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# Metal Derivatives of the Borazines. Ring Complexes

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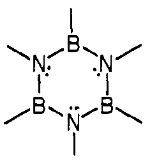
Tricarbonylchromium(0) complexes of hexamethylborazine, *B*-monophenylpentamethylborazine, *B*-monoethylpentamethylborazine, and *N*-triethyl-*B*-trimethylborazines were prepared and characterized. Infrared proton nmr and visible-ultraviolet spectra of the complexes are interpreted in terms of complexes containing puckered borazine rings $\sigma$ bonded through the ring nitrogen atoms. The results suggest that the complexed borazine rings are poorer $\pi$ acceptors than arene ligands, although the electronic environment of the $Cr(CO)_3$ moiety appears to be similar in both complex systems.

## Introduction

Borazines can be formulated as either cyclic triamines I or as cyclic compounds incorporating a $\pi$ system (II) similar to that found in benzene. A variety of physical-chemical experiments[1] indicates that the borazine nucleus in several compounds is planar; moreover, the B-N bond distances measured in, for example, $H_3B_3N_3(CH_3)_3$ (1.42 Å)[2] are shorter than that expected for a single bond (1.59 Å).[3] However, some chemical evidence exists which supports the suggestion that the nitrogen sites in a borazine ring retain some basic character. Thus, *N*-trimethylborazine reacts with hydrogen chloride to form an adduct, $(Me)_3B_3N_3(ME)_3\cdot 3HCl$, the empirical formula of which suggests that the ring nitrogen atoms have been protonated.[4]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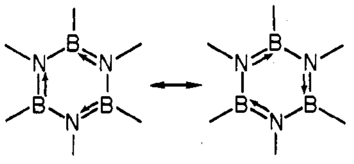
II

It would be expected that formulation of the borazine ring either as I or II might yield metal complexes similar to those formed by derivatives of hexahydrotriazine, $(CO)_3Cr\cdot\overline{NRCH_2NRCH_2NRCH_2}$ (III),[5] or by benzene $(CO)_3Cr\cdot C_6H_6$ (IV).[6] The cyclic ligand in the former complexes is a triamine; the complex has been formulated[5] to contain three nitrogen atoms $\sigma$ bonded to the $Cr(CO)_3$ moiety. In the case of IV the benzene ring is planar[7] and the compound has been described in terms of donation of the benzene $\pi$ system to the metal group. Four compounds containing complexed borazine nuclei have been reported, *viz.* $(CO)_3Cr(R)_3N_3B_3(R')_3$ ($R, R' = CH_3, C_2H_5$).[8] The available data on these compounds have been interpreted[9] to suggest that their structures are analogous to III. The results of an X-ray diffraction study of the hexaethyl derivative[10] seem to support the suggestion that the ring is nonplanar.

Our interest in the general chemistry of borazines has prompted us to prepare several other derivatives of the $Cr(CO)_3$ moiety containing a complexed borazine ring. A study of properties of these derivatives suggests that the complexed borazine rings in these compounds are not planar. A tentative preliminary report of some of our present results is available.[11]

## Experimental Section

**Equipment.** Manipulations involving air-sensitive materials were performed in a conventional vacuum line fitted with high-vacuum greased stopcocks and/or in the helium-filled drybox described previously.[12]

Proton nuclear magnetic resonance spectra were recorded on a Varian Associates (Palo Alto, Calif.) Model A-60 spectrometer, operating at a field of 14,100 G and 60 MHz. Samples were obtained at ambient temperature in dilute solutions (5–8%). Benzene, deuteriobenzene, hexafluorobenzene, chloroform, methylene chloride, and carbon tetrachloride were used as solvents with tetramethylsilane as an internal standard.

Ultraviolet–visible spectra were obtained as solutions in cyclohexane in matched 1.0-cm quartz cells fitted with septum caps or as Nujol mulls using quartz plates. The Nujol mulls were prepared with an agate mortar and pestle and were spread uniformly over a circle of filter paper. The reference was a Nujol-saturated circle of filter paper between quartz plates. The spectra obtained were of good quality and compared favorably with the cyclohexane spectra for the same compounds. Spectra were obtained at ambient temperature on a Cary 14 ultraviolet–visible spectrophotometer with accuracy to ±5 Å.

**Melting Points.** All samples were sealed in helium-filled capillary tubes and the melting points determined in a stirred oil bath with a thermometer calibrated against Eimer and Amend standard thermometers.

**Mass Spectrometry.** Mass spectra were obtained using a Bell and Howell 21491 mass spectrometer with an ionizing potential of approximately 70 eV which yielded 7 $\mu$A of current. A direct probe system was used and solid samples were introduced in capillary tubes that were opened immediately prior to introduction; liquid samples were introduced by syringe through a heated inlet system.

**Infrared Spectra.** All infrared spectra of solids were recorded in chloroform or carbon tetrachloride solution; the spectrum in the region from 700 to 800 $cm^{-1}$ was supplemented by a Nujol overlay. The liquid borazines were run as neat liquids between salt plates. The spectra of the metal carbonyl derivatives were also recorded in cyclohexane solution. Liquid cells matched within 20% with sodium chloride windows were used to record solution spectra using the pure solvent as reference.

A Beckman IR-7 infrared spectrophotometer with sodium chloride optics was used to record the spectra; wave numbers reported are accurate to $\pm 0.5$ $cm^{-1}$.

**Elemental Analyses.** Carbon, hydrogen, nitrogen, and halogen

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[1] For a review of this subject, see E. K. Mellon and J. J. Lagowski, *Advan. Inorg. Chem. Radiochem.*, 5, 259 (1963).

[2] K. P. Coffen and S. H. Bauer, *J. Phys. Chem.*, 59, 193 (1955).

[3] L. M. Trefonas, F. S. Mathews, and W. N. Lipscomb, *Acta Crystallogr.*, 14, 223 (1961).

[4] E. Wiberg and A. Bolz, *Chem. Res.*, 73, 209 (1940).

[5] A. Luttringhaus and W. Kullick, *Tetrahedron Lett.*, No. 10, 13 (1959).

[6] B. Nicholls and M. C. Whiting, *Proc. Chem. Soc., London*, 152 (1958).

[7] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1299, 1314 (1965).

[8] H. Werner, R. Prinz, and E. Deckelmann, *Chem. Ber.*, 102, 95 (1969).

[9] R. Prinz and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 6, 91(1967).

[10] G. Huttner and B. Krieg, *Angew. Chem., Int. Ed. Engl.*, 10, 512 (1971).

[11] J. J. Lagowski, *Proc. Int. Conf. Coord. Chem., 13th*, 2, 380 (1970).

[12] D. F. Burow, Ph.D. Dissertation, The University of Texas at Austin, 1966.

**Table I.** Analytical Data for Borazinetricarbonylchromium(0) Derivatives

| No. | Compound | Yield,[a] % | Mp, °C | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $(CO)_3Cr\cdot CH_3B\text{-}N(CH_3)B(CH_3)N(CH_3)B(CH_3)N(CH_3)$ | 90 | 141 | 35.94 | 6.03 | 13.97 | 37.32 | 6.20 | 14.51 |
| 2 | $(CO)_3Cr\cdot C_6H_5B\text{-}N(CH_3)B(CH_3)N(CH_3)B(CH_3)N(CH_3)$ | 18.5 | 110 dec | 46.35 | 5.56 | 11.58 | 46.01 | 5.34 | 11.28 |
| 3 | $(CO)_3Cr\cdot C_2H_5B\text{-}N(CH_3)B(CH_3)N(CH_3)B(CH_3)N(CH_3)$ | 90 | 151 dec | 38.16 | 6.40 | 13.35 | 38.97 | 6.52 | 14.42 |
| 4 | $(CO)_3Cr\cdot CH_3B\text{-}N(C_2H_5)B(CH_3)N(C_2H_5)B(CH_3)N(C_2H_5)$ | 20 | | 42.04 | 7.06 | 12.56 | 43.36 | 7.07 | 13.43 |

[a] Based on $Cr(CO)_6$ taken.

analyses were performed by Chemalytics, Tempe, Ariz. All transfers were made under nitrogen.

**Chemical Reagents.** Ethers and hydrocarbon solvents were dried by refluxing over sodium or sodium–benzophenone and then distilled under nitrogen either directly into the reaction vessel or into 1-l. bottles containing Linde 4A molecular sieves. The bottles were capped with a rubber septum and formaldehyde resin cover caps to prevent gas diffusion. Acetonitrile was refluxed over calcium hydride and distilled under nitrogen into a bottle containing fresh calcium hydride which was capped as before. Chromium hexacarbonyl (Pressure Chemical Co., Alfa Inorganics) was sublimed *in vacuo* before use. Ethylmagnesium bromide in ether solution was used as received. Hexamethylbenzene (Eastman Organic Chemicals) was used as received. Chlorobenzene was distilled prior to use as a solvent in the preparation of the borazines; a middle fraction was collected after discarding the first fraction. Methylamine hydrochloride and ethylamine hydrochloride were dried by azeotropic distillation of a mixture of the salt and anhydrous chlorobenzene prior to the addition of boron trichloride in the preparation of *N*-trialkyl-*B*-trichloroborazines.

All of the *N*-trialkylborazine derivatives were prepared under an atmosphere of argon or nitrogen using standard methods for the exclusion of moisture.

**Synthesis. *N*-Triethyl-*B*-trichloroborazine.** *N*-Triethyl-*B*-trichloroborazine was prepared by the method of Hohnstedt and Haworth[13] reported for the preparation of *N*-trimethyl-*B*-trichloroborazine. The product consisted of a solid, wet by a small amount of liquid, which was recrystallized from pentane to yield pure *N*-triethyl-*B*-trichloroborazine, mp 54–55° (lit. 55–57°,[14] 57–59° [13]).

***N*-Triethyl-*B*-trimethylborazine.** *N*-Triethyl-*B*-trimethylborazine was prepared by allowing *N*-triethyl-*B*-trichloroborazine (22.9 g, 0.0855 mol) to react with excess methylmagnesium bromide (100.0 ml, 3.0 *M*, 0.3 mol) in ethyl ether (250 ml).[13] *Anal.* Calcd for $(CH_3)_3B_3N_3(C_2H_5)_3$: C, 52.28; H, 11.70; N, 20.32. Found: C, 52.16; H, 11.30; N, 19.76. The remaining borazines were prepared and characterized as described previously.

**Tris(acetonitrile)tricarbonylchromium(0).** Tris(acetonitrile)-tricarbonylchromium(0) was prepared by a modification of the method outlined by Prinz, Werner, and Deckelmann[10] as adopted from a method outlined by Hieber.[15] The well-crystallized, granular product is stable for long periods if protected from oxygen: yield 18.70 g (96%). The infrared structure of the product was identical with that reported in the literature.

**Borazinetricarbonylchromium(0) Derivatives.** These compounds were prepared by the entrainment method of Prinz, Werner, and Deckelmann.[8] Other derivatives were prepared by substituting the appropriate borazine. The products were recrystallized from the minimum amount of benzene with cold hexane. They may be sublimed at 90° *in vacuo* without decomposition, although decomposition occurs, without melting, in the range 110–150°. Pertinent data for the borazinetricarbonylchromium(0) compounds reported here are given in Table I.

**Hexamethylbenzenetricarbonylchromium(0).** Hexamethylbenzene (3.75 g, 0.0231 mol, Eastman Organic Chemicals), hexacarbonylchromium(0) (5.0 g, 0.0227 mol), acetonitrile (0.6 ml), and *n*-octane (100 ml) were placed in a 200-ml flask fitted with reflux condenser which is connected to a pressure release, gas collection system and refluxed until gas evoluation ceased. After 24 hr 1630 ml of gas was collected at 25° compared to 1675 ml expected theoretically. The solvent was removed *in vacuo* at 50°. The unreacted hexamethylbenzene and hexacarbonylchromium(0) were sublimed into the condenser and the product was fractionally sublimed at 150°, mp 234–236° (lit.[16] 232°). *Anal.* Calcd for $(CO)_3Cr\cdot C_6(CH_3)_6$: C, 60.39; H, 6.09. Found: C, 60.68; H, 6.01.

**Table II.** Carbonyl-Stretching Frequencies of Several Complexes Containing the $Cr(CO)_3$ Moiety

| No. | Compound | Carbonyl-stretching frequencies, $cm^{-1}$: Cyclohexane A | Cyclohexane E | Nujol[a] A | Nujol[a] E |
|---|---|---|---|---|---|
| 1 | $(CH_3)_6C_6Cr(CO)_3$ | 1962 | 1888 | 1945 | 1848 |
| 2 | $(CH_3)_3B_3N_3(CH_3)_3Cr(CO)_3$ | 1963 | 1867 | 1940 | 1840 |
| 3 | $(C_6H_5)(CH_3)_2B_3N_3(CH_3)_3Cr(CO)_3$ | 1962 | 1868 | 1936 | 1830 |
| 4 | $(C_2H_5)(CH_3)_2B_3N_3(CH_3)_3Cr(CO)_3$ | 1961 | 1867 | 1940 | 1839 |
| 5 | $(CH_3)_3B_3N_3(C_2H_5)_3Cr(CO)_3$ | 1961 | 1867 | 1948 | 1845 |
| 6 | $(CH_3)_3H_3N_3C_3H_6Cr(CO)_3$[b] | | | 1900 | 1785 |
| 7 | $(CH_3CN)_3Cr(CO)_3$ | | | 1915 | 1782 |

[a] In some cases, the compounds are partially soluble in Nujol; in these instances absorption bonds also occur at the same frequencies observed in cyclohexane solution. Such bonds are omitted in this table. [b] Reference 5.

## Results

The constitution of the borazine complexes reported here may be deduced from spectroscopic data.

**Infrared Spectra. Carbonyl Frequencies.** In cyclohexane solution the carbonyl-stretching frequencies of all the borazinetricarbonylchromium(0) complexes prepared in this investigation appear near 1960 (A mode) and 1860 $cm^{-1}$ (E mode). The details in this region for the complexes and other $Cr(CO)_3$-containing compounds appear in Table II. The carbonyl-stretching frequencies for the borazine derivative are very similar to those found in hexamethylbenzenetricarbonylchromium(0) and are substantially different from those of $\sigma$-bonded cyclic triamine tricarbonylchromium(0) complexes such as those formed by hexahydro-*s*-triazine derivatives (compound **6**, Table II). Using the usual arguments for the bonding in metal carbonyls as deduced from carbonyl frequency shifts,[17] the results reported here suggest that the electronic effects of hexasubstituted borazines and hexamethylbenzene are similar, such effects arising from the sum of $\sigma$-donor $\pi$-acceptor character of the noncarbonyl ligand. The carbonyl-stretching frequencies do not necessarily reflect the conformation of the borazine ring. Thus, if the borazine ring is puckered acting as a triamine $\sigma$ donor, it would be expected to have little $\pi$-acceptor character, and the carbonyl-stretching frequency in this instance would be a measure of its relative $\sigma$-donor strength. If the borazine ring is planar, the carbonyl frequency is a measure of the $\sigma$-donor and $\pi$-acceptor character of this ligand. The fact that

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(13) D. T. Haworth and L. F. Hohnstedt, *J. Amer. Chem. Soc.*, **82**, 89 (1960).

(14) H. S. Turner and R. J. Warne, *Chem. Ind. (London)*, 526 (1968).

(15) W. Hieber, W. Abeck, and K. K. Platzer, *Z. Anorg. Allg. Chem.*, **280**, 252 (1955).

(16) E. O. Fischer, K. Ofele, H. Eisler, W. Frohlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958).

(17) G. R. Dodson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

the borazine and benzene ligands give essentially the same carbonyl frequency does not itself argue for a similar structure for these compounds as suggested previously.[9] Indeed, other evidence described here is consistent with the interpretation that the borazine ligand is puckered, which is consistent with the conformation indicated by a recent X-ray diffraction study on the ethyl derivative.[10]

**Boron–Nitrogen Stretching Frequency.** The most marked change in the spectrum of the complexed borazine relative to the uncomplexed borazine is the shift to lower frequency of the boron-nitrogen ring-stretching vibration (Table III). This shift to lower wave number is consistent with a reduction in B–N bond order. In complexed borazine rings an alternative mechanism for this decrease in bond order can arise because the nitrogen electron pair has been localized (I) in the formation of a $\sigma$-coordinate covalent bond to the chromium atom, rather than being delocalized in the B–N ring system (II). Thus, these infrared data could alternately imply that the nitrogen atom in the complex has become four-coordinate and near-tetrahedral rather than remaining three-coordinate and planar; the latter environment is found in uncomplexed borazines. A B–N ring containing three four-coordinate nitrogen atoms cannot be planar.

The results given in Table II are in agreement with the data presented previously;[9] however, the assignment[9] of a B–N single bond in a cyclic environment at 900 cm$^{-1}$ based upon the spectra of aminoboranes is in error. More appropriate models for the borazine ring complexed to a metal tricarbonyl group are the cyclic triborazanes (*e.g.*, $R_3B_3N_3R_3'\cdot 3HX$). The bands in the spectra of a large number of these compounds which appear near 1260 cm$^{-1}$ were assigned to a B–N single bond, using the usual correlation techniques.[18]

**B-$CH_3$ Vibrations.** The B-$CH_3$ absorption at 880 cm$^{-1}$ shows only insignificant shifts of one to two wave numbers to lower frequency on complexation, which is consistent with the presumption that the bonding of the boron to its substituents should be minimally affected on complexation if the rings in these complexes were puckered.

**N-$CH_3$ Vibrations.** The *N*-methyl rocking mode in borazines is, on the other hand, shifted to higher frequency on complexation (Table III). The sensitivity of this vibration to changes in the nature of the adjacent B substituents was demonstrated in an earlier publication[19] and was interpreted primarily in terms of a steric effect. The observed shift of the nitrogen methyl rocking motion (Table IV) could be a result of two related effects, the relative magnitudes of which cannot be established with the data available. The first is the change in electronic factors arising from complexation of the ring; *e.g.*, the nitrogen sites would acquire a formal positive charge if the borazine is complexed as a triamine. The second is the change in steric effects which would occur if the ring is puckered when complexation occurs; if the ring remains planar we might still expect a small change in the *N*-methyl vibrations which might be analogous to the *B*-methyl vibrations because of a decrease in the B–N bond order. Both effects would be related to a change in the hybridization of the nitrogen atom on complexation of a puckered borazine ring.

**Nuclear Magnetic Resonance. Solvent Effects.** Large solvent effects have been observed in the proton magnetic resonance of borazine and the tricarbonylchromium(0) derivatives (Table V) similar to those reported previously.[8,20] These solvent-induced shifts have been interpreted in terms of solute-solvent dipole interactions similar to those discussed in the characterization of unsymmetrical borazines.[20] Unlike the arenetricarbonylchromium(0) derivatives, the borazinetricarbonylchromium(0) complexes decomposed too rapidly in carbon tetrachloride to obtain their nmr spectra in this solvent; therefore, chloroform and methylene chloride were used to obtain solution spectra for all complexes.

**Table III.** Comparison of the Boron–Nitrogen Stretching Frequency of Borazines and Their Complexes with the $Cr(CO)_3$ Moiety

| Compound | B–N stretching frequency, cm$^{-1}$ | | |
|---|---|---|---|
| | Borazine[a] | Complex[b] | Decrease on complexation |
| $(CH_3)_3N_3B_3(CH_3)_3\cdot Cr(CO)_3$ | 1415 | 1374 | 41 |
| $(CH_3)_3N_3B_3(CH_3)_2(C_6H_5)\cdot Cr(CO)_3$ | 1423 | 1371 | 52 |
| $(CH_3)_3N_3B_3(CH_3)_2(C_2H_5)\cdot Cr(CO)_3$ | 1405 | 1373 | 32 |
| $(C_2H_5)_3N_3B_3(CH_3)_3\cdot Cr(CO)_3$ | 1430 | 1385 | 45 |

[a] $CCl_4$ solution. [b] $CHCl_3$ solution.

**Table IV.** *N*-Methyl Vibrational Change on Complexation

| Compound | *N*-Methyl vibrations, cm$^{-1}$ | |
|---|---|---|
| | Borazine | Complex |
| $(CH_3)_3N_3B_3(CH_3)_3$ | 1106[a] | 1115[c] |
| $(CH_3)_3N_3B_3(CH_3)_2(C_2H_5)$ | 1106[b] | 1115[c] |
| $(CH_3)_3N_3B_3(CH_3)_2(C_6H_5)$ | 1105, 1124[b] | 1116, 1137[c] |

[a] $CCl_4$ solution. [b] Neat liquid between salt plates. [c] $CHCl_3$ solution.

In addition to the normal benzene-type aromatic solvent induced shifts to higher field, a reverse shift has been observed for hexafluorobenzene solutions of these complexes (Table V). This effect was first described by Compton, Bertrand, and Verkade,[21] who showed that benzene and hexafluorobenzene selectively associate at the opposite ends of a dipolar molecule and also reverse their orientation.

The reverse aromatic solvent induced shift associated with hexafluorobenzene was attributed to the reversal of the positions of greatest electron density in the solvent molecule. In benzene this is the electron-rich flat side of the molecule; in hexafluorobenzene the fluorine atoms on the ring periphery are now the sites of greatest electron density. Although the anisotropic shielding zones of these two aromatic rings are similar, they orient differently with respect to a solute molecule containing a strong dipole. A net positive charge becomes associated with the flat side of benzene which leads to shielding of protons; the periphery of hexafluorobenzene molecules causes a reversal of the chemical shift.

In Table V the chemical shift of the borazines for which complexes have been made is given for each of the solvents: benzene, methylene chloride, chloroform, and hexafluorobenzene. Table IV gives the chemical shifts of the com-

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[18] G. A. Anderson, Ph.D. Dissertation, The University of Texas at Austin, 1969.

[19] L. A. Melcher, J. L. Adcock, and J. J. Lagowski, *Inorg. Chem.*, 11, 1247 (1972).

[20] J. L. Adcock, L. A. Melcher, and J. J. Lagowski, *Inorg. Chem.*, 12, 788 (1973).

[21] R. D. Compton, R. D. Bertrand, and J. G. Verkade, *J. Amer. Chem. Soc.*, 92, 2702 (1970).

**Table V.** Solvent Effects on Chemical Shifts in Borazinetricarbonylchromium(0) Complexes

| | Chemical shifts,[a] cps | | | |
|---|---|---|---|---|
| Substituent[b] | Benzene | Methylene chloride | Chloroform | Hexafluorobenzene |
| Hexamethylbenzenetricarbonylchromium(0) | | | | |
| C-CH$_3$ | 104.0 | 133.3 | 134.0 | 142.0 |
| Hexamethylborazinetricarbonylchromium(0) | | | | |
| 1,3,5-CH$_3$ (N) | 140.2 | 169.8 | 183.0 | 188.0 |
| 2,4,6-CH$_3$ (B) | 24.6 | 41.4 | 53.4 | 58.4 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-phenylborazinetricarbonylchromium(0) | | | | |
| 1-CH$_3$ (N) | 147.5 | 176.4 | 183.2 | 196.0 |
| 3,5-CH$_3$ (N) | 143.7 | 159.6 | 166.6 | 178.0 |
| 2,6-CH$_3$ (B) | 27.0 | 45.6 | 51.0 | 63.0 |
| 4-C$_6$H$_6$ (B) | 456.0 | 439.2 | 447.0 | 444.0 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-ethylborazinetricarbonylchromium(0) | | | | |
| 1-CH$_3$ (N) | 140.5 | 176.8 | 176.5 | 190.5 |
| 3,5-CH$_3$ (N) | 145.5 | 179.2 | 179.2 | 194.0 |
| 2,6-CH$_3$ (B) | 24.0 | 47.5 | 48.0 | 59.0 |
| 4-C$_2$H$_5$ (B) | 56.3[c] | 72.0[c] | 71.0[c] | 84.0[c] |
| 1,3,5-Triethyl-2,4,6-trimethylborazinetricarbonylchromium(0) | | | | |
| 1,3,5-CH$_3$ (C) | 48.0[d] | 75.8 | 72.5 | 86.0 |
| 1,3,5-CH$_2$ (N) | 169.5[d] | 191.1 | 194.2 | 205.8 |
| 2,4,6-CH$_3$ (B) | 32.2 | 48.8 | 49.2 | 60.0 |

[a] Chemical shifts are in cycles per second downfield from tetramethylsilane recorded on a 60-MHz Varian A-60 nmr spectrometer. [b] The numbering system places the unique B substituent in the 4 position. [c] Ethyl group is a sharp singlet in benzene; in the other three solvents the peak has broadened considerably but is still unresolved presumably because the solvents affect the CH$_2$ and CH$_3$ groups differently as would be expected (see ref 8). [d] CH$_2$–CH$_3$ coupling constant = 7.0 cps.

**Table VI.** Solvent Effects on Chemical Shift in Borazines

| | Chemical shift,[a] cps | | | |
|---|---|---|---|---|
| Substituent[b] | Benzene | Methylene chloride | Chloroform | Hexafluorobenzene |
| Hexamethylbenzene | | | | |
| C-CH$_3$ | 127.0 | 131.1 | 133.3 | 126.0 |
| Hexamethylborazine | | | | |
| 1,3,5-CH$_3$ (N) | 167.5 | 171.9 | 173.4 | 168.8 |
| 2,4,6-CH$_3$ (B) | 29.2 | 27.7 | 29.4 | 23.8 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-phenylborazine | | | | |
| 1-CH$_3$ (N) | 169.5 | 175.2 | 178.0 | 173.5 |
| 3,5-CH$_3$ (N) | 161.0 | 158.4 | 161.2 | 159.5 |
| 2,6-CH$_3$ (B) | 29.2 | 31.2 | 32.0 | 27.6 |
| 4-C$_6$H$_5$ (B) | 437.0 | 435.6 | 438.7 | 434.3 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-ethylborazine | | | | |
| 1-CH$_3$ (N) | 167.0 | 172.0 | 172.6 | 168.9 |
| 3,5-CH$_3$ (N) | 169.5 | 174.0 | 174.9 | 172.0 |
| 2,6-CH$_3$ (B) | 28.2 | 28.0 | 28.3 | 28.2 |
| 4-C$_2$H$_5$ (B) | 62.4[c] | 60.0[c] | 60.2[c] | 59.0[c] |
| 1,3,5-Triethyl-2,4,6-trimethylborazine | | | | |
| 1,3,5-CH$_3$ (C) | 59.8[d] | 61.0 | 62.0 | 62.5 |
| 1,3,5-CH$_2$ (N) | 195.0[d] | 197.5 | 198.5 | 196.0 |
| 2,4,6-CH$_3$ (B) | 32.0 | 29.0 | 29.5 | 26.0 |

[a] Chemical shifts are in cycles per second downfield from tetramethylsilane recorded on a 60-MHz Varian A-60 spectrometer. [b] The numbering system places the unique B substituent in the 4 position. [c] Ethyl group is unsplit; see ref 8 and 23. [d] CH$_2$–CH$_3$ coupling constant = 7.0 cps.

plexes of these borazines in the same solvents. Hexamethylbenzene and its tricarbonylchromium(0) complex are included for comparison in each of the tables.

The solvent effects for uncomplexed borazines (Table VI) are reasonably regular for the *N*-methyl groups, less so for the *B*-methyl groups. The chemical shifts in hexafluorobenzene approach those in benzene but the effect is not obvious because of the irregularity caused by local dipoles in the borazine molecules. The general observation can be made that solvent effects are small for the uncomplexed borazines (Table VI) in each of the four solvents as compared to those found in the tricarbonylchromium(0) complexes given in Table V.

In each of the complexes the *B*- or *N*-alkyl chemical shifts are uniformly shifted to lower field in the order of solvents: benzene, methylene chloride, chloroform, and hexafluorobenzene. This regularity is a direct result of a large molecular dipole in the complex along the principal symmetry axis of the borazine ring (substituents ignored) passing through the chromium atom which places a large net positive charge on the complexed ring, implying that the direction of electron density flow on complexation is to the tricarbonylchromium(0) moiety. This conclusion is supported by the reported strong electron-withdrawing effect of the phenyltricarbonylchromium(0) group.[22]

The analysis of the solvent-independent chemical shifts arising from complexation of the borazine nucleus becomes possible if we establish an internal reference. We choose to use the difference between the *B*-methyl and *N*-methyl chemical shifts for each borazine and its complex, respectively, to indicate internal changes in the ring which arise upon complexation (eq 1). Table VII lists the differences

$$\Delta' = \delta_{\mathrm{N-CH_3}} - \delta_{\mathrm{B-CH_3}} \qquad (1)$$

obtained between each type of *N*-methyl group relative to the *B*-methyl groups in the 2,6 positions in the ring. The data exhibit a general regularity in the differences calculated for every solvent; the only deviation from the value of approximately 145 cps occurs for the *N*-methyl groups in positions 3 and 5 in 1,3,5-trimethyl-2,6-dimethyl-4-phenylborazine which is consistent with the results of an earlier publication[20] where it was found that the substitution of a *B*-phenyl group adjacent to an *N*-methyl causes an upfield shift of 12.7 cps that nearly compensates for the discrepancy observed between this group of *N*-methyls and that of the remaining *N*-methyls. The greatest discrepancies occur in benzene solution which are almost certainly a result of the large aromatic solvent induced shifts resulting from orientation of benzene molecules about local dipoles in the solute and the greater probability of solute–solvent interactions occurring on the flat sides of the benzene molecule. The results in hexafluorobenzene are similar but show fewer discrepancies.

Table VIII gives the chemical shifts of the *N*-methyl group relative to the *B*-methyl group for the tricarbonylchromium(0) complexes of these borazines. Again the data exhibit a general regularity with a discrepancy for the *N*-methyl group in the 3,5 position of the 1,3,5-trimethyl-2,6-dimethyl-4-phenylborazinetricarbonylchromium(0) which is due partly to the shielding anisotropy of the 4-phenyl group adjacent to these methyl groups. As before, the greatest discrepancies occur in benzene solution for much the same reasons as for the borazines.

The differences in the Δ′ value (shown in Table IX) between the free (Table VII) and complexed (Table VIII) borazines yield a net shift difference that is due primarily to

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(22) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

**Table VII.** Chemical Shifts of *N*-Methyl Substituents in Borazines Relative to Their *B*-Methyl Substituents

| *N*-Methyl substituent position | Δ' chemical shifts,$^a$ cps<br>Benzene | Methylene chloride | Chloroform | Hexafluorobenzene |
|---|---|---|---|---|
| Hexamethylborazine | | | | |
| 1,3,5-$CH_3$ | 138.3 | 144.2 | 144.0 | 145.0 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-phenylborazine | | | | |
| 1-$CH_3$ | 140.3 | 144.0 | 146.0 | 145.9 |
| 3,5-$CH_3$ | 131.8$^b$ | 127.2$^b$ | 129.2$^b$ | 131.9$^b$ |
| 1,3,5-Trimethyl-2,6-dimethyl-4-ethylborazine | | | | |
| 1-$CH_3$ | 138.8 | 144.0 | 144.3 | 140.7 |
| 3,5-$CH_3$ | 141.3 | 146.0 | 146.6 | 143.8 |

[a] Chemical shifts are in cycles per second downfield from the *B*-methyl chemical shift defined as zero recorded on a 60-MHz Varian A-60 nmr spectrometer. $\Delta' = S(NCH_3) - S(BCH_3)$. [b] Discrepancy due to anisotropic shielding of the 4-phenyl group.

**Table VIII.** Chemical Shifts of *N*-Methyl Substituents in Borazinetricarbonylchromium(0) Complexes Relative to Their *B*-Methyl Substituents

| *N*-Methyl substituent position | Δ' chemical shifts,$^a$ cps<br>Benzene | Methylene chloride | Chloroform | Hexafluorobenzene |
|---|---|---|---|---|
| Hexamethylborazinetricarbonylchromium(0) | | | | |
| 1,3,5-$CH_3$ | 115.6 | 128.4 | 129.6 | 130.4 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-phenylborazinetricarbonylchromium(0) | | | | |
| 1-$CH_3$ | 120.5 | 130.8 | 132.2 | 133.0 |
| 3,5-$CH_3$ | 116.7$^b$ | 114.0$^b$ | 155.6$^b$ | 115.0 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-ethylborazinetricarbonylchromium(0) | | | | |
| 1-$CH_3$ | 116.7 | 129.3 | 128.5 | 131.5 |
| 3,5-$CH_3$ | 121.5 | 131.7 | 131.2 | 135.0 |

[a] Chemical shifts are in cycles per second downfield from the *B*-methyl chemical shift defined as zero on a 60-MHz Varian A-60 nmr spectrometer. $\Delta' = \delta(NCH_3) - \delta(BCH_3)$. [b] Discrepancy partly due to anisotropic shielding of the 4-phenyl group.

**Table IX.** Net Changes in Relative Chemical Shifts (Δ') in Borazine Methyl Substituents on Complexation

| *N*-Methyl substituent position | Δ'' chemical shifts,$^a$ cps<br>Benzene | Methylene chloride | Chloroform | Hexafluorobenzene |
|---|---|---|---|---|
| Hexamethylborazine *vs.* Complex | | | | |
| 1,3,5-$CH_3$ | 22.7 | 15.8 | 14.4 | 14.6 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-phenylborazine *vs.* Complex | | | | |
| 1-$CH_3$ | 19.8 | 13.2 | 13.8 | 12.9 |
| 3,5-$CH_3$ | 15.1 | 13.3 | 13.6 | 16.9 |
| 1,3,5-Trimethyl-2,6-dimethyl-4-ethylborazine *vs.* Complex | | | | |
| 1-$CH_3$ | 22.3 | 14.7 | 15.8 | 9.2 |
| 3,5-$CH_3$ | 19.8 | 14.3 | 15.4 | 8.8 |

[a] All values are in cycles per second relative to 60-MHz Varian A-60 nmr spectrometer. $\Delta'' = \Delta'$ (free) $- \Delta'$ (complexed).

changes inherent in complexation of the borazine nucleus. Aside from irregular deviations in benzene and hexafluorobenzene solution, the net effect of complexation is to decrease the chemical shift difference between the *N*-methyl substituent and the *B*-methyl substituent by about 15 cps. Because this is a relative chemical shift difference, the *N*-methyl group could be shifted upfield all or part of the net 15 cps or the *B*-methyl could be shifted downfield all or part of the 15 cps. A comparison of the *N*-methyl chemical shift and the *B*-methyl chemical shift in methylene chloride in both the borazine and the complexed borazine (Tables V and IV) indicates that the *N*-methyl chemical shifts relative to tetramethylsilane remain more nearly constant on complexation than do those for the *B*-methyls. Consequently, we conclude that the net shift difference on complexation is primarily a downfield shift of the *B*-methyl groups. The most direct interpretation of this relative deshielding of the *B*-methyl groups upon complexation of the ring is a change associated with the donation of the nitrogen electrons which were internally donated to form a $\pi$ system in the uncomplexed borazine but became associated with a tricarbonylchromium(0) moiety after complexation.

If the borazine ring remains planar upon complexation the change in the B-substituent chemical shift could be traced to either a change in the effective electronegativity of the boron atoms or to anisotropic shielding of the *N*-methyl and *B*-methyl substituent groups. The anisotropic shielding of the *B*-methyl substituents relative to the *N*-methyl substituents requires that the tricarbonylchromium(0) moiety experience a barrier to free rotation about the primary symmetry axis of the borazine ring which is consistent with our previous suggestion (*vide supra*) that the electron pairs on nitrogen atoms are localized in bond formation to the chromium atom in these complexes.

To examine electronegativity changes which may have occurred at the boron atoms upon complexation, *B*-monoethylpentamethylborazine and its $Cr(CO)_3$ derivative were prepared and studied. The chemical shift differences between the methyl and methylene groups in this compound were used as a measure of electronegativity of the boron atom.[23] The chemical shifts of the methyl and methylene components of the *B*-ethyl group are coincident and exhibit no hyperfine splitting as a consequence of the identical chemical shifts; this has also been reported for *N*-trimethyl-*B*-triethylborazine.[24] The ethyl group remained unsplit in the complexed borazine [*B*-monoethylpentamethylborazinetricarbonylchromium(0)] but was shifted to lower field (Tables V and VI). Similar results were obtained for *N*-trimethyl-*B*-triethylborazinetricarbonylchromium(0).[8] Since the difference between the methyl and methylene groups in an ethyl group bonded to an atom is related to the electronegativity of that atom,[23] we must conclude that very little change in the electronegativity of the boron atom has occurred on complexation. If the ring is planar in the complex, then the tricarbonylchromium(0) moiety must not be free to rotate about the primary symmetry axis. Under such cricumstances with octahedral (or nearly so) bonding orbitals on the chromium atom the carbon monoxide molecules with their anisotropic shielding become oriented beneath the B substituents. This arrangement requires that the net anisotropic shielding caused by the tricarbonylchromium(0) moiety exert a deshielding influence on the *B*-methyl substituents which is inconsistent with the results of Emanuel and Randall[25] who reported a general upfield shift of the methyl groups (0.169 ppm or less) for a series of methylbenzenetricarbonylchromium(0) complexes relative to the respective arene parent. These results lead to the suggestion that the magnetic anisotropy of the tricarbonylchromium(0)

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(23) B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, 77, 397 (1955).

(24) H. Noth and H. Vahrenkamp, *J. Organometal. Chem.*, 12, 23 (1962).

(25) R. V. Emanuel and E. W. Randall, *J. Chem. Soc.*, 3002 (1969).

moiety, including that of the ring–metal bonds, produces an upfield shift in the arene proton resonance of the same order of magnitude as the observed upfield shift, which means that the tricarbonylchromium(0) moiety produces almost all of the upfield shift observed for arenetricarbonylchromium(0) complexes, all other factors apparently offset each other giving a near zero effect. It is also not unreasonable to expect that the upfield shift caused by the magnetic anisotropy for the more electronically and magnetically isolated *B*-methyl protons in borazine which are complexed as puckered rings would be an order of magnitude smaller than that for the ring protons in the arene complex. In the light of the arguments developed here, the possibility of a benzenoid-type borazinetricarbonylchromium(0) with a planar ring is not a reasonable alternative, at least for the hexasubstituted borazine complexes reported in this investigation.

If, however, we assume that the borazine ring is puckered in the complex, the net deshielding observed for the *B*-methyl group is a direct consequence of the ring puckering. The *B*-methyl groups in the puckered ring are elevated to a position above the plane of the nitrogen atoms. The decrease in anisotropic shielding of the *B*-methyl group on complexation is due to the greater distance between the *B*-methyl protons and the tricarbonylchromium(0) moiety relative to the position of that methyl group in a hypothetical planar borazine complex.

**Mass Spectra.** The mass spectra of all borazinetricarbonylchromium(0) derivatives studied exhibited a molecular ion. Although the intensities of these ions varied from compound to compound, the intensities were in every case lower than that for their respective parent borazines. In some cases the fragment ions formed by the loss of two or three carbon monoxide molecules were greater in intensity than the parent borazine. To avoid expressing the intensities as fractions of the total ion current, a term is introduced which is similar to the term introduced in an earlier publication on the mass spectral analysis of borazines. The mass spectral data are discussed in terms of the "per cent relative contribution of the parent borazine" defined by eq 2, where $B$ is the intensity of the borazine ion fragment and $C$ is the intensity of the chromium-containing ion fragment(s). The complement of this percentage is defined as the "per cent relative contribution of the chromium-containing species" (% $C_P$) which allows a quantitative comparison of the relative intensities of the complexed borazine fragments to the parent borazine as well as a qualitative comparison of the relative intensities of the different complexes. To compare arenetricarbonylchromium(0) spectra to the borazine complexes an analogous set of definitions is used, *viz.* "the per cent relative contribution of the parent arene" (% $A_P$), and its complement, "the per cent relative contribution of the chromium-containing arene species" (% $C_P'$).

$$\% B_P = [B/(B + C)] \times 100\% \qquad (2)$$

The mass spectra of borazinetricarbonylchromium(0) complexes and the arenetricarbonylchromium(0) complexes have similar fragmentation patterns (Table X). Both species give a molecular ion, $C_M$; a fragment formed by the loss of two molecules of carbon monoxide, $C_M - 2(CO)$, another formed by the loss of three carbon monoxide molecules, $C_M - 3(CO)$; and finally the parent arene or borazine ion. The fragment ions characterized by the loss of two or three carbon monoxide molecules are usually more intense than the molecular ion for the borazine complexes which may be related to the relative thermal stability of these compounds as well as to the ability to stabilize a positive charge. The relative intensities of the parent molecular ion of hexamethylbenzenetricarbonylchromium(0) compared to that of hexamethylbenzene are much larger than the corresponding comparison for the compounds containing a borazine ring (Table XI), suggesting that the borazinetricarbonylchromium(0) derivatives are markedly less stable than their benzene analogs.

**Table X.** Normalized Intensities of Arene- and Borazinetricarbonylchromium(0) Fragment Ion Distributions

| Relative intensities | | | | | |
|---|---|---|---|---|---|
| $B_P$ – Me ($A_P$ – Me) | $B_P$ ($A_P$) | $C_M$ – 3(CO) – Me | $C_M$ – 3(CO) | $C_M$ – 2(CO) | $C_M$ |
| Hexamethylbenzenetricarbonylchromium(0) | | | | | |
| 5.4 | 2.3 | 0.65 | 100.00 | 9.00 | 14.70 |
| Hexamethylborazinetricarbonylchromium(0) | | | | | |
| 100.00 | 76.0 | 0.32 | 6.50 | 0.76 | 0.77 |
| *B*-Monoethylpentamethylborazinetricarbonylchromium(0) | | | | | |
| | 100.0 | 2.94 | 9.55 | 0.90 | 8.87 |
| *B*-Monophenylpentamethylborazinetricarbonylchromium(0) | | | | | |
| 24.1 | 100.0 | 3.90 | 17.70 | 1.91 | 2.42 |
| Pentamethylborazinyl-*B*-benzenetricarbonylchromium(0) | | | | | |
| 16.3 | 66.6 | 18.40 | 100.00 | 15.90 | 12.70 |
| *N*-Triethyl-*B*-trimethylborazinetricarbonylchromium(0) | | | | | |
| 100.0 | 5.8 | ~0.00 | 7.10 | 0.35 | 0.40 |

**Table XI.** Relative Per Cent Contribution of Borazine or Arene Ions Relative to the Corresponding Tricarbonylchromium(0) Complex Ions

| | % $B_P$ | % $C_M$ |
|---|---|---|
| Hexamethylbenzenetricarbonylchromium(0) | 13.7 | 86.3 |
| Hexamethylborazinetricarbonylchromium(0) | 99.0 | 1.0 |
| *B*-Monoethylpentamethylborazinetricarbonylchromium(0) | 99.0 | 1.0 |
| *B*-Monophenylpentamethylborazinetricarbonylchromium(0) | 98.0 | 2.0 |
| *N*-Triethyl-*B*-trimethylborazinetricarbonylchromium(0) | 93.4 | 6.6 |

One of the principal points relating to the ability of a borazine ring to accommodate a positive charge is the loss of a substituent at the boron site to form a borinium ion[26] and the loss of any particular combination of fragments at the nitrogen to form an immonium ion.[26] Comparison of the ring fragmentation patterns of the corresponding borazines and their tricarbonylchromium(0) complexes (Table XII) indicates that the relative intensity of the $C_M$ species to the $C_M - H$ species rises to 90.9% in the complex from 57.3% in the parent borazine for hexamethylborazinetricarbonylchromium(0); the intensity of the $C_M - CH_3$ ion, which should arise from methyl loss at the boron site, is negligible. These results suggest that the bulk of the positive charge of the radical cation is localized on the tricarbonylchromium(0) moiety.

Similar results are observed for hexamethylbenzene. The uncomplexed arene possesses 51.4% M – H character in the mass spectrum (Table XII). The $A_P$ fragment undergoes ring expansion to form the tropilium cation. However, when the arene ring is complexed to a tricarbonylchromium(0) the distribution contains only 0.7% $C_M - H$ character (Table XII).

**Electronic Absorption Spectra.** The systematic investigation and interpretation of ultraviolet–visible spectra of zero-

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(26) L. A. Melcher, J. L. Adcock, G. A. Anderson, and J. J. Lagowski, *Inorg. Chem.*, 12, 601 (1973).

**Table XII.** Relative Contribution of M to M − H Ion Distributions in Borazine Ions and the Corresponding Borazinetricarbonylchromium(0) Ion Fragments

| Borazine or arene precursor | % rel M − H character fragment ions | | |
|---|---|---|---|
| | $B_P$ ($A_P$) | $C_M$ − 3(CO) | $C_M$ |
| Hexamethylbenzene | 51.4 | 2.7 | 0.7 |
| Hexamethylborazine | 40.6 | 16.8 | 9.1 |
| *B*-Monoethylpentamethylborazine | 9.0 | 5.9 | 5.4 |
| *B*-Monophenylpentamethylborazine[a] | 31.2 | 15.2 | 10.0 |
| *N*-Triethyl-*B*-trimethylborazine | 19.1 | 4.2 | 12.8 |

[a] $Cr(CO)_3$ attached to borazine ring.

**Table XIII.** Ultraviolet-Visible Absorption Spectra of Substituted Arene- and Borazinetricarbonylchromium(0) Derivatives

| Cyclohexane solution ($\epsilon_{max} \times 10^{-4}$) | | | Nujol mull (relative absorption)[b] | | |
|---|---|---|---|---|---|
| A | B | C | A | B | C |
| $Cr(CO)_6$ | | | | | |
| 222.9 | 279.5 | | | | |
| (11.4) | (2.08) | | | | |
| Benzenetricarbonylchromium(0)[a] | | | | | |
| 218.6 | 260.0 | 308.9 | | | |
| (4.56) | (1.22) | (1.31) | | | |
| Hexamethylbenzenetricarbonylchromium(0) | | | | | |
| 219.9 | 244.0 | 325.4 | 216.4 | 248.0 | 330.5 |
| (2.03) | (0.97) | (0.76) | (4.18) | (1.44) | (2.29) |
| Hexamethylborazinetricarbonylchromium(0) | | | | | |
| 222.6 | 257.0 | 395.8 | 220.8 | 267.2 | 400.8 |
| (1.75) | (0.79) | (0.39) | (3.76) | (1.69) | (1.30) |
| *B*-Monoethylpentamethylborazinetricarbonylchromium(0) | | | | | |
| 218.7 | 267.9 | 396.5 | 219.6 | 268.6 | 396.9 |
| (1.10) | (0.38) | (0.26) | (8.23) | (2.80) | (1.88) |
| *B*-Monophenylpentamethylborazinetricarbonylchromium(0) | | | | | |
| 221.7 | 258.1 | 397.8 | 217.0 | 252.2 | 395.8 |
| (1.91) | (0.60) | (0.41) | (7.54) | (2.69) | (1.37) |
| *N*-Triethyl-*B*-trimethylborazinetricarbonylchromium(0) | | | | | |
| 221.0 | 254.3 | 392.0 | 218.0 | 264.6 | 395.1 |
| (1.75) | (0.71) | (0.45) | (9.11) | (3.60) | (2.90) |
| Tris(acetonitrile)tricarbonylchromium(0) | | | | | |
| | | | *c* | 239.7 | 397.0 |
| | | | | (7.73), | (3.89) |
| | | | | 313.2 | |
| | | | | (2.55) | |
| Tris(ammonia)tricarbonylchromium(0) | | | | | |
| | | | *c* | 265.3 | 410.0 |
| | | | | (1.82) | (1.85) |

[a] Ethanol solution (ref 28). [b] Relative absorbance for any one spectrum, not comparable to other spectra. [c] No A band observed.

valent transition metal carbonyl complexes have been only sparsely reported in the literature. Because of the paucity of data, a systematic comparison of the ultraviolet-visible spectra of borazinetricarbonylchromium(0) derivatives was undertaken in this investigation. Significant differences in the ultraviolet-visible spectra of borazine and arene derivatives were observed (Table XII). The interpretation of these spectra and the explanation for the differences observed are based primarily upon relationships suggested by Carroll and McGlynn[27] from semiempirical molecular orbital calculations on arenechromium tricarbonyls and the chromium hexacarbonyl in an attempt to provide a basis for spectral assignments. If, as has been suggested, absorption bands in metallocarbonyls below 300 mμ are due to electronic transitions involving the metal-carbon bonds of the metal carbonyl moiety (denoted hereafter as M-C bonds), bands in this region should be a characteristic feature of all compounds containing such bonds irrespective of whether the organic moiety is a conjugated diene, a cyclopentadienyl ring, or a benzene ring.[28] The M-C bands are represented by the bands designated as B in Table XIII. It was also suggested that the absorptions denoted by A in Table XIII are also M-C bands; however, this region was inadequately studied.[28] The A and B bands show a significant increase in intensity with an increase in the number of carbon monoxide ligands as illustrated by the increase in $\epsilon_{max}$ for these bonds in hexacarbonylchromium(0). A three-band pattern for the arene and borazine complexes is observed in cyclohexane and Nujol. The positions and relative intensities compare reasonably well. A possible exception to the three-band pattern is observed for tris(acetonitrile)- and tris(ammonia)tricarbonylchromium(0). However, the two spectra bands given in the B column for the acetonitrile derivative may be the result of an additional electronic transition due to the unsaturated nitrile ligand. In these complexes the strong A band is not observed. In tris(ammonia)tricarbonylchromium(0) the spectrum consists of a nearly continuous absorption with inflection points suggesting the presence of two or three bands which upon computer resolution gave the two bands tabulated. If the stronger donor character of the ligands bound to the tricarbonylchromium(0) moiety shifts the A band to shorter wavelengths as the slight trend in the A bands possibly indicates (Table XIII), the effect of the stronger donors acetonitrile and ammonia should shift the A band into the vacuum ultraviolet beyond the range of the instrument used in this investigation.

Carroll and McGlynn[27] have assigned the absorptions below 280 mμ in the ultraviolet-visible spectra of arenetricarbonylchromium complexes to transitions involving charge transfer from the transition metal to the arene ring. Assuming that the bands above 290 mμ in the tricarbonylchromium(0) derivatives listed in the C columns of Table XIII also represent electronic transitions involving charge transfer between the chromium metal atom and the noncarbonyl ligands, the absorption spectra of the borazine complexes can be interpreted. The trend in the C band is to longer wavelength along the series of compounds from benzenetricarbonylchromium(0) through the trisammonia derivatives, which is consistent with an increased donor character of the ligand in the series; however, a significant discrepancy is noted between the complexes of hexamethylbenzene and hexamethylborazine which should have the same donor character as inferred from the similarity of their infrared carbonyl-stretching frequencies. This discrepancy suggests a change in the nature of the bonding between the chromium atom and hexamethylborazine as compared to that with hexamethylbenzene. It appears that a change from π bonding in the hexamethylbenzene complex to bonding by electron pairs predominantly localized on nitrogen in the borazine might account for the difference in absorption spectra. This conclusion is supported by the similarity of the C band in the borazine complexes to the C bands in tris(acetonitrile)tricarbonylchromium(0) and tris(ammonia)tricarbonylchromium(0). However, a comparison of the M-C (A or B) bands for hexamethylbenzene- and the borazinetricarbonylchromium(0) complexes reveals a similarity between these compounds, which indicates that the M-C bands reflect the similarities of metal-carbon monoxide

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[27] D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).

[28] R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

systems as observed for the carbonyl-stretching frequencies (A mode) in the infrared spectrum and indirectly support the interpretation suggested by Lundquist and Cais that these bands are associated with metal–carbon monoxide transitions.

The similarities in the A bands and the carbonyl-stretching frequencies (A mode) of the borazine and benzene complexes indicate that the chromium–carbon monoxide bonding in these complexes is very similar. In addition, because of the similarity of the C band absorptions for acetonitrile, ammonia, and borazine complexes, it is suggested that this band correlates with the π-acceptor character as well as the donor character of the noncarbonyl ligands (arene, borazine, etc.) involved in these metal–ligand electronic transitions. This conclusion is supported by the bathochromic shifts of the C bands which occur because of conjugation by unsaturated substituents on the arene or cyclopentadienyl ligands reported by Lundquist and Cais.[28]

This interpretation suggests that the borazine ring is a significantly poorer π-acceptor ligand than is an arene moiety, although both ligands have similar donor characteristics; this is consistent with the presence of a puckered borazine ring in the complexes containing this ligand.

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**Registry No.** $Cr(CO)_6$, 13007-92-6; $(CH_3)_6C_6$, 87-85-4; $(CH_3)_3B_3N_3(CH_3)_3$, 877-07-6; $(C_6H_5)(CH_3)_2B_3N_3(CH_3)_3$, 32386-02-0; $(C_2H_5)(CH_3)_2B_3N_3(CH_3)_3$, 36972-53-9; $(CH_3)_3B_3N_3(C_2H_5)_3$, 883-29-4; $(CH_3)_6C_6 \cdot Cr(CO)_3$, 12088-11-8; $(CH_3)_3B_3N_3(CH_3)_3 \cdot Cr(CO)_3$, 41371-89-5; $(C_2H_5)(CH_3)_2B_3N_3(CH_3)_3 \cdot Cr(CO)_3$, 41371-90-8; $(C_6H_5)(CH_3)_2B_3N_3(CH_3)_3 \cdot Cr(CO)_3$, 41371-91-9; $(CH_3)_3B_3N_3(C_2H_5)_3 \cdot Cr(CO)_3$, 25895-69-6; $(CH_3CN)_3Cr(CO)_3$, 22736-49-8; $(H_3N)_3Cr(CO)_3$, 41371-94-2; pentamethylborazinyl-*B*-benzenetricarbonylchromium(0), 41375-80-8.

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# π-Coordinated Nitrile Derivatives of Halopentacarbonylmanganese(I) and -rhenium(I)

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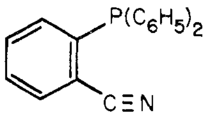
The application of *o*-cyanophenyldiphenylphosphine to the synthesis of the first π-coordinated, mononitrile–phosphine complexes of halopentacarbonyl group VII metals is described. The molecular formula of these complexes $\{[M(CO)_3LX]_y$ where $L = o\text{-}NC(C_6H_4)P(C_6H_5)_2$; M = Mn, X = Cl, Br, or I, $y = 1$; M = Re, X = Cl or Br, $y = 2\}$ and their infrared spectra are consistent with coordination of both the phosphorus atom and the C≡N bond to the group VII metal. The lowering of the C≡N stretching frequency upon π coordination of the nitrile groups to group VII metals is determined from infrared spectral measurements and is used to assess the degree of interaction between nitrile and metal in these complexes. The carbonyl-stretching frequencies are used to compare the ligand's ability to compete for metal π-electron density.

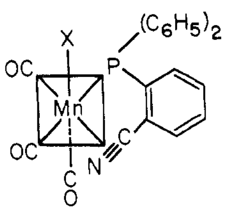
## Introduction

It has been shown that isocyanate,[2] amine-nitrile,[3-7] and dinitrile[8,9] ligands are capable of coordination through the triple bond of their nitrile groups. We now report the extension of this series by the π-coordination of a phosphine-nitrile ligand with halopentacarbonylmanganese(I) and -rhenium(I). The phosphine-nitrile used in these preparations is the ligand, *o*-cyanophenyldiphenylphosphine[10] (structure I)

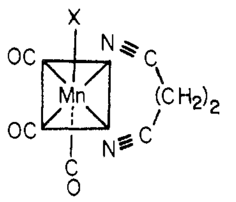


I

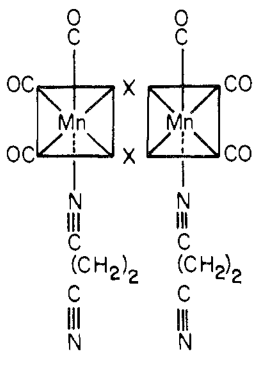
In a preliminary report of some of this material,[11] the assignment of π coordination in the manganese(I) derivatives (structure II) was in part based upon the analogous π-nitrile complexes of succinonitrile (structure III).[8,9] Although evi-



II



III



IV

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