Coordination Chemistry Reviews, 22 (1977) 185—194

METAL DERIVATIVES OF THE BORAZINES

J.J. LAGOWSKI

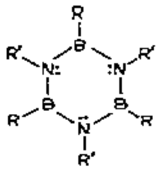
Department of Chemistry, The University of Texas, Austin, Texas 78712 (U.S.A.)

(Received 15 November 1976)

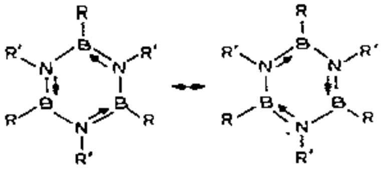
CONTENTS

A. INTRODUCTION

Borazines, which have the general formula $(RBNR')_3$, can be formulated a either cyclic triamines (I) or as cyclic π-systems (II) similar to that found in



(I)



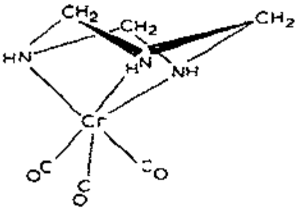
(II)

benzene. In formulation II, there are two possibilities for the arrangement of the internal dative B—N bonds. The results of a variety of physical—chemical experiments [1] suggest that the basic borazine structure is essentially planar moreover, the B—N bond distance measured in, for example, $H_3B_3N_3(CH_3)_3$ (1.42 Å) [2] is shorter than that expected for a B—N single bond (1.59 Å) [3] as would be expected from II. However, chemical evidence indicates that the nitrogen sites in the borazine ring retain some basic character. Thus, N-trimethylborazine reacts with hydrogen chloride to form an adduct, $H_3B_3N_3(CH_3)_3 \cdot 3\ HCl$, the empirical formula of which suggests that the ring nitroge atoms have been protonated [4,5].

Two fundamental types of metal derivatives would be expected of borazin formulated as a π-system (II) — complexes incorporating the ring, as in the case of arenetricarbonyl chromium(0) compounds [6—8] or the bisarenechromium(0) derivatives [9] and metal-substituted σ-derivatives.

B. RING COMPLEXES

Ring complexes would be expected from either of the extreme formulations of the borazine ring (I or II) on the basis of chemical analogy. Thus, arene-type behavior of the borazine nucleus would be expected to yield compounds analogous to arene metal carbonyls or the bisarene metal compounds. However, the aminoid character of the ring nitrogen atoms finds its analogy in the complex (III) formed between symmetrical hexahydrotriazine and the $Cr(CO_3)_3$ moiety in which the former acts as a tridentate σ-bonded ligand. Th general configuration of the triamine ligand in III might be expected to be similar to that of an N-bonded borazine.



(III)

Although several half-sandwich compounds of the type $(R_3B_3N_3R'_3)ML_3$ have been prepared, there are no substantiated reports in the open literature concerning the preparation of the corresponding full-sandwich compounds, $(R_3B_3N_3R'_3)_2M$. Attempts to prepare half-sandwich borazine-containing compounds by the interaction of metal carbonyls with a borazine in an appropriate refluxing solvent — viz., the process by which arene metal carbonyls can be prepared, have not been successful [10]. However, reaction (1) can be effected photolytically [11,18].

$$Cr(CO)_6 + R_3B_3N_3R'_3 \rightarrow (R_3B_3N_3R'_3)Cr(CO)_3 + 3\ CO \tag{1}$$

If the $Cr(CO)_3$ moiety also carries easily displaced ligands, e.g. $Cr(CO)_3L_3$ ($L{=}CH_3CN$, C_6H_5CN, $x\ C_6H_4CN$) the reaction with borazines progresses smoothly [12,13,15,17].

$$(CH_3CN)_3Cr(CO)_3 + R_3B_3N_3R'_3 \rightarrow R_3B_3N_3R'_3Cr(CO)_3 + 3\ CH_3CN \tag{2}$$

The displacement of dioxane from a binuclear complex has also been reportec [14].

$$(CO)_3Cr(\text{Dioxane})_3Cr(CO)_3 + 2\ R_3B_3N_3R'_3 \rightarrow 2\ R_3B_3N_3R'_3Cr(CO)_3 + 3\ \text{Dioxane} \tag{3}$$

In general only hexaalkyl-substituted borazines have been attached to a metal tricarbonyl moiety; the compounds formed and some important characteristics appear in Table 1.

The borazine nucleus appears to be rather easily displaced from the half-

TABLE 1

Tricarboxyl complexes of the borazines: $(CO)_3M(R_3B_3N_3R'_3)$

Metal	Borazine	MP [a]	Other properties [b]	Ref.
1. Cr	$(CH_3)_3B_3N_3(CH_3)_3$	141°(d)	IR, UV, ^{1}H NMR, ^{11}B NMR, ^{14}N NMR, ms	12, 13, 15
2. Cr	$(C_2H_5)_3B_3N_3(CH_3)_3$	150°(d)	UV, IR, ^{1}H NMR, ^{11}B NMR, ^{14}N NMR, ms	11, 12, 15
3. Cr	$(C_6H_5)(CH_3)_2B_3N_3(CH_3)_3$	110°(d)	UV, IR, ^{1}H NMR, ms	15
	$(C_2H_5)(CH_3)_2B_3N_3(CH_3)_3$	151°(d)	UV, ^{1}H NMR, ms, IR	15
4. Cr	$(CH_3)_3B_3N_3(C_2H_5)_3$	—	UV, IR, ^{1}H NMR, ms	11, 15
5. Cr	$(n\text{-}Pr)_3B_3N_3(CH_3)_3$	125°(d)	UV, IR, ^{1}H NMR, ms	17
6. Cr	$(CH_3)_3B_3N_3(n\text{-}Pr)_3$	128°(d)	UV, IR, ^{1}H NMR	17
7. Cr	$(i\text{-}Pr)_3B_3N_3(CH_3)_3$	147°(d)	UV, IR, ^{1}H NMR, ms	17
8. Cr	$(CH_3)_3B_3N_3(i\text{-}Pr)_3$	178°(d)	UV, IR, ^{1}H NMR, ms	17
9. Cr	$(C_2H_5)_3B_3N_3(C_2H_5)_3$	112°(d)	UV, IR, ^{1}H NMR, ms	17, 18
10. Mo	$(CH_3)_3B_3N_3(C_2H_5)_3$	110—120°(d)	IR	16
11. Mo	$(C_2H_5)_3B_3N_3(CH_3)_3$	—	IR	16

[a] d = Decomposition.

[b] NMR = nuclear magnetic resonance spectrum of the nucleus indicated; UV = UV visible spectrum; IR = infrared spectrum; ms = mass spectrum.

sandwich compounds. Thus $(C_2H_5)_3B_3N_3(C_2H_5)_3Cr(CO)_3$ can be readily obtained from $(C_2H_5)_3B_3N_3(CH_3)_3Cr(CO)_3$ by ring exchange with the appropriate borazine [17]. Tertiary phosphines and phosphites displace hexamethylborazine from $(CH_3)_3B_3N_3(CH_3)_3Cr(CO)_3$ under mild conditions [19]. Aryl- and alkyl-phosphites, $P(OR)_3$, yield the expected tricarbonyl derivatives

$$(CH_3)_3B_3N_3(CH_3)_3Cr(CO)_3 + 3\ L \rightarrow (CH_3)_3B_3N_3(CH_3)_3 + fac\text{-}(CO)_3CrL_3 \qquad (4)$$

$L = P(OR)_3$

whereas trialkyl- or arylphosphines produce tetracarbonyl-containing moieties.

$$3\ (CH_3)_3B_3N_3(CH_3)_3Cr(CO)_3 + 8\ L \rightarrow 3\ (CH_3)_3B_3N_3(CH_3)_3 + 4\ trans\text{-}Cr(CO)_4L_2 + CO \qquad (5)$$

$L = PR_3$

The borazine nucleus is also displaced from the half-sandwich compound by basic metal-containing ions (eqn. 6) [20]

$$(CH_3)_3B_3N_3(CH_3)_3Cr(CO)_3 + 3\ L \rightarrow (CO)_3CrL_3^{3-} + (CH_3)_3B_3N_3(CH_3)_3 \qquad (6)$$

$L = SnCl_3^-, GeCl_3^-$

Spectroscopic data suggest that the carbonyl product of reaction (6) has a meridional configuration.

A kinetic study of reaction (4) indicates a second order reaction which suggests that the rate determining step involves attack of a phosphite molecule on the half-sandwich compound. The data do not permit a distinction between attack on the complexed borazine ring or attack on the metal.

A detailed spectroscopic analysis [15] has produced a description of the structure of and electronic effects in several half-sandwich compounds. The IR spectra of these compounds [15,17] indicate the σ-donor and π-acceptor character of the borazine ring compared to that of arenes as well as the B—N bond order. Half-sandwich compounds containing borazine nuclei exhibit two carbonyl stretching frequencies, one (A mode) in the range of 1936—1945 cm^{-1} and another (E mode) in the range of 1830—1848 cm^{-1} [15,17], which are similar to the frequencies observed for the correspondingly substituted arenechromiumtricarbonyls (e.g. for $(CH_3)_6C_6Cr(CO)_3$, the A mode is at 1945 cm^{-1} and the E mode at 1848 cm^{-1}) suggesting the total electronic effect of the two ring systems is the same [21], but this conclusion does not in itself argue for a similar conformation of the ring as was originally suggested [13]. The most marked change in the spectrum of a complexed borazine ring relative to that of the free ligand is the shift to lower frequency of the B—N stretching vibration. The B—N frequency in the free ligands, which occurs at about 1400 cm^{-1}, shifts by 30—50 cm^{-1} upon complexation; the shift is not nearly as marked as that observed for the cyclic borazanes, $R_3B_3N_3R'_3 \cdot 3\ HX$, where the B—N vibration appears near 1260 cm^{-1} [4]. A shift of the B—N vibration to lower energy is interpreted as a reduction in the B—N band order which is consistent with a localization of the nitrogen electron pair for the formation of a $N \rightarrow Cr$ bond. In effect the nitrogen atom has become 4-coordinate, which should lead to a puckering of the borazine ring. In N-methyl borazines, the $N—CH_3$ rocking mode which occurs near 1106 cm^{-1} [15,17] is shifted to higher frequencies upon complexation; this shift could be the result of two effects. If the borazine nucleus is complexed through a $N \rightarrow Cr$ interaction, a change in the electronic environment would be expected; the nitrogen hybridization would change ($sp^2 \rightarrow sp^3$) and it would acquire a formal positive charge. In addition, a change in the steric environment would be expected when hexaalkyl-substituted borazines were complexed. The sensitivity of the $N—CH_3$ rocking mode to changes in the adjacent boron environments has been well documented [22].

A detailed study [15] of solvent induced chemical shifts (^1H) of $B—CH_3$ and $N—CH_3$ substituents for complexed and free borazines indicates that the complexed borazine ring is puckered with the $B—CH_3$ group elevated above the plane of the nitrogen atoms; moreover these data are consistent with a fixed (non-rotating) complexed ring system oriented so that the $B—CH_3$ groups are situated above the carbonyl groups in the $Cr(CO)_3$ moiety. A study of the methyl—methylene splitting in a series of ethyl-substituted borazanes upon complexation supports the conclusion from the IR arguments that the nitro-

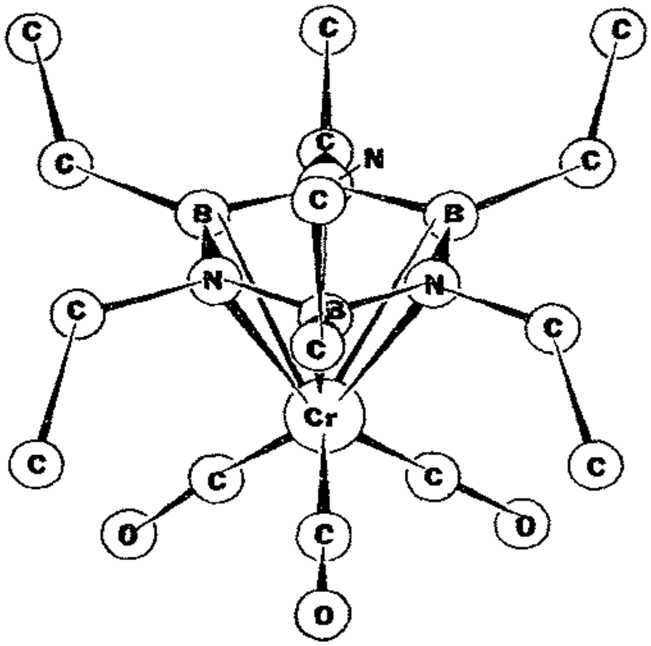


Fig. 1. The structure of hexaethylborazine chromium(0) (after ref. 23c).

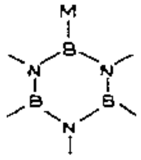
gen atom in complexed borazines has acquired a positive charge; in addition the ^{1}H NMR data indicate that the boron atom undergoes relatively little electronic change upon complexation. The electronic spectrum of the borazine chromium tricarbonyl compound also supports the suggestion that the borazine ring is a significantly poorer π-acceptor than is an arene ring even though both ligands have similar donor characteristics [15].

X-ray diffraction data on hexaethylborazine chromium tricarbonyl [23] indicates a structure similar to that deduced from the spectroscopic investigation described previously. The borazine ring is non-planar, and is centrosymmetrically complexed through the nitrogen atoms; the nitrogen atoms are located *trans* to the carbonyl groups (Fig. 1).

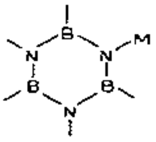
The X-ray structural data appear to be consistent with a σ-bonded interaction through the borazine nitrogen atoms. The geometry about the nitrogen sites is essentially the same as that found in the borazane $[BH_3N(CH_3)_3]_3$ which was shown to exist in a chair configuration [24]; the BNB bond angle in this borazane is 113°, whereas the corresponding angle in the borazine—metal complex has an average value of 125°. A detailed analysis of the arrangement of atoms around a nitrogen site shows that the carbon substituent is decidedly out of the plane formed by the BNB ring atoms; in two of the three positions, the carbon substituent is above the plane of these ring atoms. It can be concluded that the nitrogen atoms approach a tetrahedral configuration. The expected Cr—N single bond distance in borazine complexes is 2.18 Å, the sum of the bond radii for Cr(0) (1.48 Å [25]) and tetrahedral nitrogen (0.70 Å [26]), and should be compared with the mean observed value of 2.28 Å [23]. The carbon substituent on the boron atom is virtually coplanar with the ring atoms NBN, suggesting sp^2 hybridization of that atom. A comparison of the expected Cr—B single bond distance with the observed distance can be made using the usual bond radii arguments. First the single bond distance expected for an sp^2 boron atom can be estimated as the difference between the B—C distance in $B(CH_3)_3$ (1.56 Å [27]) and the single bond radius of sp^3 carbon (0.77 Å [26]): $B(sp^2) = 0.73$ Å). This value, combined with the single bond radius for Cr(0) (1.48 Å [25]) gives the expected value (2.21 Å) for the single bonded distance between these atoms, which is shorter than that observed experimentally (2.31 Å [23]) and suggests that the observed distance is not a bonding interaction. If the borazine ring is σ-bonded at the nitrogen sites, a decrease in the B—N bond order relative to uncomplexed borazine might be expected. Only a slight increase is observed from 1.42 Å as reported in N-trimethylborazine [2] to 1.46 Å in the complexed borazine [24]. A much greater increase in the B—N distance is expected if the borazane $H_6B_3N_3(CH_3)_6$ is taken as a reference for a single bonded B—N distance where the corresponding value is 1.59 Å [24].

C. σ-BONDED METAL SUBSTITUENTS

Theoretically, metal atoms could be substituted on two different sites of the borazine nucleus to form either B-(IV) or N-(V) substituted products.



(IV)



(V)

These two compounds, technically, would be isomers, a situation which could not be obtained in arene chemistry. It might be expected that metal substituents with filled *d* orbitals would form the stronger B-substituted derivatives, whereas metal substituents with empty *d* orbitals would form the more stable N-substituted products. In both instances enhanced stability would arise from the formation of a π-component to the metal—borazine bond. The π-component in the first instances involves M → B donation whereas N → M donation is involved in the second case.

(i) N-substituted derivatives

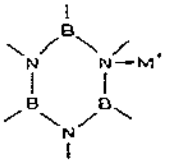
Historically, it has proven to be generally difficult to obtain unsymmetrically N-substituted borazine derivatives. N-lithioborazines are the only N-substituted derivatives available [28] and they provide the basis for the preparation of unsymmetrically N-substituted borazine. N-lithio-B-trimethylborazine, as well as a small amount of N-dilithio-B-trimethylborazine, is prepared in high yield when B-trimethylborazine is treated with methyl lithium (eqn. 7). The

$$(CH_3)_3B_3N_3H_3 + LiCH_3 \rightarrow (CH_3)_3B_3N_3H_2Li + CH_4 \qquad (7)$$

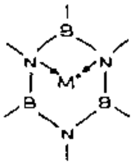
N-lithio derivatives were not characterized directly, but by the products they formed. Attempts to use N-lithioborazines to prepare other metal—borazine derivatives (e.g. eqn. 8) were unsuccessful [29].

$$(CH_3)_3B_3N_3H_2Li + HgCl_2 \not\rightarrow [(CH_3)_3B_3N_3H_2]HgCl + LiCl \qquad (8)$$

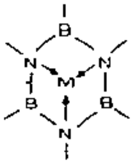
The possibility exists that borazines could form N-bonded complexes with metal ions in which the borazine nucleus may act as a mono-(VI) or possibly a bidentate (VII) ligand. Nitrogen atoms in such complexes would be typically 4-coordinate. If borazines acted as tridentate ligands (VIII), we should expect the borazine nucleus to achieve a configuration similar to that described for hexaethylborazine tricarbonyl chromium(0) [23].



(VI)



(VII)



(VIII)

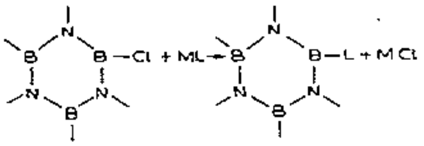
Although such complexes have not been isolated yet, there are several indications in the literature that are suggestive. The reactions of silver salts (AgX; X = CN, NO_2, NO_3 [30], ClO_4 [31]) with B-trichloroborazines produce new B-substituted derivatives (eqn. 9) which are difficult to isolate free of silver [30],

$$R_3N_3B_3Cl_3 + AgX \rightarrow R_3N_3B_3X_3 + 3\ AgCl \qquad (9)$$

suggesting that perhaps silver ions may be N-complexed.

(ii) B-substituted derivatives

The fact that borazine rings undergo substitution reactions primarily at the boron positions [1] and that stable compounds containing metal moieties bound to trivalent borane units [32] strongly suggests that stable B-substituted metal derivatives of borazines might be formed. The most obvious route to such compounds is the reaction of a B—Cl containing borazine with a metal-containing anion (e.g. eqn. (10), L = $Mn(CO)_5^-$)

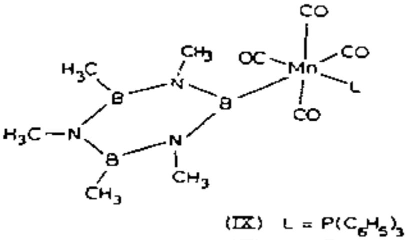


(10)

This reaction was successful for the preparation of B-silyl ($Si(C_6H_5)_3$ [33])

and B-germyl (GeR_3; R = H, C_6H_5 [34]) borazine derivatives. The IR spectrum in the B—N region of a series of B-trimetal substituted N-trimethylborazines [$(R_3M)_3B_3N_3(CH_3)_3$, M = Ge, Si, R = H, C_6H_5] indicates that $d_\pi - p_\pi$ interaction between the substituent and the boron atom increases in the order $(C_6H_5)_3Si > (C_6H_5)_3Ge > H_3Ge$ and that all these substituents are better π-donors than the corresponding B—H, B—CH_3, and B—Cl compounds [34]. Similar results are obtained for the corresponding B-disubstituted, and B-monosubstituted derivatives where they are known [34].

Attempts to synthesize borazine nuclei carrying metal carbonyl moieties σ-bonded to the boron sites have been only marginally successful [35]. Reactions of the type shown in eqn. (4) using the sodium or the bis(triphenylphosphine) iminium salts of metal carbonyl anions yielded 2-pentamethylborazinyltetracarbonyl(triphenylphosphine)manganese(0) (IX) and 2-pentamethylborazinylpentacarbonyl manganese(0) (X); the carbonyl region in the IR spectrum of the former compound (IX) indicates that the two dissimilar



(IX) L = $P(C_6H_5)_3$
(X) L = CO

substituents attached to the manganese atom are in a *cis*-arrangement. These compounds are relatively unstable thermally, yielding binuclear metal derivatives (e.g. Mn_2CO_{10}) and polymeric borazines. Both ^1H NMR and ^{11}B NMR spectra indicate that the $Mn(CO)_4P(C_6H_5)_3$ substituent releases more π-electron density to the borazine ring than does $Mn(CO)_5$. These results are in agreement with the observation that $P(C_6H_5)_3$ is a poorer π-acid and a better σ-donor than CO; replacement of a carbonyl group with $P(C_6H_5)_3$ will result in a greater electron density on the metal atom. Thus, the $Mn(CO)_4P(C_6H_5)_3$ should be able to release electrons to the boron atom more readily than a $Mn(CO)_5$ substituent. Similar results and interpretations have been obtained and offered for the B—Mn interaction in bis(dimethylamino)boronmanganesecarbonyls, $(Me_2N)_2BMn(CO)_4L$, L = CO, $P(C_6H_5)_3$ [36].

Borazine rings substituted by iron carbonyl moieties are less stable than those carrying manganese carbonyl groups but more stable than the corresponding cobalt compounds [35]. The iron-containing compounds $(CH_3)_3N_3B_3H_2Fe(CO)_4$ and $(CH_3)_3N_3B_3Cl_2Fe(CO)_2$-$\pi C_5H_5$ were shown to exist in solution using spectroscopic arguments. The compounds were prepared from the reductive reaction of N-trimethylborazine with mercury salts (eqn. 11) which had been

$$(CH_3)_3N_3B_3H_3 + HgX_2 \rightarrow Hg + H_2 + (CH_3)_3N_3B_3H_2X \qquad (11)$$

used successfully [37] for the preparation of unsymmetrical B-substituted borazines; the mercury salts of the corresponding metal carbonylate anions were employed. The iron compounds were stable in solution but there was no indication that the corresponding cobalt derivatives were formed.

ACKNOWLEDGEMENT

The generous financial support of the Robert A. Welch Foundation for the work done in these laboratories on the metal derivatives of the borazines is gratefully acknowledged.

REFERENCES

1 E.K. Mellon and J.J. Lagowski, Adv. Inorg. Chem. Radiochem., 5 (1963) 259 and refs. therein.
2 K.P. Coffen and S.H. Bauer, J. Phys. Chem., 59 (1955) 193.
3 L.M. Trefonas, F.S. Mathews and W.N. Lipscomb, Acta Crystallogr., 14 (1961) 223.
4 G.A. Anderson and J.J. Lagowski, Inorg. Chem., 14 (1975) 1845.
5 A.W. Laubengayer, O.T. Beachley, Jr. and R.F. Porter, Inorg. Chem., 4 (1965) 578.
6 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551.
7 D.A. Brown and J.R. Raju, J. Chem. Soc. A, (1966) 40.
8 W. Strohmeier, Chem. Ber., 94 (1961) 3337.
9 V. Graves and J.J. Lagowski, Inorg. Chem., 15 (1976) 577.
10 E.M. Fedneva and I.V. Krykova, Dokl. Akad. Nauk. S.S.S.R., 170 (1966) 861.
11 K. Deckelmann and H. Werner, Helv. Chim. Acta, 53 (1970) 139.
12 H. Werner, R. Prinz and E. Deckelmann, Chem. Ber., 102 (1969) 95.
13 R. Prinz and H. Werner, Angew. Chem., 79 (1967) 63; Angew. Chem., Int. Ed. Engl., 6 (1967) 91.
14 H. Werner and E. Deckelmann, Angew. Chem., 80 (1968) 564; Angew. Chem., Int. Ed. Engl., 7 (1968) 544.
15 J.J. Lagowski, Proc. 13th Int. Conf. Coord. Chem., 2 (1970) 380;
J.L. Adcock and J.J. Lagowski, Inorg. Chem., 12 (1973) 2533.
16 K. Deckelmann and H. Werner, Helv. Chim. Acta, 54 (1971) 2189.
17 M. Scotti and H. Werner, Helv. Chim. Acta, 57 (1974) 1234.
18 M. Scotti and H. Werner, J. Organometal. Chem., 81 (1974) C17.
19 E. Deckelmann and H. Werner, Helv. Chim. Acta, 52 (1969) 892.
20 B. Herber, M. Scotti and H. Werner, Helv. Chim. Acta, 58 (1975) 1225.
21 G.R. Dodson, I.W. Stolz and R.K. Sheline, Adv. Inorg. Chem. Radiochem., 8 (1966) 1.
22 L.A. Melcher, J.L. Adcock and J.J. Lagowski, Inorg. Chem., 11 (1972) 1247.
23 (a) G. Huttner and B. Krug, Angew. Chem., 83 (1971) 541.
(b) G. Huttner and B. Krug, Angew. Chem. Int. Ed. Engl., 10 (1971) 512.
(c) G. Huttner and B. Krug, Chem. Ber., 105 (1972) 3437.
24 L.M. Trefonas, F.S. Mathews and W.N. Lipscomb, Acta Crystallogr., 14 (1961) 273.
25 F.A. Cotton and D.C. Richardson, Inorg. Chem., 5 (1966) 1851.
26 L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 246.
27 H.A. Levy and L.O. Brockway, J. Am. Chem. Soc., 59 (1937) 2085.
28 (a) R.I. Wagner and J.L. Bradford, Inorg. Chem., 1 (1962) 93.
(b) R.I. Wagner and L.L. Bradford, Inorg. Chem., 1 (1962) 99.
29 R.C. Compton, Ph.D. Dissertation, The University of Texas, Austin, 1965.
30 G.L. Brennan, G.H. Dahl and R. Schaeffer, J. Am. Chem. Soc., 82 (1960) 6248.

31 M. Maclary, M.A. Thesis, The University of Texas, 1962.
32 (a) G. Schmid and H. Nöth, Z. Naturforsch., Teil B, 20 (1965) 1008.
(b) H. Nöth and G. Schmid, Allg. Prakt. Chem., 17b (1966) 610, 615.
33 A.H. Cowley, H.H. Sisler and G.E. Ryschkewitsch, J. Am. Chem. Soc., 82 (1960) 501.
34 E. Amberger and W. Stoeger, J. Organometal. Chem., 17 (1969) 287.
35 (a) L.A. Melcher, Ph.D. Dissertation, The University of Texas, Austin, 1971.
(b) D.T. Haworth and E.S. Matushek, Inorg. Nucl. Chem. Lett., (1971) 261.
36 (a) H. Nöth and G. Schmid, Angew. Chem., 75 (1963) 681.
(b) H. Nöth and G. Schmid, Angew. Chem. Int. Ed. Engl., 2 (1963) 623.
(c) H. Nöth and G. Schmid, J. Organometal. Chem., 5 (1966) 109.
(d) H. Nöth and G. Schmid, Z. Anorg. Allg. Chem., 345 (1966) 69.
37 G.A. Anderson and J.J. Lagowski, Inorg. Chem., 10 (1971) 1910.