Synthesis of Unsymmetrically Substituted Borazines. Reactions of Borazine with Silver(I) Salts

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Abstract: The reactions of $H_3B_3N_3H_3$ with a variety of silver(I) salts, Ag(I) (CN, NCO, NCS, SO_3CH_3, CO_2CH_3, CO_2CF_3, F, O, and NO_2), have been studied and many new monosubstituted borazine derivatives have been prepared. The new compounds include $H_2(NC)B_3N_3H_3$, $H_2(OCN)B_3N_3H_3$, $H_2(SCN)B_3N_3H_3$, $H_2CH_3SO_3B_3N_3H_3$, and $H_2CH_3CO_2B_3N_3H_3$ which have been characterized according to their elemental analyses and mass, infrared, ^1H, and ^{11}B nmr spectra. The spectral data suggest that the –NCO and –NCS groups have the iso structure (bonding through nitrogen), whereas the –CN group has the normal structure (bonding through carbon). The nmr data for these compounds support the hypothesis that the π electrons of borazine are delocalized, at least partially. The compounds $H_2CH_3CO_2B_3N_3H_3$ and $H_2CH_3SO_3B_3N_3H_3$ represent the first examples of compounds which can be described as borazinyl esters of organic acids.

Significant advancements have been made in the syntheses of unsymmetrically substituted borazines. The metathetical reactions of 2-chloroborazine[1–3] provide good routes to a great variety of compounds. Other preparative procedures involve the reactions of borazine with Grignard reagents,[4,5] boron tribromide,[6] and tin(IV) chloride.[3] Photochemical reactions[7] of borazine have also been used to prepare several compounds. However, there is still a large variety of compounds which cannot be prepared by any of these routes. As a part of our investigations to discover new preparative routes to unsymmetrically substituted borazines, we have studied the reactions of $H_3B_3N_3H_3$ with a variety of silver(I) salts. The silver(I) salt should react with the boron–hydrogen bonds of $H_3B_3N_3H_3$ to form a B-substituted borazine, silver metal, and hydrogen. The variety of silver salts we have studied include AgCN, –NCO, –NCS, $-CO_2CH_3$, $-CO_2CF_3$, $-SO_3CH_3$, –F, –O, and $-NO_2$. The reactions of these salts have been compared in order to determine if the anion has an effect on the reactivity and course of reaction. In addition, the new monosubstituted borazines have been fully characterized in order to study the nature of bonding between the substituent and the borazine ring and the effect of the substituent on the bonding in the borazine ring.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The pentane was dried by distillation from CaH_2. The acetonitrile was dried with phosphorus pentoxide. Borazine[8] was prepared by the $NaBH_4$ reduction of $Cl_3B_3N_3H_3$ in a glycol ether. The silver(I) salts were dried by heating *in vacuo*.

Reaction of $H_3B_3N_3H_3$ with AgX. All of the reactions of $H_3B_3N_3H_3$ with the silver(I) salts were run in a similar manner. An example is described below. The quantities of reactants, reaction medium, reaction time, mole ratio, H_2 to Ag^+, percentage yield of $H_2XB_3N_3H_3$, and temperature required for isolation of the unsymmetrically substituted borazine are given in Table I. The percentage yield of $H_2XB_3N_3H_3$ is based on the quantity of silver(I) salt reacted and the mass of the unsymmetrically substituted borazine isolated. The analyses and some physical properties of $H_2(OCN)B_3N_3H_3$, $H_2(SCN)B_3N_3H_3$, $H_2(NC)B_3N_3H_3$, $H_2CH_3CO_2B_3N_3H_3$, and $H_2CH_3SO_3B_3N_3H_3$ are given in Table II.

Table I. Reaction of $H_3B_3N_3H_3$ with Silver(I) Salts

AgX	Reaction medium	Reaction time	H_2/Ag^+, mmol	% yield, $H_2XB_3N_3H_3$	Temp,[a] °C
AgCN	C_5H_{12}	6 hr	0.515	53.6	35
AgO_2CCH_3	C_5H_{12}	5 min	0.521	32.1	−46
AgO_2CCF_3	CH_3CN	5 min	0.493	0	−46, 30
AgO_3SCH_3	CH_3CN	5 min	0.498	44.5	45
AgNCO	C_5H_{12}	6 hr	0.352	14.5	−46
AgNCS	CH_3CN	12 hr	0.0294	2.84	−46
AgF	C_5H_{12}	12 hr	0.0373	0	−78
Ag_2O	CH_3CN	12 hr	0.106	4.32	25
$AgNO_2$	CH_3CN	5 min	0.678[b]	0	−46, 30

[a] For isolation of $H_2XB_3N_3H_3$. [b] Noncondensable gas was a mixture of H_2 and N_2 as demonstrated by its mass spectrum.

Table II. Analyses and Properties of 2-Substituted Borazines

Compound	Calcd % N	Calcd % H	Exptl % N	Exptl % H	Vapor pressure,[a] mm	Mp, °C
$H_2(OCN)B_3N_3H_3$	45.9	1.64	45.8	1.61	2.4	37–38
$H_2(SCN)B_3N_3H_3$	30.4	1.42	30.3	1.42	0	24–25
$H_2(NC)B_3N_3H_3$	39.3	1.89	39.6	1.89	0	111–112
$H_2CH_3CO_2B_3N_3H_3$	30.2	1.44	31.0	1.41	1.7	0–2
$H_2CH_3SO_3B_3N_3H_3$	24.0	1.14	23.8	1.14	0	52–55

[a] At 25°.

In a typical reaction, 0.5010 g (3.00 mmol) of AgO_2CCH_3 was dissolved in 15 ml of dry CH_3CN, and then 0.3300 g (4.08 mmol) of $H_3B_3N_3H_3$ was distilled into the flask containing the silver salt using a −196° bath. The mixture was slowly warmed to room temperature with stirring. At about 0°, an orange-brown insoluble complex formed. With further warming the mixture

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Table III. Nuclear Magnetic Resonance Data for 2-Substituted Borazines, $H_2XB_3N_3H_3$

	X									
	OCN		SCN		CN		CH_3CO_2		CH_3SO_3	
	Proton Data									
Solvent	CCl_4	CCl_4	C_5H_{10}	CH_3CN	CH_3CN	$CDCl_3$	CCl_4	C_5H_{10}	CH_3CN	
Mol % solute	5	2	5	5	5	2	5	5	5	25
NH δ, ppm	−5.02	−5.10	−5.00	−5.83	−6.48	−6.00	−5.52	−5.55	−5.63	−5.59
J, Hz	52	53	54	55	56	56	44	44	50	49
BH δ, ppm	−4.40	a	−4.42	a	−4.25	a	−4.42	−4.42	a	a
J, Hz	133		138		138		136	136		
CH δ, ppm							−2.03	−2.03	−3.10	−3.05
	Boron-11 Data									
	−25.2		−25.2			−22.9	−25.3[b]		−25.1[b]	
	−29.7		−29.8			−26.9				
	−38.5		−38.5			−35.9	−35.4[c]		−36.9[c]	

[a] Not observable. [b] More intense line. [c] Less intense line.

turned black and hydrogen evolution occurred rapidly. After approximately 1 hr, the mixture was frozen at −196° and the H_2 was measured with a Toepler pump-gas buret assembly. The volatile, condensable products were then fractionated using −46° and −196° traps. The excess $H_3B_3N_3H_3$ was not separated from the pentane (−196° trap).

Mass Spectra. The mass spectra of the new compounds prepared in this study were recorded by using a Perkin-Elmer Hitachi Model RMU 6-E mass spectrometer. All spectra had the correct *m/e* cutoff values expected for the parent which confirmed the molecular mass and purity of the new compounds.

Infrared Spectra. The infrared spectra were recorded in the range 4000–630 cm^{-1}, by means of a Beckman IR-5A spectrometer. The spectra of $H_2(OCN)B_3N_3H_3$ and $H_2CH_3CO_2B_3N_3H_3$ were taken on samples in the gas phase in a 10-cm cell. The spectra of $H_2(SCN)B_3N_3H_3$, $H_2(NC)B_3N_3H_3$, and $H_2CH_3SO_3B_3N_3H_3$ were taken on samples as Nujol and Kel-F mulls and/or CCl_4 and $CHCl_3$ solutions.

The following gives the spectral frequencies in reciprocal centimeters (intensity s, strong; m, medium; w, weak; sh, shoulder). The frequencies of the mulling agents or solvents have been omitted.

$H_2(OCN)B_3N_3H_3$. 3484 (m), 2605 (sh), 2541 (sh), 2291 (vs), 1524 (s), 1486 (sh), 1465 (sh), 1446 (vs), 1426 (sh), 1390 (w), 1360 (m), 1265 (w), 1104 (sh), 1085 (m), 1051 (m), 931 (sh), 918 (m), 719 (m), 712 (sh), 645 (m).

$H_2(SCN)B_3N_3H_3$. 3447 (m), 2600 (sh), 2545 (sh), 2110 (vs), 2064 (vs), 1478 (sh), 1467 (vs), 1454 (sh), 1441 (vs), 1422 (sh), 1369 (s), 1351 (m), 1260 (m), 1208 (w), 1185 (m), 1059 (w), 1019 (w), 972 (w), 917 (m), 904 (s), 885 (m), 707 (s), 650 (w), 630 (m).

$H_2(NC)B_3N_3H_3$. 3403 (m), 2591 (sh), 2510 (m), 2232 (w), 1471 (sh), 1449 (vs), 1435 (vs), 1389 (sh), 1362 (m), 1339 (sh), 1285 (m), 1255 (w), 1105 (w), 917 (sh), 905 (s), 758 (s), 707 (m), 660 (m), 640 (s). (The spectra of the mulls showed splitting of the NH and BH modes.)

$H_2CH_3CO_2B_3N_3H_3$. 3469 (m), 3005 (vw), 2600 (sh), 2528 (m), 1760 (m), 1582 (sh), 1469 (vs), 1438 (w), 1406 (sh), 1388 (m), 1291 (m), 1247 (s), 1181 (m), 935 (sh), 922 (m), 886 (m).

$H_2CH_3SO_3B_3N_3H_3$. 3425 (m), 2914 (w), 2822 (w), 2787 (w), 2630 (sh), 2524 (m), 1486 (sh), 1467 (sh), 1456 (vs), 1423 (sh), 1390 (w), 1379 (w), 1338 (m), 1328 (m), 1285 (m), 1181 (m), 1136 (m), 1127 (m), 985 (m), 922 (m), 901 (m), 860 (w), 784 (m), 678 (m), 665 (m), 645 (m).

Nuclear Magnetic Resonance Spectra. The ^1H nmr spectra were recorded at 100 MHz by means of a Varian Model HA-100 spectrometer. The ^{11}B nmr spectra were recorded at 15.871 MHz with a Varian Model HR-60 spectrometer. The reference compounds were tetramethylsilane and boron trifluoride diethyl etherate. The chemical shifts of the ^{11}B spectra were determined using the side-band technique. The chemical shifts and coupling constants for the monosubstituted derivatives are given in Table III.

Results and Discussion

The reaction of $H_3B_3N_3H_3$ with a silver(I) salt, a new reaction in borazine chemistry, has been studied, and many new monosubstituted derivatives have been prepared. The reactivities of the salts Ag^ICN, -NCO, -NCS, $-SO_3CH_3$, $-CO_2CH_3$, $-CO_2CF_3$, -F, -O, and $-NO_2$ have been studied, and the new compounds $H_2(NC)B_3N_3H_3$, $H_2(OCN)B_3N_3H_3$, $H_2(SCN)B_3N_3H_3$, $H_2CH_3SO_3B_3N_3H_3$, and $H_2CH_3CO_2B_3N_3H_3$ have been isolated. No borazine derivatives were isolated from the reactions of $AgCO_2CF_3$ (F and NO_2).

The idealized equation for the reaction of $H_3B_3N_3H_3$ with a silver(I) salt (AgX) is given in eq 1. There are

$$AgX + H_3B_3N_3H_3 \longrightarrow H_2XB_3N_3H_3 + Ag + {}^1/_2H_2 \qquad (1)$$

several aspects of this particular reaction which are synthetically and experimentally attractive. The extent of reaction is readily monitored by the hydrogen evolution, and the monosubstituted borazine is easily isolated as it is the only product of the reaction which is volatile and condensable. Using the data from Table I the salts AgCN, $AgCO_2CH_3$, $AgCO_2CF_3$, and $AgSO_3CH_3$ apparently reacted according to the idealized equation; 0.5 mol of hydrogen per mole of Ag^+ was formed during the reaction, and the yield of the monosubstituted borazine, with the exception of $H_2CF_3CO_2B_3N_3H_3$, was quite high. There was no $H_2CF_3CO_2B_3N_3H_3$ isolated from the reaction mixture. It was probably formed but apparently decomposed before it could be isolated. It should be noted that $H_2CH_3CO_2B_3N_3H_3$ was also observed to decompose at 25°, but much less readily than $H_2CF_3CO_2B_3N_3H_3$. For the case of AgNCO, only about 80% of the expected quantity of H_2 was formed and the yield of $H_2(OCN)B_3N_3H_3$ was small. The salts AgNCS, AgF, and Ag_2O reacted to give silver metal, but only a small quantity of H_2 was formed and the yield of the monosubstituted borazines was either very small or zero. In addition the quantity of $H_3B_3N_3H_3$ consumed per mole of AgX was much less than one (0.336, AgNCS; 0.197, AgF; and 0.446, Ag_2O). Therefore, one could envision that species such as $H_3B_3N_3H_3 \cdot 3HSCN$ and $(F_2BNH_2)_x$, as well as many others, could be formed in these reactions. The reaction of $AgNO_2$ with $H_3B_3N_3H_3$ is even more complicated and surprising. The noncondensable gas formed in the reaction was a mixture of H_2 and N_2. These results suggest that $H_3B_3N_3H_3$ can reduce NO_2^- to N_2. It is certainly quite clear that the reactions of $H_3B_3N_3H_3$ with silver(I) salts are exceedingly complex and depend on the nature of the anion. However, we have not been able to elucidate any correlation between the nature of the reaction and the silver(I) salts.

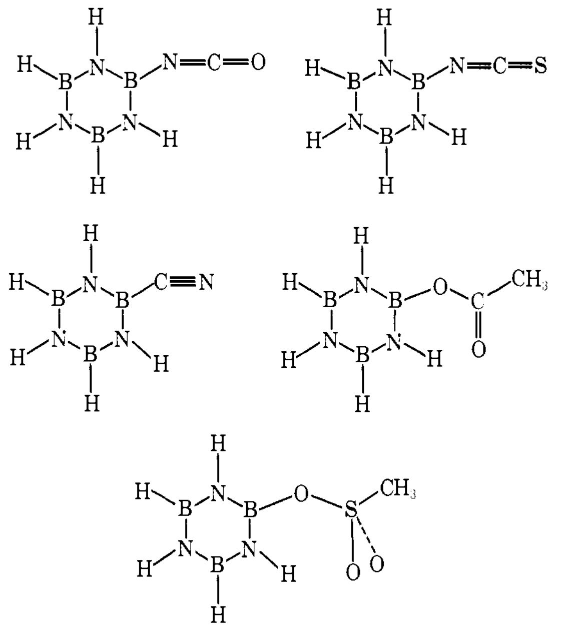

Figure 1. Structures of monosubstituted borazines.

The compounds $H_2(OCN)B_3N_3H_3$, $H_2(SCN)B_3N_3H_3$, $H_2(NC)B_3N_3H_3$, $H_2CH_3CO_2B_3N_3H_3$, and $H_2CH_3SO_3B_3N_3H_3$, which have been prepared by this reaction, have been fully characterized according to their elemental analyses and mass, infrared, ^1H, and ^{11}B nmr spectra. There are several possible structures as well as modes and types of bonding possible in these compounds. The structures shown in Figure 1 are consistent with all of our data.

The pseudohalides, CN, NCS, and NCO, are ambidentate ligands. Our spectroscopic data indicate that the CN group has the normal structure (bonding through carbon), whereas the groups NCS and NCO have the iso structure (bonding through nitrogen). The infrared spectrum of $H_2(NC)B_3N_3H_3$ exhibits a band at 2232 cm^{-1} which is characteristics of the CN stretch in nitriles. Aromatic nitriles[9] absorb in the region 2225–2240 cm^{-1}, whereas isonitriles absorb at lower frequencies. The spectrum of $H_2(SCN)B_3N_3H_3$ has a doublet in the antisymmetric NCS stretching region (2170, 2090 cm^{-1}) which is characteristic of the isothiocyanate structure.[10,11] The frequency of the symmetric NCS stretching mode (885 cm^{-1}) for $H_2(SCN)B_3N_3H_3$ is also consistent with the isothiocyanate structure.[12,13] The frequency region[12,13] expected for a thiocyanate structure is much lower, 690–720 cm^{-1}. The antisymmetric and symmetric NCS stretching frequencies[14] for $(SCN)_3B_3N_3H_3$ were observed at 2083 and 972 cm^{-1}, respectively. Further comparisons[14] are also possible between the spectra of $H_2(OCN)B_3N_3H_3$ and $(OCN)_3B_3N_3H_3$. The antisymmetric stretching frequencies were observed at 2291 and 2287 cm^{-1}, respectively. The corresponding frequency[11] for C_6H_5NCO was observed at 2285 cm^{-1}. The isocyanate structure in $(OCN)_3B_3N_3H_3$ was further confirmed by reaction with amines.[15] The similarities between the nmr chemical shifts (Table III) of the NH protons and the boron atoms bound to the substituent in $H_2(SCN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$ further suggest that both compounds have the iso structure, bonding through nitrogen. If the group NCO were bound through oxygen instead of nitrogen, one would expect a smaller chemical shift relative to borazine. The assignment of the symmetric NCO stretching frequency for $H_2(OCN)B_3N_3H_3$ is uncertain, just as for C_6H_5NCO[10,11] and $(OCN)_3B_3N_3H_3$.[14] The two possible frequencies are at 1085 and 1524 cm^{-1} for $H_2(OCN)B_3N_3H_3$. The corresponding frequency is either 1108[10] or 1448[11] cm^{-1} in C_6H_5NCO and 1042 or 1545 cm^{-1} in $(OCN)_3B_3N_3H_3$.

The ^1H and ^{11}B nmr data for the compounds are given in Table III. The ^1H spectra of all five compounds were typical of monosubstituted borazines,[1,2] an NH triplet, a BH quartet, and a CH singlet. In all cases the NH protons which are ortho and para to the substituent are magnetically equivalent. The ^{11}B spectra of $H_2CH_3CO_2B_3N_3H_3$ and $H_2CH_3SO_3B_3N_3H_3$ were also typical of monosubstituted borazines,[1,2] unsymmetrical doublets. The more intense line[2] is believed to be due to the superposition of a BX singlet and one line of the BH doublet. The less intense line is believed to be due to the other line of the BH doublet. The ^{11}B spectra of $H_2(OCN)B_3N_3H_3$ and $H_2(SCN)B_3N_3H_3$ were unique, as they exhibited three lines, two of which were more poorly defined than the other. Two of these lines should be due to the BH doublet and the third line to the BX singlet. In both cases we have assumed that the line due to the boron bound to the substituent was the line at the highest field. In the case of $H_2(NC)B_3N_3H_3$, the ^{11}B nmr spectrum might be three lines, or possibly two if one is very broad. The spectrum is certainly unclear.

Earlier proton nmr data for a series of B-monosubstituted borazines[1] were consistent with the hypothesis that the π electrons of borazine are delocalized, at least partially, and substituents interact with this π system by means of a resonance effect to alter the π-electron density at the ortho and para positions. Furthermore, the boron-11 nmr data were observed to be a measure of the extent of the π interaction between the substituent and the ring, and were related to the change in π-electron density at the para position and, consequently, the relative chemical shifts of the para NH proton. This correlation[1] between the relative boron-11 chemical shift for the boron bound to the substituent and the relative para NH proton chemical shift is given in Figure 2. The data for the substituents OCN–, SCN–, CH_3CO_2–, and CH_3SO_3– have been added to the original graph.[1] The substituents OCN– and SCN– support the correlation, whereas substituents CH_3CO_2– and CH_3SO_3– apparently do not. The relative chemical shifts for the NH protons of $H_2CH_3CO_2B_3N_3H_3$ and $H_2CH_3SO_3B_3N_3H_3$ should be 0.48 and 0.19 ppm farther upfield, respectively, in order to correlate with the ^{11}B–X data. It should also be noted that the spectra for $H_2CH_3SO_3B_3N_3H_3$ were run as solutions in CH_3CN. This solvent could also produce a paramagnetic shift.

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The compound, $H_2CH_3SO_3B_3N_3H_3$, is insoluble in nonpolar solvents.

The ^1H and ^{11}B data for $H_2(NC)B_3N_3H_3$ are confusing. If the cyanide group is acting normally as an electron-attracting substituent, the ortho and para NH protons should be shifted downfield relative to $H_3B_3N_3H_3$, and they are. The boron atom bound to the substituent should probably also be shifted downfield. There is one line in the ^{11}B spectrum at −35.9 ppm, which is downfield from $H_3B_3N_3H_3$ (−29.2 ppm). The relative chemical shift of this line does, however, correlate reasonably well with the relative NH proton shift in CH_3CN solution (see Figure 2). However, this leaves the lines at −26.9 and −22.9 ppm for the B–H doublet. This gives a coupling constant of 63 Hz from the ^{11}B spectrum, whereas the ^1H spectrum suggests 138 Hz, a confusing situation. The two lines at −35.9 and −26.9 ppm give a coupling constant of 143 Hz, but this leaves the line at −22.9 ppm for the boron bound to the cyanide. The line at −22.9 ppm is upfield from $H_3B_3N_3H_3$ (−29.2 ppm), which is apparently inconsistent with the properties of the cyanide group, an electron-attracting substituent.

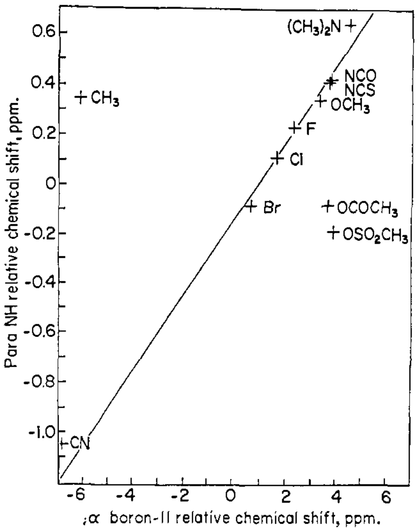

Figure 2.

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Stereochemically Nonrigid Organometallic Molecules. XXIX. Cycloheptatrienediiron Hexacarbonyl[1,2]

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Abstract: The crystal and molecular structures and other properties of cycloheptatrienediiron hexacarbonyl have been investigated. The molecule in the crystal has approximate mirror symmetry with the iron atoms lying on opposite sides of the mirror plane; the nmr spectrum strongly suggests, though it cannot prove, that the same structure persists in solution. A systematic name which refers to this structure explicity is (1,2,3-*trihapto*-4,5,6-*trihapto*cycloheptatri-1,3,5-ene)diiron(Fe-Fe) hexacarbonyl. A simple formalism which, however, should not be taken as a precise and literal description of the electronic structure, considers the π-electron system of the C_7H_8 ring to be divided into two adjacent allyl groups, each of which forms a π complex with one of the iron atoms. The C–C bonds in the allyl groups have an average length of 1.401 ± 0.008 Å and the Fe–C(allyl) distances have average values of 2.15 ± 0.03 Å to the outer atoms and 2.042 ± 0.003 Å to the center atoms. The Fe–Fe distance is 2.87 Å. This structure contrasts strikingly with the structures of $C_8H_8Ru_2(CO)_6$ and $C_8H_{10}Fe_2(CO)_6$, in which the M–M axes are turned nearly 90° toward the direction of a possible mirror plane analogous to the one found in $C_7H_8Fe_2(CO)_6$, but are nevertheless skew and quite unsymmetrically bonded. The significance of this structural difference on the interpretation of the fluxional behavior of the C_8H_8 and C_8H_{10} compounds is considered. $C_7H_8Fe_2(CO)_6$ crystallizes in the space group *Pbca* with unit cell dimensions $a = 24.269 \pm 0.006$, $b = 11.431 \pm 0.003$, and $c = 9.732 \pm 0.003$ Å, $Z = 8$; $D(\text{calcd}) = 1.83$ g cm^{-3}; $D(\text{obsd}) = 1.85 \pm 0.01$ g cm^{-3}. The structure was solved and refined using 3111 reflections collected on a counter diffractometer with Mo Kα radiation. Corrections were made for absorption, secondary extinction, and anomalous effects of the Zr filter on background estimates of low-angle reflections. All atoms other than hydrogen were refined anisotropically; hydrogen atoms all refined well isotropically. Final conventional and weighted residuals were 6.1 and 4.2%, respectively.

According to simple but generally reliable rules concerning valence in olefin–metal carbonyl molecules, each of the metal atoms in groups such as $(OC)_3Fe\text{–}Fe(CO)_3$ and $(OC)_3Ru\text{–}Ru(CO)_3$ would be considered to lack three electrons of a closed-shell (noble

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[1] Previous paper in this series: J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, **93**, 3592 (1971).

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[3] NSF Predoctoral Fellow, 1966–1970.