 1-Mesitylimidazole (0.744 g, 4.00 mmol), 3-bromopropanoic acid (0.629 g, 4.11 mmol), and dry toluene (20 mL) were heated in a pressure tube to 130 °C for a period of 3 h. After cooling to ambient temperature, the mixture was filtered, and the grayish-white residue was washed twice with dry ether and then dried in the vacuum oven at 60 °C for 2 h to give product **12** (1.193 g, 88%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.68 (br, 1H), 9.50 (s, 1H), 8.13 (s, 1H), 7.92 (s, 1H) 7.14 (s, 2H), 4.47 (t, J = 6.6 Hz, 2H), 3.03 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (75.9 MHz, DMSO-d_6): δ 171.8, 140.3, 138.0, 134.4, 131.2, 129.3, 123.8, 123.1, 45.3, 33.4, 20.6, 16.9.

1-Mesityl-3-(2-carboxyethyl)imidazolium (4). Compound **12** (1.00 g, 2.95 mmol) and Na$_2$CO$_3$ (0.170 mg, 1.60 mmol) in water (10 mL) were heated to reflux for 2 min. The solvent was removed under reduced pressure, and the solid residue was extracted with hot acetone (3 × 20 mL) and filtered. The filtrate was reduced to 10 mL under vacuum, and compound **4** was obtained by cooling this solution to −20 °C (0.698 g, 92%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.41 (s, 1H), 8.07 (s, 1H), 7.86 (s, 1H) 7.13 (s, 2H), 4.36 (t, J = 6.3 Hz, 2H), 2.47 (t, J = 6.3 Hz, 2H), 2.32 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (75.9 MHz, DMSO-d_6): δ 172.4, 140.1, 137.7, 134.5, 131.3, 129.2, 123.3, 123.2, 47.7, 37.9, 25.9, 20.6, 17.0.

1-(2,6-Diisopropylphenyl)-3-(2-carboxyethyl)imidazolium bromide (13). The preparation was the same as that described for **12** from 1-(2,6-diisopropylphenyl)imidazole (0.840 g, 3.68 mmol) and 3-bromopropanoic acid (0.568 g, 3.71 mmol) to give compound **13** (1.324 g, 94%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.62 (br, 1H), 9.63 (s, 1H), 8.19 (s, 1H), 8.08 (s, 1H) 7.62 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 4.50 (d, J = 6.0 Hz, 2H), 3.04 (t, J = 6.0 Hz, 2H), 2.25 (m, 2H), 1.13 (d, J = 6.3 Hz, 6H), 1.12 (d, J = 6.3 Hz, 6H). ^{13}C NMR (75.9 MHz, DMSO-d_6): δ 171.8, 145.2, 138.2, 131.5, 130.5, 125.0, 124.4, 123.2, 45.4, 33.2, 28.0, 23.8.

1-(2,6-Diisopropylphenyl)-3-(2-carboxyethyl)imidazolium (5). Compound **13** (1.250 g, 3.28 mmol) was deprotonated with Na$_2$CO$_3$ (0.202 g, 1.91 mmol) in water (10 mL) as described for compound **12** to give **5** (0.897 g, 91%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.60 (s, 1H), 8.17 (s, 1H), 8.08 (s, 1H) 7.62 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 4.50 (d, J = 6.0 Hz, 2H), 3.04 (t, J = 6.0 Hz, 2H), 2.26 (m, 2H), 1.13 (d, J = 6.3 Hz, 6H), 1.12 (d, J = 6.3 Hz, 6H). ^{13}C NMR (75.9 MHz, DMSO-d_6): δ

171.8, 145.2, 138.3, 131.5, 130.6, 125.0, 124.4, 123.2, 45.4, 33.2, 28.0, 23.9, 23.8.

Bis(1-butyl-3-(2-sulfonatoethyl)imidazol-2-ylidene)silver Sodium Salt (6). Imidazolium **1** (670 mg, 2.0 mmol) and Ag$_2$O (470 mg, 2.0 mmol) were added to a round-bottom flask while in the drybox. Upon removing the flask from the drybox, water (72 mL) deoxygenated with N$_2$ was added via syringe. The reaction was allowed to stir for 2.5 h at room temperature. Sodium chloride (117 mg, 2.0 mmol) was then added to the reaction mixture. The reaction mixture was then filtered and the filtrate dried under vacuum. The crude product was then dissolved in MeOH, filtered, and dried. This process was repeated. The crude product was recrystallized from 2-propanol to give complex **6** (333.6 mg, 56%). ^{1}H NMR (360 MHz, D$_2$O): δ 7.55 (s, 1H), 7.49 (s, 1H), 4.65 (t, J = 6.0 Hz, 2H), 4.25 (t, J = 6.9 Hz, 2H), 1.88 (t, J = 7.7 Hz, 2H), 1.35 (quint, J = 6.9 Hz, 2H), 0.96 (t, J = 7.74, 6.9, 3H). ^{13}C NMR (90.5 MHz, D$_2$O w/MeOH spike): δ 182.0, 123.08, 123.0, 50.4, 50.0, 45.7, 31.8, 19.3, 13.2.

Bis(1-mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene)silver Sodium Salt (7). Zwitterion **2** (0.6159 g, 1.997 mmol), deoxygenated water (72 mL), and silver(I) oxide (0.5532 g, 2.387 mmol) were placed in a round-bottom flask and allowed to stir at 50 °C for 7 h. Sodium chloride (0.1439 g, 2.46 mmol) was then added to the reaction mixture. The reaction mixture was then filtered, and the filtrate was dried. Complex **7** (0.663 g, 89%) was obtained as a pale yellow solid after recrystallization with 2-propanol. ^{1}H NMR (500 MHz, D$_2$O): δ 7.43 (s, 1H), 7.16 (s, 1H), 7.08, (s, 2H), 4.08 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 7.7 Hz, 2H), 2.38 (s, 3H), 2.14 (quint, J = 6.9, 4.3 Hz, 2H), 1.84 (s, 6H). ^{13}C NMR (90.5 MHz, D$_2$O w/MeOH spike): δ 180.6 (dd, $^1J(^{107}$Ag$-^{13}$C) = 180.3 Hz, $^1J(^{109}$Ag$-^{13}$C) = 207.6 Hz), 140.4, 136.3, 135.9, 129.6, 123.8, 122.4, 50.1, 48.4, 27.0, 21.0, 17.3. ESI-MS (negative ion, 1:1 H$_2$O/CH$_3$CN, 0.1% HCO$_2$H): calcd for [C$_{30}$H$_{38}$AgN$_4$S$_2$O$_6$]$^-$ 721.1, 723.1; found 721.2, 723.2.

Bis(1-(2,6-diisopropylphenyl)-3-(3-sulfonatopropyl)imidazol-2-ylidene)silver Sodium Salt (8). **8** was prepared in the same manner as **7** using **3** (0.7057 g, 2.014 mmol) and Ag$_2$O (0.5475 g, 2.363 mmol) to give an orange solid (0.6627 g, 79%). X-ray-quality crystals were obtained by slow diffusion of ether into a solution of **8** in DMSO. ^{1}H NMR (500 MHz, D$_2$O): δ 7.61 (t, J = 7.8 Hz,-1H), 7.50 (s,1H), 7.42, (d, J = 7.8 Hz, 2H), 7.37 (s, 1 H), 3.84 (t, J = 6.7 Hz, 2H), 2.39 (t, J = 7.8 Hz, 2H), 2.24 (quint, J = 6.7 Hz, 2H), 2.00 (m, 2H), 1.04 (d, J = 6.7 Hz 12H). ^{13}C NMR (90.5 MHz, DMSO): δ 182.7 (d, $^1J(^{107/109}$Ag$-^{13}$C) = 193.9 Hz), 145.2, 134.7, 129.9, 124.3, 123.7, 122.4, 49.5, 47.4, 24.0, 23.6, 23.5. ESI-MS (negative ion, 1:1 H$_2$O/CH$_3$CN, 0.1% HCO$_2$H): calcd for [C$_{36}$H$_{50}$AgN$_4$S$_2$O$_6$]$^-$ m/z 805.2, 807.2; found m/z 805.2, 807.2.

Bis(1-mesityl-3-(2-carboxylatoethyl)imidazol-2-ylidene)silver Sodium Salt (9). Complex **9** was prepared as described for **7** from zwitterion **4** (0.606 g, 2.35 mmol), deoxygenated water (50 mL), Ag$_2$O (0.547 g, 2.38 mmol), and sodium chloride (0.137 g, 2.36 mmol) and was obtained as a pale yellow solid (0.321 g, 42%) after recrystallization from dry THF. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.65 (s, 1H), 7.32 (s, 1H), 6.94 (s, 2H), 4.30 (t, J = 6.6 Hz, 2H), 2.42 (t, J = 6.6 Hz, 2H), 2.35 (s, 3H), 1.65 (s, 6H). ^{13}C NMR (75.9 MHz, DMSO-d_6): δ 180.8 (dd, $^1J(^{107}$Ag$-^{13}$C) = 181.6 Hz, $^1J(^{109}$Ag$-^{13}$C) = 209.5 Hz), 173.7, 138.1, 135.7, 134.3, 128.7, 122.6, 121.9, 49.1, 40.3, 20.7, 17.0. ESI-MS (negative ion, 1:1 H$_2$O/CH$_3$CN, 0.1% HCO$_2$H): calcd for [C$_{30}$H$_{34}$AgN$_4$O$_4$]$^-$ m/z 621.2, 623.2; found m/z 621.3, 623.3.

Bis(1-(2,6-diisopropylphenyl)-3-(2-carboxylatoethyl)imidazol-2-ylidene)silver Sodium Salt (10). Complex **10** was prepared as described for **7** from zwitterion **5** (0.660 g, 2.20 mmol), Ag$_2$O (0.513 g, 2.22 mmol), and sodium chloride (0.128 g, 2.20 mmol) and was obtained as a grayish-white solid (0.537 g, 62%) after recrystallization from a mixture of dry pyridine/toluene (1:2). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.72 (s, 1H), 7.46 (s, 1H), 7.39 (t,

Table 2. Crystallographic Data for Compounds 2·H₂O, 3·0.5H₂O, and 8·4DMSO

	2·H₂O	**3·0.5H₂O**	**8·4DMSO**
formula	$C_{15}H_{22}N_2O_4S$	$C_{18}H_{27}N_2O_{3.5}S$	$C_{44}H_{74}AgN_4NaO_{10}S_6$
fw	326.41	359.48	1142.29
color/habit	colorless/plate	colorless/fragment	amber/petal
cryst size (mm³)	$0.42 \times 0.38 \times 0.04$	$0.56 \times 0.26 \times 0.22$	$0.72 \times 0.34 \times 0.32$
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	8.1383(10)	26.380(4)	12.5852(10)
b (Å)	8.3237(11)	8.1346(12)	12.9823(10)
c (Å)	12.7636(17)	17.813(3)	18.9730(15)
α (deg)	81.437(2)	90	104.370(1)
β (deg)	81.868(2)	105.124(2)	103.9960(10)
γ (deg)	78.118(2)	90	98.9130(10)
V (Å³)	831.16(19)	3690.2(10)	2836.5(4)
Z	2	8	2
D_{calc} (g/mol)	1.304	1.294	1.337
T (K)	173(2)	173(2)	173(2)
μ (mm⁻¹)	0.214	0.197	0.636
$F(000)$	348	1544	1200
θ range (deg)	2.52 to 28.28	2.37 to 28.29	2.42 to 28.32
index ranges (h, k, l)	−6/10, ±10, −12/16	−32/34, −7/10, −23/22	±16, −17/16, ±24
no. of reflns collected	5363	11 461	28 527
no. of indep reflns/R_{int}	3754/0.0173	4379/0.0361	13 564/0.0192
no. of obsd reflns [$I > 2\sigma(I)$]	3006	3069	11 647
no. of data/restraints/params	3754/0/288	4379/0/331	13 564/0/607
R1/wR2 [$I > 2\sigma(I)$]^a	0.0416/0.1125	0.0406/0.0936	0.0476/0.1292
R1/wR2 (all data)^a	0.0542/0.1190	0.0696/0.1041	0.0553/0.1359
GOF (on F^2)^a	1.070	1.036	1.039

^{a} R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 4.28 (d, J = 6.3 Hz, 2H), 2.35 (t, J = 6.3 Hz, 2H), 2.11 (m, 2H), 1.01 (d, J = 6.3 Hz, 6H), 0.80 (d, J = 6.3 Hz, 6H). ¹³C NMR (75.9 MHz, DMSO-d_6): δ 180.7 (dd, $^1J(^{107}Ag-^{13}C)$ = 182.4 Hz, $^1J(^{109}Ag-^{13}C)$ = 210.8 Hz), 173.1, 145.2, 134.8, 129.8, 124.1, 123.6, 122.1, 49.2, 40.3, 27.7, 24.2, 23.5. ESI-MS (negative ion, 1:1 H₂O/CH₃CN, 0.1% HCO₂H): calcd for $[C_{36}H_{46}AgN_4O_4]^-$ m/z 705.3, 707.3; found m/z 705.4, 707.4.

Bis(1-mesityl-3-(3-sulfonatopropylsodium salt)imidazol-2-ylidene)palladium Diiodide (11). Zwitterion **2** (308 mg, 1.00 mmol), sodium iodide (224.9 mg, 1.50 mmol), potassium *tert*-butoxide (168 mg, 1.50 mmol), and palladium acetate (112 mg, 0.500 mmol) were added to a round-bottom flask while in the drybox. Upon removing the flask from the drybox, dry, deoxygenated DMSO (5 mL) was added via syringe. The reaction was allowed to stir for 3 h at 50 °C under nitrogen. The DMSO was removed by vacuum distillation at ~50 °C. The remaining residue was rinsed with ether (3 × 10 mL). Removal of the ether was accomplished via cannula filtration. The crude product was then extracted with cold methanol. The methanol solution was quickly added to cold acetonitrile via cannula filtration resulting in precipitation of the product. The methanol extraction/precipitation process was repeated several times. The precipitated material was then washed with cold acetonitrile (3 × 10 mL) to give **11** as an off-white solid (55.0 mg, 11%). ¹HNMR (500 MHz, DMSO-d_6): δ. 7.47 (d, J = 1.57 Hz, 2H), 7.12 (d, J = 1.6 Hz, 2H), 6.79 (s, 4H), 4.57 (t, J = 7.1 Hz, 4H), 2.41 (s, 6H), 2.36 (m, 8H), 1.87 (s, 12H). ¹³C NMR (90.5 MHz, DMSO): δ 166.7, 137.3, 135.87, 135.4, 129.2, 124.8, 122.4, 50.7, 48.7, 26.3, 21.6, 21.0. ESI-MS (negative ion, 1:1 H₂O/CH₃CN, 0.1% HCO₂H)): calcd for $[C_{30}H_{38}I_2N_4NaPdS_2O_6]^-$ 996.9; found 997.1. Calcd for $[C_{30}H_{39}I_2N_4PdS_2O_6]^-$ 975.0; found 975.1. Calcd for $[C_{30}H_{38}IN_4PdS_2O_6]^-$ 847.0; found 847.1. Calcd for $[C_{30}H_{38}I_2N_4PdS_2O_6]^{2-}$ 487.0; found 487.0. The expected isotope distribution for a palladium-containing compound was observed for each ion. The reported value is the most intense peak.

Electrospray Mass Spectra. Mass spectrometry analyses were performed on a Micromass Q-ToF 2 mass spectrometer (Micromass, Manchester, UK). The samples were dissolved in 50/50 acetonitrile/ water containing 0.1% formic acid and injected into a 1 μL/min flow of the same solvent. The flow was introduced into the nano-LC interface of the mass spectrometer. The mass spectra (electro-spray ionization) were recorded in the negative ion mode.

X-ray Crystal Structure Determination. X-ray crystallographic data collection was performed using a Bruker SMART diffracto-meter with a CCD area detector, using graphite-monochromated Mo Kα radiation. The SHELXTL software, version 5, was used for refinement.[42] Absorption corrections were made with SAD-ABS.[43] ORTEP and other structural drawings were made with SHELXTL[42] and ORTEP-3.[44,45]

Crystallographic data for compounds **2·H₂O**, **3·0.5H₂O**, and **8·4DMSO** can be found in Table 2. In each structure, the non-hydrogen atoms were readily located and refined anisotropically. For compounds **2·H₂O** and **3·0.5H₂O**, all hydrogen atoms were located from a difference Fourier map and refined isotropically. For the structure of compound **8·4DMSO**, the hydrogen atoms were geometrically constrained and placed in calculated positions 0.95 Å from the bonded carbon and allowed to ride on that atom. After initial structure solution, high thermal motion was observed for C16 on one of the isopropyl substituents and for the DMSO solvent molecules, which led to an investigation of disorder. It was not possible to resolve reasonable disorder models for each atom, thus atoms C16, C25, and C24 were refined at full occupancy and the resulting thermal ellipsoids are large. Only the disordered DMSO solvent molecule containing atom S6 could be adequately resolved. The observed DMSO solvent disorder is over two sulfur positions, such that the molecule shares its oxygen and two carbon atoms. The two sulfur positions were refined at 50% occupancy in alternate least-squares cycles.

(42) Sheldrick, G. M. *SHELXTL*, Version 5.05; Siemens Analytical X-Ray Instruments, Inc., 1996.
(43) Sheldrick, G. M. *SADABS*, Program for Semiempirical Absorption Correlation of Area Detector Data; University of Göttingen: Germany, 1996.
(44) Burkitt, M. *Methods Enzymol.* **1994**, *234*, 66.
(45) Farrugia, J. *Appl. Crystallogr.* **1997**, *30*, 565−566.

Supporting Information Available: NMR and ESI-MS spectra for compounds **2**−**11**, additional ORTEP diagrams for **2**·H_2O, **3**·0.5H_2O, and **8**·4DMSO, and full crystallographic data for **2**·H_2O, **3**·0.5H_2O, and **8**·4DMSO in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060552B