Table I. Spectral Properties of $Cp_2MM'(CO)_4$ (M, M' = Mo, W)

M	M'	IR, ν_{CO}, cm^{-1}	^1H NMR, δ	^{13}C NMR, δ
Mo	Mo	1900, 1850	5.22^a, 4.65^b	105.6, 195.9^b
Mo	W	1950, 1890, 1835^d	5.36, 5.30^a	92.9, 92.1, 229.7^c (231.7, 227.9 (J_{WC} = 218 Hz))^e
W	W	1885, 1830	5.2^a	92.6, 222.7^c

[a] $CDCl_3$ solvent, ambient temperature (~30 °C). [b] C_6D_6 solvent, ambient temperature. [c] CD_2Cl_2 solvent, $T = 30$ °C. [d] KBr disk. [e] Toluene-d_8, $T = -50$ °C.

$Cp_2Mo_2(CO)_4$, $Cp_2MoW(CO)_4$, and $Cp_2W_2(CO)_4$. The identity of each fraction was confirmed by its mass spectrum. Recrystallization of the $Cp_2MoW(CO)_4$ from CH_2Cl_2/heptane gave pure material, yield ca. 30% (based on $Mo_2 + W_2 = 2MoW$). Anal. Calcd for $C_{14}H_{10}MoO_4W$: C, 32.2; H, 1.92. Found: C, 32.3; H, 2.05.

Results and Discussion

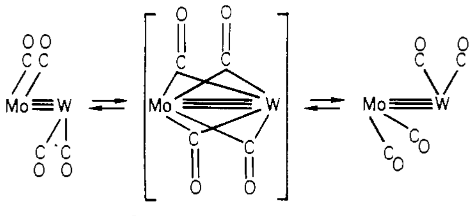
The use of the high-boiling ether, diglyme or bis(2-methoxyethyl) ether, in place of toluene[7] or xylene[8] as solvent for the thermal decarbonylation of $Cp_2M_2(CO)_6$ to $Cp_2M_2(CO)_4$ (M = Mo, W) shortens the requisite reaction time and gives purer product. With sufficient care to exclude oxygen, no recrystallizations are necessary to obtain analytically or spectroscopically (NMR) pure product. The pure solids may be handled in air for hours, but over a period of several weeks or months, progressive deterioration of the samples is evident. Solutions are rapidly attacked by oxygen, giving dark insoluble solids and $Cp_2M_2(CO)_6$, formed by the reaction of $Cp_2M_2(CO)_4$ with the CO liberated by the oxidation process.

The reaction shown in eq 5 must be nearly thermoneutral

$$\mathrm{Mo{\equiv}Mo + W{\equiv}W \rightleftarrows 2Mo{\equiv}W} \tag{5}$$

since the yields of the Mo_2, MoW, and W_2 dimers were in an *approximate* 1:2:1 ratio (determined by ^1H NMR of the crude mixture), as expected for a statistical distribution. This result suggests that *at the reaction temperature*, the triply bonded species are all essentially at equilibrium with the CO in the system and hence are in equilibrium with each other and with the respective singly bonded dimers. As the CO is swept out of the system the equilibrium is gradually shifted to the triply bonded dimers.

At room temperature, the heteronuclear complex, $Cp_2MoW(CO)_4$, displays two resonances for the Cp groups in both the ^{13}C and ^1H NMR spectra (see Table I) as expected. However, only one resonance is observed for the carbonyl groups. In the solid state, $Cp_2Mo_2(CO)_4$ has disordered carbonyls that can be interpreted as a "stop-action" photograph of a fluxional process in which the carbonyls hop from one metal to another across the triple bond:[13,14]



(6)

Also, Jemmis et al.[15] have calculated that only a small energy difference exists between a tetrabridged structure (e.g., the proposed intermediate in eq 6) and the observed semibridging structures. The synthesis of the heteronuclear dimer, $Cp_2MoW(CO)_4$, has given us the first opportunity to study the process indicated in eq 6.

A variable-temperature NMR study of the MoW dimer showed that, below −10 °C, the carbonyl ^{13}C resonances split into two peaks. At −50 °C, the low-temperature limit has peaks at 231.7 and 227.9 ppm. The latter resonance is assigned to the carbonyls bonded to the tungsten atom due to its satellites (J_{WC} = 218 Hz). This coupling constant is considerably larger than the typical 130 Hz observed for many $W(CO)_5L$ complexes[16] and suggests that a higher fraction of s-character is present in the W–CO bonded of the multiply bonded dimer. One also notes that the carbonyl bonded to Mo in the MoW dimer is considerably deshielded with respect to the Mo_2 dimer (δ 231.7 vs. 195.9), whereas the shieldings of the carbonyls on W are more similar in the two compounds (δ227.9 and 222.7, respectively). Since *both* sets of resonances are shifted downfield, it is unlikely that the shifts are caused entirely by a polarity, e.g. $Mo^{\delta+}{\equiv}W^{\delta-}$, in the MoW bond (the electronegativity of W may be slightly higher than that of Mo due to the lanthanide contraction[17]). More likely, the cause of these shifts may be found in changes in the paramagnetic shift contributions, which depend on the energy differences between filled and empty orbitals in the complex.

The peak shapes corresponding to various temperatures were calculated as a function of exchange rate with the program DNMR-3A.[18] An Arrhenius plot was fitted by a least-squares procedure to give an activation energy of 10.4 ± 0.3 kcal/mol for the fluxional process. Jemmis et al.[15] calculated the energy surface interconnecting the semibridged and quadruply bridged structures to be relatively flat. Their EHMO method predicted the (μ-CO)$_4$ structure to be about 2 kcal *lower* in energy than the observed semibridged structure. However, they pointed out that the quadruply bridged structure has a near degeneracy that would tend to give an open-shell configuration subject to a second-order Jahn–Teller distortion. Consequently, deformations of the ground-state, semibridged structure to the quadruply bridged structure would be disfavored. Our value for the activation energy of the carbonyl exchange (eq 6) places an upper limit of ca. 10 kcal/mol on the energy difference between these two structures.

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Registry No. $Cp_2Mo_2(CO)_6$, 12091-64-4; $Cp_2W_2(CO)_6$, 12091-65-5; $Cp_2Mo_2(CO)_4$, 56200-27-2; $Cp_2MoW(CO)_4$, 65995-85-9; $Cp_2W_2(CO)_4$, 62853-03-6; W, 7440-33-7; Mo, 7439-98-7.

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(13) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

(14) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034.

(15) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576.

(16) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; pp 159–164.

(17) Little, E. J.; Jones, M. M. *J. Chem. Educ.* **1960**, *37*, 231.

(18) Quantum Chemistry Program Exchange, Program No. 165, Bloomington, IN.

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Synthesis, Characterization, and Properties of Stable Chromium(III) Aryl Isocyanide Complexes

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The chemistry of homoleptic isocyanide complexes of chromium has been of interest[1-15] to organometallic chemists

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(1) L. Malatesta, A. Sacco, and S. Ghielmi, *Gazz. Chim. Ital.*, **82**, 516 (1952).

since the synthesis of the zerovalent hexacoordinate aryl isocyanide derivatives by Malatesta[1,2] in the early 1950s. During the last 10 years, these compounds have been the subject to several electrochemical[7-10] and photochemical investigations,[11-14] showing that, although the Cr(0) complexes are formally isoelectronic with $Cr(CO)_6$, they possess strikingly different properties.[15] $Cr(CNAr)_6$, unlike $Cr(CO)_6$, can be sequentially oxidized in electrochemically reversible one-electron steps to produce the hexacoordinate Cr(I), Cr(II), and Cr(III) derivatives.[7] On the basis of these electrochemical results, Treichel et al.[8] isolated salts of the Cr(I) and Cr(II) derivatives by stoichiometrically oxidizing the zerovalent complexes with Ag^+ in acetone. However, the much more positive Cr(III)/Cr(II) formal potentials precluded the synthesis of the Cr(III) complexes by this route.[16] Complexes of the form $Cr(CNAr)_6{}^{3+}$ have been proposed as products in the disproportionation reaction (reaction 1) utilized in the synthesis of $Cr(CNAr)_6{}^0$, but no salts of the former have been isolated from this reaction.

$$3Cr_2(OAc)_4{\cdot}2H_2O + 36CNAr \rightarrow 2Cr(CNAr)_6{}^0 + 4Cr(CNAr)_6{}^{3+} + 12OAc^- + 6H_2O \quad (1)$$

While extending[17] the previous electrochemical studies, we became interested in isolating the Cr(III) derivatives to complete the series.[18] This unprecedented series affords the opportunity to systematically study the structure, bonding, and reactivity of complexes in which the metal attains four different oxidation states while maintaining identical ligation. By utilizing the powerful oxidants NO^+[19] and $SbCl_5$[20] at −25 °C, we have effected the synthesis and isolation of salts containing the $Cr(CNAr)_6{}^{3+}$ cations.

Experimental Section

Reagents. The synthesis of the starting materials $Cr(CNPh)_6$, $Cr(2,6\text{-DMP})_6$, and $Cr(2,6\text{-DiPP})_6$ have been previously reported.[17] $Cr(2,6\text{-DMP})_6BF_4$ was prepared by the method of Treichel[8] substituting $AgBF_4$ for $AgPF_6$. $NOBF_4$ (Pfaltz and Bauer) and $SbCl_5$ (Aldrich) were used as received. Omnisolv methylene chloride and hexane were purchased from MCB and dried over activated alumina. AR grade anhydrous diethyl ether (Mallinckrodt) was protected from air and used as received.

Sample Handling. Because the solid Cr(III) products and their solutions are extremely mositure sensitive, they were handled by using either Schlenk techniques or a glovebag flushed with prepurified tank nitrogen. Nujol used for the infrared mull spectra was dried over $CaSO_4$. Even with extreme care, samples and solutions sometimes showed evidence of reaction with water. Many of the critical physical measurements were conducted on days of low absolute atmospheric humidity to enhance the effectiveness of the methods used to exclude moisture.

Physical Measurements. Infrared spectra were obtained as Nujol mulls on either a Beckman 4250 or a Perkin-Elmer 283. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and MHW Laboratories, Phoenix, AZ. The magnetic moment measurement was made on the solid material by the Faraday method.

Preparation of the Compounds. $Cr(2,6\text{-DMP})_6(BF_4)_3$. A test tube with a total volume of about 60 mL was charged in a glovebag with 50.0 mg of $NOBF_4$ (0.43 mmol), 74.3 mg (0.08 mmol) of $Cr(2,6\text{-DMP})_6BF_4$, and a stir bar, sealed with a serum stopper, and flushed with dry nitrogen. The tube was then placed in a low-temperature bath at −25 °C. Twenty milliliters of dry CH_2Cl_2 at −25 °C was transferred by cannula into the tube. The stirred solution underwent a series of color changes over 4 h, which terminated in a maroon solution. Fifty milliliters of cold, dry hexane was then added, precipitating a dark maroon microcrystalline solid. The mixture was filtered at −25 °C through a medium frit, yielding 76.5 mg of $Cr(2,6\text{-DMP})_6(BF_4)_3$ (87% yield). Characteristic IR bands: $\bar{\nu}$(CN) 2214 cm^{-1} (s), $\bar{\nu}$(ring) 1588 cm^{-1} (m). Anal. Calcd for $C_{54}H_{54}N_6CrF_{12}B_3$: C, 58.99; H, 4.95; N, 7.64. Found: C, 58.95; H, 5.03; N, 7.45. Magnetic data: $\chi_M{}^{cor} = +6331 \times 10^{-6}$ cgsu/mol (diamagnetic correction -647×10^{-6} cgsu/mol), giving $\mu_{eff}(24\ °C) = 3.89\ \mu_B$.

$Cr(CNPh)_6(SbCl_6)_3$. A tube with a total volume of about 60 mL was charged with 105 mg of solid $Cr(CNPh)_6$ (0.15 mmol) and a stir bar and sealed. The tube was degassed with dry nitrogen by using flush/evacuate cycles and immersed in the −25 °C low-temperature bath. Twenty milliliters of dry CH_2Cl_2 was transferred by cannula into the tube through a glass stopcock equipped with a serum stopper. As the cold solution was stirred, 0.15 mL of $SbCl_5$ (1.2 mmol) was added by syringe. The solution immediately darkened and after several minutes deposited purple microcrystals. After an additional 4 h of stirring, the mixture was filtered through a medium frit. The solid product (250 mg, 95% yield) was washed with dry hexane. Characteristic IR bands: $\bar{\nu}$(CN) 2208 cm^{-1} (s), $\bar{\nu}$(ring) 1583 cm^{-1} (s). Anal. Calcd for $C_{42}H_{30}N_6CrCl_{18}Sb_3$: C, 30.13; H, 1.81; N, 5.02. Found: C, 29.92; H, 2.09; N, 5.00.

$Cr(2,6\text{-DMP})_6(SbCl_6)_3$. A method virtually identical with that used for the phenyl isocyanide complex was used for this case, with the exception that the product, which was partially soluble in cold CH_2Cl_2, was precipitated as dark purple microcrystals on addition of 30 mL of cold, dry hexane. One hundred milligrams of $Cr(2,6\text{-DMP})_6$ (0.12 mmol) yielded 164 mg of $Cr(2,6\text{-DMP})_6(SbCl_6)_3$ (75%). Characteristic IR bands: $\bar{\nu}$(CN) 2188 cm^{-1} (s), $\bar{\nu}$(ring) 1587 cm^{-1} (s). Anal. Calcd for $C_{54}H_{54}N_6CrCl_{18}Sb_3$: C, 35.20; H, 2.95; N, 4.56; Cl, 34.64. Found: C, 35.03; H, 3.03; N, 4.46; Cl, 34.38.

$Cr(2,6\text{-DiPP})_6(SbCl_6)_3$. The method used was the same as for the 2,6-DMP compound. One hundred milligrams of $Cr(2,6\text{-DiPP})_6$ (0.085 mmol) yielded 148 mg of blue microcrystalline $Cr(2,6\text{-DiPP})_6(SbCl_6)_3$ (80% yield). Characteristic IR bands: $\bar{\nu}$(CN) 2180 cm^{-1} (vs), $\bar{\nu}$(ring) 1585 (s). Anal. Calcd for $C_{78}H_{102}N_6CrCl_{18}Sb_3$: C, 42.99; H, 4.72; N, 3.86. Found: C, 42.74; H, 4.79; N, 3.81.

$Cr(2,6\text{-DMP})_6(BF_4)_2{\cdot}8H_2O{\cdot}HBF_4$. A solid sample (~20 mg) of $Cr(2,6\text{-DMP})_6(BF_4)_3$ exposed to air for 4 days yielded an orange powder. IR spectrum: $\bar{\nu}$(CN) 2147 cm^{-1} (vs), $\bar{\nu}$(ring) 1588 cm^{-1} (m). Anal. Calcd for $C_{54}H_{71}N_6O_8CrF_{12}B_3$: C, 52.11; H, 5.75; N, 6.75. Found: C, 52.40; H, 5.44; N, 6.74.

Discussion

Treatment of $Cr(2,6\text{-DMP})_6{}^+$ or $Cr(2,6\text{-DMP})_6$ (2,6-DMP = 2,6-dimethylphenyl isocyanide) with an excess of either $NOBF_4$ or $SbCl_5$ in dry CH_2Cl_2 at −25 °C results in a rapid sequence of color changes terminating in a dark solution, which on standing at −25 °C deposits microcrystals of the maroon $BF_4{}^-$ or purple $SbCl_6{}^-$ salts of the $Cr(2,6\text{-DMP})_6{}^{3+}$ cation. Filtration of the solution under dry nitrogen affords ~85% yield of the microcrystalline compounds which are stable at room temperature in the absence of water. The infrared

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(2) L. Malatesta and A. Sacco, *Atti Accad. Naz. Linci, Cl. Sci. Fis., Mat. Nat., Rend.* [8] **13**, 264 (1952).

(3) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

(4) K. R. Mann, M. Cimolino, C. L. Geoffroy, G. S. Hammond, A. A. Orio, G. Albertin, and H. B. Gray, *Inorg. Chim. Acta*, **16**, 97 (1976).

(5) K. R. Mann, Ph.D. Thesis, California Institute of Technology, 1976.

(6) Evert Ljungström, *Acta Chem. Scand., Ser. A*, **A32**, 47 (1978).

(7) P. M. Treichel and G. J. Essenmacher, *Inorg. Chem.*, **15**, 146 (1976).

(8) G. J. Essenmacher and P. M. Treichel, *Inorg. Chem.*, **16**, 800 (1977).

(9) P. M. Treichel, D. W. Firsich, and G. J. Essenmacher, *Inorg. Chem.*, **18**, 2405 (1979).

(10) W. S. Mialki, T. E. Wood, and R. A. Walton, *J. Am. Chem. Soc.*, **102**, 7105 (1980).

(11) K. Iuchi, S. Asada, and A. Sugimori, *Chem. Lett.*, 801 (1974).

(12) K. Iuchi, S. Asada, T. Kinugasa, K. Kanamori, and A. Sugimori, *Bull. Chem. Soc. Jpn.*, **49**, 577 (1976).

(13) K. R. Mann, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **99**, 306 (1977).

(14) H. B. Gray, K. R. Mann, N. S. Lewis, J. A. Thich, and R. M. Richman, *Adv. Chem. Ser.*, No. **168**, 44 (1978).

(15) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th ed., Wiley, New York, 1980, pp 93–95.

(16) The electrochemical syntheses of $Cr(CNR)_6{}^{3+}$ complexes, where R = alkyl, have been unsucessfully attempted: W. S. Mialki, D. E. Wigley, T. E. Wood, and R. A. Walton, *Inorg. Chem.*, **21**, 480 (1982).

(17) D. A. Bohling, J. F. Evans, and K. R. Mann, *Inorg. Chem.*, **21**, 3546 (1982).

(18) These complexes are isoelectronic with vanadium(II) alkyl isocyanide complexes that have been recently characterized by: L. D. Silverman, J. C. Dewan, C. M. Giandomenico, and S. J. Lippard, *Inorg. Chem.*, **19**, 3379 (1980); L. D. Silverman, P. W. R. Corfield, and S. J. Lippard, *ibid.* **20**, 3106 (1981).

(19) N. G. Connelly and J. D. Davies, *J. Organomet. Chem.*, **38**, 385 (1972).

(20) $SbCl_5$ has been used in chlorinated organic solvents to produce powerfully oxidizing organic cation radicals: F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. c*, 2719 (1969).

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

spectra of these two compounds exhibit single, very strong $\tilde{\nu}$(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 pseudooctahedral 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 $\tilde{\nu}$(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 $\tilde{\nu}$(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 $\tilde{\nu}$(CN) stretch in the infrared spectrum at 2147 cm^{-1}. Upon further, prolonged exposure to air, this solid becomes light green, with the $\tilde{\nu}$(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 $\tilde{\nu}$(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 $\tilde{\nu}$(CN) stretching frequency. For example, for Ar = Ph: $n = 0$, $\tilde{\nu}$(CN) 1975 cm^{-1}; $n = 1$, $\tilde{\nu}$(CN) 2065 cm^{-1}; $n = 2$, $\tilde{\nu}$(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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