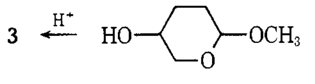
Table I. Rates of Acidic Solvolysis of Several Bicyclic Acetals[6]

Acetal	k_1, sec^{-1}	Acid concn. C_{HA}, M	Relative reactivity
2	5.3×10^{-3}	6.3×10^{-4}	6.9×10^5
3	1.8×10^{-3}	6.3×10^{-3}	2.5×10^4
1	1.8×10^{-4}	6.3×10^{-3}	2.5×10^3
7	5.8×10^{-5}	6.3×10^{-1}	7.7 (ref 1)
8			1 (ref 1)

tion of the bicyclization technique described above gave 2,7-dioxabicycloheptane **3** in 85% yield (by gc), bp 47° (30 mm). It could also be made from 2-methoxy-5-hydroxytetrahydropyran[5] (**6**) in 39% yield.

$$HOCH_2CHOHCH_2CH_2CH(OCH_3)_2 \xrightarrow{H^+}$$

5



6

Tremendous differences in reactivity among these compounds were indicated by measurements of their rates of acid-catalyzed solvolysis (Table I). In the series **2**, **3**, **1**, 6,8-dioxabicyclo[3.2.1]octane (**7**), and dimethyl acetal (**8**), the half-lives increased by a factor of $>10^2$ as the total acid concentration was increased by a factor of 10^3. The approximate relative reactivities under these conditions thus span more than five powers of ten. These differences are traceable to ring strain and anomeric effect. Work is currently under way to establish the respective contributions of undissociated acid and of oxonium ion.

These new monomers are expected to be of interest in studies of polymerization to polysaccharide analogs,[1,2,7] the thermochemistry of acetals,[8] and the study of acetal solvolysis mechanisms and lysozyme action.[9]

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A Platinum(II) Complex Containing a Metallodithiocarboxylate Ligand

Sir:

Although thiocarbonyl complexes of several metals are now known,[1] none has been reported for Pt(II). In our attempts to prepare such a complex, we not only found evidence for the formation of a reactive platinum thiocarbonyl complex but also observed that it is slowly converted into a very stable Pt(II) complex containing the novel metallodithiocarboxylate bidentate ligand, the first ligand of this type to be observed. The molecular structure of the complex has been established by an X-ray crystallographic investigation.

When 0.46 g of *trans*-$(Ph_3P)_2Pt(Cl)[C{=}S)OMe]$[2a] in 15 ml of CH_2Cl_2 was stirred under 1 atm of BF_3 for 18 hr at 25°, the solution changed from pale to deep yellow. The BF_3 and solvent were removed under a stream of N_2 leaving a yellow oil which solidified on gently warming under vacuum. While attempts to recrystallize and purify the solid yielded only oils, the compound did exhibit a strong band in its infrared spectrum at 1400 cm^{-1} in a position characteristic of the thiocarbonyl ligand;[1] it also exhibited a broad absorption at 1050 cm^{-1} typical of the BF_4- ion. This evidence together with the presence of only phenyl proton resonances in its pmr spectrum suggested that the compound could be formulated as $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$.[2b] While C, H, Cl, S, and F analyses of the compound were close to this composition, they were not satisfactory. That $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$ was the predominant compound in the solid, however, was supported by its ready reaction with MeOH and Me_2NH in CH_2Cl_2 at 25° to give the following known and expected[3] products in 60–70% yield.

$$(Ph_3P)_2Pt(Cl)(CS)^+ \begin{array}{l} \xrightarrow{MeOH} (Ph_3P)_2Pt(Cl)[C({=}S)OMe]^2 \\ \xrightarrow{Me_2NH} (Ph_3P)_2Pt(Cl)[C({=}S)NMe_2]^4 \end{array} \quad (1)$$

When a CH_2Cl_2 solution of the impure $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$ was shaken with a small amount of H_2O, the 1400-cm^{-1} absorption of the CS ligand disappeared and a new band appeared at 2115 cm^{-1}. The position of this product band was identical with that of a sample of $[(Ph_3P)_2Pt(Cl)(CO)]BF_4$ prepared by a different route.[5]

$$(Ph_3P)_2Pt(Cl)(CS)^+ + H_2O \longrightarrow (Ph_3P)_2Pt(Cl)(CO)^+ + H_2S \quad (2)$$

This reaction presumably proceeds *via* H_2O attack at the thiocarbonyl carbon atom as proposed for the conversion of the CS ligand in $W(CO)_5(CS)$ into a C≡NR group on reaction with primary amines.[6] Even the solid $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$ undergoes slow hydrolysis according to eq 2 when exposed to the atmosphere for several hours.

If a solution of $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$ in CH_2Cl_2-hexane is allowed to stand under an air atmosphere at 25° for 1 to 2 days, air-stable yellow crystals (35–40% yield) suitable for X-ray analysis are formed. When recrystallized from acetonitrile-ethyl ether, the compound analyzes correctly for $[Cl(Ph_3P)_2Pt(CS_2)Pt(PPh_3)_2]BF_4$. *Anal.* Calcd: C, 53.3; H, 3.65; Cl, 2.16; S, 3.91. Found: C, 52.6; H, 3.51; Cl, 1.69; S, 4.12. The compound is stable on heating in air up to its melting point, 258-261°. It is a 1:1 electrolyte in CH_2Cl_2 solution and exhibits a broad band at 1050 cm^{-1} in its infrared spectrum characteristic of the BF_4^- anion.

The crystal used for the structure determination of this compound contained approximately 0.2 mol of CH_2Cl_2 per mole of complex. Data were collected on a fully automated Syntex $P2_1$ four-circle diffractometer using monochromatic Cu Kα (1.5418 Å) radiation. There are four molecules of complex in the unit cell which belongs to the common space group $P2_1/c$. Diffractometer measured cell constants for the monoclinic unit cell are a = 15.577 (1), b = 16.539 (3),

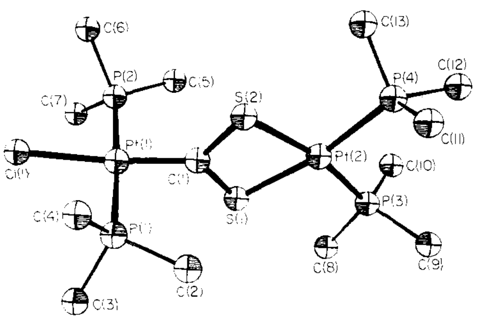

Figure 1. A computer generated perspective drawing of $[Cl(Ph_3P)_2Pt(CS_2)Pt(PPh_3)_2]BF_4 \cdot 0.2CH_2Cl_2$. The phenyl carbons of the PPh_3 groups have been omitted for clarity.

and $c = 27.190$ (2) Å and $\beta = 95.061$ (7)°. A total of 5351 reflections were judged observed after correction for Lorentz, polarization, and background effects. All 90 nonhydrogen atoms were located using heavy atom methods. Full-matrix least-squares refinement[7] varying positional and anisotropic thermal parameters for the atoms of the complex and positional and occupancy parameters for the solvent converged to the present discrepancy index of 0.07.

The computer generated drawing (Figure 1) of the dimeric cation shows a square-planar geometry about each of the platinum atoms with the two planes being perpendicular (89.97°) to each other. Donor groups to Pt(2) involve P(3) and P(4) of the two Ph_3P ligands and two sulfur atoms of the metallodithiocarboxylate ligand, $(Ph_3P)_2(Cl)Pt(CS_2^-)$. Structurally this ligand is similar to the familiar dithio acid $(R\text{-}CS_2^-)$, xanthate $(RO\text{-}CS_2^-)$, and dithiocarbamate $(R_2N\text{-}CS_2^-)$ ligands.[8,9] The Pt(2)-S(1), 2.353 (5) Å, and Pt(2)-S(2), 2.361 (5) Å, bond distances are similar to an average value of 2.32 Å reported for the Pt-S bond distances in the dithiocarbamate complex, $(Et_2NCS_2)_2Pt$.[10] The S(1)-Pt(2)-S(2) bond angle is 72.4 (2)° as compared to 75.5° for the analogous angle in the above-mentioned dithiocarbamate complex. The C(1)-S(1), 1.709 (21) Å, and C(1)-S(2), 1.692 (20) Å, bond distances and the S(1)-C(1)-S(2) bond angle (109.9 (9)°) are very similar to related parameters reported[8,9] for a variety of dithiocarbamate and xanthate complexes. The Pt(1)-C(1) bond distance (1.950 (15)Å) is among the shortest Pt-C(sp^2) distances known. In the Pt-carbene complexes where this bond might be expected to be shortened due to multiple bonding, the values[11-13] range from 1.98 to 2.13 Å. For the complex *cis*-$PtCl_2(PEt_3)[C(OMe)(NHPh)]$ where the bond distance[14] is 1.98 (2) Å, Cotton and Lukehart[13] have estimated a Pt-C(sp^2) bond order of 1.2 suggesting the presence of some Pt to C π-bonding. The shortness (1.95 Å) of the Pt(1)-C(1) bond in the metallodithiocarboxylate ligand suggests Pt to C π-bonding occurs here as well. Further structural details can be found in Tables I-III (supplementary material).

While we have not been able to definitively establish the path which leads from the impure $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$ to the metallodithiocarboxylate complex, a possible route is one which involves initial slow hydrolysis (eq 2) of the reactive thiocarbonyl complex by small amounts of atmospheric moisture. This could be followed by attack of H_2S produced in reaction 1 on unreacted thiocarbonyl complex (eq 3). The resulting metallodithiocarboxylate ligand could then react (eq 4) with the carbonyl complex generated in reaction 1 to give the dimeric product. Support for reaction 3 derives from the mechanism postulated for the reaction of $(R_3P)_2Pt(Cl)(CO)^+$ with H_2O to form CO_2 and $(R_3P)_22Pt(Cl)H$. It involves H_2O attack at the carbonyl carbon atom.[15] In the formation of the metallodithiocarboxylate complex, the concentration of H_2O is important. At high concentrations, only the carbonyl complex is produced as noted above (eq 2). Very low concentrations presumably allow reactions 3 and 4 to occur, resulting in the formation of the dimeric product.

$$(Ph_3P)_2Pt(Cl)(CS)^+ + H_2S \longrightarrow (Ph_3P)_2Pt(Cl)(CS_2^-) + 2H^+ \qquad (3)$$

$$(Ph_3P)_2Pt(Cl)(CS_2^-) + (Ph_3P)_2Pt(Cl)(CO)^+ \longrightarrow [(Ph_3P)_2(Cl)Pt(CS_2)Pt(PPh_3)_2]^+ + Cl^- + CO \qquad (4)$$

The unusually high stability of this metallodithiocarboxylate complex suggests that it will be possible to synthesize other complexes bearing this general type of ligand.

Supplementary Material Available. The fractional coordinates (Table I), bond distances (Table II), and important bond angles (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-656.

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On the Alleged Intermediacy of a Silacyclopropane in the Pyrolysis of Phenyltrimethylsilyldiazomethane

Sir:

The synthesis, isolation, and characterization of the long elusive silacyclopropane ring system by Seyferth[1] can be expected to remove inhibitions from the proposal of such compounds as reactive intermediates. Earlier this year Ando