Inorg. Chem. **1983**, *22*, 1563-1565

spectra of these two compounds exhibit single, very strong $\bar{\nu}$(CN) stretches at 2214 and 2188 cm^{-1}, respectively. The elemental analyses that were obtained for these compounds are in excellent agreement with their formulation as $Cr(2,6\text{-}DMP)_6(BF_4)_3$ and $Cr(2,6\text{-}DMP)_6(SbCl_6)_3$. Measurement of the magnetic susceptibility at 24 °C of the BF_4^- salt gave a value of 3.89 μ_B for the magnetic moment, consistent with the spin-only value expected for three unpaired electrons residing on a pseuodoctahedral Cr(III) center.

Similar reactions were carried out on the unsubstituted parent compound, $Cr(CNPh)_6$, using $NOBF_4$, $NOPF_6$, or $SbCl_5$ as the oxidant. Solid compounds were isolated in each case, which exhibited $\bar{\nu}$(CN) stretching frequencies at about 2210 cm^{-1}. However, only in the case of $SbCl_5$ was an analytically pure compound obtained. $Cr(CNPh)_6(SbCl_6)_3$ is a deep purple microcrystalline solid, which exhibits an intense $\bar{\nu}$(CN) stretching frequency at 2208 cm^{-1}, indicative of an extremely electron-deficient environment at the Cr(III) center.[21]

The isolation and thermal stability of these chromium(III) isocyanide derivatives are surprising in view of their highly oxidizing nature. While the formal reduction potentials for the CrL_6^{3+}/CrL_6^{2+} couples are quite positive for L = phenyl isocyanide and 2,6-DMP (+0.73 and +0.82 V, respectively, vs. corrected AgCl/Ag in CH_2Cl_2 with 0.1 M TBAH as the electrolyte),[17] the isolation of $Cr(2,6\text{-}DiPP)_6(SbCl_6)_3$ (2,6-DiPP = 2,6-diisopropylphenyl isocyanide), with a formal Cr(III)/Cr(II) reduction potential of +1.27 V vs. AgCl/Ag, is particularly amazing. This latter compound was obtained as a blue microcrystalline solid, which is stable in the absence of water, as are the other Cr(III) complexes described here.

The oxidizing nature of these compounds is illustrated by their solid-state reactivity. Remarkably, in solid $Cr(2,6\text{-}DMP)_6(BF_4)_3$, the $Cr(2,6\text{-}DMP)_6^{3+}$ cation is *cleanly* reduced to $Cr(2,6\text{-}DMP)_6^{2+}$ simply by exposing the solid to the atmosphere for several days. The color of the solid sample lightens from the maroon color of the Cr(III) complex to the orange color characteristic of the corresponding Cr(II) complex. The analysis of the resulting solid agrees closely with the formulation $Cr(2,6\text{-}DMP)_6(BF_4)_2\cdot 8H_2O\cdot HBF_4$, and the compound exhibits an intense $\bar{\nu}$(CN) stretch in the infrared spectrum at 2147 cm^{-1}. Upon further, prolonged exposure to air, this solid becomes light green, with the $\bar{\nu}$(CN) band at 2147 cm^{-1} disappearing, as a new band at 1650 cm^{-1} indicative of isocyanide ligand hydrolysis grows in. At this time, we can only speculate that the reducing atmospheric component in this system is water, which reduces the Cr(III) complex to the Cr(II) complex. The less sterically hindered $Cr(CNPh)_6^{3+}$ cation appears decidedly more reactive with the atmosphere, bypassing completely the reduction stage, proceeding directly to the ligand hydrolysis stage after only a few hours. We intend to investigate these solid-state transformations more completely in the future.

Perhaps the most interesting chemistry these Cr(III) complexes exhibit is the extreme lability of the isocyanide ligands in room-temperature solutions, confirming observations made in cyclic voltammetric measurements on $Cr(2,6\text{-}DMP)_6^{3+}$ and $Cr(2,6\text{-}DiPP)_6^{3+}$.[17] While "typical" Cr(III) complexes undergo ligand exchange with first-order rate constants on the order of 10^{-6} s^{-1} ($Cr(H_2O)_6^{3+}$), room-temperature dissolution of the $Cr(CNAr)_6^{3+}$ complexes in acetone, acetonitrile, or propylene carbonate leads to instantaneous bleaching. These solutions show strong bands in the infrared region near 2120 cm^{-1}, characteristic of the $\bar{\nu}$(CN) stretching frequency of uncoordinated aryl isocyanides. These apparently facile ligand replacement reactions can also be contrasted to the behavior of the zerovalent low-spin d^6 $Cr(CNPh)_6$ complex, which exhibits a first-order ligand-exchange rate constant of 2.8×10^{-7} s^{-1} at 20 °C.[22]

In view of these facile ligand replacement reactions, the apparent ease of hydrolysis in the solid state, and the strongly oxidizing nature of these Cr(III) complexes, we conclude that the further development of their chemistry will yield quite interesting results.

Acknowledgment. This work was supported by the U.S. Army Research Office.

Registry No. $Cr(2,6\text{-}DMP)_6(BF_4)_3$, 85135-14-4; $Cr(CNPh)_6(SbCl_6)_3$, 85150-70-5; $Cr(2,6\text{-}DMP)_6(SbCl_6)_3$, 85135-15-5; $Cr(2,6\text{-}DiPP)_6(SbCl_6)_3$, 85135-16-6; $Cr(2,6\text{-}DMP)_6(BF_4)_2$, 85135-17-7; $Cr(2,6\text{-}DMP)_6BF_4$, 85135-18-8; $Cr(CNPh)_6$, 17375-15-4; $Cr(2,6\text{-}DMF)_6$, 82456-65-3; $Cr(2,6\text{-}DiPP)_6$, 82456-71-1.

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(21) There is a correlation between the Cr oxidation state in $Cr(CNAr)_6^{n+}$ compounds and the $\bar{\nu}$(CN) stretching frequency. For example, for Ar = Ph: $n = 0$, $\bar{\nu}$(CN) 1975 cm^{-1}; $n = 1$, $\bar{\nu}$(CN) 2065 cm^{-1}; $n = 2$, $\bar{\nu}$(CN) 2161 cm^{-1} (data from ref 7).

(22) G. Cetini and O. Gambino, *Ann. Chim.* (*Rome*), **53**, 236 (1963).

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Preparation of Iodobenzene Dimethoxide. A New Synthesis of $[^{18}O]$Iodosylbenzene and a Reexamination of Its Infrared Spectrum

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Iodosylbenzene has found use as an oxygen-transfer reagent by both organic and inorganic chemists.[1,2] Its use was the key to the isolation of several high-valent porphyrin complexes by the groups of Groves and Hill.[2] Despite the wide use of iodosylbenzene, its physical and chemical properties are poorly understood by many researchers. Iodosylbenzene is a polymer, linked by I-O-I bonds, rather than a monomer, PhI=O or PhI^+O^-, as is sometimes supposed. This idea is not new, having been proposed by Bell in 1960 on the basis of the IR spectrum.[3] This work was overlooked by Banks in his 1966 review of polyvalent iodine compounds and by many later workers.[1g-h,4-8]

Not recognizing that iodosylbenzene is polymeric has caused some researchers to misinterpret its solubility[1g,4-9] and infrared spectral properties.[7,10] We wish to report that the high solubility of iodosylbenzene in methanol is due to a solvolysis reaction that forms iodobenzene dimethoxide, $PhI(OMe)_2$ (**1**). This is the first reported example of an acyclic dialkoxyiodinane. The ease of hydrolysis of **1** back to iodosylbenzene has led to a method for ^{18}O-labeling of iodosylbenzene using only a 3-fold excess of $[^{18}O]$water. In contrast, a 30-fold excess of $[^{18}O]$water was used in a recently published procedure for preparing $[^{18}O]$iodosylbenzene by the base hydrolysis of iodobenzene dichloride.[2e] Our ability to prepare pure highly labeled iodosylbenzene has allowed us to reinvestigate the IR spectrum of iodosylbenzene. This was made necessary by substantial discrepancies that exist between the results of recent 20% labeling experiments and an earlier investigation of the IR spectrum of iodosylbenzene.[10,11]

Experimental Section

Methanol was distilled from magnesium dimethoxide. Iodosylbenzene was made by literature methods.[12] All infrared spectra were

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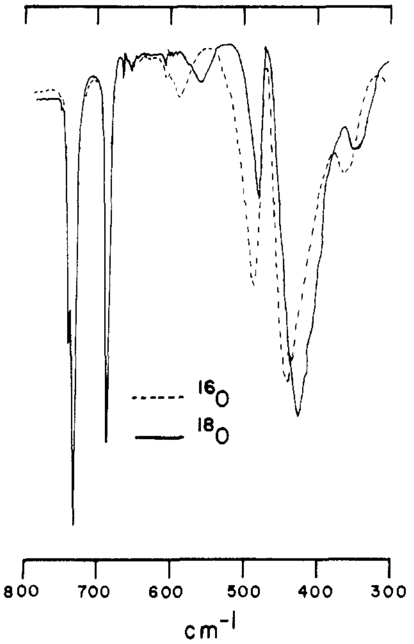

Figure 1. Comparison of the infrared spectra of ^{16}O and 82 atom % ^{18}O-labeled iodosylbenzene. These spectra were recorded as KBr pellets with a 1% concentration of iodosylbenzene.

recorded on a Perkin-Elmer 597 spectrometer as Nujol mulls using CsI windows and as KBr pellets with a PhIO concentration of 1%. ^{1}H NMR spectra were recorded on the UCB-200 FT NMR spectrometer at 201.95 MHz. MS analysis was performed on a Kratos MS-12 mass spectrometer. [^{18}O]Water was obtained from Alfa. Flame-dried glassware and an inert atmosphere were used in the synthesis and handling of PhI(OMe)$_2$.

Synthesis of Iodobenzene Dimethoxide. Yellow iodosylbenzene, 2.00 g (9.09 mmol), was stirred for 15 min with 20 mL of methanol. There was initial rapid formation of a milky white suspension followed by its slow nearly complete dissolution. Molecular sieves powder, 3-Å pore size, 2.00 g, was added and the mixture stirred for 2 h. After filtration through a medium-porosity fritted-glass filter, all solvent was removed and the resultant white solid dried under vacuum for 10 h. The solid was recrystallized from 35 mL of hot hexane (freshly distilled from P_2O_5). After the mixture was cooled to −70 °C in a 2-propanol/dry ice bath, 1.85 g (75% yield) of white needles was collected. The compound was stored under a N_2 atmosphere at −30 °C. Anal. Calcd for $C_8H_{11}IO_2$: C, 36.11, H, 4.17; I, 47.69. Found: C, 35.86; H, 4.03; I, 47.88. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.70 (s, 6 H), 7.47 (m, 3 H), 7.94 (m, 2 H). IR (CCl_4 solution): ν(C–H) 2915, 2886, 2800 cm^{-1}; ν(C–O) 1013 cm^{-1} (very intense).

Synthesis of [^{18}O]Iodosylbenzene. PhI(OMe)$_2$, 1.00 g (3.7 mmol), suspended in 7 mL of ether, was treated with 0.20 mL (10 mmol) of 91% ^{18}O-labeled water added by syringe. A yellow precipitate formed immediately. After the mixture was stirred for 30 min, all the solvent was removed in vacuo, and the solid was dried for 8 h. The yellow solid was suspended in ether and then collected on a fritted-glass filter in air. The solid was washed with ether and acetone and then dried under vacuum. The yield was 0.80 g (96%). Anal. Calcd for C_6H_5IO: C, 32.48; H, 2.27; I, 57.20. Found: C, 32.38; H, 2.28; I, 57.57. IR: 1568, 1377, 1303, 1175, 1065, 1011, 997, 918, 741, 736, 686 cm^{-1}. For the IR spectral region below 800 cm^{-1}, see Figure 1. The ^{18}O content was found to be 82 ± 3%, on the basis of spectral analysis of triphenylphosphine oxide prepared by reaction of the labeled iodosylbenzene with triphenylphosphine dissolved in dichloromethane.

Iodosylbenzene Oxygen-Exchange Reactions. (a) Back-Substitution Reaction. [^{18}O]Iodosylbenzene, 50 mg, was dissolved in 0.50 mL of methanol. [^{16}O]Water, 0.1 mL, was added. All the solvent was removed in vacuo and the solid dried under vacuum for 2 h. The IR spectrum was identical with that of [^{16}O]iodosylbenzene.

(b) Water-Exchange Experiments. Portions (25 mg) of powdered [^{18}O]iodosylbenzene were stirred for 5 h with 5 mL of each of the following solutions: (1) distilled water; (2) phosphate buffer, pH 10; (3) 10% v/v methanol/water. No exchange of the ^{18}O was observed under any of the above conditions on the basis of the IR spectrum of the reisolated iodosylbenzene. In boric acid buffer, pH 4, the iodosylbenzene decomposed.

Results and Discussion

Iodosylbenzene is very insoluble in most organic solvents. Upon dissolution in acetic acid, it is known to react to form iodobenzene diacetate, PhI(OAc)$_2$.[3,13] It is a common practice to use alcohols as the solvent for iodosylbenzene.[1g,4–6,9,10] We were surprised at the exceedingly high solubility of iodosylbenzene in methanol, >0.5 g/mL, and thought that this might be due to a solvolysis reaction.

A number of compounds were found in the literature that contain alkoxy groups bound to iodine(III); however, no report of the preparation of such a compound from iodosylbenzene was found. Removal of the solvent from a methanol solution of iodosylbenzene was found to give a white crystalline compound contaminated with some yellow iodosylbenzene. Drying of the methanol solution with molecular sieves gave a purer product that could be recrystallized from hexane. The elemental analysis and the IR and NMR spectra identified the compound as iodobenzene dimethoxide, PhI(OMe)$_2$ (**1**).

Iodobenzene dimethoxide is a white crystalline solid soluble in all organic solvents tested, including acetone, ether, benzene, carbon tetrachloride, and hexane. The structure of **1** is expected to be T-shaped, with the two lone pairs occupying equatorial sites of an imaginary trigonal bipyramid, as is the case for other iodinanes.[8,14,15]

The literature on arylalkoxyiodinanes has been reviewed by Amey and Martin.[15] Representative compounds prepared previously include **2**,[16] **3**,[17] **4**,[7] **5**,[15] and **6**.[18] A simple acyclic dialkoxyiodinane, **1**, has not been previously isolated.

It has been shown by Baker[7] and Martin[15,17] that the five-membered rings in **4**–**6** are quite stable to hydrolysis. However, the acyclic RO–I moieties in **4** and **5** can be hydrolyzed by base to make the corresponding hydroxy compound.[6,15,17]

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(1) (a) Takaya, T.; Enyo, H.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1032. (b) Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1975**, *97*, 421. (c) Gustafsson, J. A.; Bergman, J. *FEBS Lett.* **1976**, *70*, 276. (d) Gustafsson, J. A.; Rondahl, L.; Bergman, J. *Biochemistry* **1979**, *18*, 865. (e) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (f) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413. (g) Lichtenberger, F.; Nastainczyk, W.; Ullrich, V. *Biochem. Biophys. Res. Commun.* **1976**, *70*, 939. (h) Moriarty, R. M.; Gupta, S. C.; Hu, H.; Berenschot, D. R.; White, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 686.

(2) (a) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613. (b) Hill, C. L.; Schardt, B. C. *Ibid.* **1980**, *102*, 6374. (c) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6375. (d) Schardt, B. C.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1981**, 765. (e) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363. (f) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964.

(3) Bell, R.; Morgan, K. J. *J. Chem. Soc.* **1960**, 1209.

(4) Gragerov, I. P.; Levit, A. F. *Zh. Obshch. Khim.* **1963**, *33*, 544.

(5) Willner, I.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Chem. Commun.* **1980**, 964.

(6) Moriarity, R. M.; John, L. S.; Du, P. C. *J. Chem. Soc., Chem. Commun.* **1981**, 641.

(7) Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow., A. J. *J. Chem. Soc.* **1965**, 3721.

(8) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.

(9) (a) Prikule, D.; Neilands, O. *Latv. PSR* Zinat. *Akad. Vestis, Kim. Ser.* **1972**, 743; *Chem. Abstr.* **1973**, *78*, 83966*d*. (b) Shannon, P.; Bruice, T. C. *J. Am. Chem. Soc.* **1981**, *103*, 4580.

(10) Heimbrook, D. C.; Sligar, S. C. *Biochem. Biophys. Res. Commun.* **1981**, *99*, 530.

(11) Siebert, H.; Handrich, M. *Z. Anorg. Allg. Chem.* **1976**, *426*, 173.

(12) Lucas, H. J.; Kennedy, E. R.; Formo, M. W. "Organic Syntheses"; Wiley: New York, 1955; Collect Vol. III, p 483.

(13) Sharefkin, J. G.; Saltzman, H. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 660.

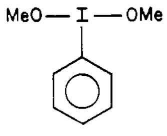
(14) Etter, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5326.

(15) Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 1779.

(16) Tanner, D. D.; Gidley, G. C. *Can. J. Chem.* **1968**, *46*, 3537.

(17) G. F. Koser; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 4988.

(18) Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1982**, *47*, 1024.



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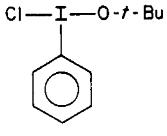

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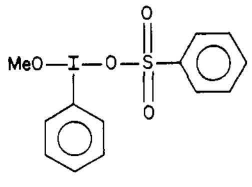

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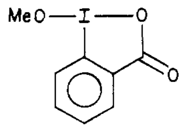

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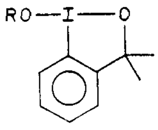

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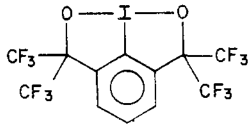

6

The addition of water to the solid or to solutions of **1** results in the immediate formation of iodosylbenzene, eq 1. This

$$\underset{\mathbf{1}}{\mathrm{PhI(OCH_3)_2}} + \mathrm{H_2O} \rightleftharpoons \underset{\mathbf{7}}{\mathrm{(PhIO)}_n} + \mathrm{2CH_3OH} \quad (1)$$

contrasts sharply with the requirement for base in order to form iodosylbenzene from iodobenzene dichloride and iodobenzene diacetate.[19]

The formulation of **7** as a polymer species containing I–O–I bonds was first discussed by Bell in 1960 and subsequently by Siebert in 1976.[3,11] This polymeric formulation for iodosylbenzene explains its very low solubility in most solvents and its ready disproportionation into iodobenzene and iodoxybenzene in the solid state.[20]

In Siebert's detailed IR and Raman spectral study, four absorption bands were found that could not be directly related to bands observed in iodobenzene. The two intense broad IR absorption bands at 490 and 443 cm^{-1} he assigned as the principal I–O–I group vibrations. Two weak bands observed at 360 and 591 cm^{-1} were believed to result from combination frequencies.[11]

A more recently published 20% ^{18}O-labeling experiment reported finding oxygen-sensitive absorptions at 1066, 735, and 690 cm^{-1}. No observations were reported for the IR spectral region below 600 cm^{-1}.[10]

The ^{18}O content of the iodosylbenzene used in the present labeling study was determined by mass spectral analysis of triphenylphosphine oxide prepared from the iodosylbenzene and found to be 82 ± 3%.

We observed no oxygen-sensitive absorptions in the IR spectrum of iodosylbenzene at frequencies >600 cm^{-1}. The results of the previously reported labeling study were probably due to the presence of impurities introduced by their method of ^{18}O incorporation.

The spectra we obtained for labeled and unlabeled iodosylbenzene are shown in Figure 1, for $\nu < 800$ cm^{-1}. In the ^{16}O spectrum, the bands described by Siebert are readily observed. Upon ^{18}O labeling, the most definitive change in the spectrum is the shift of the weak 590 cm^{-1} band to 560 cm^{-1}. This frequency is very close to that observed for the antisymmetric stretching frequency ν(I–O–I) in some other compounds: 595 cm^{-1}, iodine pentoxide;[21] 585 cm^{-1}, (μ-oxo)bis(nitrato)diphenyldiiodine(III);[22] 587 cm^{-1}, 1,1′-oxybis(1,2-benziodoxol-3(1*H*)-one).[11] Rather than being a combination band as thought by Siebert, the 590 cm^{-1} is probably the antisymmetric stretching frequency ν(I–O–I) of iodosylbenzene.

The bands at 490 and 443 cm^{-1} are quite broad. A major portion of the intensity for the 443-cm^{-1} band is probably due to a ring deformation mode that occurs in iodobenzene at 448 cm^{-1}.[3,11] Overlaying this ring deformation mode is an oxygen-sensitive absorption, occurring in the region of the spectrum found for a symmetric stretching frequency ν(I–O–I).[20] The bands at 490 and 360 cm^{-1} are also oxygen sensitive. Assignment to specific vibrational bands would be difficult to make.

One of the purposes of the previous labeling study was to determine whether or not the oxygen in iodosylbenzene can be exchanged with water.[10] There is some evidence in the literature that this exchange is possible,[4,8] and there are also claims that it is not.[2a,c] We have confirmed that no exchange occurs in neutral or basic water nor in a solution that is 10% v/v methanol/water at 25 °C.

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE-7909730) is acknowledged.

Registry No. **1**, 85083-59-6; **1** polymer, 85083-60-9; [^{18}O]-iodosylbenzene, 80572-92-5.

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[19] (a) Lucas, H. J.; Kennedy, E. R. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 482. (b) Saltzman, H.; Sharefkin, J. G. *Ibid.*, 1973; Collect. Vol. V, p 658.

[20] Lucas, H. J.; Kennedy, E. R. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 485.

[21] Sherwood, P. M. A.; Turner, J. J. *Spectrochim. Acta, Part A* **1970**, *26A*, 1975.

[22] Dasent, W. E.; Waddington, T. C. *J. Chem. Soc.* **1960**, 3350.