chloroperoxybenzoic acid to produce methyl trifluoromethyl sulfoxide in 78% yield. Traces of $CF_3SO_2CH_3$ and unreacted CF_3SCH_3 were removed by trap-to-trap distillation. $CF_3SO_2CH_3$ was retained at −20° while $CF_3S(O)CH_3$ was stopped in a trap cooled to −30°. The infrared spectrum of $CF_3SO_2CH_3$ at 4 Torr showed the following bands: 1397 (vs), 1330 (w), 1246 (vs), 1210 (vs), 1146 (vs), 960 (m) (pqr), 780 (w-m), 742 (w-m), 540 (m) (pqr), and 484 (w-m) cm^{-1}. Mass spectral fragments included $M - CH_3^+$, $M - CF_3^+$, and CF_3^+. A quartet at ϕ 79.5 ($J_{H-F} = 1$ Hz) occurred in the ^{19}F nmr spectrum and a quartet at δ 3.1 occurred in the ^1H nmr spectrum.

Properties of Methyl Trifluoromethyl Sulfoxide. $CF_3S(O)CH_3$ existed as a colorless liquid at room temperature. Its infrared spectrum contained the following bands: 2899 (w), 1425 (w), 1245 (w), 1210 (vs), 1170, 1164 (m) (doublet), 1125 (s), 960 (w-m), 740 (w) cm^{-1}. The ^{19}F nmr spectrum showed a quartet at ϕ 76.6 (J_{H-F} = 1.1 Hz) and the ^1H nmr spectrum showed a quartet at δ 2.75. A mass spectrum showed ions attributed to M^+, $CFSO^+$, CF_3^+, and CH_3SO^+. Fluorine analysis gave 47.0% (calcd 47.8%).

Preparation of CF_3SCF_2H. Reaction of CF_2HCO_2Ag (7 mmol) with CF_3SCl (5 mmol) at 25° for 10 min produced the colorless compound $CF_2HC(O)OSCF_3$, which was retained in a trap at −78° during trap-to-trap distillation. $CF_2HC(O)OSCF_3$ was photolyzed in a 1-l. Pyrex bulb for 1 hr to produce CF_2HSCF_3 (75%). Large amounts of CF_3SSCF_3 (25%) which formed during the photolysis were removed by gas chromatography.

Properties of CF_2HSCF_3. CF_2HSCF_3 existed as a gas at room temperature which condensed to a colorless liquid. The ^1H nmr spectrum showed a triplet at δ 7.06 ($J_{H-F} = 55.6$ Hz) while the ^{19}F nmr spectrum showed a triplet for the CF_3 resonance (J_{F-F} = 7.0 Hz) at ϕ 38.4 and a doublet of quartets for the CF_2H resonance at ϕ 93.2. The infrared spectrum showed the following absorbance bands: 3005 (w), 1321 (m), 1192 (vs), 1168 (vs), 1142 (vs), 1095 (vs), 794 (m), 761 (m), 482 (vw) cm^{-1}. The major ions observed in the mass spectrum were attributed to M^+, $C_2F_4SH^+$, CF_2S^+, CF_3^+, CFS^+, and CF_2H^+. Fluorine analysis gave 61.0% (calcd 62.5%).

Reaction of CF_2HSCF_3 with *m*-$ClC_6H_4CO_3H$. CF_3SCF_2H (2.5 mmol) was condensed into a vessel containing excess *m*-chloroperoxybenzoic acid. After 7 days at 25°, no reaction had occurred.

Preparation of $(CF_3S)_2CH_2$. The reaction of 6 g of $Hg(SCF_3)_2$ in a 10-ml thick-walled Pyrex tube with 1.5 g of CH_2I_2 at 80° gave approximately quantitative conversion to $(CF_3S)_2CH_2$.

Properties of $(CF_3S)_2CH_2$. Bis(trifluoromethylthio)methane existed as a colorless liquid at 25° and froze to a colorless solid. The gas-phase infrared spectrum had the following absorption bands: 1305 (w), 1238 (m), 1185 (vs), 1154 (vs), 1113 (vs), 821 (w), 763 (m), 738 (w, sh), 450 (w) cm^{-1}. Mass spectral species included M^+, $CF_3SCH_2^+$, CF_3S^+, $CH_2S_2^+$, CF_3^+, CH_2S^+, and CHS^+. The ^1H nmr spectrum contained a singlet at δ 4.35 and likewise the ^{19}F nmr spectrum had a singlet at ϕ 42.8. *Anal.* Calcd: F, 52.9; S, 29.70; C, 16.65; H, 0.92. Found: F, 52.9; S, 29.73; C, 16.50; H, 0.91.

Reaction of $(CF_3S)_2CH_2$ with *m*-$ClC_6H_4CO_3H$. Oxidation of 2 mmol of $(CF_3S)_2CH_2$ with 4.4 mmol of *m*-$ClC_6H_4CO_3H$ at 25° for 4 days resulted in a mixture of involatile compounds. Isolation of two major components was effected by gas chromatography; they were tentatively identified as $CF_3SCH_2S(O)CF_3$ (~65%) and $CF_3SCH_2SO_2CF_3$ (~10%).

The product believed to be $CF_3SCH_2S(O)CF_3$ was a colorless liquid at 25° and had the following infrared spectrum: 3010 (w), 1412 (w), 1390 (w), 1215-1200 (vs, br), 1163 (s-vs), 1123 (s), 830 (w), 765 (w), 748 (w) cm^{-1}. Ions present in the mass spectrum confirming the proposed structure were $CF_3SCH_2S(O)^+$, $CF_3S(O)^+$, $CF_3SCH_2^+$, CF_3S^+, CF_3^+, SO^+, and SCH_2^+. The ^1H nmr spectrum showed a single resonance at δ 4.93 while the ^{19}F nmr displayed quartets ($J_{CF_3-CF_3} = 0.6$ Hz) at ϕ 42.3 (CF_3S) and 73.9 ($CF_3S(O)$).

The structure of $CF_3SCH_2SO_2CF_3$ was proposed on the basis of ^{19}F nmr data with resonances at ϕ 44.0 and 79.6 and the presence of an SO_2 asymmetric stretch in the infrared spectrum.

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Registry No. CF_3SCH_3, 421-16-9; $(CF_3S)_2Hg$, 21259-75-6; CH_3I, 74-88-4; $CF_3SOC(O)CH_3$, 42530-92-7; ClF, 7790-89-8; *trans*-$CF_3SF_4CH_3$, 42530-93-8; *m*-$ClC_6H_4CO_3H$, 937-14-4; $CF_3SO_2CH_3$, 421-82-9; $CF_3S(O)CH_3$, 2697-49-6; CF_2HCO_2Ag, 383-88-0; CF_3SCl, 421-17-0; CF_2HSCF_3, 371-72-2; $(CF_3S)_2CH_2$, 819-67-0; $CF_3SCH_2S(O)CF_3$, 42530-99-4.

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Assignment of the Photoelectron Spectra of $Mn(CO)_5CH_3$ and $Mn(CO)_5CF_3$

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Study of the electronic structure of the series of compounds $Mn(CO)_5X$ (X = H, Cl, Br, I, CH_3, CF_3) *via* photoelectron spectroscopy has provided considerable insight into the nature of the bonding in these systems.[1] Of particular interest have been the ionizations occurring at less than 12 eV, which have been found to be sensitive to the nature of the group X. Using the criterion that the area under an ionization band should reflect the orbital degeneracy for orbitals with closely similar localization properties, the original workers concluded that the metal e orbital is above the metal b_2 orbital for all complexes of the series except $Mn(CO)_5CH_3$.[2] This assignment has recently been confirmed for the pentacarbonylmanganese halides with the aid of the pe spectrum of $Mn(CO)_4(CNCH_3)Br$.[3] The spectra of the perfluoromethyl and methyl complexes however exhibited significant deviations from the trends observed in the spectra of the halide complexes. Using the intensity assignment criterion for these spectra leads to some unusual conclusions regarding the bonding in these systems. In the perfluoromethyl complex the ratio of the first to second band has become 3:1, suggesting a considerable enhancement of the ionization cross section of the e orbital over the b_2 orbital in this molecule. This may indicate that these orbitals possess significantly different localization properties from the e and b_2 orbitals in the corresponding halides. Nevertheless the assignment was in accord with qualitative expectations concerning the orbital ordering. In the methyl complex the ratio of the first two bands is 1:2, suggesting a reversal in the order of the e and b_2 ionizations. To rationalize this unexpected inversion of the e and b_2 levels it has been proposed that the e orbital is stabilized below the b_2 orbital through back-bonding into the π^* levels of the methyl group. However, such an interpretation of the band assignment does not conform with the other properties of the methyl complex.[4,5] In any event, the two spectra appeared to indicate a substantial change in the character of the e and b_2 levels from that observed in the pentacarbonylmanganese halides.

Approximate molecular orbital calculations on these two molecules using our method[6] did not support these interpretations. Instead, the calculations show that another ioniza-

(1) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, 47, 112 (1969).

(2) The metal levels of the CH_3 and CF_3 complexes may be quite closely described by the local C_{4v} symmetry of the $Mn(CO)_5$ portion.

(3) D. L. Lichtenberger, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, 12, 702 (1973).

(4) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1, 143 (1964).

(5) F. A. Cotton and R. M. Wing, *J. Organometal. Chem.*, 9, 511 (1967).

(6) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 768 (1972).

tion, that arising from the σ-bonding a_1 orbital between the methyl or perfluoromethyl ligand and the metal, should lie in the same region of the spectra as the metal e and b_2 ionizations. This unexpected additional band offers an alternative assignment of the spectra which does not require the assumption of appreciable back-bonding to the methyl ligand. It was postulated that the observed intensity changes were due to a near degeneracy of the perfluoromethyl a_1 with the metal e orbital in the first band of the $Mn(CO)_5CF_3$ spectrum, and a near degeneracy of the methyl a_1 with the metal b_2 orbital in the second band of the $Mn(CO)_5CH_3$ spectrum. Because of our recent success in observing the previously undetected ionization from the a_1 level in the halogen complexes (in accord with our calculations on these complexes), we decided to reexamine the spectra of $Mn(CO)_5CH_3$ and $Mn(CO)_5CF_3$ to determine if there is indeed evidence for a third ionization in the region of the e and b_2 bands.

Figure 1 shows a close look at the ionization region of interest for these two molecules. It is readily apparent that three separate ionizations are responsible for the line shapes observed here. In $Mn(CO)_5CF_3$ the first ionization possesses a distinct shoulder, and in $Mn(CO)_5CH_3$ the second ionization appears as a doublet of peaks of nearly equal intensity. Taking a closer look at just the top of these bands and curve fitting with gaussian peaks further confirm these observations. Thus our theoretical prediction of the additional a_1 orbital ionization in the region of the e and b_2 ionizations is substantiated by the well-defined spectra, and the particular peaks where the near degeneracies occur are in accord with our earlier proposal.

While we have strong convictions concerning the validity of our band assignments, an alternative assignment exists that cannot be entirely ruled out with the present experimental evidence. The alternative assignment is based on a recent *ab initio* calculation on $Mn(CO)_5CH_3$.[7] This calculation supports the placement of the a_1 ionization in the region of the e and b_2 ionizations. However, the authors propose that the first ionization may be due to the a_1 orbital followed by the ionizations of the nearly degenerate e and b_2 orbitals in the second band. Making assignments from the ground-state eigenvalues of either calculation involves a degree of risk because of the uncertainty in Koopmans' theorem, not to mention the uncertainty of approximations in our calculational method or the limited basis set in the *ab initio* calculations. The experimental IP's and splittings are within the range of uncertainty of both interpretations. If one were to accept assignment of the first ionization to the a_1 orbital, it would require acceptance of considerable enhancement of the ionization cross section for this a_1 orbital over that observed for a_1 levels in general.[3] It is well known however that cross sections are sensitive to the atomic character and therefore intensities may not form a firm guideline for assignment through curve analysis. Further information, such as that obtained from variation of the ionization energy or angle, or study of other complexes containing metal to methyl bonds, may prove helpful.

Regardless of the ultimate validity of one or the other assignments, this study shows that special care must be exercised in assigning the ionizations of photoelectron spectra. Many separate ionizations often occur very close in energy, and key ionizations may possess very low cross sections.

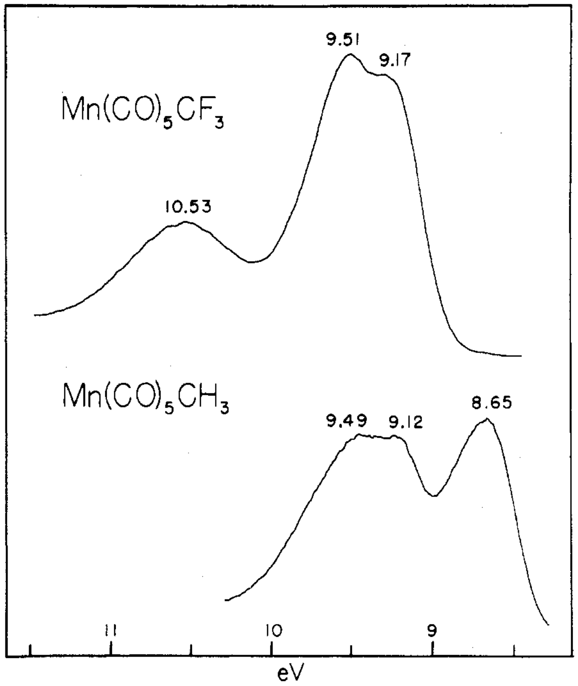

Figure 1. Low-energy photoelectron spectra of $Mn(CO)_5CF_3$ and $Mn(CO)_5CH_3$.

Due to the nature of the experiment these ionizations are often difficult to resolve or detect. Also, the unexpected occurrence of physical processes other than direct ionization, such as autoionization, may alter the spectra of similar molecules. Incorrect assignments for any of these reasons may have serious implications to the interpretation of the bonding in the system, as illustrated by the molecules studied here. The expected anomalies observed for the perfluoromethyl and methyl spectra with respect to the halide spectra are explained simply by the existence of the additional unexpected a_1 band as predicted by both calculations. This stresses the value of using theoretical calculations as an aid to interpreting the results of photoelectron spectroscopy.

Experimental Section

Spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. Full sweeps of the base line with argon present both prior to and subsequent to the spectra determination indicated no system contamination. All spectra were determined with an electron analyzer energy of 2.00 eV, typically yielding a half-width for the major argon peak of 24 meV at approximately 40,000 counts/sec. Both compounds were prepared according to standard techniques and analyzed by infrared spectroscopy. A given experimental determination of a spectrum consisted of a series of single observations, each observation requiring approximately 5 min of data collection time. Observations were repeated until all the sample introduced into the spectrometer had been depleted (generally 1 hr of data collection) to ensure that there was no transient behavior such as instrumental drift or contamination. It was more difficult to resolve the bands in $Mn(CO)_5CF_3$ than in $Mn(CO)_5CH_3$ due to slight instrumental instability obscuring the shape of the peak of the ionization band and the danger of contamination with $Mn(CO)_5COCF_3$. When the experiment was completed and comparison of each observation indicated no substantial differences, the observations were then summed to yield the well-defined spectra. In both cases each single observation is only a less well-defined representation of the final sum but still illustrates the same line shape. Both experiments were repeated after a period of 1 month to ensure reproducibility. Displayed spectra are the raw experimental data and were produced by the instrument's recorder. Peak positions were determined at their maxima with fitted gaussians on a linear base line, with data points weighted relative to their value. The uncertainty of the placement of these positions may be as large as 0.1 eV for the least well-defined band.

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(7) M. B. Hall, M. F. Guest, and I. H. Hillier, *Chem. Phys. Lett.*, 15, 592 (1972).

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Registry No. $Mn(CO)_5CF_3$, 13601-14-4; $Mn(CO)_5CH_3$, 13601-24-6.

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Preparation and Properties of Ethoxycarbonyl(tetraphenylporphinato)rhodium(III)

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Recent interest in unusual rhodium[1,2] porphyrins and the possible applications of these compounds as model systems for vitamin B_{12} have prompted us to report the synthesis of a novel porphine containing a rhodium-bound alkoxycarbonyl group.

The general area of alkoxycarbonyl complexes of transition metals has recently been reviewed by Angelici[3] and he has presented many examples (including rhodium complexes) of the general reaction

$$L_nMCO^{z+} + OR^- \rightarrow L_nMCOOR^{(z-1)+}$$

Angelici has also pointed out that the reactivity of a metal-bound CO in the analogous reaction with amines can often be correlated with the force constant or stretching frequency of the CO in question. Generally, CO groups exhibiting absorptions below 2000 cm^{-1} are not reactive. Inasmuch as Cl(TPP)RhCO[4] exhibits a CO stretching absorption at 2100 cm^{-1}, we expected it to be susceptible to attack by an alkoxy anion.

Friedrich and Moskophidis[5] have examined the reaction between cobalt corrinoids and carbon monoxide in alcoholic solution. They observed the formation of the alkoxycarbonyl derivative of the Co(III) corrinoid but not of the Co(II) species.

Experimental Section

Dichlorotetracarbonyldirhodium was prepared by the method of McCleverty and Wilkinson.[6]

The reaction of $(TPP)H_2$ and $[Rh(CO)_2Cl]_2$ was carried out by the methods of Fleischer and coworkers.[7-9] The previously reported product, ClTPPRhCO, was purified by an indirect route because it was not stable enough to withstand chromatography. Crude Cl(TPP)RhCO was dissolved in 2:1 $CHCl_3$-C_2H_5OH and allowed to evaporate slowly to dryness producing a residue possessing an infrared spectrum containing no carbonyl absorption at 2100 cm^{-1} and a visible spectrum with peaks at 422, 538, and 571 nm, identical with that of a sample of the reported compound (TPP)RhCl. This residue was redissolved in benzene and chloroform and chromatographed on alumina to obtain pure (TPP)RhCl. The carbonylation of (TPP)RhCl to produce a pure sample of the known compound Cl(TPP)RhCO was carried out in methylene chloride under 1 atm of CO at room temperature for 12 hr. The product crystallized quantitatively and was suction filtered, washed with a few milliliters of ether or hexane, and air-dried. The CO absorption was observed at 2100 cm^{-1}.

Ethoxycarbonyl(tetraphenylporphinato)rhodium(III) ((TPP)Rh-$COOC_2H_5$). A 10-mg sample of Cl(TPP)RhCO was dissolved in 150 ml of methylene chloride and a dilute solution of sodium ethoxide in ethanol was added until the reaction mixture turned orange-red. The solvents were immediately removed under reduced pressure at 60°. The residue was washed with a few milliliters of water and ethanol, chromatographed twice with benzene–chloroform on alumina, and recrystallized from chloroform–ethanol. Spectral peaks were observed at 418 and 526 nm in $CHCl_3$ and 1700 cm^{-1} in KBr. *Anal.* Calcd for $C_{44}H_{28}N_4RhCOOC_2H_5$: C, 71.58; H, 4.19; N, 7.11; Rh, 13.06. Found: C, 71.37; H, 4.33; N, 7.00; Rh, 12.72. The nmr spectrum ($CDCl_3$) showed peaks at τ 1.2 (sharp s, pyrrole H), 1.8 (m, phenyl H), 2.2 (m, phenyl H), 8.7 (q, CH_2), and 10.8 (t, CH_3).

Instrumentation. Infrared and visible spectra were recorded on a Perkin-Elmer Model 521 and a Cary Model 14, respectively. Molecular weights in Fisher Spectrograde methylene chloride were determined on a Hitachi Perkin-Elmer Model 115 vapor pressure osmometer at 31.5° using benzil as a standard. Solute concentrations were in the 10 mm range. Magnetic susceptibilities were measured on polycrystalline powders by the Faraday method using a Cahn RG electrobalance. The molar diamagnetic susceptibility of $(TPP)H_2$ was measured as -386×10^{-6} cgsu/mol. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E spectrometer by direct introduction of the sample above 250°. The pyrolysis products were introduced as gases, the pyrolysis being conducted outside the spectrometer. The nmr spectrum was recorded at 220 MHz on a Varian spectrometer.

Results and Discussion

Duplication of the conditions employed by Fleischer[7-9] and coworkers for the reaction between $[Rh(CO)_2Cl]_2$ and $(TPP)H_2$ in refluxing benzene or glacial acetic acid produced the previously reported products, $H_2ORh(TPP)Cl$, EtOHRh-(TPP)Cl, and ClRh(TPP)CO. In addition, a small amount of material exhibiting an infrared absorption at 1700 cm^{-1} was also obtained and the low frequency for the carbonyl absorption led us to suspect that an alkoxylcarbonyl may have been produced. Because of the poor yield of that material a direct synthesis was sought and accomplished by the reaction of ClRh(TPP)CO and $NaOC_2H_5$ in ethanol which essentially quantitatively produced $(TPP)RhCOOC_2H_5$. This product exhibits a strong CO stretching absorption at 1700 cm^{-1}, far below that expected for a terminal CO group. The molecular weight observed in CH_2Cl_2 requires a monomeric formulation and thus eliminates the possible bridging of CO groups between two rhodium porphine molecules. The maintenance of the oxidation state of the rhodium at III is indicated by the diamagnetism of the product. The high-field position found for the ethyl group in the nmr spectrum is due to the anisotropic effect of the porphine ring current and is similar to that observed for the axial acyl group in $(TPP)RhCOCH_3$.[1]

The mass spectrum of $(TPP)RhCOOC_2H_5$ is presented in Table I. It is noteworthy that no fragments are observed which correspond to $(TPP)RhCO^+$, $(TPP)RhOC_2H_5^+$, and $COOC_2H_5^+$. The large peak for CO_2^+ is derived from the alkoxycarbonyl as indicated by the absence of a peak at *m/e* 32 indicating the absence of air. Presumably then the peak at *m/e* 28 is likewise due to CO^+ rather than N_2^+. In

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(1) B. R. James and D. V. Stynes, *J. Chem. Soc., Chem. Commun.*, 1261 (1972).

(2) Z. Yashida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Lett.*, 1077 (1972).

(3) R. J. Angelici, *Accounts Chem. Res.*, 5, 335 (1972).

(4) TPP is the dianion of tetraphenylporphine.

(5) W. Friedrich and M. Moskophidis, *Z. Naturforsch. B*, 26, 879 (1971).

(6) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8, 211 (1966).

(7) E. B. Fleischer and N. Sadasivan, *Chem. Commun.*, 159 (1967).

(8) N. Sadasivan and E. B. Fleischer, *J. Inorg. Nucl. Chem.*, 30, 591 (1968).

(9) E. B. Fleischer, R. Thorp, and D. Venerable, *Chem. Commun.*, 475 (1969).