trend in ν(M–P) as expected on the basis of our arguments, except for the first member. Since the appropriate k_1 and k_2 values given by Cotton[2] for the carbonyl groups are slightly smaller for these complexes than for the analogous $P(OCH_3)_3$ compounds and hence also for the $P(OCH_2)_3CCH_3$ analogs (see above), the general shift toward smaller values of ν(M–P) in the $P(C_6H_5)_3$ complexes (except the monosubstituted one) can be ascribed to the slightly lower π-bonding properties of $P(C_6H_5)_3$ compared to $P(OR)_3$ and the larger mass effect of the former ligand. The reason(s) for the peculiarly larger ν(M–P) value found for $Mo(CO)_5P(C_6H_5)_3$ (204 cm^{-1}) compared to $Mo(CO)_5P(OCH_2)_3CCH_3$ (195 cm^{-1}) is (are) not known at this time. The same obtains for the situation found with $Ni(CO)_3P(C_6H_5)_3$ (192 cm^{-1})[29] *vs.* $Ni(CO)_3P(OCH_2)_3CCH_3$ (143 cm^{-1}) (Table VI). No ν(M–P) values are available for higher substitution complexes of the Ni–$P(C_6H_5)_3$ series for comparison with the $Ni(CO)_{4-x}(P(OCH_2)_3CCH_3)_x$ series, however. If the higher ν(M–P) values in these two $P(C_6H_5)_3$ complexes are due to stronger M–P bonds, it is strange that a similar disparity is not found in the trend of the k_1 and k_2 values for the carbonyl modes in the case of the molybdenum complexes. It is tentatively proposed, therefore, that at least in the molybdenum mono $P(C_6H_5)_3$ complex, some other effect (coupling to another mode perhaps) operates to raise the frequency of the M–P mode. Because the M–P stretching region is quite free of other absorptions in the polycyclic phosphite complexes utilized in this research, further studies on other polycyclic phosphorus ligands exhibiting a variety of ligand properties as well as PF_3[30] are in progress.[31]

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[31] NOTE ADDED IN PROOF.—Recently Singh, *et al.* [S. Singh, P. P. Singh, and R. Rivest, *Inorg. Chem.*, **7**, 1236 (1968)], were unable to assign any bands in the spectra of $Fe(CO)_4P(C_6H_5)_3$ and *trans*-$Fe(CO)_3(P(C_6H_5)_3)_2$ in the 700–200 cm^{-1} region and suggested that coupling with M–C modes brought the ν(M–P) absorptions below the 200 cm^{-1} limit of their instrument. Inasmuch as our work and that of Chalmers, *et al.*,[20] indicates that ν(M–P) stretches frequently appear below 200 cm^{-1} for zerovalent phosphorus complexes, we suggest that ν(M–P) in all probability occurs below 200 cm^{-1} and that it is not necessary to invoke the coupling argument at this time.

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Metal-Stabilized Thionitroso Compounds

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Reaction between $(t\text{-}C_4H_9N)_2S$ and $Fe(CO)_5$ in hexane at ambient temperature produced an alkylthionitroso complex, $Fe_2(CC)_6(t\text{-}C_4H_9NS)$ (**1**), in small yield whereas $(C_6H_5N)_2S$ with $Fe(CO)_5$ or with $Fe_2(CO)_9$ yielded azobenzene as the main isolable product. The phenyl analog of **1**, $Fe_2(CO)_6(C_6H_5NS)$ (**2**), was obtained by treating C_6H_5NSO with $Fe_2(CO)_9$. On the basis of infrared, nmr, and mass spectroscopy the structures for **1** and **2** were deduced.

Studies on reactions of sulfur diimides $(RN)_2S$ with metals or metal compounds have been undertaken in expectation of formation of nitrene or metal-stabilized nitrene complexes. Generally facile cleavage of the N–S bond or abstraction of the sulfur atoms takes place under mild reaction conditions giving rise to a variety of products depending upon the substituent R or the metal. Thus, the reaction of $(t\text{-}C_4H_9N)_2S$ with $Ni(C_5H_5)_2$ or with $(C_5H_5NiCO)_2$ produced a cluster complex, $(NiC_5H_5)_3(t\text{-}C_4H_9N)$, which may be regarded as a nitrene complex,[1] whereas the reaction with $Co(C_5H_5)(CO)_2$ gave a binuclear complex, $(CoC_5H_5)_2(t\text{-}C_4H_9NCON\text{-}t\text{-}C_4H_9)$,[1,2] which was supposedly derived from a nitrene complex intermediate, $Co(C_5H_5)(CO)(t\text{-}C_4H_9N)$. Treating dodecacarbonyltriiron with C_6H_5NCO, Pauson, *et al.*,[3] prepared a similar iron carbonyl complex, $Fe_2(CO)_6(C_6H_5NCONC_6H_5)$, which was called an "ureylene" complex.[4]

We now wish to describe the reaction of $(RN)_2S$ or RNSO with iron carbonyls which affords iron carbonyl complexes of thionitrosoalkane or -benzene.

Reaction of $(t\text{-}C_4H_9N)_2S$ with $Fe(CO)_5$ was carried out in hexane, under irradiation with sunlight, to give an orange, diamagnetic, crystalline complex (**1**), mp 48–50°, in 3% yield. It is thermally stable and fairly volatile. The elemental analysis and molecular weight measurement (mass spectrometry) corresponded to the molecular formula $Fe_2(CO)_6(t\text{-}C_4H_9NS)$, indicat-

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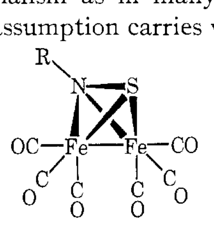
ing that we have here another new type of reaction. Characterization of complex **1** was facilitated by its good solubility in not only aromatic but also paraffinic hydrocarbons. Thus, the infrared spectrum showed six carbonyl stretching bands, four of which were of strong intensity resembling the reported absorptions for hexacarbonyldiiron complexes, *e.g.*, $Fe_2(CO)_6(o\text{-}SC_6H_4NH)$[5] or $Fe_2(CO)_6(o\text{-}SC_6H_4S)$.[5] An absorption at 705 cm^{-1} of medium intensity was assigned to an N–S single bond stretching frequency.[6] In the nmr spectrum a sharp singlet due to the *t*-butyl protons appeared at τ 9.38 which is higher than the chemical shift (τ 8.64) of free $(t\text{-}C_4H_9N)_2S$. If a nitrogen atom of a ligand coordinates to metal primarily through its lone-pair electrons, a small downfield shift compared to the free ligand is generally observed for the alkyl protons adjacent to the nitrogen atom.[7] Hence the upfield shift may be considered to be indicative of σ bonding between the nitrogen atom and $Fe(CO)_3$. However, since an anisotropic deshielding effect due to coordination to metal is sensitive to the stereochemistry of complexes and since the comparison must be made between free and the same ligand coordinated, the argument here involving different species, $(RN)_2S$ and RNS, suffers somewhat from ambiguity.

When $(C_6H_5N)_2S$ was treated similarly with $Fe(CO)_5$ or $Fe_2(CO)_9$ azobenzene was obtained as the main product together with a trace amount of aniline, no tractable iron complex being formed. C_6H_5NSO with $Fe_2(CO)_9$ in benzene, however, produced an orange, diamagnetic complex (**2**), mp 65–67°, in 1.6% yield. The molecular formula corresponds to $Fe_2(CO)_6(C_6H_5NS)$. This is less soluble in paraffinic hydrocarbons than in aromatic solvent. Complex **2** showed six carbonyl stretching bands quite similar to those of **1** and also an N–S stretching band at 721 cm^{-1}. The mass spectra of **1** and **2** show the molecular ions, $RNSFe_2(CO)_6^+$, fragment ions, $RNSFe_2(CO)_n^+$ (n = 0–5), formed by successive loss of six carbonyl ligands, and the ligand ion RNS^+. Other prominent peaks are $NSFe_2^+$ and SFe_2^+ for **1** and $CNSFe_2^+$, SFe_2^+, and $C_6H_5NSFe_2^{2+}$ for **2**. Thus the infrared and mass spectra consistently suggest that RNS is involved in **1** and **2** where the nitrogen–sulfur bond order is likely reduced to that of a single bond. All of these physical properties appear to conform well with a proposed structure depicted below. We postulated that the two iron atoms attain the inert gas formalism as in many iron(0) carbonyl complexes. The assumption carries with it an implication that both of the lone pairs on the nitrogen and sulfur atoms participate in the coordination forming two bridges.



1, R = $t\text{-}C_4H_9$
2, R = C_6H_5

This is the first reported example of an alkyl- or arylthionitroso complex. A phenylnitroso complex of the formula $[Fe(CO)_3(C_6H_5NO)]_2$[8] was reported to have been made by the reaction of $C_6H_5NO_2$ with $Fe(CO)_5$. The stoichiometry is different and hence we have the structure involving no iron–iron bond. It is noteworthy that free thionitrosoalkane or -arene had not been reported to be isolated while it can be stabilized by complexation. Doubtless, RNS tends to polymerize and a tetrametic form $(R\text{–}NS)_4$[9] has been reported so far.

Experimental Section

Reaction of $(t\text{-}C_4H_9N)_2S$ with $Fe(CO)_5$.—A mixture of 2.0 g (10 mmol) of $Fe(CO)_5$ and 1.8 g (10 mmol) of $(t\text{-}C_4H_9N)_2S$ dissolved in 15 ml of hexane was stirred at room temperature under irradiation with diffuse sunlight for 20 hr. After removal of the black precipitate by filtration, the filtrate was chromatographed on alumina under a nitrogen atmosphere using hexane as an eluent to give a yellow eluate from which was obtained orange solids stable to air. Sublimation at 60° under vacuum (1 mm) gave 60 mg of an orange crystalline complex (**1**), mp 48–50°. *Anal.* Calcd for $C_{10}H_9NO_6SFe_2$: C, 31.76; H, 2.46; N, 3.60; O, 25.43; mol wt, 383. Found: C, 31.36; H, 2.37; N, 3.65; O, 25.07; mol wt, 383 (measured by mass spectrometry). The infrared spectrum recorded on a Jasco Model DS-402G grating spectrophotometer using Nujol mull showed carbonyl stretching bands at 2069 (s), 2030 (vs), 1999 (vs), 1996.5 (s), 1988.5 (m), and 1980 (w) cm^{-1} and a band due to the *t*-butyl group at 1175 cm^{-1}. A medium-intensity band appeared at 705 cm^{-1}, a region of N–S single-bond stretching. In the far-infrared region were observed a number of unassignable absorptions at 641 (m), 619 (w), 593 (m), 570 (s), 492 (w), 477 (w), 450 (w), 440 (w), and 362 (w) cm^{-1}. In the nmr spectrum measured by a 100-Mc Model JNM 4H-100 of Japan Electron Optics Laboratory in benzene solution was observed a sharp singlet at τ 9.38 assignable to the *t*-butyl protons. This implies that the complex is diamagnetic. The mass spectrum was recorded on a Hitachi Type RMU-7HR at Takeda Chemical Industries Ltd.

Reaction of $(C_6H_5N)_2S$ with $Fe(CO)_5$ or with $Fe_2(CO)_9$.—A mixture of 1.0 g (4.7 mmol) of $(C_6H_5N)_2S$ and 0.46 g (2.4 mmol) of $Fe(CO)_5$ in 10 ml of cyclohexene was refluxed for 20 hr to give a dark brown oil from which was obtained, upon alumina chromatography using a hexane–benzene mixture as an eluent, 84 mg of azobenzene as the main isolable product. Further elution with benzene gave a trace amount of aniline but no complex product. Similarly a mixture of 0.32 g (1.5 mmol) of $(C_6H_5N)_2S$ and 0.36 g (1 mmol) of $Fe_2(CO)_9$ in 10 ml benzene was heated at 40° for 2 hr to give 30 mg of azobenzene. Irradiation with sunlight of the reaction mixture did not alter the reaction course.

Reaction of C_6H_5NSO with $Fe_2(CO)_9$.—A mixture of 1.2 g (3.3 mmol) of $Fe_2(CO)_9$ and 0.97 g (7 mmol) of C_6H_5NSO, prepared by the established method,[10] in 20 ml of benzene was heated at 40–45° for 3 hr. Alumina chromatography using a hexane–benzene mixture as an eluent followed by recrystallization from hexane gave an orange crystalline complex, mp 65–67°. *Anal.* Calcd for $C_{12}H_5NO_6SFe_2$: C, 35.78; H, 1.25; N, 3.47; O, 23.82; mol wt, 403. Found: C, 36.21; H, 1.41; N, 3.46; O, 24.96; mol wt, 403. The infrared spectrum shows carbonyl stretching bands at 2071 (s), 2034 (vs), 1999 (vs), 1998.5 (vs),

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1995 (m), and 1985 (w) cm^{-1}, which resemble the carbonyl bands for 1. An absorption at 721 cm^{-1} is assignable to the N–S stretching band. Two absorptions at 755 and 682 cm^{-1} are the CH out-of-plane deformation bands for the monosubstituted benzene. In the far-infrared region were observed absorptions at 642 (m), 617 (s), 583 (s), 561 (s), ~475 (w, b), 445 (w), and 397 (w, b) cm^{-1}.

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Some Aspects of the Stereochemistry of Amine Oxide Metal Complexes

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Vibrational and electronic spectra and magnetic data are correlated to show that complexes of the type $M(R\text{-}PyO)_6{}^{n+}(ClO_4)_n$ (R–PyO = pyridine N-oxide or a substituted derivative) do not have octahedral (O_h) symmetry. Similarly the copper complexes $Cu(R\text{-}PyO)_4(ClO_4)_2$ do not have D_{4h} symmetry. The argument employs data from the literature as well as some novel vibrational (infrared) and low-temperature electronic spectroscopic data. A new five-coordinate derivative $Co(2\text{-}CH_3PyO)_5(ClO_4)_2$ (2-CH_3PyO = 2-picoline N-oxide) is characterized.

Complexes of type $ML_6{}^{n+}$, where L is a polyatomic monodentate ligand, generally have electronic, vibrational, and magnetic properties close to those anticipated for an octahedral complex even though such a molecule will not, in general, belong to the point group O_h.[2] The *effective* symmetry of the molecule is determined not only by the geometric site symmetry of the ion but also by the electronic symmetry, governed by the degree of interaction between the metal ion wave functions and the ligand wave functions. This is particularly marked with bidentate ligands where the properties of species such as $ML_3{}^{n+}$, where L is an unsaturated molecule such as bipyridyl, deviate considerably from octahedral behavior;[3] with saturated systems such as ethylenediamine, the deviation is very much smaller.[2,4] Pyridine N-oxide and its substituted derivatives are known to react with a wide range of metal ions forming complexes of considerable current interest.[5,6]

This ligand appears to be one of the very few monodentate ligands whose hexakis complexes have properties indicative of a marked variation from regular octahedral symmetry. This variation from the expected octahedral behavior is the main topic of discussion in this paper. During the course of our investigation a novel five-coordinate cobalt(II) complex of 2-picoline N-oxide was synthesized. This is also discussed.

Experimental Section

Electronic diffuse reflectance spectra were recorded with a Beckman DK2A instrument. The low-temperature transmittance spectra were obtained, by the method outlined by Rowley and Drago,[7] using a Cary 14 instrument. Vibrational spectra were recorded with Perkin-Elmer Models 21 and 257 spectrophotometers. Magnetic moments were determined using the Gouy method with a 1.5-in. pole piece Newport electromagnet. Mercury tetrathiocyanatocobaltate(II) was used as calibrant.

The new complexes reported in this paper were prepared by the following general technique. The metal salt (1 g) and the ligand (1 g) were each dissolved in hot alcohol (20 ml). The solutions were filtered and mixed. The mixture was then kept at 0° for 24 hr. The products were recrystallized from the same solvent, washed with diethyl ether, and dried under reduced pressure. Table I lists the analytical data and also the alcohol (methanol or ethanol) used for each synthesis. In the case of the complex $Fe(4\text{-}NO_2PyO)_6(ClO_4)_2$ 1 g each of the metal salt and ligand were refluxed in ethanol (10 ml) for 5 min. *Note: This complex may detonate* and care should be taken in handling it. The other complexes described here were not observed to be liable to explosion. The unusually intense color of this complex and of the corresponding manganese(II) complex is due to the presence of a relatively low-energy charge-transfer band and to the absorption of the $-NO_2$ group. The detailed nature of the charge-transfer absorption in pyridine N-oxide metal complexes, which has been briefly commented upon,[8] is the subject of a future paper.[9]

The five-coordinate complex $Co(2\text{-}CH_3PyO)_5(ClO_4)_2$ was prepared using a total of 25 ml rather than 40 ml of solvent as in the general method. Prolonged cooling at 0° is required to induce crystallization. This cobalt complex has a conductivity of 207 mhos mol^{-1} cm^{-2} at an approximately 5×10^{-5} *M* concentration in nitromethane. This may be compared with the conductivities of $(C_2H_5)_4N^+Br^-$ and $Co(3\text{-}CH_3PyO)_6(ClO_4)_2$ being 127 and 206 mhos mol^{-1} cm^{-2} at similar temperature and concentration, in nitromethane. A value of about 200 mhos mol^{-1}

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