frequencies in *trans*-bis-(glycinato)-platinum(II), 3231 and 3083 cm.$^{-1}$, indicating that the NH_2 groups are coordinated to copper(II) in a *trans* arrangement.

The third high frequency peak in Fig. 2 is attributed to the O–H stretching vibration. It is much weaker, less broad, and at a higher frequency than the corresponding absorption by dichlorobis-(glycine)-platinum(II), in which intra- and intermolecular C=O · · ·H—O hydrogen bonds are important.

The frequency of the carbonyl peak, 1659 cm.$^{-1}$, compares with 1658 cm.$^{-1}$ in chelated dichloro-(ethyl glycinate)-copper(II), 1711 cm.$^{-1}$ in dichlorobis-(glycine)-platinum(II) in which only the nitrogen atoms of the glycine molecules are coordinated, and with about 1605 cm.$^{-1}$ for the antisymmetric O=C—O stretching vibration in bis-(glycino)-copper(II) monohydrate. The 1659 cm.$^{-1}$ peak in the spectrum of bis-(glycine)-copper(II) trichlorocuprate(I) indicates the presence of C=O —Cu bonds. This is the only complex known to the authors containing chelated neutral glycine ligands. We were unable to prepare similar complexes by adding other metal halides and hydrogen chloride to solutions of metal glycinates.

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Some Reactions of Bis-(iron tricarbonyl nitrosyl)-mercury

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Reaction between $Hg[Fe(CO)_3NO]_2$ and tris-(dimethylamino)-phosphine yields the complexes $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$ and $(Tdp)_2Fe(NO)_2$, depending on the reaction conditions. Reaction between $Hg[Fe(CO)_3NO]_2$ and bis-(trifluoromethyl)-dithietene yields a nitrosyl derivative of stoichiometry $C_4F_6S_2FeNO$. Reaction between $Hg[Fe(CO)_3NO]_2$ and triphenylphosphine yields the substitution product $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$.

The compound $Hg[Fe(CO)_3NO]_2$, described recently by Hieber and Beutner,[1] was prepared and characterized independently in this laboratory prior to appearance of the original report. In the present paper substitution reactions of $Hg[Fe(CO)_3NO]_2$ are described.

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double beam machine with sodium chloride optics. In addition, the metal carbonyl and nitrosyl regions of the infrared spectra of selected compounds were taken in halocarbon oil mulls and recorded on a Perkin-Elmer Model 112 single-beam machine with CaF_2 optics. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, New York. Melting points were taken in capillaries and are uncorrected.

Materials.—Triphenylphosphine was purchased from Metal and Thermit Co., Rahway, New Jersey. Tris-(dimethylamino)-phosphine[2,3] and bis-(trifluoromethyl)-dithietene[4] were prepared by published procedures.

Bis-(iron tricarbonyl nitrosyl)-mercury.—The procedure which we used for the preparation of $Hg[Fe(CO)_3NO]_2$ was very similar to that of Hieber and Beutner[1] involving the reaction between the anion $[Fe(CO)_3NO]^-$ and aqueous mercury(II) cyanide. Material recrystallized from dichloromethane was used for these reactions. It was found necessary to store $Hg[Fe(CO)_3NO]_2$ in a refrigerator.

Reaction between $Hg[Fe(CO)_3NO]_2$ and Triphenylphosphine.[4a]—Upon stirring a solution of 1.35 g. (2.5 mmoles) of $Hg[Fe(CO)_3NO]_2$ and 2.62 g. (10 mmoles) of triphenylphosphine in 50 ml. of thiophene-free benzene at room temperature for several hours, a fine yellow-orange precipitate gradually formed. After 22 hr. this precipitate was filtered, washed with 50 ml. of dichloromethane, and dried to give 1.72 g. (68% yield) of $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$, which on heating turned brown above 200°. The compound $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ is a yellow-orange powder considerably more stable than the unsubstituted $Hg[Fe(CO)_3NO]_2$. Like $Hg[Co(CO)_3P(C_6H_5)_3]_2$,[5] $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ is very sparingly soluble in organic solvents.

Anal. Calcd. for $C_{40}H_{30}N_2P_2HgFe_2O_6$: C, 47.3; H, 3.5; N, 2.8; P, 6.1; Hg, 19.8. Found: C, 46.9; H, 3.0; N, 3.0; P, 5.8; Hg, 19.7.

Infrared Spectrum.—C–H bands too weak to be unequivocally observed; metal carbonyl bands at 1980 (w), 1950 (m), and 1905 (s) cm.$^{-1}$; metal nitrosyl bands at 1712 (s) and 1705 (s) cm.$^{-1}$; other bands at 1475 (w), 1430 (w), 1375 (vw), 1263 (vw), 1175 (vw), 1090 (w), 1025 (vw), 992 (vw), 745 (w), 705 (w), and 691 (m) cm.$^{-1}$.

Preparation of $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$.—A mixture of 1.5 g. (2.77 mmoles) of $Hg[Fe(CO)_3NO]_2$, 2.5 ml. (~2.5 g., 15.4 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of thiophene-free benzene was refluxed ~6 hr. under nitrogen with magnetic stirring. After cooling to room temperature the reaction mixture was filtered by gravity. Solvent was removed from the orange filtrate at ~30 mm. The resulting orange crystalline residue was recrystallized twice from mixtures of dichloromethane and hexane and washed with pentane to give 0.34 g. (19% yield) of orange crystals of $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$, which on heating gradually turned black above ~135°.

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[1] W. Hieber and H. Beutner, *Z. anorg. allgem. Chem.*, **320**, 101 (1963).

[2] To minimize confusion and the use of several types of brackets tris-(dimethylamino)-phosphine will be abbreviated as Tdp in formulas.

[3] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

[4] C. G. Krespan, *ibid.*, **83**, 3434 (1961).

[4a] NOTE ADDED IN PROOF.—Since this paper was accepted, the compound $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ has been described independently by Hieber and Klingshirn [W. Hieber and W. Klingshirn, *Z. anorg. allgem. Chem.*, **323**, 292 (1963)]. They also described several other $Hg[Fe(CO)_2(NO)PR_3]_2$ compounds.

[5] W. Hieber and R. Breu, *Ber.*, **90**, 1259 (1957).

Anal. Calcd. for $C_{17}H_{36}N_8P_2Fe_2O_7$: C, 32.0; H, 5.6; N, 17.5; P, 9.7; Fe, 17.5. Found: C, 30.8, 31.4; H, 5.8, 5.8; N, 16.6, 17.2; P, 9.1, 9.5; Fe, 16.6.

Infrared Spectrum.—C–H bands at 2970 (sh), 2910 (w), 2875 (w), 2840 (sh), and 2800 (sh) cm.$^{-1}$; metal carbonyl bands at 2025 (m), 1963 (s), and 1860 (s) cm.$^{-1}$; metal nitrosyl bands at 1755 (s) and 1634 (s) cm.$^{-1}$; other bands at 1475 (w), 1455 (w), 1435 (sh), 1400 (vw), 1275 (m), 1170 (m), 1055 (w), 965 (s), and 768 (s) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Methyl resonance observed at 7.23 τ (triplet, outer peaks separated by 10.2 c.p.s.).

Conductivity.—A molar conductance of 156 ± 7 mhos was found by measurements on acetone solutions of three concentrations in the range 4.2×10^{-4} to 1.4×10^{-3} M.

Preparation of $(Tdp)_2Fe(NO)_2$.—The same quantities of $Hg[Fe(CO)_3NO]_2$ and tris-(dimethylamino)-phosphine as used in the preparation of $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$ were refluxed in benzene solution for 20 hr. rather than only 6 hr. Extraction of the evaporated reaction mixture with five 10-ml. portions of pentane (in which the ionic derivative is insoluble) gave a red solution which deposited 0.53 g. (43% yield) of $(Tdp)_2Fe(NO)_2$, m.p. 99–101°, on cooling in a −78° bath. Sublimation at 120° (0.1 mm.) gave the analytical sample as a dark red sublimate which appeared purple-brown when powdered. The compound became liquid upon standing in closed vials at 25°.

Anal. Calcd. for $C_{12}H_{36}N_8P_2FeO_2$: C, 32.6; H, 8.1; N, 25.3; P, 14.0; mol. wt., 442. Found: C, 32.8; H, 8.1; N, 25.2; P, 14.4; mol. wt., 423.

Infrared Spectrum.—C–H bands at 2960 (vw, sh), 2900 (sh), 2850 (m), and 2780 (sh) cm.$^{-1}$; metal nitrosyl bands (Perkin-Elmer 112 machine, halocarbon oil mull) at 1657 (s) and 1697 (s) cm.$^{-1}$; other bands at 1475 (sh), 1455 (w), 1428 (sh), 1390 (w), 1290 (w), 1265 (m), 1175 (s), 1145 (vw), 1054 (w), 967 (s), 950 (s), 942 (sh), 743 (w), and 692 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Methyl resonance observed at 7.46 τ (doublet, $J = 9.3$ c.p.s.).

Reaction between $Hg[Fe(CO)_3NO]_2$ and Bis-(trifluoromethyl)-dithietene.—A mixture of 2.0 g. (3.7 mmoles) of $Hg[Fe(CO)_3NO]_2$, 1.0 ml. (~1.6 g., 7.0 mmoles) of bis-(trifluoromethyl)-dithietene, and 50 ml. of thiophene-free benzene was refluxed 7 hr. under nitrogen with magnetic stirring. After the reaction period was over, the reaction mixture was allowed to cool to room temperature. The reaction mixture was filtered by gravity and the solvent removed from the black filtrate at ~30 mm. The black residue was dried 2 hr. at 25° (0.6 mm.). It was then transferred to a sublimer and the product sublimed out at 100–120° (0.5–0.1 mm.) through glass wool for 18 hr. to give 0.39 g. (18% yield) of a black crystalline sublimate of empirical composition $C_4F_6S_2FeNO$.

Anal. Calcd. for $C_4F_6S_2FeNO$: C, 15.4; H, 0.0; F, 36.5; S, 20.5; N, 4.5; Fe, 18.0. Found: C, 15.6; H, 0.0; F, 36.3; S, 20.3; N, 4.6; Fe, 18.0.

Infrared Spectrum.—Metal nitrosyl bands (Perkin-Elmer 112 machine, halocarbon oil mull) at 1777 (w), 1799 (w), 1815 (s), 1832 (s), and 1882 (s) cm.$^{-1}$; carbon–carbon double bond band at 1530 cm.$^{-1}$; carbon–fluorine bands at 1235 (s), 1175 (s), and 1157 (s) cm.$^{-1}$; other bands at 1110 (w), 890 (w), 882 (w), and 710 (m) cm.$^{-1}$.

F^{19} N.m.r. Spectrum.—Single resonance in tetrahydrofuran solution at 60 p.p.m. upfield from internal $CFCl_3$. Only a weak spectrum was obtained.

Discussion

When $Hg[Fe(CO)_3NO]_2$ is allowed to react with triphenylphosphine at room temperature, a simple substitution process takes place as represented by the equation

$$Hg[Fe(CO)_3NO]_2 + 2P(C_6H_5)_3 \longrightarrow Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2 + 2CO$$

This reaction is entirely analogous to the reaction between $Hg[Co(CO)_4]_2$ and triphenylphosphine to give $Hg[Co(CO)_3P(C_6H_5)_3]_2$.[5]

When tris-(dimethylamino)-phosphine was used in place of triphenylphosphine in the reaction with $Hg[Fe(CO)_3NO]_2$, a mixture of the expected substitution product $Hg[Fe(CO)_2(NO)(Tdp)]_2$ and a mercury-free decomposition product was obtained at room temperature as indicated by analyses. If the reaction is carried out in boiling benzene for 6 hr. rather than at room temperature, formation of an orange mercury-free solid of composition $(Tdp)_2Fe_2(CO)_5(NO)_2$ takes place as represented by the equation

$$Hg[Fe(CO)_3NO]_2 + 2Tdp \longrightarrow (Tdp)_2Fe_2(CO)_5(NO)_2 + CO + Hg$$

This new iron nitrosyl complex appears to be completely analogous to the yellow crystalline complex of composition $(Tdp)_2Co_2(CO)_7$ obtained from dicobalt octacarbonyl and tris-(dimethylamino)-phosphine.[6] The iron complex $(Tdp)_2Fe_2(CO)_5(NO)_2$ was found to exhibit a relatively high conductivity in acetone solution supporting an ionic formulation $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$, entirely analogous to the formulation $[(Tdp)_2Co(CO)_3][Co(CO)_4]$ for the reaction product from tris-(dimethylamino)-phosphine and dicobalt octacarbonyl.[7] Indeed the values found for the molar conductances of the two compounds (~155 mhos) are almost identical.

The infrared and proton n.m.r. spectra also support the formulation of $(Tdp)_2Fe_2(CO)_5(NO)_2$ as $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$. Thus in the infrared spectrum the carbonyl bands at 1963 and 1860 cm.$^{-1}$ and the nitrosyl band at 1634 cm.$^{-1}$ may be attributed to the $Fe(CO)_3NO^-$ anion[8] and the carbonyl band at 2025 cm.$^{-1}$ and the nitrosyl band at 1755 cm.$^{-1}$ to the $(Tdp)_2Fe(CO)_2NO^+$ cation. The proton n.m.r. spectrum of $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$ exhibits a triplet due to the 36 equivalent methyl protons split by the two phosphorus atoms almost identical with the triplet observed in the proton n.m.r. spectrum of $[(Tdp)_2Co(CO)_3][Co(CO)_4]$.[6,7]

If the reaction between $Hg[Fe(CO)_3NO]_2$ and tris-(dimethylamino)-phosphine in boiling benzene is carried out for 20 hr. rather than for only 6 hr., the iron nitrosyl derivative produced in the largest quantity appears to be $(Tdp)_2Fe(NO)_2$,[9] presumably formed according to the equation

$$Hg[Fe(CO)_3NO]_2 + 2Tdp \longrightarrow (Tdp)_2Fe(NO)_2 + (1/n)[HgFe(CO)_4]_n + 2CO$$

This iron nitrosyl complex is a substitution product of

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(6) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(7) The presence of two nonequivalent iron atoms in $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$ is also suggested by Fe^{57} Mössbauer resonance studies on this compound (G. K. Wertheim and R. H. Herber, private communication). Two quadrupole split resonances were observed.

(8) Compare W. Beck, *Ber.*, **94**, 1214 (1961), where values of 1984 and 1881 cm.$^{-1}$ are given for the carbonyl bands and 1651 cm.$^{-1}$ for the nitrosyl band in $Fe(CO)_3NO^-$ based on spectra obtained in solutions in acetone and in diethylene glycol dimethyl ether.

(9) In one of the experiments a red-orange liquid more volatile than $(Tdp)_2Fe(NO)_2$ was also observed; this may be the compound $(Tdp)FeCO(NO)_2$.

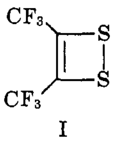
$Fe(CO)_2(NO)_2$ similar to previously reported compounds.[10] The tendency for $Hg[Fe(CO)_3NO]_2$ to produce $Fe(CO)_2(NO)_2$ on heating alone[1] makes the formation of a derivative of $Fe(CO)_2(NO)_2$ on heating with tris-(dimethylamino)-phosphine not at all surprising.

The proton n.m.r. spectrum of $(Tdp)_2Fe(NO)_2$, like that of the isoelectronic $(Tdp)_2Ni(CO)_2$,[6] exhibits a doublet rather than a triplet due to the 36 equivalent methyl protons. This indicates that the phosphorus–phosphorus coupling in $(Tdp)_2Fe(NO)_2$ is so small that each methyl proton is split by only one of the phosphorus atoms. This further confirms the observation that the coupling between the two phosphorus atoms in a tetrahedral system is much smaller than the coupling between the two phosphorus atoms in the *trans* positions of a trigonal bipyramidal or octahedral system.[6]

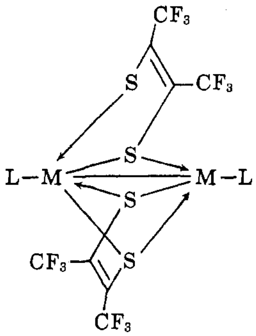
When $Hg[Fe(CO)_3NO]_2$ was allowed to react for 7 hr. in boiling benzene with bis-(trifluoromethyl)-dithietene (I), complete displacement of carbon monoxide occurred to produce a black derivative of stoichiometry $C_4F_6S_2FeNO$, apparently according to the equation

$$Hg[Fe(CO)_3NO]_2 + 2C_4F_6S_2 \longrightarrow 2C_4F_6S_2FeNO + Hg + 6CO$$

This iron nitrosyl derivative $C_4F_6S_2FeNO$ appears to be related to the isoelectronic black compound of stoichiometry $C_4F_6S_2CoCO$ isolated from the reaction between bis-(trifluoromethyl)-dithietene and dicobalt octacarbonyl.[11] Unfortunately, $C_4F_6S_2FeNO$ like $C_4F_6S_2CoCO$ was too sparingly soluble in benzene for a molecular weight determination by the vapor pressure osmometer. The F^{19} n.m.r. spectrum of this nitrosyl derivative indicated it to be diamagnetic. The volatility and diamagnetism of these compounds suggest them to be dimeric and a consideration of related derivatives of bis-(trifluoromethyl)-dithietene (I)[11] suggests structures with four sulfur bridges for $[C_4F_6S_2CoCO]_2$ (II) and $[C_4F_6S_2FeNO]_2$ (III).



I



II, M = Co, L = CO
III, M = Fe, L = NO

No iron nitrosyl derivatives of interest were isolated from the reactions between $Hg[Fe(CO)_3NO]_2$ and certain olefinic hydrocarbons such as cyclopentadiene, cyclooctatetraene, and cycloheptatriene. No evidence for the formation of derivatives of the type $(RC{\equiv}CR)Fe_2(CO)_4(NO)_2$ isoelectronic with the known compounds $(RC{\equiv}CR)Co_2(CO)_6$[12] was obtained in the reactions of $Hg[Fe(CO)_3NO]_2$ with diphenylacetylene and with hexafluorobutyne-2. Reaction between $Hg[Fe(CO)_3NO]_2$ and *p*-anisyl isonitrile gave a green reaction mixture from which nothing of interest was isolated.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance.

[10] M. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957); W. Hieber, W. Beck, and H. Tengler, *Z. Naturforsch.*, **15b**, 411 (1960); D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962).

[11] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[12] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *ibid.*, **78**, 120 (1956); M. R. Tirpak, C. A. Hollingworth, and J. W. Wotiz, *J. Org. Chem.*, **25**, 687 (1960); J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

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Oxygen-18 Tracer Studies on the Reduction of Uranyl Ion by Chromium(II)[1]

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Oxygen-18 tracer experiments have been carried out on the reaction between UO_2^{+2} and Cr(II) in aqueous perchloric acid. Evidence is presented suggesting efficient transfer of oxygen from UO_2^{+2} to Cr(II) under conditions where the reaction between the excess Cr(II) and intermediate is rapid. The results of oxygen-transfer experiments are given at 0 and 25°. The results at 25° and low H^+ are interpreted in terms of an activated complex containing Cr–O–U–O–Cr bonds.

Introduction

Newton and Baker[2] have studied the reaction between U(VI) and Cr(II) in perchloric acid and have found that the reaction is complicated in that the reactants disappear much faster than final products appear. When the reactants are mixed in acid solution a rapid reaction occurs, followed by a slower reaction which yields the final products U(IV) and Cr(III). The stoichiometry of the net reaction is

[1] A preliminary account of this work was presented at the 7th International Conference on Coordination Chemistry, Stockholm, June, 1962.

[2] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).