resonance occurs at about δ −1.2 ppm. (Negative chemical shifts are downfield from the reference tetramethylsilane, TMS.) Since this peak nearly coincides with the center peak of the ammonia triplet, its assignment was confirmed by observing the spectrum at several $Na(CH_3)_2NBH_3$ concentrations. The relative intensity of the peak assigned to the $(CH_3)_2NBH_3^-$ methyl resonance increased with increasing $(CH_3)_2NBH_3^-$ concentration. No peaks attributable to the borane resonances could be resolved. The pmr spectra of the $(CH_3)_2HNBH_3$ and $(CH_3)_2NBH_3^-$ solutions were recorded periodically over a period of several weeks. During this time no $(CH_3)_2NH$ was ever detected and no evidence for the formation of species such as $H_2NBH_3^-$ or H_3NBH_3 could be obtained. These observations strongly imply that no transamination of either $(CH_3)_2HNBH_3$ or $(CH_3)_2NBH_3^-$ occurs with ammonia over extended periods under the conditions used in this study.

In 12 N HCl $Na(CH_3)_2NBH_3$ hydrolyzes in a few minutes

$$Na(CH_3)_2NBH_3 + 3H_2O + H^+ \longrightarrow 3H_2 + B(OH)_3 + (CH_3)_2NH + Na^+$$

Titrations of aqueous solutions of $Na(CH_3)_2NBH_3$ with 0.05 N HCl, however, yield typical weak base–strong acid titration curves which indicate that the equilibrium

$$(CH_3)_2NBH_3^- + H_2O \rightleftharpoons (CH_3)_2HNBH_3 + OH^-$$

is established prior to the hydrolysis of the BH_3 group. The pmr chemical shift of the methyl protons in aqueous $(CH_3)_2NBH_3^-$ solutions is nearly identical with the chemical shift of the methyl groups in neutral aqueous solutions of $(CH_3)_2HNBH_3$ demonstrating that the equilibrium lies far to the right. Further supportive evidence for this reaction is the fact that $(CH_3)_2HNBH_3$ can be isolated from and seen in the mass and infrared spectra of $Na(CH_3)_2NBH_3$ which has been placed in contact with moist air. In these mass spectra, peaks which could have arisen from the hydrolysis of $H_2NBH_3^-$ were either completely absent or present in trace amounts (under 2% of the most intense peak) lending further evidence to the supposition that transamination did not occur during the preparation of $(CH_3)_2NBH_3^-$.

The hydrolysis of the borane group is too rapid at 25° to allow the base dissociation constant, K_b, to be conveniently determined from potentiometric titration data. However, at 20° this hydrolysis is slow enough to permit reproducible data to be obtained. A K_b of $1.76\ (\pm 0.33) \times 10^{-4}$ was obtained as the average of 24 values calculated[8] from data taken on four potentiometric titrations of solutions 0.05–0.005 M in $Na(CH_3)_2NBH_3$. The error is expressed to a 95% confidence level.

It is interesting to compare the properties of $(CH_3)_2NBH_3^-$ and $(CH_3)_2HNBH_3$ with those of similar alkylamines and alkylammonium ions. The aqueous equilibrium of $(CH_3)_2NBH_3^-$ and its formation from $(CH_3)_2HNBH_3$ are analogous to the well-known amine hydrolysis reaction and characteristic reduction of ammonium ions with sodium in liquid ammonia.[9] The methyl pmr signals of $(CH_3)_2NBH_3^-$ (δ −1.2 ppm) and $(CH_3)_2HNBH_3$ (δ −2.5 ppm)[10] appear at a higher field than those of trimethylamine (δ −2.2 ppm)[11] and trimethylammonium ion (δ −2.9 ppm),[11] respectively, compounds in which the BH_3 moiety has formally been replaced by an isoelectronic CH_3^+ group. This may well reflect a greater electron density about the methyl groups in the borane compounds than in the compounds containing the CH_3^+ group with its higher nuclear charge and consequent greater electron-withdrawing ability. Similarly the base dissociation constants at 20° for $(CH_3)_2NBH_3^-$ and $(CH_3)_3N$[12] of 1.76×10^{-4} and 5.50×10^{-5}, respectively, also may reflect the relative electron-withdrawing power of the BH_3 and CH_3^+ groups since the electron density about and, thus, basicity of the nitrogen should be related inversely to the electron-withdrawing power of the groups attached to it.

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[8] L. Meites and H. C. Thomas, "Advanced Analytic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 90.

[9] G. W. Watt, *Chem. Rev.*, **46**, 289 (1950).

[10] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965), reported δ_{CH_3} −2.52 ppm in $CDCl_3$ and −2.41 ppm in 1,4-dioxane. In this study δ_{CH_3} −2.48 ppm has been observed in D_2O solutions.

[11] Data from E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 641 (1957), converted to TMS reference.

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The Preparation of a Technetium Iron Carbonyl Anion

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A technetium diiron dodecacarbonyl anion has been prepared that is analogous to the manganese compound reported by Anders and Graham[2] and the rhenium compound reported by Evans, Hargaden, and Sheline.[3] Ditechnetium decacarbonyl[4] (119 mg, 0.25 mmol; Pressure Chemical Co., Pittsburgh, Pa.) and 196 mg (1.0 mmol) of iron pentacarbonyl were dissolved in 150 ml of freshly distilled (over lithium aluminum hydride) tetrahydrofuran (THF) under a dry nitrogen atmosphere, and the solution was irradiated for 1 hr by an A-H6 high-pressure mercury (General Electric Co.) arc lamp at a distance of about 1 ft. During the first few minutes of irradiation, the

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Table I

Infrared Spectra of $(C_2H_5)_4NMFe_2(CO)_{12}$ (M = Tc, Mn, or Re)

Element	Absorption frequency, cm^{-1}							
Tc	2077 w	2008 m	1987 s		1943 m	1903 w	1815 w	1783 w
Mn[2]	2063 vw	1999 m	1990 s	1972 m	1944 m	1903 w	1827 w	1785 w
Re[3]	2075 w	2006 m	1991 s		1946 m	1903 w	1814 w	1785 w

Table II

Yield Dependence on Group VIIb Element and Solvent

	THF or ether		*n*-Hexane	
Element	Linear	Triangular	Linear	Triangular
Tc	None	High	Trace	Moderate
Mn	Moderate	Moderate[a]	High	None
Re	None	High	Low	Moderate

[a] Required prolonged (4-hr) irradiation.

solution changed color very dramatically: from almost colorless to yellow to orange to red in less than 5 min, then to a very deep red-violet after extended irradiation. After irradiation, excess (1 mmol) tetraethylammonium bromide in ethanol was added to stabilize the anion, and the solvent was removed under high vacuum. The residue was extracted several times with *n*-hexane to remove the unreacted carbonyls. The infrared spectrum in the carbonyl stretch region of a THF solution of the salt is remarkably similar to the spectra of the analogous manganese and rhenium compounds; the infrared absorption bands for the three anions are given in Table I.

The first group VIIb diiron dodecacarbonyl anion reported was prepared by the reaction of the pentacarbonylmanganese anion with iron pentacarbonyl in diglyme.[2] It is not known whether this reaction is general for all of the group VIIb elements. The photochemical reaction, however, of a group VIIb carbonyl with iron pentacarbonyl is a general reaction—all members of this series have now been prepared by this method. The products of this preparation depend on the particular group VIIb element and the solvent employed; the principal products being a neutral linear $M_2Fe(CO)_{14}$ species and a triangular anionic $MFe_2(CO)_{12}^-$ species. The usual differences in properties of transition elements within a group are not very apparent in the structures of their metal carbonyls,[5] but the typical difference between elements of the first transition series and those in the second and third series is quite obvious in the reactions of their carbonyls. The formation of the neutral linear species is favored by manganese and *n*-hexane as the solvent, and the triangular anionic species is favored by technetium and rhenium and polar solvents, such as THF or diethyl ether; the element and solvent dependence is summarized in Table II.

The striking similarity of the infrared carbonyl stretch spectra of the manganese and rhenium compounds to that of triiron dodecacarbonyl led previous workers[2,3] to propose an $Fe_3(CO)_{12}$-like structure in which the apical *cis*-$Fe(CO)_4$ moiety is replaced by a *cis*-$M(CO)_4^-$ group, where M = Mn or Re; the same structure is also proposed for the technetium iron carbonyl anion.

All known isotopes of technetium are radioactive, and the isotope used in this work was ^{99}Tc (a fission product available from Oak Ridge National Laboratory, Oak Ridge, Tenn). This isotope can be safely used with standard radiochemical precautions[6] in ordinary laboratory glassware and equipment because of its long half-life (2.1×10^5 years) and its decay mode involves only a low-energy β particle (maximum energy, 0.29 MeV).[7] Since the average β-particle energy is about 0.1 MeV, the β radiation and attendant bremsstrahlung are attenuated to dose rates of 1 mr/hr, and less, at a distance of 1 ft by ordinary laboratory glassware.[8] Personnel and equipment were monitored with a thin (1.4-mg/cm^2) end-window Geiger portable survey meter.

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The Synthesis of Potassium Isothiocyanatopentacyanocobaltate(III)[1a]

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In our previous study of the substitution of water in the aquopentacyanocobaltate(III) ion by thiocyanate ion[2] we did not isolate the reaction product and, therefore, could not establish whether the sulfur- or nitrogen-

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