Inorg. Chem. **2000,** *39,* 3724−3727

Ethylene Oxide and Propylene Sulfide Complexes of Silver(I): Synthesis and Characterization of $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$

H. V. Rasika Dias* and Ziyun Wang

Department of Chemistry and Biochemistry,
The University of Texas at Arlington,
Arlington, Texas 76019-0065

Received November 17, 1999

Introduction

The silver-catalyzed partial oxidation of ethylene to ethylene oxide is one of the most important and thoroughly investigated industrial processes.[1−12] Silver−ethylene and silver−ethylene oxide species are two possible intermediates formed on the silver catalyst surface during the reaction. Remarkably, despite the interest, very little is known about structures and properties of silver coordination complexes containing either ethylene or ethylene oxide ligands.[13−16] Recently, we reported on the synthesis of one of these complexes, the silver−ethylene adduct $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2-C_2H_4)$,[17] using a highly fluorinated tris(pyrazolyl)borate ligand (where $HB(3,5-(CF_3)_2Pz)_3$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate).[18−20] Unlike the typical silver(I)−ethylene complexes, $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2-C_2H_4)$ does not lose ethylene under reduced pressure.[14−16] Therefore, its properties can be investigated conveniently using a variety of techniques, including X-ray crystallography. In this paper, we describe the successful utility of the $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand in the isolation of the ethylene oxide adduct $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$. A related sulfur derivative containing the propylene sulfide ligand has also been synthesized, and spectroscopic and structural data of this silver adduct, $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$, are also presented for comparison.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz). Proton and carbon chemical shifts are reported in parts per million versus Me_4Si. ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$ spectrum. Infrared spectra were recorded on a BioRad 40S spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer model 2400 CHN analyzer. The synthesis of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$[17] was carried out as reported previously. Ethylene oxide and propylene sulfide were purchased from commercial sources.

Synthesis of $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$. A sample of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ (300 mg, 0.37 mmol) was dissolved in about 10 mL of hexane. Ethylene oxide (OC_2H_4) was bubbled into this solution for about 5 min at room temperature. The reaction mixture was cooled to −20 °C to obtain colorless crystals of $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$ in quantitative yield. Mp: 68−70 °C. ^1H NMR ($CDCl_3$): δ 2.74 (s, 4H, CH_2), 6.92 (s, 3H). ^{19}F NMR ($CDCl_3$): δ −59.1 (d, $^5J(F,H) = 3.6$ Hz), −62.0 ($^4J(F,Ag) = 1.6$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 41.2 (CH_2), 106.2 (CH), 119.1 (q, $^1J(C,F) = 271$ Hz, CF_3), 120.3 (q, $^1J(C,F) = 269$ Hz, CF_3), 140.7 (q, $^2J(C,F) = 43.4$ Hz, CCF_3), 143.3 (q, $^2J(C,F) = 38.1$ Hz, CCF_3). Anal. Calcd for $C_{17}H_8F_{18}N_6BOAg$: C, 26.42; H, 1.04; N, 10.87. Found: C, 26.68; H, 0.81; N, 11.25.

Synthesis of $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$. A sample of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ (300 mg, 0.37 mmol) was dissolved in about 10 mL of hexane. Propylene sulfide (SC_3H_6) (30 mg, 0.37 mmol) was added to this solution at room temperature and stirred overnight. This mixture was concentrated and cooled to −20 °C to obtain colorless crystals of $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$ in >90% yield. Mp: dec around 90 °C. ^1H NMR ($CDCl_3$): δ 1.72 (d, 3H, $J = 6.1$ Hz, CH_3), 2.69 (dd, 1H, $J = 2.1$, 7.1 Hz, CH_2), 3.14 (dd, 1H, $J = 2.1$, 6.9 Hz, CH_2), 3.57 (m, 1H, CH), 6.89 (s, 3H). ^{19}F NMR ($CDCl_3$): δ −59.0 (d, $^5J(F,H) = 3.6$ Hz), −61.9 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.5 (CH_3), 32.2, 37.5, 106.1 (CH), 119.2 (q, $^1J(C,F) = 271$ Hz, CF_3), 120.4 (q, $^1J(C,F) = 269$ Hz, CF_3), 140.1 (q, $^2J(C,F) = 39.8$ Hz, CCF_3), 143.2 (q, $^2J(C,F) = 38.1$ Hz, CCF_3). Anal. Calcd for $C_{18}H_{10}F_{18}N_6BSAg$: C, 26.92; H, 1.26; N, 10.47. Found: C, 27.25; H, 0.95; N, 10.24.

Crystallographic Data Collection and Structure Determinations. Cell parameters of $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$ were determined using 38 reflections. The structure was solved by direct methods, followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the Bruker SHELXTL 5.1 software package.[21] The C−C unit of the ethylene oxide moiety was disordered over two sites and was refined with occupancies of 0.54 and 0.46. A minor rotational disorder was observed for fluorines on C26 and C37 and was modeled successfully. All non-hydrogen atoms were refined anisotropically. The hydrogen atom on B was located from the difference map. The remaining hydrogens were included in the calculated positions.

Cell parameters of $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$ were determined using 34 reflections. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atom on B was located from the difference map. The remaining hydrogens were included in the calculated positions.

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(1) Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1991; p 392.
(2) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265.
(3) Kilty, P. A.; Sachtler, W. M. H. *Catal. Rev. Sci. Eng.* **1974**, *10*, 1.
(4) Verykios, X. E.; Stein, F. P.; Coughlin, R. W. *Catal. Rev. Sci. Eng.* **1980**, *22*, 197.
(5) Sachtler, W. M. H.; Backx, C.; Van Santen, R. A. *Catal. Rev. Sci. Eng.* **1981**, *23*, 127.
(6) Bertole, C. J.; Mims, C. J. *J. Catal.* **1999**, *184*, 224.
(7) Wang, C.-B.; Deo, G.; Wachs, I. E. *J. Phys. Chem. B* **1999**, *103*, 5645.
(8) Miller, G. J.; Metson, J. B.; Bowmaker, G. A.; Cooney, R. P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4149.
(9) Plischke, J. K.; Benesi, A. J.; Vannice, M. A. *J. Catal.* **1992**, *138*, 223.
(10) Fernandes, E. F.; Benesi, A. J.; Vannice, M. A. *J. Phys. Chem.* **1994**, *98*, 8498.
(11) Sajkowski, D. J.; Boudart, M. *Catal. Rev. Sci. Eng.* **1987**, *29*, 325.
(12) Bielanski, A.; Haber, J. *Oxygen in Catalysis*; Marcel Dekker: New York, 1991; p 279.
(13) Lancashire, R. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 5, p 775.
(14) Fackler, J. P., Jr. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1987; Vol. 7, p 3829.
(15) Pruchnik, F. P. *Organometallic Chemistry of the Transition Elements*; Plenum: New York, 1990.
(16) Quinn, H. W.; Tsai, J. H. *Adv. Inorg. Radiochem.* **1969**, *12*, 217.
(17) Dias, H. V. R.; Jin, W.; Wang, Z. *Inorg. Chem.* **1997**, *36*, 6205−6215.
(18) Dias, H. V. R.; Lu, H.-L.; Ratcliff, R. E.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1975−1976.
(19) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317−2328.
(20) Renn, O.; Venanzi, L. M.; Marteletti, A.; Gramlich, V. *Helv. Chim. Acta* **1995**, *78*, 993−1000.
(21) *SHELXTL (Version 5.1)*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

10.1021/ic991334w CCC: $19.00

Table 1. Crystal Data and Summary of Data Collection and Refinement

	[HB(3,5-$(CF_3)_2$Pz$)_3$]-Ag(OC_2H_4)	[HB(3,5-$(CF_3)_2$Pz$)_3$]-Ag(SC_3H_6)
empirical formula	$C_{17}H_8AgBF_{18}N_6O$	$C_{18}H_{10}AgBF_{18}N_6S$
formula weight	772.97	803.06
space group	$P\bar{1}$	$P\bar{1}$
T, K	293(2)	183(2)
λ, Å	0.71073	0.71073
a, Å	8.2200(10)	8.1647(12)
b, Å	11.913(2)	12.709(2)
c, Å	15.2675(13)	14.849(2)
α, deg	67.214(9)	66.305(13)
β, deg	76.346(9)	76.535(10)
γ, deg	71.053(11)	75.040(11)
V, Å^3	1293.3(3)	1348.4(3)
Z	2	2
ρ (calcd), g/cm^3	1.985	1.978
μ, mm^{-1}	0.935	0.972
R1 (all data)[a]	0.0356	0.0562
wR2 (all data)[b]	0.0721	0.1289

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(OC_2H_4)

Ag−O	2.249(2)	C(1)−C(2)	1.429(17)
Ag−N(32)	2.345(2)	C(1A)−C(2A)	1.420(18)
Ag−N(12)	2.363(2)	N(11)−N(12)	1.360(3)
Ag−N(22)	2.382(2)	N(11)−B	1.560(4)
O−C(1A)	1.327(10)	N(21)−N(22)	1.357(3)
O−C(1)	1.338(9)	N(21)−B	1.564(4)
O−C(2)	1.407(11)	N(31)−N(32)	1.354(3)
O−C(2A)	1.414(12)	N(31)−B	1.566(3)

O−Ag−N(32)	127.93(10)	C(2)−O−Ag	129.2(9)
O−Ag−N(12)	136.19(10)	C(2A)−O−Ag	130.2(10)
N(32)−Ag−N(12)	81.65(8)	O−C(1)−C(2)	61.0(7)
O−Ag−N(22)	130.30(11)	O−C(2)−C(1)	56.3(6)
N(32)−Ag−N(22)	80.18(8)	O−C(1A)−C(2A)	61.8(7)
N(12)−Ag−N(22)	80.43(8)	O−C(2A)−C(1A)	55.9(6)
C(1)−O−C(2)	62.7(8)	N(11)−B−N(21)	109.7(2)
C(1A)−O−C(2A)	62.3(8)	N(11)−B−N(31)	110.2(2)
C(1A)−O−Ag	142.3(8)	N(21)−B−N(31)	110.0(2)
C(1)−O−Ag	142.9(6)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(SC_3H_6)

Ag−N(12)	2.344(4)	C(2)−C(3)	1.430(12)
Ag−N(32)	2.363(4)	N(11)−N(12)	1.341(6)
Ag−S	2.3925(16)	N(11)−B	1.559(8)
Ag−N(22)	2.402(4)	N(21)−N(22)	1.362(6)
S−C(1)	1.796(8)	N(21)−B	1.568(8)
S−C(2)	1.819(8)	N(31)−N(32)	1.359(6)
C(1)−C(2)	1.512(13)	N(31)−B	1.560(8)

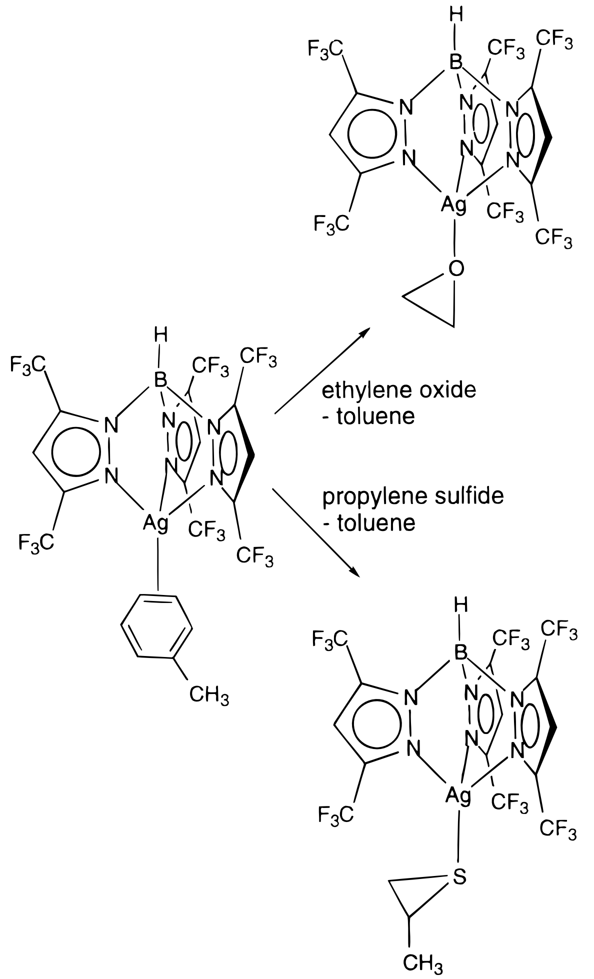
N(12)−Ag−N(32)	79.83(15)	C(2)−S−Ag	109.6(3)
N(12)−Ag−S	128.02(12)	C(2)−C(1)−S	66.1(4)
N(32)−Ag−S	140.13(11)	C(3)−C(2)−C(1)	118.2(8)
N(12)−Ag−N(22)	79.32(15)	C(3)−C(2)−S	121.3(7)
N(32)−Ag−N(22)	79.94(15)	C(1)−C(2)−S	64.5(4)
S−Ag−N(22)	127.92(11)	N(11)−B−N(31)	110.4(4)
C(1)−S−C(2)	49.5(4)	N(11)−B−N(21)	110.3(4)
C(1)−S−Ag	113.3(3)	N(31)−B−N(21)	109.4(4)

Cell dimensions and structure refinement data of [HB(3,5-$(CF_3)_2$-Pz$)_3$]Ag(OC_2H_4) and [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(SC_3H_6) are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

Results and Discussion

The treatment of [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(η^2-toluene) with ethylene oxide (ca. 1 atm) in hexane at room temperature, followed by cooling, afforded [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(OC_2H_4) as a colorless crystalline solid in excellent yield (Scheme 1).

Scheme 1



Notably, [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(OC_2H_4) does not lose ethylene oxide under reduced pressure. It was characterized by NMR (^{1}H, ^{19}F, and ^{13}C) spectroscopy, elemental analysis, and X-ray diffraction.

The ^{1}H NMR spectrum taken in $CDCl_3$ shows a resonance at 2.74 ppm due to the CH_2 protons of the coordinated ethylene oxide. The free ethylene oxide displays the corresponding peak at a relatively higher field (2.54 ppm).[22] The ^{13}C NMR spectrum displays a resonance at δ 41.2, corresponding to carbons of the CH_2 unit (cf. free ligand at 40.6 ppm).[23,24] The ethylene oxide adsorbed on the Ag/SiO_2 surface shows a peak at the same chemical shift value.[10] The ^{19}F NMR spectrum of [HB(3,5-$(CF_3)_2$Pz$)_3$]Ag(OC_2H_4) shows two signals (δ −59.1, −62.0), as expected for the −CF_3 groups on the 3- and 5-positions of the pyrazolyl groups. Both signals appear as doublets. The doublet at δ −59.1, which corresponds to trifluoromethyl groups on the pyrazole ring 5-positions, is believed to be due to long-range coupling to the hydrogen atom on boron.[19,25] Similar splitting has been observed for most of the metal complexes

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(22) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 214.

(23) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 237.

(24) Davis, S. G.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 861.

(25) Dias, H. V. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1996**, *15*, 2994−3003.

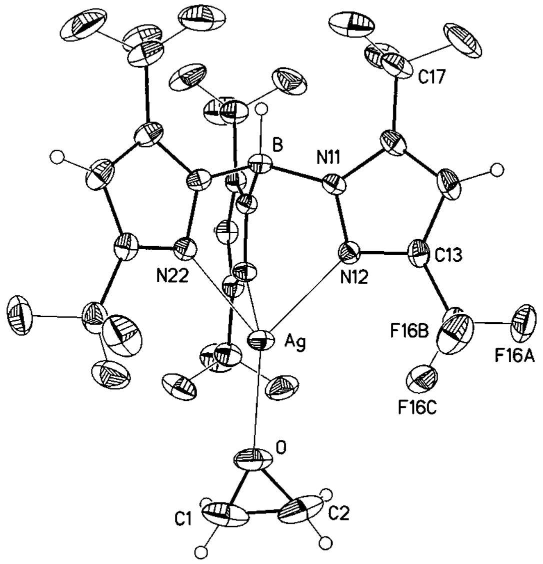

Figure 1. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4).

derived from the [HB(3,5-$(CF_3)_2Pz)_3$]$^-$ ligand. The doublet structure at δ −62.0, which corresponds to trifluoromethyl groups on the pyrazole ring 3-positions, is probably due to spin−spin coupling to the silver atom.[17]

The X-ray crystal structure of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) is illustrated in Figure 1. It features a pseudotetrahedral silver ion with the oxygen atom of ethylene oxide occupying one of the sites. The Ag−O bond distance of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) (2.249(2) Å) is very close to the corresponding value of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(THF) (2.234(4) Å).[17,26] The angle defined by the Ag−O vector and the midpoint of the OC_2 plane is about 146°. The THF moiety of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(THF) shows a relatively smaller tilt (the angle defined by the Ag−O vector and the centroid of the THF moiety is about 164°), perhaps due to steric reasons. For comparison, the corresponding angle of the cadmium(II) epoxide derivative [HB(3-(Ph)Pz)$_3$]Cd(CH_3CO_2)L (where L = cyclohexene oxide or propylene oxide) is about 140°.[27] Unfortunately carbon atoms of the ethylene oxide moiety in [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) are disordered over two sites. Therefore, C−C and C−O bond distances of the ethylene oxide unit are not very reliable for a detailed discussion.

The silver adduct [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) represents the first thermally stable, well-characterized molecule containing silver−ethylene oxide bonding. The isolation of molecules such as [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) is challenging due to (i) the low affinity of the soft silver(I) toward neutral oxygen-based donors[28] and (ii) the weak donor properties of the ethylene oxide ligand (because of the high s-character of orbitals containing donor electrons).[29] The stability of the ethylene oxide complex [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) may largely be a result of the unique steric/electronic properties of the fluorinated tris(pyrazolyl)borate ligand.[25] The [HB(3,5-$(CF_3)_2Pz)_3$]$^-$ is a weak donor.[25,30,31] Therefore, the coordination of silver(I) ion to the [HB(3,5-$(CF_3)_2Pz)_3$]$^-$ ligand may not significantly reduce the electrophilic character at the silver site. This allows the formation of a relatively strong Ag−OC_2H_4 σ-bond. The steric protection afforded by the [HB(3,5-$(CF_3)_2Pz)_3$]$^-$ ligand to the Ag−OC_2H_4 moiety further enhances the stability of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4).

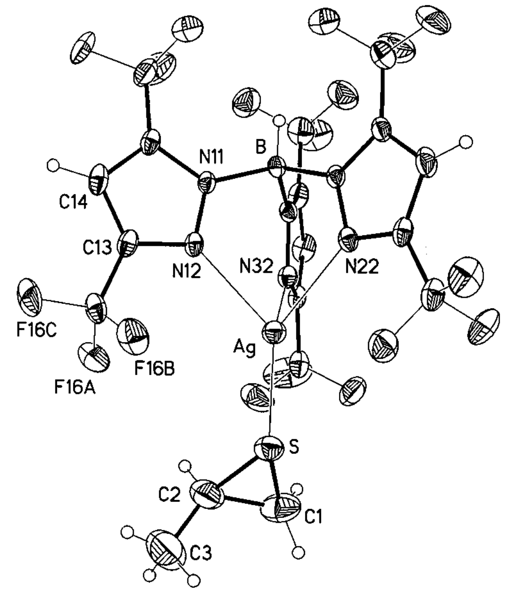

Figure 2. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6).

The related propylene sulfide derivative [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6) was obtained by the treatment of [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(η^2-toluene) with propylene sulfide in hexane. Although [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6) is an air-stable solid, it should preferably be stored at 0 °C because crystals of this compound slowly deteriorate at room temperature. ^{1}H NMR signals of the metal-coordinated propylene sulfide [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6) (δ 1.72, 2.69, 3.14, 3.57) appear at relatively lower field values compared to the corresponding resonances of the free propylene sulfide (δ 1.51, 2.11, 2.50, 2.91).[32] The ^{13}C NMR chemical shift values of the thiirane ring carbons also show a significant downfield shift. The ^{19}F NMR spectrum of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6) in $CDCl_3$ displays two signals (δ −59.0, −61.9) in the normal region for [HB(3,5-$(CF_3)_2Pz)_3$]Ag complexes.[17]

The X-ray crystal structure of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6) is shown in Figure 2. The silver atom adopts a distorted pseudotetrahedral geometry. The Ag−S bond distance of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(SC_3H_6) (2.3925(16) Å) is somewhat shorter than the typical Ag−S bond lengths for silver dialkyl thioether adducts.[33] The propylene sulfide moiety shows a significantly larger tilt (compared to the ethylene oxide analogue) toward the tris(pyrazolyl)borate ligand (Figure 3). The angle defined by the Ag−S vector and the midpoint of the SC_2 plane is about 114°. This is not unusual, as the sulfur atom prefers a more pyramidal geometry.[34]

Propylene sulfide is used as a monomer in various metal-catalyzed polymerization processes.[29,35−40] It is also a good

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(26) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 267−268.

(27) Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 538.

(28) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 27.

(29) Darensbourg, D. J.; Niezgoda, S. A.; Holtcamp, M. W.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* **1997**, *36*, 2446.

(30) Dias, H. V. R.; Kim, H.-J. *Organometallics* **1996**, *15*, 5374−5379.

(31) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 3687−3694.

(32) Integrated Spectral Data Base System for Organic Compounds.http://www.aist.go.jp/RIODB/SDBS (accessed 1999).

(33) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(34) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2332.

(35) Inoue, S.; Aida, T.; Watanabe, Y.; Kawaguchi, K. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 365.

(36) Watanabe, Y.; Aida, T.; Inoue, S. *Macromolecules* **1990**, *23*, 2612.

(37) Dumas, P.; Guerin, P.; Sigwalt, P. *Fr. Nouv. J. Chim.* **1980**, *4*, 95.

(38) Dumas, P.; Girault, J. P.; Guerin, P. *Fr. Polym. Bull.* **1980**, *2*, 257.

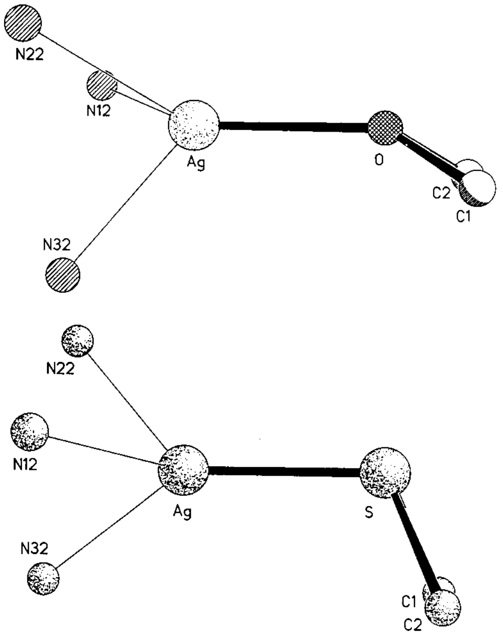

Figure 3. N_3Ag-OC_2 and N_3Ag-SC_2 moieties of $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$ showing silver–ligand bonding.

sulfur atom donor to metal ions.[41−48] However, structurally characterized metal–propylene sulfide species (or any other thiiranes) are rare.[34,49−52] To our knowledge, the complex presented herein represents the only structurally characterized example containing silver–thiirane bonding.

Acknowledgment. The authors thank The Robert A. Welch Foundation for support of this work. The authors also acknowledge The University of Texas at Arlington for providing funds in purchasing the Siemens P4 single crystal X-ray diffractometer.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of $[HB(3,5-(CF_3)_2Pz)_3]Ag(OC_2H_4)$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag(SC_3H_6)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Dumas, P.; Guerin, P. *Can. J. Chem.* **1978**, *56*, 925.

(40) Mogan, D. R.; Wragg, R. *Makromol. Chem.* **1969**, *125*, 220.

(41) Hao, L.; Xiao, J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 2165.

(42) Uhl, W.; Grauoner, R.; Hiller, W.; Neumayer, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 62.

(43) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Organometallics* **1996**, *15*, 2428.

(44) Baranger, A. M.; Hanna, T. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 10041.

(45) Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770.

(46) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chem.* **1994**, *33*, 1416.

(47) Kovacs, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1131.

(48) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

(49) Abel, E. W.; Cooley, N. A.; Kite, K.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Dawes, H. M. *Polyhedron* **1989**, *8*, 887.

(50) Yee, G. T.; Noll, B. C.; Williams, D. K. C.; Sellers, S. P. *Inorg. Chem.* **1997**, *36*, 2904.

(51) Adams, R. D.; Queisser, J. A.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 10674.

(52) Adams, R. D.; Yamamoto, J. H.; Holmes, A.; Baker, B. J. *Organometallics* **1997**, *16*, 1430.