tungsten,[2] dimanganese decacarbonyl,[3] iron pentacarbonyl,[4] dicobalt octacarbonyl,[5] and nickel tetracarbonyl[6] result in complete removal of carbonyl groups. The compatibility of nitrate and carbonyl ligands has, nevertheless, been demonstrated by the preparation of the compound nitratopentacarbonylmanganese(I), $Mn(CO)_5NO_3$. However, reaction of dimanganese decacarbonyl with excess dinitrogen tetroxide in petroleum ether (bp 40–60°) gives rise to a mixture of products,[3] the principal constituents being nitrato- and nitropentacarbonylmanganese(I). A rather complicated extraction and fractional crystallization procedure is then necessary for the isolation of the pure nitrato complex, which is involatile.

In contrast, the reaction of dirhenium decacarbonyl with excess liquid dinitrogen tetroxide (alone or mixed with acetonitrile) leads directly to the production of nitratopentacarbonylrhenium(I), presumably according to the equation $Re_2(CO)_{10} + 2N_2O_4 \rightarrow 2Re(CO)_5NO_3 + 2NO$. This product can be purified by vacuum sublimation at 100°.

Experimental Section

Dirhenium decacarbonyl was obtained from Strem Chemicals Inc. and used without further purification. Liquid dinitrogen tetroxide was prepared and purified as described elsewhere.[7] All organic solvents were dried and purified by standard techniques.

Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer as mulls in Nujol and Halocarbon oil, using polythene-protected cesium iodide windows.

Carbon content was determined by a "wet-combustion" method. The material was oxidized in a closed system with a mixture of chromic oxide, phosphoric acid, fuming sulfuric acid, and potassium iodate. The carbon dioxide produced was determined by absorption.[8] Rhenium was determined by vigorous oxidation with 70% perchloric acid to perrhenate which was estimated by the method of Headridge.[9] Nitrogen was determined by the Dumas method.

Preparation of $Re(CO)_5NO_3$.—Liquid dinitrogen tetroxide (10 ml) was added to dirhenium decacarbonyl (1 g) at 0° in a vessel vented to the atmosphere through phosphoric oxide. On warming slowly to 20°, the carbonyl dissolved to give a green N_2O_3 solution which was shaken for 3 hr at this temperature; no precipitation occurred. On removal of the nitrogen oxides under vacuum at 20°, a buff-colored powder remained. *Anal.* Found: Re, 43.8; C, 16.4. On heating this powder to 100° under vacuum, a white crystalline sublimate was obtained. *Anal.* Calcd for $Re(CO)_5NO_3$: Re, 47.9; C, 15.5; N, 3.61. Found: Re, 47.5; C, 15.3; N, 3.75; 70% yield based on $Re_2(CO)_{10}$. The same reaction, using a mixture of dinitrogen tetroxide and acetonitrile, gave an identical product, so that the course of the reaction is apparently unaffected by a cosolvent having a high dielectric constant and appreciable electron pair donating ability.

Results and Discussion

Nitratopentacarbonylrhenium(I) is a white crystalline solid which is indefinitely stable, even in moist air. At atmospheric pressure, it decomposes without melting at 125–130°. The compound is soluble in most polar solvents and can be recrystallized from methanol. It is insoluble in water, benzene, cyclohexane, petroleum ether, carbon tetrachloride, *sym*-tetrachloroethane, and carbon disulfide. Cryoscopic measurements of molecular weight in nitrobenzene gave values of 260 (0.0125 *M*) and 281 (0.0200 *M*) indicating appreciable dissociation of the nitratocarbonyl at these concentrations (calcd for $Re(CO)_5NO_3$: 388). This may well be due to solvent coordination with release of ionic nitrate groups, as occurs with some derivatives of $Mn(CO)_5NO_3$.[10] The compound is diamagnetic (χ_m at 24° by the Gouy method is -243.9×10^{-6} cgs unit) as expected for Re(I). The infrared spectrum of nitratopentacarbonylrhenium(I) shows a marked similarity to those of the rhenium pentacarbonyl halides in the carbonyl stretching region,[11] the M–C–O deformation region, and the M–C stretching region,[12] confirming the presence of octahedrally coordinated Re(I). The nitrate bands in the spectrum of $Re(CO)_5NO_3$ are simple and clearly defined and are closely analogous to those of nitratopentacarbonylmanganese(I)[3] in which nitrate coordination is considered to be unidentate.

A detailed examination of the solution properties, the Raman spectrum, and the X-ray crystallography of $Re(CO)_5NO_3$ is in progress. The crystallography is particularly important since no truly unidentate nitrate group has yet been confirmed by this method.

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The Preparation of Sodium Tris(2,2′-bipyridine)ferrate(−I)[1]

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A number of 2,2′-bipyridine complexes with metals in low oxidation states, including tris(2,2′-bipyridine)iron(0), have been reported in recent years.[2–5] In this note we report the preparation of sodium tris(2,2′-bipyridine)ferrate(−I).

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The compound was prepared in anhydrous 1,2-dimethoxyethane (DME) by the addition of a solution of Na^+bipy^- in excess to solid, anhydrous $Fe(bipy)_3Cl_2$ under rigorously anhydrous, oxygen-free conditions in an evacuated vessel. The reaction was

$$3Na^+bipy^- + Fe(bipy)_3Cl_2(s) = NaFe(bipy)_3 + 3bipy + 2NaCl(s)$$

$NaFe(bipy)_3$ was not formed quantitatively but could be produced in good yield. It was moderately soluble in DME but considerably less soluble than Na^+bipy^- and free bipyridine, which therefore could be washed out of the reaction mixture with DME although with some loss of the product, $NaFe(bipy)_3$. The $NaFe(bipy)_3$ remaining was isolated from insoluble products by being dissolved in DME, transferred through a filter to a separate compartment of the vessel, and deposited as a black powder upon evaporation of the DME.

The isolated product oxidized at once upon exposure to air. Chemical analyses were made for sodium, iron, chloride, carbon, hydrogen, and nitrogen. Spot tests for chloride showed that it was absent in the isolated product. A weighed sample of the oxidized product was dissolved and treated with hydrogen peroxide to oxidize the iron to iron(III). Hydrous iron(III) oxide was precipitated with ammonia, filtered, and analyzed for iron by the oxine method. The filtrate was analyzed for sodium by the sodium zinc uranyl acetate method.

Samples from three different experimental runs gave Fe:Na:C:H:N ratios of 1.00:1.02:31.8:27.5:6.19, 1.00:1.06:34.2:35.8:6.39, and 1.00:1.10:35.7:33.3:6.84. The theoretical ratios for $NaFe(bipy)_3$ are 1.00:1.00:30.0:24.0:6.00. The deviations from theoretical ratios were probably due to Na^+bipy^-, free bipyridine, and DME impurities remaining in the product. A practical limit to the number of times a sample could be washed was dictated by the solubility of the product and the need for a sample of sufficient size for the analyses. The $NaFe(bipy)_3$ may have been solvated with some DME still remaining in the air-oxidized product. In a fourth run the isolated product was heated to 90–125° in an oil bath. At these temperatures most of the DME and bipyridine impurities were volatilized. The analysis on the oxidized product of this run gave Fe:Na:C:H:N ratios of 1.00:1.04:31.1:27.3:6.12. After being heated, the isolated product was approximately 98.1% $NaFe(bipy)_3$, 1.3% Na^+bipy^-, and 0.6% free bipyridine. A quantitative determination of total DME driven off when the product was heated would require a larger amount of product than we could isolate at a time.

The reductions of $FeCl_3$ in DME solution and of solid $Fe(bipy)Cl_3$ by excess Na^+bipy^- in DME solution were attempted. The moderately soluble products were isolated in a separate compartment of the reaction vessel. Analyses showed that the Na:Fe ratio was between 1:1 and 2:1, which implied that the product was probably a mixture of Fe(−II) and Fe(−I) compounds.

The salmon-colored solution of $NaFe(bipy)_3$ in DME had absorption peaks at 352, 509, 535, and 700 mμ with molar extinction coefficients of 33×10^3, 12×10^3, 12×10^3, and 5×10^3 M^{-1} cm^{-1}, respectively. The spectrum is shown in Figure 1. For comparison the spectrum of $Fe(bipy)_3$ in DME[6] and that of Na^+bipy^- in DME are also shown. The spectra of these two iron compounds are similar to the spectrum of Na^+bipy^-. The Na^+bipy^- spectrum had peaks at 840, 750, 558, 527, 385.5, and 257.5 mμ with molar extinction coefficients of 0.9×10^3, 0.6×10^3, 4.8×10^3, 5.0×10^3, 25.1×10^3, and 5.8×10^3 M^{-1} cm^{-1}, respectively.

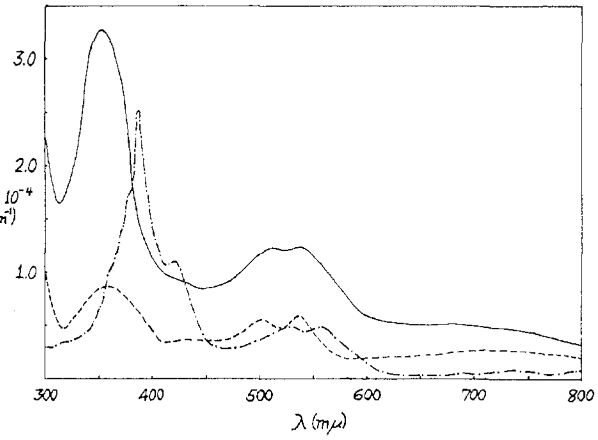

Figure 1.—Absorption spectra of $NaFe(bipy)_3$, $Fe(bipy)_3$, and Na^+bipy^- in DME: ———, $NaFe(bipy)_3$: — — —, $Fe(bipy)_3$: — · —, Na^+bipy^-.

A sample large enough for accurate bulk magnetic susceptibility measurement by the Gouy method could not be isolated.

The esr spectrum was obtained on a sample of solid $NaFe(bipy)_3$, which had been well washed before isolation to rid it of soluble impurities. The line was symmetrical, 2.8 gauss wide, and had a g value of 2.0031. To show that this line was not due to Na^+bipy^-, the esr spectrum of crystalline Na^+bipy^- was obtained. Solid Na^+bipy^- gave an asymmetric esr signal with $g_{\perp} = 2.0046$ and $g_{\parallel} = 2.0033$. Furthermore, inadequately washed samples of $NaFe(bipy)_3$ showed the characteristic esr spectrum of solid Na^+bipy^-, which decreased in intensity with additional washing, leaving only the esr spectrum of $NaFe(bipy)_3$.

The g value of 2.0031 is very close to the spin-only value of 2.0023 and indicates that the unpaired electrons in $NaFe(bipy)_3$ occupy molecular orbitals composed mainly of ligand orbitals. The similarity of the visible and near-ultraviolet spectra of Na^+bipy^- and $NaFe(bipy)_3$ is consistent with the esr evidence.

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