with $\epsilon_{HCrO_4^-} = 228$ at 420 mμ. The error limits of the constant were derived from the individual measurements by means of propagations of error calculations, taking into account the standard deviations of volume, time, and absorbance measurements. As the best value $K = (1.24 \pm 0.14) \times 10^4$ (for equal concentrations of the reactants) can be taken. At 420 mμ the molar absorptivity is 1040 ± 40 $cm^{-1}\ M^{-1}$.

Absorption Spectrum.—The spectrum recorded using the flow device is a superposition of the spectra of the different ionic species existing in solution. After correction for $HCrO_4$– the absorption spectrum given in Figure 3 was found for the intermediate. The reaction is faster in an excess of thiosulfate, and it shows an induction period with chromate in excess. The measurements were, therefore, carried out in a slight excess of chromate, in order to avoid an appreciable decay of the chromatothiosulfate during the flow from the mixing chamber to the light path in the cell. The calculations were made for the time of mixing. The absorption curve shows a maximum at 390 mμ with ϵ_{max} 1400 $cm^{-1}\ M^{-1}$. This value was found also in a high excess of $HS_2O_3^-$.

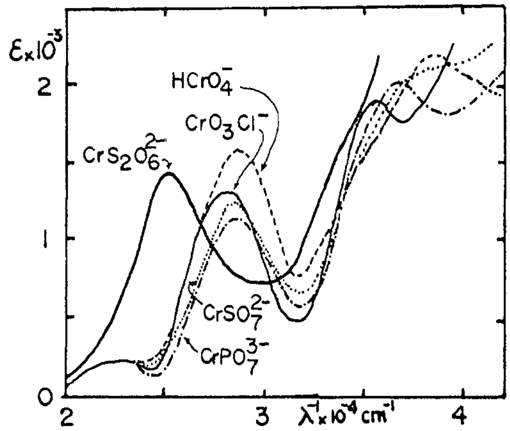

Figure 3.—Absorption spectra of some Cr(VI) compounds.

Absorption curves for $HCrO_4^-$, CrO_3Cl^-, $CrSO_7^{2-}$, and $CrPO_7^{3-}$ as determined by us are included in Figure 3. In every case they are in good agreement with published spectra for these species.[6–9]

Discussion

The band at 390 mμ can be ascribed to a charge-transfer transition, as can the 350 mμ band for $HCrO_4^-$.[10] A number of other species having a Cr–O–R group (*e.g.*, where R is PO_3, SO_3, or $COCH_3$[11]) also have an absorption maximum near 350 mμ. The chlorochromate ion[7,8] has a maximum slightly shifted toward longer wavelengths.

The nature of the R group apparently does not affect the position of the charge-transfer band, but the exchange of the oxygen atom with a chlorine atom of low electronegativity shifts the absorption band to lower frequencies. The even more pronounced shift in the case of the chromatothiosulfate is consistent with the assumption that the sulfur atom acts as a bridge rather than an oxygen atom, and therefore the probable formula of the intermediate is $^-O_3CrSSO_3^-$. The formation of this ion can be assumed to take place by the displacement of OH^- in the $HCrO_4^-$ ion by the sulfur of the $HS_2O_3^-$ ligand.

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The Reaction of Borazines with Sodium Biphenylide

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The formation of alkali metal derivatives of the borazines, *e.g.*, $LiN_3(CH_3)_2B_3(CH_3)_3$, was first reported by Wagner and Bradford.[1] However, attempts to methylate B-methyl- and B-phenylborazines at the nitrogen positions with alkali metal–ammonia solutions or with alkali metal amides led to addition products rather than to the expected alkali metal derivatives.[2] The alkali metals react with solutions of aromatic hydrocarbons such as biphenyl in tetrahydrofuran and other ethers to form solutions of radical anions (eq 1) which can also be used as metalating agents.[3] Thus, it might reasonably be expected that these solutions could be used to prepare alkali metal borazine derivatives.

$$C_6H_5C_6H_5 + Na \longrightarrow C_6H_5C_6H_5\cdot^- + Na^+ \qquad (1)$$

Experimental Section

Blue-green solutions of sodium biphenylide in anhydrous tetrahydrofuran or ethylene glycol dimethyl ether were prepared according to the procedure of Scott, Walker, and Hansley;[4] aliquots of these solutions were hydrolyzed and titrated with standard acid before use.

B-Trimethylborazine and B-trimethyl-N-methylborazine were prepared from the copyrolysis of $(CH_3)_3BNH_3$ and $(CH_3)_3BNH_2CH_3$ and were isolated by conventional methods.[1] B-Triphenylborazine was obtained by the reaction of phenylmagnesium bromide with B-trichloroborazine.[5] Pentacarbonylmanganese

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bromide was prepared by the reaction of $Mn_2(CO)_{10}$ with bromine.[6] The other reagents were the purest products commercially available; the boiling points and/or melting points of these reagents corresponded to the accepted literature values and the substances were not further purified.

The reactions were conducted in conventional ground-glass equipment under an inert atmosphere. Solutions of air-sensitive compounds were transferred with a syringe through rubber septums. Air-sensitive solids were manipulated in a drybox, the atmosphere of which was equilibrated with the liquid sodium–potassium eutectic mixture. Vapor phase chromatography was conducted with an Aerograph Autoprep using 30% Carbowax 20M on an acid-washed 30–60 Chrom W support.

Reactions of $(CH_3)_3B_3N_3(CH_3)H_2$ with $Na^+(C_{12}H_{10})\cdot^-$.—To a solution of $(CH_3)_3B_3N_3(CH_3)H_2$ (0.791 g, 5.82 mmol) in 75 ml of tetrahydrofuran in a nitrogen-filled flask was added dropwise with stirring 10 ml of 0.54 *M* $Na^+(C_{12}H_{10})\cdot^-$ (5.4 mmol). Initially the reaction mixture possessed a yellow metallic appearance, but it became red-orange before the addition of the $Na^+(C_{12}H_{10})\cdot^-$ solution was complete. Methyl iodide (0.36 ml, 5.9 mmol) was then added to the reaction mixture and the color immediately discharged leaving a yellow-brown turbid solution. The reaction mixture was stirred overnight and filtered to remove the sodium iodide. Vapor-phase chromatography of the liquid which remained after removal of the solvent from the filtrate showed it to consist of $(CH_3)_3B_3N_3(CH_3)H_2$ and $(CH_3)_3B_3N_3(CH_3)_2H$ in the ratio of 1.6:1, corresponding to a 38% conversion of the original borazine. The retention times for the two peaks assigned to $(CH_3)_3B_3N_3(CH_3)H_2$ and $(CH_3)_3B_3N_3(CH_3)_2H$ were identical with those of authentic samples of the individual compounds. The mixture of the borazines was fractionally distilled at atmospheric pressure to give a pure sample of $(CH_3)_3B_3N_3(CH_3)_2H$, bp 185–190° (lit.[1] 187–188°); this fraction exhibited an infrared spectrum identical with that of an authentic sample as well as with that reported in the literature.[1]

Reaction of $(C_6H_5)_3B_3N_3H_3$ with $Na^+(C_{12}H_{10})\cdot^-$.—To a solution of $(C_6H_5)_3B_3N_3H_3$ (2.30 g, 7.77 mmol) in 100 ml of dry ethylene glycol dimethyl ether under nitrogen was added dropwise with stirring 15.0 ml of 0.54 *M* sodium biphenylide (8.1 mmol). Each drop of the reagent was decolorized as it mixed with the borazine solution which gradually acquired a red-orange color. The addition of methyl iodide (0.50 ml, 8.2 mmol) to the reaction mixture caused immediate precipitation of sodium iodide. The reaction mixture was then allowed to reflux for 2 hr, cooled, and filtered twice. The solvent was removed *in vacuo* from the filtrate and the residue was extracted with petroleum ether (bp 90–100°) to remove unreacted biphenyl; the remaining solid was $(C_6H_5)_3B_3N_3H_3$; mp 177.5–179°; lit.[5] 179–182°. No N-methylated borazine derivatives were detected among the products.

Reactions of Solutions of $Na^+(C_{12}H_{10})\cdot^-$ Containing Methylborazines.—The reactions between tetrahydrofuran solutions of the alkali metal derivatives of the B-methylated borazines and compounds containing active halogen atoms such as $Mn(CO)_5Br$, $(C_6H_5)_3SnCl$, and $(C_6H_5)_2PCl$ were investigated as possible routes to the formation of N-substituted borazines. The details of the reaction with $(C_6H_5)_3SnCl$ are given as illustrative of the conditions employed and the results obtained.

B-Trimethyl-N-methylborazine (1.711 g, 17.57 mmol) and 42 ml of 0.23 *M* $Na^+(C_{12}H_{10})\cdot^-$ (9.2 mmol) were allowed to react in 50 ml of anhydrous tetrahydrofuran. To the resulting red solution was added 3.853 g (10 mmol) of $(C_6H_5)_3SnCl$. The red color immediately discharged with the formation of a fine precipitate of NaCl which could not be completely removed by filtration. The filtrate was fractionally distilled *in vacuo* to yield 1.156 g of the starting borazine, identified by its gas chromatographic retention time and infrared spectrum. The solid residue from the distillation was washed with petroleum ether (bp 60–70°) to remove biphenyl and recrystallized from benzene to give 2.24 g of $(C_6H_5)_6Sn_2$; mp 226–228.5°; lit.[6] 228–232°. The infrared spectrum of this product was identical with that of an authentic sample of $(C_6H_5)_6Sn_2$.

Similar results were obtained when $Mn(CO)_5Br$ and $(C_6H_5)_2PCl$ were added to solutions containing B-methylborazine anions generated from the reaction of the corresponding borazine with a solution of sodium naphthalenide. Thus, $Mn(CO)_5Cl$ and $(C_6H_5)_2PCl$ were converted in high yield to $Mn_2(CO)_{10}$ and $(C_6H_5)_4P_2$,[7] respectively.

Exploratory qualitative esr experiments were conducted in an attempt to establish the presence of radicals in the $NaC_{12}H_{10}$ solutions containing borazines. The esr spectrum (Varian epr Model V-4502) of the blue-green solution of $Na^+(C_{12}H_{10})\cdot^-$ in tetrahydrofuran exhibited the nine-line structure (total line width of 24 G) predicted and found by DeBoer and Weissman.[8] If these solutions were allowed to stand for long periods of time, they turned yellow but gave the same esr spectra as the blue-green solutions. However, on exposure to air the blue-green solutions turned orange-red and no longer gave an esr signal.

A solution of B-trimethyl-N-methylborazine in tetrahydrofuran did not react with a potassium mirror. Addition of biphenyl to the mixture caused the immediate development of a color and the solution gave a weak esr spectrum that was essentially the same as that for $Na^+(C_{12}H_{10})\cdot^-$; the signal rapidly decreased in intensity. B-Triphenylborazine in tetrahydrofuran rapidly reacted with a potassium mirror to give a red solution possessing a spectrum consisting of a single line 26 G wide which could not be resolved further. The addition of biphenyl to this solution did not affect the esr spectrum.

Discussion

The addition of B-methyl- or B-phenyl-substituted borazines to solutions of $Na^+(C_{12}H_{10})\cdot^-$ in tetrahydrofuran causes the characteristic blue-green color of the latter to change to red; gas liberation does not occur in the course of these reactions. In the case of B-triphenylborazine, reaction with $Na^+(C_{12}H_{10})\cdot^-$ apparently results in electron transfer to form a borazine radical anion (eq 2), as was observed in the reaction

$$(C_6H_5)_3B_3N_3H_3 + C_{12}H_{10}\cdot^- \rightleftharpoons (C_6H_5)_3B_3N_3H_3\cdot^- + C_{12}H_{10} \quad (2)$$

of this borazine with metal–ammonia solutions[2] and in the reversible one-electron polarographic reduction of B-phenyl-substituted borazines.[9] This borazine radical anion can also be obtained directly from the reaction of B-triphenylborazine with an alkali metal in tetrahydrofuran as indicated by the esr data. The failure to form N-methylated derivatives of B-triphenylborazine from the reaction of methyl iodide with reaction mixtures containing $(C_6H_5)_3B_3N_3H_3\cdot^-$ indicates that the latter does not lose hydrogen readily to form the expected anion (eq 3). The absence of hydrogen

$$(C_6H_5)_3B_3N_3H_3\cdot^- \longrightarrow (C_6H_5)_3B_3N_3H_2^- + 0.5H_2 \quad (3)$$

from the products does not necessarily support this argument since reduction of biphenyl would be expected[10] to occur under the conditions of the experiment (*vide infra*). However, the formation of NaI and the recovery of B-triphenylborazine from the reactions of solutions containing $(C_6H_5)_3B_3N_3H_3\cdot^-$ with methyl iodide are consistent with this interpretation.

In contrast with B-triphenylborazine, B-methyl-substituted borazines undergo slightly more complex

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reactions with solutions of $Na^+(C_{12}H_{10})\cdot^-$. The methylation of $(CH_3)_3B_3N_3(CH_3)H_2$ in the presence of $Na^+(C_{12}H_{10})\cdot^-$ indicates that an alkali metal borazine derivative has been formed. The absence of hydrogen evolution in the reaction of the B-methylborazine with $Na^+(C_{12}H_{10})\cdot^-$ suggests that the biphenylide ion acts as a base removing a proton from the borazine to give an anion (eq 4) which can be subsequently alkylated

$$C_{12}H_{10}\cdot^- + (CH_3)_3B_3N_3(CH_3)H_2 \longrightarrow C_{12}H_{11}\cdot + (CH_3)_3B_3N_3(CH_3)H^- \quad (4)$$

$$(CH_3)_3B_3N_3(CH_3)H^- + CH_3I \rightleftarrows (CH_3)_3B_3N_3(CH_3)_2H + I^- \quad (5)$$

(eq 5). The red color of the solution is attributed to the presence of a carbanion formed by the reaction of the biphenyl radical, formed according to eq 4, with excess $Na^+(C_{12}H_{10})\cdot^-$ (eq 6).[10] The equilibria rep-

$$C_{12}H_{11}\cdot + C_{12}H_{10}\cdot^- \rightleftarrows C_{12}H_{11}^- + C_{12}H_{10} \quad (6)$$

resented by eq 4 and 6 must be reversible in the presence of substances that are easily reduced, as indicated by the isolation of coupled products when either $Mn(CO)_5Br$, $(C_6H_5)_3SnCl$, or $(C_6H_5)_2PCl$ was added to solutions of $Na^+(C_{12}H_{10})\cdot^-$ containing B-methylborazines. The isolation of $Mn_2(CO)_{10}$, $(C_6H_5)_6Sn_2$, and $(C_6H_5)_4P_2$, respectively, indicates that reduction occurs (eq 7) rather than the expected re-

$$2C_{12}H_{10}\cdot^- + 2MX \longrightarrow 2C_{12}H_{10} + MM + 2X^- \quad (7)$$
$$(MX = Mn(CO)_5Br, (C_6H_5)_3SnCl, (C_6H_5)_2PCl)$$

action of the borazine anion with halo compounds (*cf.* eq 5). The data presented here suggest that it is unlikely that a B-methylborazine radical anion is formed in these systems and are consistent with the fact that borazines of this type do not give a polarographic reduction wave, in contrast with the B-phenylborazines.[9]

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Low-Frequency Infrared Spectral Studies on Triphenylphosphine, -arsine, and -stibine Derivatives of Iron and Molybdenum Carbonyl Complexes

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Monosubstituted derivatives of iron carbonyl, $Fe(CO)_4\cdot L$, are expected[1] to have four possible configurations based on the position of L in trigonal-bipyramidal and rectangular-pyramidal structures of iron pentacarbonyl, $Fe(CO)_5$. Cotton and Parish made an attempt to study the configuration of monotriphenylphosphine iron tetracarbonyl, $Fe(CO)_4(C_6H_5)_3P$. On the basis of the number of carbonyl stretching vibrations observed for this monosubstituted iron carbonyl complex, they were able to conclude that $Fe(CO)_4\cdot L$ species are very probably trigonal bipyramidal and the model with the L in an axial position (C_{3v}) is strongly favored. An attempt has been made to establish the structure of $Fe(CO)_4\cdot L$ derivatives by analyzing the 700–200-cm^{-1} region. Triphenylphosphine, -arsine, and -stibine have been used as the substituting ligands (L). The structural configurations for the $Mo(CO)_5\cdot L$ and the $Fe(CO)_3\cdot 2L$ types of complexes are well established.[1,2] As an extension to the above studies, infrared spectra of $Mo(CO)_5\cdot L$ and $Fe(CO)_3\cdot 2L$ complexes using triphenylphosphine. -arsine, and -stibine ligands (L) have been recorded in the low-frequency region for a discussion of the metal-ligand (M–L) vibrations in the substituted iron and molybdenum carbonyl complexes.

Experimental Section

Iron and molybdenum carbonyls were purchased from Alfa Inorganics, Inc., and were used as such for preparing complexes. Reagent grade tetrahydrofuran from Fisher Chemicals was refluxed over lithium aluminum hydride and distilled. The middle fraction of the distillate was used as solvent. Triphenylphosphine (LP), -arsine (LA), and -stibine (LS) were obtained from K & K Laboratories and were dried under vacuum before use. All of the compounds were handled in a drybox flushed with nitrogen, and the reactions were carried out under a nitrogen atmosphere. The iron and molybdenum carbonyl complexes were prepared by the methods described in the literature,[3,4] and their compositions were confirmed by their melting points and elemental analyses. The infrared spectra of the complexes and the ligands were taken in the form of Nujol mulls supported on cesium iodide disks. A Perkin-Elmer 621 double-beam infrared spectrophotometer was used for recording the spectra.

Results and Discussion

The infrared spectral data of substituted iron and molybdenum carbonyl complexes have been summarized in Table I. The selection rules for stretching and deformation modes of vibration for possible configurations of the substituted metal carbonyls as derived by standard group theoretical methods[2,5] have been given in Table II. The C–M–C bending vibrations occur at frequencies below the range we have studied and therefore have not been considered in Table II. Low-frequency infrared spectra of the ligands LP, LA, and LS are well assigned[6] and can be nicely distinguished from the rest of the spectra.

Four possible structures have been proposed[1] for the $Fe(CO)_4\cdot L$ complexes derived from the trigonal-bipyramidal (TBP) and the rectangular-pyramidal (RP) configurations of iron pentacarbonylFe, $(CO)_5$.

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