Table IIIA. Atomic Positional Parameters for 3[a]

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Rh(3) | 0.10808 (4) | 0.44528 (4) | 0.29666 (2) |
| Br(1) | 0.15686 (5) | 0.32874 (5) | 0.39598 (3) |
| Br(2) | 0.28032 (5) | 0.26288 (6) | 0.18850 (4) |
| P(1) | −0.00997 (13) | 0.34912 (13) | 0.23514 (8) |
| P(2) | 0.47492 (14) | 0.01962 (14) | 0.28169 (9) |
| C(1) | −0.0097 (6) | 0.6248 (5) | 0.3893 (3) |
| C(2) | 0.1356 (6) | 0.5829 (6) | 0.3986 (4) |
| B(4) | −0.0380 (6) | 0.6157 (6) | 0.2891 (4) |
| B(5) | −0.0772 (8) | 0.7591 (7) | 0.3747 (5) |
| B(6) | 0.0300 (8) | 0.7374 (7) | 0.4451 (5) |
| B(7) | 0.2183 (7) | 0.5399 (7) | 0.3107 (5) |
| B(8) | 0.1088 (6) | 0.5638 (6) | 0.2365 (4) |
| B(9) | −0.0047 (7) | 0.7261 (7) | 0.2799 (5) |
| B(10) | 0.0353 (8) | 0.8006 (7) | 0.3745 (5) |
| B(11) | 0.1699 (9) | 0.6886 (8) | 0.3951 (6) |
| B(12) | 0.1530 (8) | 0.6791 (8) | 0.2934 (5) |
| H(P2) | 0.3672 (54) | 0.1037 (53) | 0.2673 (33) |
| H(1) | −0.0486 (55) | 0.6139 (55) | 0.4237 (35) |
| H(2) | 0.1633 (55) | 0.5478 (55) | 0.4354 (35) |
| H(4) | −0.1129 (54) | 0.6084 (52) | 0.2616 (33) |
| H(5) | −0.1691 (54) | 0.8178 (54) | 0.3955 (33) |
| H(6) | 0.0014 (51) | 0.7787 (52) | 0.5098 (34) |
| H(7) | 0.3099 (56) | 0.4926 (52) | 0.3094 (33) |
| H(8) | 0.1490 (49) | 0.5185 (50) | 0.1621 (33) |
| H(9) | −0.0510 (52) | 0.7733 (52) | 0.2406 (33) |
| H(10) | 0.0244 (51) | 0.8903 (55) | 0.3994 (33) |
| H(11) | 0.2346 (53) | 0.7046 (52) | 0.4290 (34) |
| H(12) | 0.2122 (53) | 0.6942 (52) | 0.2653 (33) |

[a] Units of each esd, in parentheses, are those of the least-significant digit of the corresponding parameter.

less than 3 times their standard deviations were considered to be unobserved and were omitted from subsequent calculations.

**Solution and Refinement of the Structure.** The coordinates of the rhodium atom and two bromine atoms were determined by solution of a three-dimensional Patterson map, and a subsequent Fourier summation resulted in the location of all non-hydrogen atoms. The six phenyl groups and the benzene solvate were described as rigid $C_6$ hexagons with C–C = 1.39 and C–H = 1.0 Å. The 11 hydrogen atoms of the $C_2B_9H_{11}$ cage and the remaining hydrogen atom of the cation were located on difference maps. After several cycles of full-matrix least-squares refinement, with anisotropic thermal parameters for Rh, Br, P, and the cage $C_2B_9$ atoms and isotropic thermal parameters for the remaining atoms, convergence was reached with $R$[23] = 0.046 and $R_w = 0.054$. The refinement included positional and anisotropic thermal parameters for Rh, P, Br, and the $C_2B_9$ cage, positional and isotropic thermal parameters for the hydrogen atom of the cation, group and carbon isotropic thermal parameters for the phenyl groups and benzene molecules, and positional parameters for the remaining nongroup hydrogen atoms (Table IIIA). For the latter hydrogen atoms, $B$ was set at 1.0 + $B$ of the carbon atom to which the hydrogen atom is attached. The "goodness of fit" was 1.576, defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, with $N_o$ (number of observations) = 6054 and $N_v$ (number of variables) = 275. On a final difference map, the highest peak is 0.5 e/Å$^3$. There are six such peaks, all within 1 Å of $PPh_3$ or $HPPh_3^+$.

Scattering factors for Rh, Br, P, C, and B were taken from ref 25 and for H from Stewart, Davidson, and Simpson.[24] Real and imaginary terms for anomalous scattering were taken from ref 25. The function $\sum w||F_o| - |F_c||^2$ was minimized in the refinement.

The final observed and calculated structure factors are available as supplementary material.

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**Registry No.** **1**, 53687-46-0; **2**, 68914-09-0; $[HPPh_3]$[**3**], 87226-21-9; K[18-crown-6][**3**], 87226-23-1; **5**, 82807-97-4; K[18-crown-6][**6**], 87226-29-7; $[(n\text{-}C_4H_9)_4N]$[**7**], 87226-25-3; $[Et_4N]$[**8**], 87226-27-5; $[Et_4N]$[*closo*-3-$Ph_3P$-3-CO-3,1,2-$RhC_2B_9H_{11}$], 8226-31-1; $BF_3$, 7637-07-2; $B_2H_6$, 19287-45-7; $BBr_3$, 10294-33-4; benzhydroxamic acid chloride, 698-16-8; bromoform, 75-25-2.

**Supplementary Material Available:** Atomic thermal parameters for **3** (Table IIIB) and a listing of structure factor amplitudes for $[HPPh_3]$[*closo*-3-$Ph_3P$-3,3-$Br_2$-3,1,2-$RhC_2B_9H_{11}$] (22 pages). Ordering information is given on any current masthead page.

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# Notes

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## Crystal and Molecular Structure of ($\eta^5$-Pentamethylcyclopentadienyl)(trifluoromethanesulfonato)iron(II) Dicarbonyl: A Strong Electrostatic Iron–Triflate Interaction

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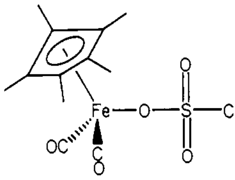
We wish to report here the X-ray crystallographic study of ($\eta^5$-pentamethylcyclopentadienyl)(trifluoromethanesulfonato)iron(II) dicarbonyl (**1**), the first transition-metal triflate to be so characterized.

Although a wide range of organometallic complexes containing sulfur–oxygen ligands has been reported in recent years,[1] a relatively small number of sulfonato complexes of transition metals has been described.[2-6] Much of the interest in these complexes stems from the behavior of the sulfonate group, which has the capacity to function as a mono-, di-, or tridentate ligand and to vary its mode of bonding. Thus, in $(CO)_5Re(OSO_2R)$ (R = $CH_3$, $C_6H_5$, $p\text{-}CH_3C_6H_4$),[4] normal monodentate coordination appears to be observed. Multidentate behavior is observed with titanium in $(TiCl_2(OSO_2CF_3)_2)_2$[2] and $(TiCl_3(OSO_2CF_3))_x$.[2]



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[‡] U.S. Army Research Office.

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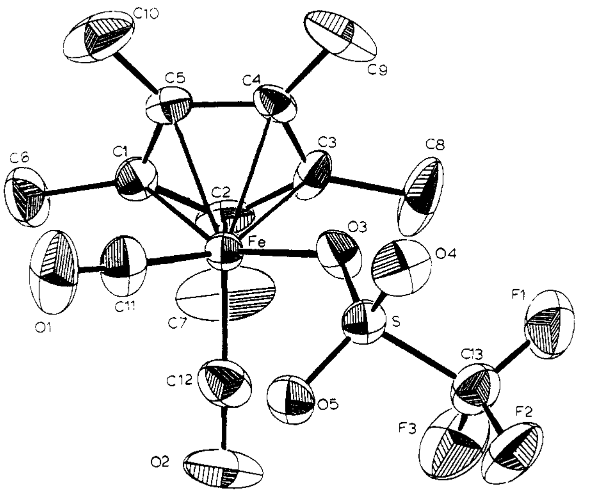

**Figure 1.** ORTEP view of **1** showing the atomic labeling scheme. Non-hydrogen atoms are represented by 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Complexes containing trifluoromethanesulfonate ($OSO_2CF_3$, triflate) ligands show a special propensity to ionize easily. Sargeson et al. have reported that the (triflato)cobalt(III) ammine complex $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ undergoes very rapid and efficient substitution to form a wide range of complexes.[6] Facile substitution reactions of the "nearly coordinatively unsaturated" $Mn(CO)_5(OSO_2CF_3)$[3a] also occur. In this system, the triflate ligand was proposed to be only nominally coordinated to manganese. These reactions parallel the ability of triflate to function as a good leaving group in nucleophilic substitution reactions at carbon in organic compounds.[7]

**Results and Discussion**

The crystal structure consists of monomeric $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeOSO_2CF_3$ units that are well separated from each other. A view of the complex is given in Figure 1. Selected bond distances and angles are listed in Table I.

The coordination geometry about the iron atom is roughly octahedral with the pentamethylcyclopentadienyl group (Cp′) occupying three ligand sites and the carbonyl and triflate ligands positioned in the other three sites.

The bond distances and angles involving the carbonyl ligands are comparable to values reported for related systems.[8,9] The Fe–Cp′ bond distances in **1** range from 2.069 (5) to 2.108 (5) Å, with an average $Fe\text{–}C_{ring}$ distance of 2.090 (15) Å, and are similar to those found in $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeSO_2CH_2CH{=}CH(Ph)$ (average 2.115 (16) Å)[8] and in $[\eta^5\text{-}C_5(CH_3)_5]_2Fe$ (average 2.050 (2) Å).[10] In **1**, the C–C bond distances and angles in the pentamethylcyclopentadienyl ligand are normal. The ring carbons are nearly planar, with no atom deviating from the plane by more than 0.023 (6) Å.

Although the triflate group is an ambidentate ligand that can act as a bridging group, in **1** it is coordinated in a monodentate fashion by an oxygen linkage. Whereas no structural data on transition-metal-coordinated triflate ligands are available, there are several reports concerning the structure of the uncoordinated triflate anion.[11] A comparison of these data to the results obtained for **1** indicates that the structure of the triflate group is relatively unchanged by metal coordination. Overall, the triflate ligand assumes a staggered conformation around the S–C bond. The average C–F bond length in **1** of 1.311 (10) Å is close to the values found in the free anion,[11] and the S–C bond distance of 1.805 (6) Å compares well with the distances found in the anion[11] as well as with the value of 1.817 (5) Å expected for a S–C bond.[12] The repulsions between the oxygen atoms in **1** are apparently greater than those between oxygen and the trifluoromethyl group. Consequently, the O–S–O and F–S–O angles are greater than 109.5° while the C–S–O and F–C–F angles are less than 109.5°. These differences have also been observed in the free anion.[11] In the triflate anion the three sulfur–oxygen bond lengths are relatively short and essentially equal (average 1.43 Å), denoting an equivalent degree of multiple bonding in each of the sulfur–oxygen bonds. In the coordinated structure, **1**, only a slight difference is seen. The bond distances from the tetrahedral sulfur atom to the terminal oxygens, O(4) and O(5), are 1.406 (4) and 1.414 (4) Å, respectively, while the distance from sulfur to the linking oxygen, O(3), is longer at 1.454 (3) Å. The short S–O(4) and S–O(5) bond lengths are indicative of multiple bonding ($d_\pi\text{–}p_\pi$) between sulfur and the terminal oxygen atoms[15] and are within the range expected for S–O bonds.[11-14] The S–O(3) bond distance is shorter than the S–O single-bond lengths reported for organic tosylates such as **2**[12] and other related structures where the S–O(3) bond is largely covalent in nature. The relatively short S–O(3) bond distance of 1.454 (3) Å in **1** also indicates substantial multiple bonding in the S–O(3) bond. Overall, therefore, the S–O bonding in the coordinated triflate

Table I. Selected Bond Distances (Å) and Bond Angles (deg) in $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeOSO_2CF_3$ (1)

A. Bond Distances

| | | | |
|---|---|---|---|
| Fe–C(1) | 2.069 (5) | Fe–C(5) | 2.108 (5) |
| Fe–C(2) | 2.085 (5) | Fe–C(11) | 1.750 (6) |
| Fe–C(3) | 2.086 (5) | Fe–C(12) | 1.765 (7) |
| Fe–C(4) | 2.101 (4) | Fe–O(3) | 2.007 (3) |
| O(1)–C(11) | 1.159 (9) | S–C(13) | 1.805 (6) |
| O(2)–C(12) | 1.154 (10) | C(13)–F(1) | 1.309 (6) |
| S–O(3) | 1.454 (3) | C(13)–F(2) | 1.303 (7) |
| S–O(4) | 1.406 (4) | C(13)–F(3) | 1.323 (10) |
| S–O(5) | 1.414 (4) | | |

B. Bond Angles

| | | | |
|---|---|---|---|
| Fe–C(11)–O(1) | 175.9 (4) | C(11)–Fe–C(12) | 92.5 (3) |
| Fe–C(12)–O(2) | 175.8 (5) | C(12)–Fe–O(3) | 97.0 (2) |
| Fe–O(3)–S | 133.2 (2) | O(3)–Fe–C(11) | 96.8 (2) |
| O(3)–S–O(5) | 112.3 (2) | S–C(13)–F(1) | 111.6 (5) |
| O(3)–S–O(4) | 113.9 (2) | S–C(13)–F(2) | 111.5 (5) |
| O(4)–S–O(5) | 117.7 (2) | S–C(13)–F(3) | 111.5 (5) |
| O(5)–S–C(13) | 103.7 (3) | F(1)–C(13)–F(2) | 107.6 (6) |
| O(4)–S–C(13) | 104.9 (3) | F(2)–C(13)–F(3) | 107.3 (6) |
| O(3)–S–C(13) | 102.1 (3) | F(1)–C(13)–F(3) | 107.2 (6) |

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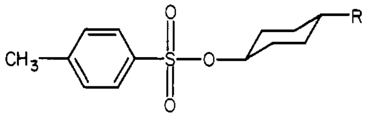

**2**

R = H: S–O = 1.57 (1) Å; S=O = 1.43 (1), 1.44 (1) Å
R = *t*-Bu: S–O = 1.561 (2) Å; S=O = 1.426 (2), 1.427 (2) Å

ligand strongly resembles, but is not identical with, the bonding arrangement in the free anion.

The Fe–O(3) bond length of 2.007 (3) Å is a normal value for an iron–oxygen single bond and agrees well with the Fe–O distance of 2.004 (10) Å reported for $(\eta^3\text{-CHCHCH}_2)\text{Fe}(\text{CO})_3[\text{OS}(\text{OBF}_3)]$[16] and the bond length of 1.957 (2) Å observed in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{O}_2\text{CH})$.[17] Thus, the Fe–O(3) bond distance in **1** gives no evidence that the triflate ligand is only weakly associated with the metal; rather, it indicates a relatively strong interaction between the iron atom and the triflate ligand. This is borne out by a mass spectroscopic analysis of **1**, which resulted in only the formation of the molecular ion M$^+$, not the Cp′(CO)$_2$Fe$^+$ cation, in contrast to the case of other organometallic salts.[18]

The normal Fe–O(3) bond length coupled with the observation that the coordinated triflate is relatively undistorted from the free anion suggests that the iron–triflate interaction is a moderately strong one but is predominantly *ionic* in nature. These solid-state results suggest that, even though metal–triflate complexes may be highly labile, the electrostatic interaction between the triflate anion and the metal cation may be substantial. Thus, implications concerning solution-state structures based solely on the lability of such complexes should be made cautiously.

## Experimental Section

**Synthesis of $[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{FeOSO}_2\text{CF}_3$ (1).** Complex **1** was obtained from the decomposition of $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Fe}{=}\text{CHC}_6\text{H}_5]^+(\text{OSO}_2\text{CF}_3)^-$. $[\text{C}_5\text{Me}_5](\text{CO})_2\text{FeCH}(\text{C}_6\text{H}_5)\text{OCH}_3$[19] (0.16 g, 0.43 mmol) dissolved in 17 mL of 2,2,4-trimethylpentane was treated at 0 °C with $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ (0.115 g, 0.52 mmol) in an equal volume of the same solvent. Precipitation of a tarry, deep red solid occurred. The supernatant was decanted under N$_2$ and the solid washed with additional solvent and then redissolved in 8 mL of anhydrous ether. The resulting clear, deep red ether solution was concentrated under nitrogen until red crystals began to precipitate. After the mixture was cooled by stages to −78 °C, the supernatant liquid was decanted and the deep red, air-stable crystals of **1** were pumped free of solvent (0.10 g, 50% yield).[20] IR (CH$_2$Cl$_2$): 2040, 1998, cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 1.70 (s). Molecular ion peak: *m/e* 396 (field desorption MS). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{O}_5\text{F}_3\text{SFe}$: C, 39.41; H, 3.82; S, 8.09; Fe, 14.10. Found: C, 39.15; H, 3.76; S, 7.84; Fe, 13.92.

**X-ray Data Collection and Reduction.** Diffraction data were collected at 20 °C on an Enraf-Nonius CAD-4 automated diffractometer using a graphite monochromator. Crystal data and data collection parameters are listed in Table II.

A total of 4328 reflections were collected, and the data were processed in the usual manner,[21] using a value of 0.01 for *p* in the estimation of the standard deviations. The intensities were corrected for Lorentz–polarization effects and for absorption by using an empirical correction based on $\psi$ scans.

**Table II.** Crystal and Data Collection Parameters for $[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{FeOSO}_2\text{CF}_3$ (1)

| | |
|---|---|
| cryst dimens | 0.15 × 0.25 × 0.55 mm |
| calcd density | 1.57 g cm$^{-3}$ |
| cryst system | orthorhombic |
| space group | *Pbca*, $D_{2h}^{15}$ |
| systematic absences | $k = 2n + 1$ for $0kl$<br>$l = 2n + 1$ for $h0l$<br>$h = 2n + 1$ for $hk0$ |
| molecules/unit cell | 8 |
| cell constants | $a$ = 14.350 (3) Å<br>$b$ = 27.304 (9) Å<br>$c$ = 8.533 (3) Å |
| cell vol | 3346.3 Å$^3$ |
| linear abs coeff, $\mu$ | 10.9 cm$^{-1}$ |
| range of transmission factors | 0.910–1.000 (0.976 av) |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.710 69 Å) |
| takeoff angle | 2.6° |
| reflcns measd | $+h, +k, +l$ |
| scan mode | $\omega$-2$\theta$ |
| scan width | $(A + B \tan \theta)°$; $A = 1.1$, $B = 0.35$ |
| scan range | $3° \leqslant 2\theta \leqslant 55°$ |
| prescan rate | 10° min$^{-1}$ |
| bkgd scan width | 25% of scan width |
| scan rate | variable (1.25–10° min$^{-1}$) |
| total reflcns | 4338 |
| reflcns with $I \geqslant 3\sigma(I)$ | 1442 |

**Table III.** Final Positional Parameters[a] for $[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{FeOSO}_2\text{CF}_3$

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Fe | 0.03012 (6) | 0.10725 (3) | 0.1860 (1) |
| S | −0.0912 (1) | 0.12762 (6) | −0.1198 (2) |
| F(1) | −0.1818 (3) | 0.2027 (2) | −0.2252 (6) |
| F(2) | −0.1129 (4) | 0.2153 (2) | −0.0106 (6) |
| F(3) | −0.0354 (4) | 0.2124 (1) | −0.2214 (6) |
| O(1) | −0.0734 (4) | 0.0159 (2) | 0.2053 (8) |
| O(2) | −0.1132 (3) | 0.1638 (2) | 0.3477 (6) |
| O(3) | −0.0033 (3) | 0.1252 (2) | −0.0350 (5) |
| O(4) | −0.1687 (3) | 0.1125 (2) | −0.0313 (6) |
| O(5) | −0.0833 (3) | 0.1098 (2) | −0.2749 (5) |
| C(1) | 0.1251 (4) | 0.0875 (2) | 0.3571 (7) |
| C(2) | 0.1265 (4) | 0.1384 (2) | 0.3395 (8) |
| C(3) | 0.1508 (4) | 0.1498 (2) | 0.1836 (8) |
| C(4) | 0.1691 (4) | 0.1050 (2) | 0.1088 (7) |
| C(5) | 0.1551 (4) | 0.0677 (2) | 0.2153 (7) |
| C(6) | 0.1116 (6) | 0.0595 (3) | 0.5074 (9) |
| C(7) | 0.1091 (6) | 0.1746 (3) | 0.4704 (11) |
| C(8) | 0.1606 (6) | 0.1998 (3) | 0.1172 (12) |
| C(9) | 0.2002 (5) | 0.0992 (4) | −0.0562 (9) |
| C(10) | 0.1728 (6) | 0.0147 (3) | 0.1896 (12) |
| C(11) | −0.0346 (5) | 0.0530 (2) | 0.1940 (9) |
| C(12) | −0.0588 (4) | 0.1412 (3) | 0.2791 (9) |
| C(13) | −0.1064 (5) | 0.1928 (3) | −0.1450 (9) |

[a] *x*, *y*, and *z* are fractional coordinates. Estimated standard deviations in parentheses.

**Structure Solution and Refinement.** The solution and refinement of the structure were carried out on a PDP-11 computer using programs supplied by Enraf-Nonius.[21] Atomic scattering factors were taken from Cromer and Waber,[22a] and the anomalous dispersion factors $\Delta f'$ and $\Delta f''$ were taken from Cromer.[22b]

The position of the iron atom was deduced from a Patterson map. Subsequent calculations of difference Fourier maps allowed the positions of the other non-hydrogen atoms to be determined. Least-squares refinement of these positions with isotropic temperature factors resulted in $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.110$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.111$. The hydrogens were placed at calculated positions[23] with isotropic temperature factors and were

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(19) This compound was obtained by methylation of $\text{C}_5\text{Me}_5(\text{CO})_2\text{FeCOCH}_3$ followed by hydride reduction using procedures previously reported: Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

(20) A more general route to triflate complexes of the type $\text{Cp}(\text{CO})_2\text{FeOSO}_2\text{CF}_3$ and $\text{Cp}'(\text{CO})_2\text{FeOSO}_2\text{CF}_3$ involves cleavage of alkyl derivatives with triflic acid in CH$_2$Cl$_2$: Humphrey, M. B.; Williams, G. O., unpublished results.

(21) The programs used during data collection and reduction were supplied by Enraf-Nonius. All programs used for structure solution and refinement were part of the Structure Determination Package (SDP) provided by B. Frenz through Enraf-Nonius.

(22) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2A; (b) Table 2.3.1.

not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to $R = 0.049$ and $R_w = 0.042$. The final cycle of least-squares refinement contained 1442 observations and 208 variables, and a final difference Fourier map showed no feature greater than 0.16 e Å$^{-3}$. The atomic positional parameters obtained from the final least-squares cycle along with their estimated standard deviations are given in Table III.

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**Registry No.** **1**, 79001-07-3; $[C_5Me_5(CO)_2Fe{=}CHC_6H_5]^+(OSO_2CF_3)^-$, 87101-25-5; $[C_5Me_5](CO)_2FeCH(C_6H_5)OCH_3$, 87101-26-6; $Me_3SiOSO_2CF_3$, 27607-77-8.

**Supplementary Material Available:** Tables of anisotropic thermal parameters for the non-hydrogen atoms of **1**, positional and thermal parameters for the hydrogen atoms in **1**, additional bond distances and angles in **1**, a least-squares plane calculation of the pentamethylcyclopentadienyl ligand in **1**, and observed and calculated structure factors for **1** (15 pages). Ordering information is given on any current masthead page.

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[23] Positions were calculated from $d$(C–H) = 0.95 Å with the program HYDRO.

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# Isomeric 2-(Arylazo)pyridine Complexes of $OsCl_2$ and $OsBr_2$

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and Animesh Chakravorty*

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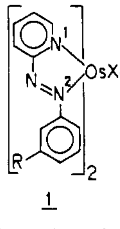
The ruthenium chemistry of unsaturated nitrogenous ligands—2,2′-bipyridine (bpy) being the prototype—has developed rapidly[1] in recent times primarily due to the relevance of this chemistry to photophysical, photochemical, and redox phenomena. In comparison to this the progress in the corresponding chemistry of osmium has been very slow.[2-5] Indications are strong, however, that this area also abounds in fascinating spectroscopic and electron-transfer phenomena.[6-9] With this background and in logical continuation to our program[10] on the chemistry of ruthenium, we have initiated research on osmium chelates of certain classes of unsaturated nitrogenous ligands. In this first report we describe the synthesis, spectra, and redox properties of the osmium(II) complexes $OsX_2L_2$ (**1**), where X = Cl and Br and L is 2-(phenylazo)pyridine (R = H; pap) and 2-($m$-tolylazo)pyridine (R = Me; tap). The ruthenium chemistry of L has developed to a considerable extent[10-14] during the last few years, but nothing is known about the corresponding osmium chemistry.



**1**

## Results and Discussion

**Synthesis.** The reaction of L with $(Et_4N)_2OsX_6$ in 2-methoxyethanol

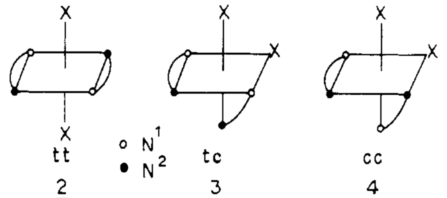
$$OsX_6{}^{2-} + 2L \rightarrow OsX_2L_2 + 4X^- \qquad (1)$$

proceeds slowly but smoothly. When the reaction mixture is concentrated and cooled, dark-colored crystals of composition $OsX_2L_2$ (isomer A) result in about 70% yield. Isomeric purity was tested by $^1H$ NMR (see below) and TLC on silica gel using 1:1 benzene–dichloromethane as developer. From the mother liquor another isomer (B) of the complex is isolated (yield 10–15%) in pure form with use of chromatographic techniques. Even when L is used in excess of 2 mol, only $OsX_2L_2$ is isolated from reaction 1; no $OsL_3{}^{2+}$ appears to be formed.

Isomer A dissolves in common organic solvents ($C_6H_6$, $CH_2Cl_2$, $CH_3CN$, etc.) to give blue-violet solutions. Solutions of the isomer B are red-violet. All complexes are diamagnetic in the crystalline state and are nonelectrolytic in nitromethane and acetonitrile.

The reduction of osmium from +4 to +2 state in reaction 1 is probably brought about by the alcoholic solvent. The ruthenium complexes, $RuX_2L_2$, similarly arise[11] from the spontaneous reductive (+3 → +2) chelation of $RuX_3$ with L in methanol.

**Isomer Characterization.** $RuX_2L_2$ occurs in three isomeric forms[10,13] designated as trans–trans ($tt$, **2**), trans–cis ($tc$, **3**) and cis–cis ($cc$, **4**) on the basis of the relative positions within the pairs $N^1,N^1$ and $N^2,N^2$. The structures of the $tc$ and $cc$ isomers of $RuCl_2(pap)_2$ are accurately known from three-dimensional X-ray work.[10,12] The IR spectra of the three isomers differ significantly in the region 4000–300 cm$^{-1}$.



**2** **3** **4**

The vibration spectra of the isomer A of $OsCl_2(pap)_2$ and $tc$-$RuCl_2(pap)_2$ (**3**) are nearly superposable in the above region except for frequency shifts particularly in the $\nu_{N=N}$ region

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