sistent with the presence of $\mu$-oxo bridges in these compounds.

**4. Conclusions.** The solvolysis of hexaphenylditin by carboxylic acids produces compounds with the empirical formula $Sn(O_2CR)_3$. Spectroscopic evidence discussed above establishes that there are two distinct types of tin, one Sn(II) and the other Sn(IV). The Sn(II) is in a very distorted environment which is rather sensitive to the nature of the carboxylate ligand coordinated to it, while the Sn(IV) is in a nearly regular environment and is much less influenced by the nature of ligand. Comparison with the analogous $Sn(O_2CR)_2$ and $Sn(O_2CR)_4$ compounds clearly shows that these new compounds are not mixtures of the corresponding Sn(II) and Sn(IV) species. Vibrational spectroscopy suggests that the carboxylate ligands bridge the Sn(II) and Sn(IV) atoms. If all of the carboxylate groups were involved in bridging the tin atoms, then a polymeric structure would be most likely. However, there is strong evidence that some of the carboxylates are present in the form of coordinated anhydride, and furthermore the lack of any significant Mössbauer absorption at room temperature, while not conclusive, argues against a polymeric structure.

We have noted above the good correlation between our Mössbauer data and those obtained by Harrison and coworkers for $[Sn^{II}Sn^{IV}O(O_2CC_6H_4\text{-}o\text{-}NO_2)_4THF]_2$. The structure of $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2\cdot C_6H_6$ recently reported by us[8] is also very similar in structure to Harrison's compound. It was obtained by a modification of the preparation reported here and contains a molecule of benzene, but no trifluoroacetic anhydride, and one coordination site in the equatorial plane about the tin(II) site is vacant. All of the spectroscopic evidence presented on the compounds reported here indicates that they have the same basic structure as these two compounds.[7,8] The central cluster of two Sn(II) and two Sn(IV) atoms would then be held together by two $\mu_3$-oxo bridges and eight carboxylate ligands, each of which would bridge a Sn(IV) and a Sn(II). In this way the Sn(IV) atoms could achieve six-coordination from two $\mu_3$-bridging oxygens, which are cis to one another, and from four carboxylate oxygens to give an almost regular octahedral arrangement. Around the Sn(II) atoms a pentagonal-bipyramidal arrangement is proposed with a bridging oxygen in one apical position and the nonbonding electron pair in the other apical site. In the equatorial plane, four positions are envisaged as being occupied by four carboxylate oxygens, and the fifth position, which is vacant in $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2\cdot C_6H_6$ and occupied by THF in $[Sn^{II}Sn^{IV}O(O_2CC_6H_4\text{-}o\text{-}NO_2)_4THF]_2$, is assumed to be occupied by an oxygen from a coordinated anhydride molecule.

The molecules are then best formulated as $[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$. We are presently attempting to obtain single crystals of one of these compounds containing anhydride that would be suitable for X-ray crystallographic analysis.

**Acknowledgment.** The Natural Sciences and Engineering Research Council of Canada is thanked for financial support.

**Registry No.** $Sn(O_2CCF_3)_3$, 82661-20-9; $Sn(O_2CCCl_3)_3$, 82661-21-0; $Sn(O_2CCHCl_2)_3$, 82661-22-1; $Sn(O_2CCH_2Cl)_3$, 82661-23-2; $Sn(O_2CCH_3)_3$, 82665-07-4; $Sn(O_2CCF_2CF_2CF_3)_3$, 82661-24-3; $Sn(O_2CC(CH_3)_3)_3$, 82661-25-4; $Sn(O_2CCF_3)_4$, 16424-89-8; $Sn(O_2CCCl_3)_4$, 82661-27-6; $Sn(O_2CCHCl_2)_4$, 66096-29-5; $Sn(O_2CCH_2Cl)_4$, 62487-22-3; $(C_6H_5)_6Sn_2$, 1064-10-4; $(C_6H_5)_4Sn$, 595-90-4; $Sn(O_2CC_3F_7)_4$, 82661-26-5.

---

Contribution from the Department of Chemistry,
University of Regina, Regina, Saskatchewan S4S 0A2, Canada

# Preparation and Crystal and Molecular Structure of a Novel Cleavage Product from the Reaction of a Bis(tertiary arsine) with $Re_2(CO)_{10}$

RICHARD J. BARTON, SHENGZHI HU,[1] LYNN M. MIHICHUK,* and BEVERLY E. ROBERTSON

*Received November 17, 1981*

The bis(tertiary arsine) *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$ reacts with $Re_2(CO)_{10}$ to give a compound of formula $C_{11}H_6AsF_6O_5Re$, the structure of which was determined by X-ray crystallography. The compound crystallizes in the space group $P\bar{1}$ with $a = 8.189$ (3) Å, $b = 8.950$ (2) Å, $c = 25.471$ (3) Å, $\alpha = 101.49$ (1)°, $\beta = 90.28$ (2)°, $\gamma = 116.78$ (2)°, and $Z = 4$. The structure was refined by blocked full-matrix least squares, with 5690 unique reflections, to $R = 0.046$ and $R_w = 0.056$. The coordination around Re is close to octahedral. An $-As(CH_3)_2$ group has been cleaved from the ligand. The $Re(CO)_4$ unit is coordinated to the remaining arsenic atoms and to a CO group, which has inserted between the rhenium atom and the olefinic carbon atom to form a five-membered ring.

## Introduction

Many of the reactions of bis(tertiary phosphines and arsines) with metal carbonyls afford simple carbonyl-substituted complexes.[2] However there are also many reports of reactions resulting in novel products as a result of ligand rearrangement or cleavage of ligand moieties.[3] In particular, the reactions of $M_2(CO)_{10}$ (M = Mn, Re) with cis-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$ afforded two different types of complexes.[3a] The Mn reaction resulted in a novel complex containing a fluorinated $\pi$-allyl group.[4] We had previously reported[3a] that the rhenium system gave a complex containing a $CH_2O$ fragment $\sigma$ bonded to rhenium through either the carbon or oxygen atom on the basis of spectroscopic evidence.

In order to verify the above findings, we determined the molecular structure of the complex that is described below.

## Experimental Section

The fluorinated arsine ligand (L–L) was prepared as described in the literature.[5] Infrared spectra were recorded on a Perkin-Elmer 457 instrument. $^{19}F$ and $^1H$ NMR spectra were recorded by using Varian T-60 and XL-100 spectrometers with chemical shifts given

---

(1) Visiting Scholar, Department of Chemistry, University of Amoy, Amoy, People's Republic of China.

(2) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stibine Complexes of the Transition Elements"; Elsevier: New York, 1979.

(3) See, for example: (a) Cullen, W. R.; Mihichuk, L.; Einstein, F. W. B.; Field, J. S. *J. Organomet. Chem.* **1974**, *73*, C53. (b) Cobbledick, R. E.; Cullen, W. R.; Einstein, F. W. B.; Mangayarkarasy, W. *Inorg. Chem.* **1981**, *20*, 186. (c) Chia, L. S.; Cullen, W. R.; Harborne, D. A. *Can. J. Chem.* **1972**, *50*, 2182. (d) Einstein, F. W. B.; Jones, R. D. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2563. (e) Barrow, M. J.; Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A.; Wilson, F. B. *J. Chem. Soc., Chem. Commun.* **1973**, 583. (f) Patel, H. A.; Fischer, R. G.; Carty, A. J.; Naik, D. V.; Palenik, G. J. *J. Organomet. Chem.* **1973**, *60*, C49.

(4) Einstein, F. W. B.; Field, J. S. *J. Chem. Soc., Dalton Trans.* **1975**, 172.

(5) Crow, J. P.; Cullen, W. R.; Herring, F. G.; Sams, J. R.; Tapping, R. L. *Inorg. Chem.* **1971**, *10*, 1616.

in ppm upfield from internal $CFCl_3$ ($^{19}F$) and downfield from internal $Me_4Si$ ($^1H$). Mass spectra were measured with an AEI MS-9 instrument. Melting points were determined in sealed evacuated capillaries with a Gallenkamp apparatus. Microanalyses were performed by Mr. P. Borda, Chemistry Department, University of British Columbia.

**Reactions of (L–L) with Dirhenium Decacarbonyl.** $Re_2(CO)_{10}$ (1 g, 1.5 mmol) and (L–L) (1.7 g, 4.5 mol) in 375 mL of degassed benzene were irradiated for 85 min with a 450-W Hanovia lamp placed in a water-cooled quartz jacket. The reaction was monitored by observing the disappearance of $Re_2(CO)_{10}$ with use of infrared spectroscopy. The final solution was dark orange (initially colorless). The benzene was removed under reduced pressure and the red oil chromatographed on a Florisil column under nitrogen. Petroleum ether (bp 30–60 °C) eluted a pale yellow band of unreacted ligand (0.5 g). A 2–10% diethyl ether/98–90% petroleum ether mixture eluted an orange band, which afforded oily orange crystals. Recrystallization from a methylene chloride/hexane mixture at −20 °C gave dark orange air-stable crystals of formula $C_{11}H_6AsF_6O_5Re$ (0.4 g, 22%); mp 151–152 °C.

Reaction between $Re_2(CO)_{10}$ and excess (L–L) in refluxing toluene or xylene resulted in complete decomposition.

Anal. Calcd for $C_{11}H_6AsF_6O_5Re$: C, 22.26; H, 1.01; F, 19.22. Found: C, 22.02; H, 1.10; F, 18.90.

The mass spectrum showed peaks due to the parent ion followed by loss of four carbonyl groups.

The IR spectrum ($C_6H_{12}$ solution) gave carbonyl frequencies at 2100 (m), 2021 (s), 1995 (s, br), 1981 (vs), and 1610 (m) $cm^{-1}$ ($CH_2Cl_2$ solution).

The $^1H$ NMR spectrum ($CDCl_3$ solution) showed a singlet at 2.13 ppm ($As–CH_3$). The $^{19}F$ NMR spectrum ($CH_2Cl_2$ solution) consisted of quartets centered at 53.2 and 59.1 ppm ($CF_3$); $J(F,F)$ = 12.4 Hz.

**X-ray Diffraction Studies.** Crystals of the compound displayed a complex variety of diffraction patterns. Examination of several crystals revealed that two crystalline phases are present and that the crystals range from being entirely of the phase reported here, which is triclinic ($P\bar{1}$), to crystals that consisted mainly of an orthorhombic phase (one of *Cmc*2$_1$, *C*2*cm*, or *Cmcm*) but that retained some of the triclinic phase. It is reasonable to assume that, under the proper crystallization conditions, crystals of the pure orthorhombic phase might be obtained.

The transformation (100/120/121), when applied to the triclinic axes, produces a pseudosymmetric cell similar to that of the orthorhombic phase, but with $\alpha = 95°$ and $\beta$ and $\gamma$ near 90°. The diffraction pattern, when indexed according to the new cell produced by the transformation, is also pseudosymmetric and approximates the Laue symmetry and extinction pattern of the orthorhombic phase. In particular very few reflections with $h + 2k = 0$ and $l = 2n + 1$ (indexed in the triclinic phase) with $I > 2\sigma(I)$ were observed because of the presence of the pseudo-*c*-glide operation. In the orthorhombic phase the *c* glide becomes exact, the angles become 90°, and the Laue symmetry is *mmm*.

Crystals of the orthorhombic phase also contained some volume of the triclinic phase in two orientations related by a mirror plane. All of the crystal volume present showed a common $c^*$ axis. The reflections belonging to the two orientations of the triclinic phase appeared as satellite reflections on either side of the peaks belonging to the orthorhombic phase. These satellite reflections could also have been interpreted as an incommensurate modulation associated with the $c^*$ direction, if a complete examination of several crystals had not been undertaken. We trust that the implications for structure determinations based on a very limited study of reciprocal space are clear.

The orthorhombic phase has one molecule per asymmetric unit if the space group is *Cmc*2$_1$ or *C*2*cm* and would be disordered with 0.5 molecule/asymmetric unit in the space group *Cmcm*. The triclinic phase has half the volume of that of the orthorhombic phase with 2 molecules/asymmetric unit.

A summary of crystal data and intensity collection is given in Table I. A total of 9364 independent data were collected in the range 3° < 2$\theta$ < 60° on a modified Picker diffractometer and reduced to structure amplitudes by using X RAY 76.[6] The structure was also solved and refined with X RAY 76.

**Table I.** Summary of Crystal Data and Intensity Collection

| | |
|---|---|
| formula | $C_{11}H_6AsF_6O_5Re$ |
| fw | 593.1 |
| $a$ | 8.189 (3) Å |
| $b$ | 8.950 (2) Å |
| $c$ | 25.471 (3) Å |
| $\alpha$ | 101.49 (1)° |
| $\beta$ | 90.28 (2)° |
| $\gamma$ | 116.78 (2)° |
| $V$ | 1623.6 Å$^3$ |
| $Z$ | 4 |
| density | 2.44 g cm$^{-3}$ (calcd); 2.43 g cm$^{-3}$ (obsd) (by flotation) |
| space group | $P\bar{1}$ |
| crystal dimens | 0.40 × 0.07 × 0.11 mm |
| temp | 20 °C |
| radiation | Mo K$\bar{\alpha}$ |
| scan speed | 2° min$^{-1}$ |
| 2$\theta$ limits | 3–60° |
| unique data obsd | 9364 |
| final no. of parameters | 577 |
| $R$ ($\Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$) | 0.046 |
| $R_w$ ($\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w F_o^2)^{1/2}$ | 0.056 |

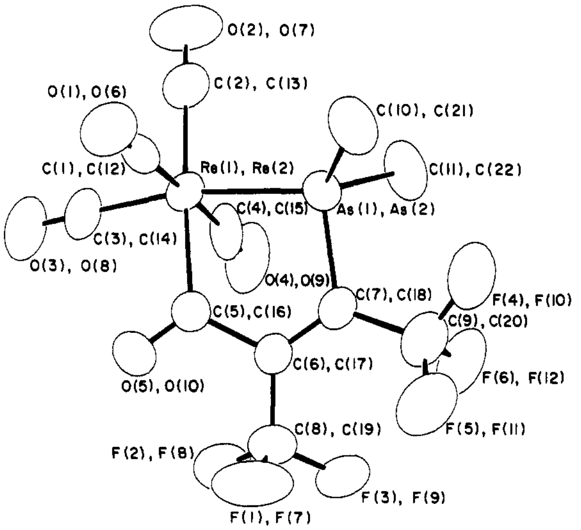


**Figure 1.** View of the molecule giving the atomic numbering scheme.

The data were corrected for the effects of absorption. Corrections were not made for the effects of secondary extinction. The structure was solved by the Patterson and heavy-atom methods with the assumption of space group $P\bar{1}$ and 2 molecules/asymmetric unit. The structure was refined by blocked full-matrix least squares by using the 5690 reflections for which $I > 2\sigma(I)$. The positions of many of the hydrogen atoms could not be inferred from the difference map and could not be inferred from geometrical considerations. Therefore hydrogen atoms were not included in the refinement. The scattering factors for the Re and As atoms were modified to account for the effect of dispersion.[7] The estimated standard deviations, $\sigma$, were based on the counting statistics of the individual reflections plus the variation in the standard reflections, and the weights of the individual reflections used in the least squares were taken as $1/(\sigma^2(F_o) + 10^{-3}F_o^2)$. Final positional parameters for the atoms of both molecules in the asymmetric unit are listed in Table II. Tables of observed and calculated structure amplitudes, thermal parameters, and nonessential bond lengths and bond angles are available as supplementary material.

## Results and Discussion

It is interesting to note that the reaction previously reported of (L–L) with $Mn_2(CO)_{10}$ only gave a product upon heating whereas the reaction with $Re_2(CO)_{10}$ only gave a product upon ultraviolet irradiation and in each case a different novel species was obtained.

---

(6) Stewart, J. M., Ed. "X RAY System (1976)", Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

(7) "International Tables of X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. 3.

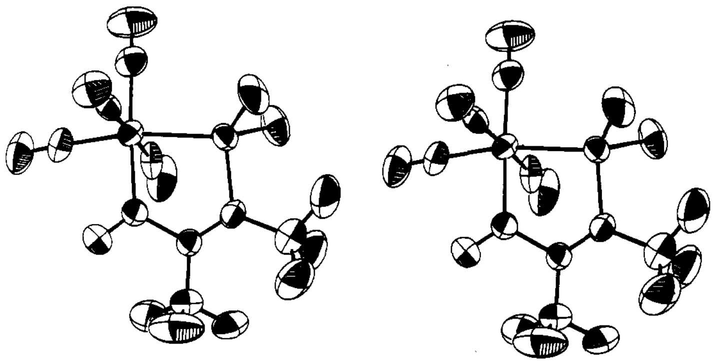


**Figure 2.** Stereoview of one of the two independent molecules in the asymmetric unit.

**Table II.** Fractional Atomic Coordinates (×$10^4$)

| | *x* | *y* | *z* |
|---|---|---|---|
| Re(1) | 3189.9 (5) | 1106.0 (5) | 4133.8 (1) |
| As(1) | 1468.9 (1.3) | 2617.8 (1.3) | 3891.8 (4) |
| F(1) | 7600 (12) | 6610 (10) | 3441 (3) |
| F(2) | 7234 (12) | 4179 (12) | 2980 (3) |
| F(3) | 5740 (10) | 5332 (9) | 2712 (3) |
| F(4) | 1315 (14) | 5449 (14) | 3465 (4) |
| F(5) | 4045 (12) | 6838 (9) | 3269 (4) |
| F(6) | 2126 (13) | 4570 (12) | 2711 (3) |
| O(1) | 4385 (12) | 3428 (10) | 5289 (3) |
| O(2) | −33 (15) | −1771 (13) | 4533 (5) |
| O(3) | 6065 (15) | −93 (13) | 4362 (4) |
| O(4) | 2316 (17) | −958 (15) | 2945 (4) |
| O(5) | 6980 (10) | 3849 (12) | 4007 (4) |
| C(1) | 3907 (13) | 2568 (12) | 4865 (4) |
| C(2) | 1132 (19) | −738 (15) | 4387 (5) |
| C(3) | 4978 (16) | 319 (15) | 4281 (5) |
| C(4) | 2586 (16) | −266 (14) | 3377 (5) |
| C(5) | 5347 (14) | 3234 (13) | 3868 (4) |
| C(6) | 4863 (12) | 4162 (12) | 3491 (4) |
| C(7) | 3279 (14) | 4195 (12) | 3498 (4) |
| C(8) | 6372 (17) | 5084 (17) | 3158 (5) |
| C(9) | 2748 (19) | 5298 (17) | 3226 (6) |
| C(10) | 843 (17) | 4014 (17) | 4463 (5) |
| C(11) | −704 (16) | 1411 (17) | 3360 (5) |
| Re(2) | 3576.2 (5) | 2329.4 (5) | 876.7 (1) |
| As(2) | 6953.7 (1.3) | 4226.4 (1.3) | 1112.9 (4) |
| F(7) | 5050 (14) | 8869 (10) | 1540 (3) |
| F(8) | 3354 (11) | 7148 (10) | 2003 (3) |
| F(9) | 6140 (12) | 8649 (9) | 2265 (3) |
| F(10) | 10185 (10) | 7755 (11) | 1527 (4) |
| F(11) | 8939 (11) | 7972 (11) | 2266 (3) |
| F(12) | 9060 (11) | 7972 (11) | 2266 (3) |
| O(6) | 3842 (13) | 3021 (11) | −283 (3) |
| O(7) | 3663 (18) | −1104 (13) | 431 (4) |
| O(8) | −622 (12) | 961 (13) | 641 (4) |
| O(9) | 3271 (13) | 1719 (12) | 2047 (3) |
| O(10) | 2501 (11) | 5214 (11) | 996 (4) |
| C(12) | 3784 (15) | 2769 (13) | 139 (5) |
| C(13) | 3651 (18) | 161 (15) | 606 (4) |
| C(14) | 949 (17) | 1352 (15) | 739 (5) |
| C(15) | 3363 (15) | 1945 (13) | 1631 (4) |
| C(16) | 3846 (13) | 4835 (12) | 1152 (4) |
| C(17) | 5362 (12) | 6364 (11) | 1503 (3) |
| C(18) | 6955 (13) | 6381 (12) | 1493 (4) |
| C(19) | 4990 (17) | 7778 (15) | 1823 (5) |
| C(20) | 8753 (16) | 7852 (15) | 1753 (5) |
| C(21) | 8572 (15) | 4794 (16) | 537 (5) |
| C(22) | 8306 (16) | 3748 (18) | 1638 (5) |

**Table III.** Important Bond Lengths (Å)

| | | | |
|---|---|---|---|
| Re(1)-As(1) | 2.498 (2) | Re(2)-As(2) | 2.498 (1) |
| Re(1)-C(1) | 1.96 (1) | Re(2)-C(12) | 1.99 (1) |
| Re(1)-C(2) | 1.98 (1) | Re(2)-C(13) | 1.95 (1) |
| Re(1)-C(3) | 1.95 (2) | Re(2)-C(14) | 1.92 (1) |
| Re(1)-C(4) | 1.99 (1) | Re(2)-C(15) | 2.01 (1) |
| Re(1)-C(5) | 2.17 (1) | Re(2)-C(16) | 2.19 (1) |
| As(1)-C(7) | 1.97 (1) | As(2)-C(18) | 1.98 (1) |
| As(1)-C(10) | 1.95 (1) | As(2)-C(21) | 1.97 (1) |
| As(1)-C(11) | 1.96 (1) | As(2)-C(22) | 1.96 (2) |
| C(1)-O(1) | 1.14 (1) | C(12)-O(6) | 1.14 (2) |
| C(2)-O(2) | 1.12 (2) | C(13)-O(7) | 1.14 (2) |
| C(3)-O(3) | 1.14 (2) | C(14)-O(8) | 1.16 (2) |
| C(4)-O(4) | 1.12 (1) | C(15)-O(9) | 1.12 (1) |
| C(5)-O(5) | 1.21 (1) | C(16)-O(10) | 1.22 (2) |
| C(5)-C(6) | 1.54 (2) | C(16)-C(17) | 1.55 (1) |
| C(6)-C(7) | 1.31 (2) | C(17)-C(18) | 1.30 (2) |
| C(6)-C(8) | 1.51 (2) | C(17)-C(19) | 1.52 (2) |
| C(7)-C(9) | 1.52 (2) | C(18)-C(20) | 1.50 (1) |

**Table IV.** Important Bond Angles (Deg)

| | | | |
|---|---|---|---|
| Re(1)-C(1)-O(1) | 178 (1) | Re(2)-C(12)-O(6) | 177 (1) |
| Re(1)-C(2)-O(2) | 179 (2) | Re(2)-C(13)-O(7) | 177 (1) |
| Re(1)-C(3)-O(3) | 178 (1) | Re(2)-C(14)-O(8) | 175 (1) |
| Re(1)-C(4)-O(4) | 176 (1) | Re(2)-C(15)-O(9) | 179 (1) |
| C(3)-Re(1)-As(1) | 168.0 (3) | C(14)-Re(2)-As(2) | 167.0 (4) |
| C(5)-Re(1)-As(1) | 78.8 (4) | C(16)-Re(2)-As(2) | 79.1 (3) |
| Re(1)-As(1)-C(7) | 100.2 (4) | Re(2)-As(2)-C(18) | 100.3 (3) |
| As(1)-C(7)-C(6) | 115 (1) | As(2)-C(18)-C(17) | 116.0 (6) |
| C(5)-C(6)-C(7) | 120 (1) | C(16)-C(17)-C(18) | 120 (1) |
| Re(1)-C(5)-C(6) | 120 (1) | Re(2)-C(16)-C(17) | 121 (1) |

The infrared spectrum shows four terminal CO bonds indicative of a $Re(CO)_4$ unit and a band at 1610 $cm^{-1}$ indicative of a ketonic CO of a metal–acyl complex.[8,9] The ketonic CO stretching frequency in metal acyls is lower (1600–1650 $cm^{-1}$) than that found for organic ketones (~1725 $cm^{-1}$).

The $^{19}F$ NMR spectrum shows two inequivalent $CF_3$ resonances, indicating an asymmetric grouping about the C═C moiety. For substantiation of the above spectroscopic results the crystal structure of the complex was determined.

## Description of the Structure

A view of the molecule giving the atomic numbering scheme is shown in Figure 1. A stereoview of one of the two independent molecules in the asymmetric unit is shown in Figure 2. An $-As(CH_3)_2$ group has been cleaved from the ligand, and a CO group has inserted between the rhenium and the olefinic carbon atom.

The Re–As bond lengths (average 2.50 Å) (see Table III) are somewhat shorter than previously reported Re–As distances (average 2.57 Å)[10,11] and shorter than the value predicted from covalent radii.[12] This shortening is thought to be due to some double-bond character in the Re–As bond caused by ($d\pi$–$d\pi$) back-donation from the Re atom. The angles subtended at the Re atom deviate substantially from

---

(8) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161.

(9) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds"; Methuen: London, 1968; Vol. 2.

(10) Maslen, E. N.; Dewan, J. C.; Kepert, D. L.; Trigwell, K. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1974**, 2128.

(11) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1201.

(12) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

octahedral values (see Table IV): C(2)–Re(1)–As(1) (97.6°), C(13)–Re(2)–As(2) (98.2°), C(3)–Re(1)–As(1) (168.0°), C(14)–Re(2)–As(2) (167.0°), C(5)–Re(1)–As(1) (78.8°), and C(16)–Re(2)–As(2) (79.1°).

The two molecules in the asymmetric unit are chemically identical. The Re(1)–C(5)–O(5) and Re(2)–C(16)–O(10) angles are 125.5 (9) and 124.2 (6)°, respectively. Also the torsional angles [C(3)–Re(1)–C(5)–O(5)] and [C(14)–Re(2)–C(16)–O(10)] are –24.9 (1.0) and –27.5 (9)°, respectively. The only apparent source of these distortions is electrostatic repulsions between the atoms O(5) and O(10) on the bridging carbonyl groups and the atoms O(3) and O(8) on the carbonyl groups trans to the As atoms. The decrease in the angles As(1)–Re(1)–C(5) and As(2)–Re(2)–C(16) from 90° also contributes to an increase in the O(3)–O(5) and O(8)–O(10) separations, but the origin of this distortion is not clear. Idealized geometry at each of the atoms in the rings would lead to nonclosure of the rings. The sp$^2$ character of the carbon atoms maintains their endocyclic ring angles near 120°. Therefore, the strain is manifested at both the As and Re atoms in each ring. The orientations of the $CF_3$ groups are then fixed by their repulsive interactions with O(5) and O(10) and between themselves, as shown in Figure 2.

The nature of the deviations of the geometry of the rings from planarity was analyzed with the procedure of Cremer and Pople.[13] The puckering of five-membered rings is defined by a phase angle $\phi$, whose value is a measure of the relative contribution of the twist and envelope conformations to the deviations from planarity of the ring atoms and $q$, the amplitude of puckering for the ring. For reference purposes, the value of $q$ for the furanoid ring of sucrose is 0.353.[14] The procedure utilizes the torsional angles about the ring bonds and may be applied to rings with unequal bond lengths such as in the present case.

The values of $q$ for the rings in molecule 1 and molecule 2 are 0.280 and 0.240, which indicates a substantial degree of puckering. The values of $\phi$ for the ring in molecule 1 and molecule 2 are 15.9 and 15.0°. A result of 0° would correspond to the envelope conformation, and a result of 18° would correspond to the twist conformation. On the basis of this criterion, the ring conformation is clearly twist.

The structure of the complex is consistent with the spectroscopic results discussed above.

**Acknowledgment.** This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of operating grants to L.M.M., B.E.R., and R.J.B., by the special program for scholars of Canada and the People's Republic of China, and by the University of Regina in the form of funds for computing.

**Registry No.** $C_{11}H_6AsF_6O_5Re$, 82113-00-6; $Re_2(CO)_{10}$, 14285-68-8.

**Supplementary Material Available:** Tables of the observed and calculated structure amplitudes, final thermal parameters, and nonessential bond lengths and bond angles (41 pages). Ordering information is given on any current masthead page.

---

[13] Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

[14] Brown, G. M.; Levy, H. A. *Acta Crystallogr.* **1973**, *29*, 790.

---

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

# Structures of (Carbonato)bis(2,2′-bipyridine)cobalt(III) and (Carbonato)bis(1,10-phenanthroline)cobalt(III) Complexes

ERIC C. NIEDERHOFFER,[1] ARTHUR E. MARTELL,* PHIL RUDOLF, and ABRAHAM CLEARFIELD

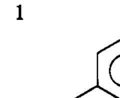
*Received January 27, 1982*

The crystal and molecular structures of *cis*-(carbonato)bis(2,2′-bipyridine)cobalt(III) nitrate pentahydrate, *cis*-$[Co(C_{10}H_8N_2)_2CO_3]NO_3{\cdot}5H_2O$ and *cis*-(carbonato)bis(1,10-phenanthroline)cobalt(III) bromide tetrahydrate, *cis*-$[Co(C_{12}H_8N_2)_2CO_3]Br{\cdot}4H_2O$, have been determined by single-crystal X-ray diffraction methods. The former compound conforms to the monoclinic space group $C2/c$ ($Z = 4$) with cell parameters $a = 10.931$ (4) Å, $b = 16.039$ (2) Å, $c = 14.435$ (2) Å, $\beta = 101.94$ (2)°, and $V = 2476$ (2) Å$^3$. Full-matrix least-squares refinement on 1306 unique reflections with $I > 3\sigma(I)$ gave $R_F = 0.046$ and $R_{wF} = 0.059$. The other compound also conforms to the space group $C2/c$ ($Z = 8$) with cell parameters $a = 28.251$ (8) Å, $b = 12.500$ (2) Å, $c = 14.299$ (3) Å, $\beta = 91.42$ (2)°, and $V = 5048$ (3) Å$^3$. Refinement of 1640 unique reflections with $I > 3\sigma(I)$ gave $R_F = 0.049$ and $R_{wF} = 0.058$. Both compounds contain cations that are slightly distorted from ideal octahedral geometry. The structural parameters are considered with respect to similar *cis*-(carbonato)polyaminecobalt(III) complexes. Ligand field and vibrational assignments are presented for these complexes. Analysis of the electronic absorption transitions $^1T_{1g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ and $^1T_{2g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ yields values of $10Dq$ and $B$.

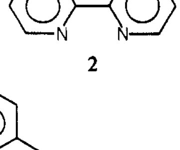
## Introduction

Considerable attention has been directed toward understanding the mechanisms of irreversible autoxidation reactions of cobalt dioxygen complexes. Much of the previous work has been concerned with the role of the ligand, with some structural verification of the resulting products.[2-5]

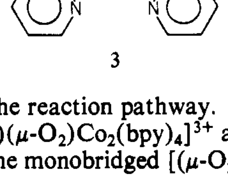
The presence of 2,2′-bipyridine (bpy, **1**), 1,10-phenanthroline (phen, **2**), or 2,2′,-2″-terpyridine (terpy, **3**) in the coordination sphere simplifies the reaction pathway. Autoxidation of the dibridged $[(\mu\text{-OH})(\mu\text{-O}_2)Co_2(bpy)_4]^{3+}$ and $[(\mu\text{-OH})(\mu\text{-O}_2)Co_2(phen)_4]^{3+}$ or the monobridged $[(\mu\text{-O}_2)Co_2(terpy)_2(L)_2]^{4+}$ (L = bpy or phen) in aqueous solution has been shown to result



1



2



3

---

[1] Abstracted in part from a dissertation to be submitted by Eric C. Niederhoffer to the Faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Harris, W. R.; Bess, R. C.; Martell, A. E.; Ridgway, T. H. *J. Am. Chem. Soc.* **1977**, *99*, 2958.

[3] Martell, A. E.; Harris, W. R. *J. Mol. Catal.* **1980**, *7*, 99.

[4] Harris, W. R.; Martell, A. E. *J. Coord. Chem.* **1980**, *10*, 107.

[5] McKenzie, E. D. *J. Chem. Soc. A* **1969**, 1655.

0020-1669/82/1321-3734$01.25/0