oil with clean ^{1}H NMR and mass spectra.

General Procedure for the Conversion of Sulfoxides 1 to α-Fluoro Thioethers 2. A flame-dried, round-bottomed flask fitted with rubber septa was purged with N_2 and charged with anhydrous CH_2Cl_2 or $CHCl_3$ (20 mL), 1 (10 mmol), and $SbCl_3$ (68 mg, 0.3 mmol). The resulting solution was cooled to ~4 °C (ice-bath cooling is unnecessary on a 1-mmol scale) and DAST (2.31 mL, 2.82 g, 17.5 mmol) was injected. After 15 min the ice bath was removed and stirring at ambient temperature was continued until TLC (EtOAc/hexane, 1:4) indicated complete consumption of starting 1 (normally 1.5–5 h). The reaction mixture was poured into vigorously stirred ice-cold saturated $NaHCO_3$ (20 mL) and stirring was continued for 30 min. The mixture was extracted with $CHCl_3$ (2 × 30 mL) and the combined organic phase was washed with $NaHCO_3/H_2O$ (10 mL), H_2O (20 mL), and $NaCl/H_2O$ (20 mL), dried ($MgSO_4$), and evaporated to give a brown oil. This crude product was usually oxidized directly to the sulfoxides 3 or sulfones 4. Purification by flash chromatography (EtOAc/hexane, 1:15) or Kugelrohr distillation afforded pure **2a** and **2h** (see Table I).

General Procedure for the Oxidation of α-Fluoro Thioethers 2 to α-Fluoro Sulfoxides 3. A solution of MCPBA (1.02 g of 85% reagent, 5 mmol) in $CHCl_3$ (30 mL) was added dropwise to a cooled (-30 °C) stirred solution of crude 2 (5 mmol) in $CHCl_3$ (30 mL). TLC (EtOAc/hexane, 1:4) indicated complete oxidation after ~5 min. The reaction mixture was worked up as in the above procedure for **1h**. The oily residue was purified by flash chromatography (EtOAc/hexane, 1:10 to 1:3) or Kugelrohr distillation (**3a**) to give the α-fluoro sulfoxides 3 as slightly yellow oils. Careful chromatography separated the diastereomeric pairs of enantiomers of **3b**, **3c**, **3d**, and **3h** (yields and ^{1}H NMR and mass spectral data are given for the stereoisomeric mixtures in Table I).

[(Fluoromethyl)sulfonyl]benzene[21] (4a). A solution of MCPBA (4.46 g of 85% reagent, 22 mmol) in $CHCl_3$ (70 mL) was added dropwise to a cooled (-10 °C), stirred solution of **2a** (1.42 g, 10 mmol, based on starting **1a**) in $CHCl_3$ (30 mL). The reaction mixture was allowed to warm to ambient temperature and was stirred for an additional 4 h. Workup as described for **1h** afforded **4a** (1.57 g, 90%) as colorless crystals (see Table I).

[(Fluoromethyl)sulfonyl]methane.[7] Dimethyl sulfoxide (0.71 mL, 0.78 g, 10 mmol) was converted to [(fluoromethyl)thio]methane according to the general procedure for 1 → 2 (except the combined solution in $CHCl_3$ (~100 mL) after drying ($MgSO_4$) was not evaporated owing to product volatility). This solution was cooled to -10 °C and oxidized as in the above procedure for **4a**. The reaction mixture was concentrated to ~15 mL, cooled at 0 °C, and filtered. The filtrate was dried ($KHCO_3/MgSO_4$, 3:1) and evaporated to give a solidified yellow oil. Kugelrohr distillation at 55 °C/0.4 mmHg gave 0.85 g (76% based on starting dimethyl sulfoxide) of [(fluoromethyl)sulfonyl]methane as a slightly yellow solidified oil, mp 40–42 °C (lit.[7] mp 40–43 °C): ^{1}H NMR δ 3.01 (s, 3, CH_3), 5.12 (d, J = 46.8 Hz, 2, CH_2F); MS m/z 112 (M^+, 18), 97 ($M - CH_3$, 89), 79 ($M - CH_2F$, 100), 63 (81).

Acknowledgment. We thank the American Cancer Society (Grant No. CH-405) and the Polish Academy of Sciences (Grant No. CPBP 01.13.1) for generous financial support.

Registry No. **1a**, 20696-08-6; **1b**, 127594-85-8; **1c**, 127594-86-9; **1d**, 114045-23-7; **1e**, 73610-10-3; **1f**, 127594-87-0; **1g**, 127594-88-1; **1h**, 127594-89-2; **1i**, 127594-90-5; **1j**, 127594-91-6; **2a**, 60839-94-3; **2b**, 127594-92-7; **2c**, 127594-93-8; **2d**, 127594-94-9; **2e**, 127594-95-0; **2f**, 127594-96-1; **2g**, 127594-97-2; **2h**, 127594-98-3; **2i**, 1535-67-7; **2j**, 81931-98-8; **3b** (isomer 1), 127594-99-4; **3b** (isomer 2), 127595-00-0; **3c** (isomer 1), 127595-01-1; **3c** (isomer 2), 127595-02-2; **3d** (isomer 1), 127595-03-3; **3d** (isomer 2), 127595-04-4; **3e**, 94404-43-0; **3f**, 127595-05-5; **3g**, 127595-06-6; **3h** (isomer 1), 127595-07-7; **3h** (isomer 2), 127595-08-8; **4a**, 20808-12-2; DAST, 38078-09-0; p-$MeOC_6H_4S(CH_2)_3CO_2Et$, 127594-84-7; $Br(CH_2)_3CO_2Et$, 2969-81-5; p-$MeOC_6H_4SH$, 696-63-9; $SbCl_3$, 10025-91-9; MeS(O)Me, 67-68-5; FCH_2SMe, 65038-44-0; FCH_2SO_2Me, 94404-44-1.

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A 1:1 Complex of Silver with a Cofacial Stilbene: ((Z)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene)silver(I) Triflate

James E. Gano,* Girija Subramaniam,* and
Ronald Birnbaum

Bowman-Oddy Laboratories, Department of Chemistry,
University of Toledo, Toledo, Ohio 43606

Received January 3, 1990

Sterically congested stilbene, (Z)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (1) was recently shown to possess face-to-face or cofacial benzene rings.[1,2] The π-electron-rich cleft in this simple molecule, Scheme I, offers an interesting site for complexation. The exterior faces of the rings in 1, in contrast to related cofacial hydrocarbons,[3] were thought to be unlikely complexation sites due to the proximity of the large *tert*-butyl groups. Similarly, stereoisomer 2 would not be expected to form complexes. Finally, steric hindrance should prevent complexation of 1 and 2 at the normally preferred site of interaction, the central double bond. As a validation of these concepts, the preparation and characterization of the first metal complex of this system, the silver trifluoromethanesulfonate (silver triflate, AgOTf) complex, is described below.

Results

Attempts to detect a silver ion complex of 1[1] by ^{1}H NMR with silver nitrate in ethanol or silver triflate in either tetrahydrofuran (THF) or methanol gave no indication of appreciable complexation. A stoichiometric solution of 1 and silver triflate was prepared in dry tetrahydrofuran. Evaporation of the solvent produced colorless crystals of a new material, 3, which melted at 195–196 °C, in contrast to 1, mp = 89–90 °C, and which readily dissolved in chloroform, in contrast to silver triflate. The ^{1}H NMR and ^{13}C NMR spectra of 3 (Table I) were similar to 1 but all resonances were shifted downfield. Silver triflate in excess of the 1:1 stoichiometry did not effect the observed ^{1}H NMR chemical shifts of 3. In contrast, a 100% excess (2:1 for 1:silver triflate) of 1 shifted the observed resonances to points equidistant between those of 1 and 3. Although the ^{1}H NMR spectrum of 3 showed no changes when a normal $CDCl_3$ solution was cooled, similar treatment of a very dilute, 0.00038 M, solution showed some peak broadening and coalescence at the lowest temperature, -50 °C. Stereoisomer 2 showed no ^{1}H NMR evidence for complex formation in the presence of silver triflate. Crystals of the new complex were stable to moisture and oxygen. Slight darkening occurred upon exposure to room

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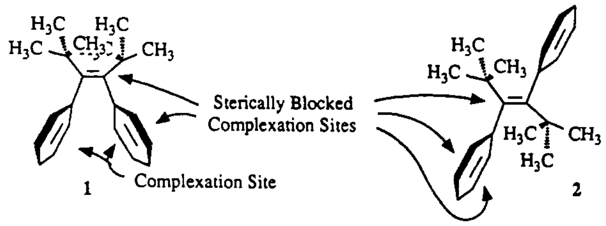
Table I. Comparison of ^1H NMR Chemical Shifts, δ, of 1 and 3 in $CDCl_3$[c]

	^1H NMR				^{13}C NMR					
	$(CH_3)_3C$	ortho	meta	para	$(CH_3)_3C$	$(CH_3)_3C$	[C=C, ipso]	ortho[a]	meta[a]	para
1	1.249	6.666	6.870	6.774	33.50	35.93	[146.9, 147.4][b]	130.0	126.2	123.9
3[c]	1.31	6.84	7.20	7.13	33.5	36.1	[147.9, 148.2][b]	131.2	124.0	119.1
Δδ	0.06	0.27	0.39	0.33	−0.0	0.2		1.2	−2.2	−4.7

[a] Assigned on the basis of the relative magnitude of the downfield shift in the silver complex. [b] Assignment uncertain. [c] The certainty of δ for 3 is reduced because a small fraction is dissociated at the concentration used in the measurements.

Scheme I



light over a period of weeks. Melting of 3 occurred without decomposition.

Determination of a stability constant for formation of complex 3 in chloroform-*d* from NMR data was desirable. The low solubility of silver triflate in chloroform prevented preparation of the concentrated solutions needed for application of the standard Benesi–Hildebrand equation.[4] Instead, ^1H NMR measurements were recorded for a series of chloroform-*d* solutions of differing concentrations wherein the ratio of added 1 to added silver triflate was maintained to be 1:1. An equation to describe the system was derived based on the simple equilibrium in eq 1. The

$$1 + \text{AgOTf} \underset{}{\overset{K_{\text{complex}}}{\rightleftharpoons}} 1\text{:AgOTf} \qquad (1)$$

data was fit to that equation with a nonlinear regression analysis. Both the stability constant, K_{complex}, and the ^1H NMR chemical shift of 3 at the meta position were taken as variables. Since the largest difference in chemical shift between 1 and 3 was observed at the meta position, that resonance was used for the plot. This experiment gave $K_{\text{complex}} = 3700 \pm 300\ M^{-1}$ and $\delta_3^{\text{meta}} = 7.213 \pm 0.004$. A plot of K_{complex} as a function of concentration is presented in Figure 1. Considering the large experimental error imposed by the relatively small chemical shift range, the plot gives the expected straight line.

Competitive complexation experiments were performed to compare the stability of 3 with other known, stable silver:arene complexes. Simple aromatic compounds, like *m*-xylene or bibenzyl, showed no effect on the ^1H NMR spectrum of 3 in a 1:1 chloroform-*d* solution. A more rigorous test was provided by the very efficient silver ligand, [2.2.2]paracyclophane (4). In a 45:1:3 solution of 1, 4, and silver triflate, there was no evidence of any uncomplexed 4.

Single-crystal X-ray diffraction analysis was performed on a sample of 1 crystallized from dichloromethane. Analysis of the diffraction data went smoothly and ultimately provided $R = 0.040$. The resulting structure is shown in perspective in Figure 2. A packing diagram is shown in Figure 3.

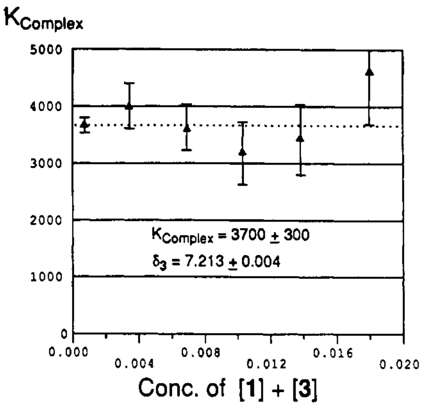


Figure 1. Plot of the stability constant, K_{complex}, as a function of the sum [1] + [3]. Throughout, the stiochiometry of added 1 and added AgOTf = 1:1.

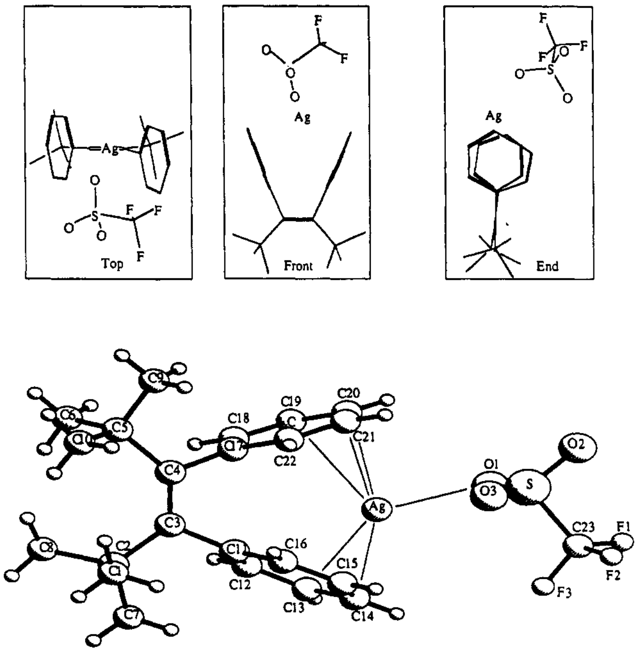


Figure 2. Structure of 3 from X-ray crystal structure determination. Line drawings have H atoms omitted. Views are along exactly perpendicular axes. Perspective drawing generated with PLUTO.

Discussion

All previously reported silver complexes of simple arenes, including the seemingly related silver:bibenzyl complex, have been unstable substances which decomposed without the presence of ligand vapor and protection from moisture.[5] More elaborately structure arenes, like 4, form three-coordinated complexes 5 and 6, which are stable, crystalline solids.[6,7] Thus, complex 3 is the simplest, stable silver:

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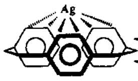
arene complex reported to date.


4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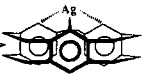
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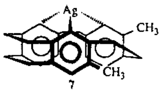
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Complex 3 showed the downfield-shifted ^{1}H NMR spectrum characteristic of materials such as 5 and 6. The absence of any change in the ^{1}H NMR spectrum of 3 upon addition of excess (i.e. >1:1) silver triflate showed >95% of the ligand was complexed to silver triflate. The absence of separate signals in the ^{1}H NMR spectrum of a 2:1, 1:silver triflate sample, however, showed a rapid equilibrium existed between complexed and uncomplexed ligand. Similar results are reported for 6–7, but not for 5.[7] Furthermore, both these observations provide evidence for a 1:1 (or n:n) complex. The absence of complex formation with 2 supported the contention that steric hindrance by the *tert*-butyl groups eliminated complex formation on the outside face of the phenyl or, in contrast to other observations,[8] with the double bond in either 1 or 2.

It was desirable to obtain a quantitative measure of the stability of 3. The results in Figure 1 show the stability constant in chloroform-*d* to be 3700 M^{-1}. Although this number is large, there still remained a few percent of disassociated 3 in solution at our highest concentrations studied, ~0.02 M. This explains the slight discrepency between measured, Table I, and calculated, Figure 1, values for δ_3^{meta}.

Since stability constants have not been reported for other complexes in chloroform, competitive complexation experiments were performed to obtain relative stabilities. Simple arenes such as *m*-xylene and bibenzyl were unable to compete with 1 for the silver ion in 1:1:1 chloroform-*d* solutions. Competitive complexation experiments have been reported in studies of the more elaborate triaryl complexes 5–7.[7] By combining those results with our experiments, the relative stability constants for the known, highly stable silver:arene complexes can be shown to be K^5_{comp}:K^6_{comp}:K^7_{comp}:K^3_{comp} = 2.4:1.0:0.11:≲0.01, respectively.

The X-ray crystal structure, Figure 2, was informative. The geometry of the ligand in 3 is very similar to the geometry of the uncomplexed ligand 1.[2] This relationship, which has been noted in other silver:arene complexes,[7] might suggest that the arene–silver bond is not strong enough to form if that would require a substantial distortion of the ligand geometry. The planes defined by the phenyl rings in 3 are essentially perpendicular to the plane defined by the central double bond. The slight lengthening, 0.01–0.015 Å, of the *t*-Bu—C= bond in 3 compared to 1 probably reflects delocalization of the positive charge on the phenyl rings onto the central carbon of the *t*-Bu group. The phenyl rings are planar. The 8.3° (Ph—C=C—Ph) twist about the central double bond in 3 (Figure 2, End) is twice that in 1 (4.45°). Both phenyl groups in 3 are slightly tilted toward the silver ion, leading to a pyramidalization of the ipso carbons ($\angle C_4C_{17}C_{20}$ = 175.9°, $\angle C_3C_{11}C_{14}$ = 177.98°). The ipso–ipso and meta–meta distances, 2.64 Å and 3.17 (3.28) Å, are less than the van der Waals distance, 3.4 Å, normally seen between aromatic rings.

As anticipated, the silver ion is found in the cleft between and approximately equidistant from the phenyl rings in 3. The bonding pattern differs between the two rings. Silver is bound directly to the para position, Ag–C(20) = 2.579 (4) Å, of one ring and in a bridged pattern between the meta, Ag–C(13) = 2.510 (5) Å, and para, Ag–C(14) = 2.583 (5) Å, positions of the other ring. None of the Ag–C distances in 3 approach the shortest value in the range of distances, 2.40–2.69 Å, reported for 5 and 6. Silver bound to a corner and silver bound to an edge are both observed bondings patterns in silver:arene complexes, the former in 6 and the latter in 5. Thus, the presence of two different Ag–C bonding patterns in 3 is probably due to minor factors such as crystal packing forces. Lines drawn from silver to the para positions of each ring make acute angles, 85.16° and 83.28°, with their respective ring planes; therefore, the silver lies above the interior of the phenyl ring. Silver lies 0.70 Å above a line connecting the para positions. Both 5 and 6 have silver 0.24 Å above a plane defined by the nearest carbons but in these examples the silver is not over the phenyl ring. The Ag–(para carbon) line in 6 makes an angle of 105° with the plane of the ring. The shortest Ag–O distance, 2.356 (3) Å, in 3 is shorter than the 2.41–2.49 Å observed for 5 and 6, as expected. Reduced ligand stabilization, suggested by the longer Ag–C distances, must be compensated for by the increased Ag–O interaction.[7] All features of the crystal structure, bond lengths and pyramidalization at the ipso carbon, suggest the silver ion has been forced to bind in a site that is slightly larger than optimum.

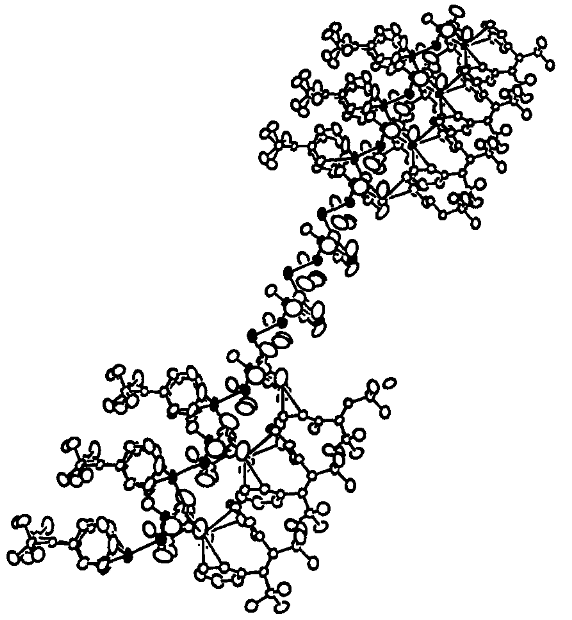

Figure 3. ORTEP plot of a section of the continuous polymeric chain formed by 3 in the solid state. The organic ligand has been removed in the center section of the chain to reveal the silver triflate units. The continuous –Ag–O–S–O– chain has been designated by blackened atoms.

In the crystal the AgOTf:1 units form straight columns, organic on the exterior and inorganic in the interior, which are laid side by side lengthwise (Figure 3). Although there are two short Ag–O distances, 2.356 (3) and 2.433 Å, to each silver, only one is to an oxygen of the triflate in the same asymmetric unit (Figure 2, Top). The two short O–Ag–O bonds are part of a continuous, zigzag, ...O–Ag–O–S–O–Ag–O–S..., chain extending in a helical fashion through the crystal as shown in the center portion of Figure 3, where the organic portions have been removed. The organic ligands 1 extend out from this chain on alternating sides. In contrast, silver complexes 5 and 6 were both found to crystallize in monomeric units. The bibenzyl:silver complex is also polymeric.

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Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*(A2)
Ag	0.90981 (2)	0.29118 (4)	0.79232 (1)	5.536 (7)
S	1.08600 (7)	0.5724 (1)	0.84826 (5)	5.50 (2)
F1	1.2444 (2)	0.4880 (6)	0.8261 (2)	11.9 (1)
F2	1.2643 (3)	0.5364 (6)	0.9324 (2)	13.6 (1)
F3	1.1999 (4)	0.3299 (5)	0.8873 (2)	13.3 (2)
O1	1.0283 (2)	0.4791 (5)	0.7908 (1)	7.22 (8)
O2	1.1067 (3)	0.7222 (4)	0.8270 (2)	7.8 (1)
O3	1.0573 (3)	0.5644 (5)	0.9092 (2)	9.6 (1)
C1	0.6862 (3)	0.0438 (6)	1.0238 (2)	6.7 (1)
C2	0.6651 (2)	−0.0028 (4)	0.9490 (2)	4.46 (7)
C3	0.6895 (2)	0.1340 (4)	0.9061 (1)	3.34 (6)
C4	0.6377 (2)	0.2597 (4)	0.8743 (2)	3.25 (6)
C5	0.5352 (2)	0.3270 (4)	0.8700 (2)	3.99 (7)
C6	0.4533 (3)	0.2518 (7)	0.8113 (3)	7.2 (1)
C7	0.7301 (3)	−0.1459 (5)	0.9491 (2)	6.4 (1)
C8	0.5596 (3)	−0.0658 (5)	0.9141 (2)	6.4 (1)
C9	0.5332 (3)	0.5027 (6)	0.8586 (3)	8.1 (1)
C10	0.5138 (3)	0.3146 (6)	0.9379 (2)	6.4 (1)
C11	0.7915 (2)	0.1197 (4)	0.9025 (1)	3.60 (6)
C12	0.8095 (3)	0.0389 (5)	0.8500 (2)	4.90 (8)
C13	0.9043 (3)	0.0295 (6)	0.8469 (2)	6.47 (9)
C14	0.9811 (3)	0.1044 (6)	0.8971 (2)	8.1 (1)
C15	0.9635 (3)	0.1876 (6)	0.9519 (3)	7.2 (1)
C16	0.8699 (3)	0.1910 (5)	0.9534 (2)	5.13 (9)
C17	0.6849 (2)	0.3539 (4)	0.8314 (2)	3.75 (6)
C18	0.6641 (3)	0.3180 (5)	0.7613 (2)	5.26 (9)
C19	0.7122 (3)	0.3937 (6)	0.7215 (2)	7.0 (1)
C20	0.7794 (3)	0.5091 (6)	0.7509 (2)	7.6 (1)
C21	0.7986 (3)	0.5484 (5)	0.8203 (3)	7.2 (1)
C22	0.7520 (2)	0.4721 (5)	0.8611 (2)	5.37 (9)
C23	1.2037 (4)	0.4765 (7)	0.8744 (2)	7.7 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

Summary and Conclusions

The combination of a nearly optimal complexing cleft and steric hindrance to alternative complexation sites in (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (**1**) provides the opportunity for formation of unusually stable metal complexes with predictable structures. Complex **3**, in the solid phase, is shown to be a 1:1 complex. The silver ion is located between the cleft formed by the phenyl rings. Individual units are connected in a polymeric chain. Further work is in progress to establish the extent of the series of metal complexes of **1**.

Experimental Section

((*Z*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene)silver(I) Triflate (3). In Ethanol. A solution was prepared containing 15.1 mg (0.052 mmol) of **1** and 9.5 mg (0.055 mmol) of silver nitrate in 0.625 mL of absolute ethanol by being heated at 80 °C in a water bath. ^{1}H NMR analysis showed a 0.03 ppm downfield shift of the aromatic resonances in **1**. **In THF.** Solid **1** (17.0 mg, 0.058 mmol) and silver triflate (16.7 mg, 0.065 mmol) were sealed in a flask under argon with a rubber septum. Freshly distilled (sodium benzophenone ketyl) THF (4 mL) was added via syringe. After stirring for 1 h, the solvent was removed under vacuum, giving a white solid. Trituration with $CDCl_3$ and removal of solvent under vacuum gave colorless crystals of **3**, which displayed the same ^{1}H NMR spectrum after melting, mp = 195–196 °C, as before melting. In the presence of ethanolic HCl, **3** gave a white precipitate. **3**: ^{13}C NMR[1] (see Table I); ^{1}H NMR (see Table I). Anal. Calcd: C, 50.28; H, 5.14. Found: C, 49.56; H, 5.28. Since decreasing the concentration to obtain a UV spectrum also decreased the fraction of complexed ligand, it was not possible to obtain a satisfactory spectrum even with short pathlength cells. More concentrated solutions showed tailing of the UV absorption out to 300 nm.

Determination of K. A stock solution of **3** in $CDCl_3$ (0.018 M) was diluted to give six samples over the concentration range 0.018 to 0.0007 M. ^{1}H NMR spectra were measured at 400 MHz (VXR-400). The chemical shift of the most downfield signal in the most downfield triplet ($\delta = 6.870$ in **1**) was recorded. The data was fitted to the following equation:

$$\delta_{obs} = (\delta_1[1] + \delta_3[3])/([1] + [3])$$

$$= (\delta_1[1] + \delta_3(S - [1]))/S \qquad S = [1] + [3]$$

The chemical shifts for pure **1**, pure **3**, and the equilibrating mixture are δ_1, δ_3, and δ_{obs}, respectively.

X-ray Analysis of 3. A colorless crystal of $C_{23}H_{28}AgF_3O_3S$ crystallized from dichloromethane having approximate dimensions of 0.20 × 0.16 × 0.06 mm was mounted on a glass fiber in a random orientation. Data collection was performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer. The monoclinic cell parameters and calculated volume are $a = 14.469$ (5), $b = 8.541$ (2), and $c = 20.386$ (4) Å, $\beta = 109.96$ (2)°, $V = 2368.1$ Å^3. For $Z = 4$ and $M_r = 549.41$ the calculated density is 1.54 g/cm^3. The space group was determined to be $P2_1/c$. The data were collected at a temperature of 21 ± 1° using the ω–2θ scan technique. Data were collected to a maximum 2θ of 52.0°. A total of 5186 reflections were collected, of which 4984 were unique. A total loss in intensity of 4.1% was measured. An anisotropic decay correction was applied ranging from 0.990 to 1.063 with an average value of 1.022. The linear absorption coefficient is 9.7 cm^{-1} for Mo Kα radiation. Relative transmission coefficients ranged from 0.916 to 0.999 with an average value of 0.969. The structure was solved by direct methods and refined by full matrix least squares. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. Only the 3479 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 280 variable parameters and converged (largest parameter shift was 0.02 times its esd) with unweighted and weighted agreement factors of $R_1 = \sum|F_o - F_c|/\sum F_o = 0.040$, $R_2 = (\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2} = 0.062$. The standard deviation of an observation of unit weight was 2.17. All calculations were performed on a VAX11/750 computer using SDP/VAX.[9] Final atomic positions are given in Table II.

Acknowledgment. A gift of **4** was kindly provided by V. Boekelheide. Financial support from The Ohio Research Challenge Program (J.G.) and the Arts and Sciences College X-ray Facility and the technical assistance of Sean Klopfenstein and discussions with Alan Pinkerton are gratefully acknowledged.

Supplementary Material Available: Experimental details, table of bond distances, table of bond angles, and table of dihedral angles for X-ray structure **3** (13 pages). Ordering information is given on any current masthead page.

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[9] Frenz, B. A. "The Enraf-Nonius CAD 4 SDP - A Real-time System for Concurent X-Ray Data Collection and Crystal Structure Determination" in *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R. van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

Regioselective Reductions of Diacids: Aspartic Acid to Homoserine

Bing Gong and David G. Lynn*

Searle Chemistry Laboratory, 5735 Ellis Avenue, The University of Chicago, Chicago, Illinois 60637

Received December 22, 1989

Intermediary metabolism centers on the controlled interconvertion of low-molecular weight, heavily functionalized carbon compounds, many containing repetitive functionalities. Examples include the polyhydroxylated compounds of glycolysis and the Calvin cycle, the di- and tricarboxylic acids of the Krebs cycle, and the diamino and