Reactions of Decaborane Derivatives with Bis(diphosphine) Complexes of Iridium, and the Crystal Structure of *cis*-Bis[1,2-bis(diphenylphosphino)ethane]dihydroiridium(III) Tetradecahydrononaborate(1−), [Ir(dppe)$_2$H$_2$][B$_9$H$_{14}$]

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The four- and five-co-ordinate iridium(I) cations $[Ir(dppe)_2]^+$ and $[Ir(CO)(dppe)_2]^+$ react with $B_{10}H_{14}$, $B_{10}H_{13}$(Cl-6), and $[B_{10}H_{13}]^-$ to give a number of ionic compounds. The reaction between $[Ir(dppe)_2]Cl$ and $B_{10}H_{13}X$ (X = H or 6-Cl) yields $[Ir^{III}Cl(dppe)_2H][B_{10}H_{12}X]$. The complex $[Ir(CO)(dppe)_2]Cl$ reacts with $[B_{10}H_{13}]^-$, in methanol solution, to give $[Ir^{I}(CO)(dppe)_2][B_{10}H_{13}]$ and, as a product of methanolic degradation, $[Ir^{III}(dppe)_2H_2][B_9H_{14}]$. The latter crystallizes as pale yellow needles in the orthorhombic space group *Ccca* with a = 15.456(4), b = 23.936(4), c = 28.529(7) Å, and Z = 8. The $[B_9H_{14}]^-$ anion is grossly disordered, but it is possible to determine the structure of the cation.

THE bis(diphosphine) complexes $[Ir(dppe)_2]X$ and $[Ir(CO)(dppe)_2]X$ [dppe = 1,2-bis(diphenylphosphino)ethane] have been known for many years, and their reactions extensively studied.[1-6] The four-co-ordinate complex $[Ir(dppe)_2]X$ is of particular interest because its behaviour resembles that of the well known complex $[Ir(CO)Cl(PPh_3)_2]$.[7,8] For example, it reacts with dihydrogen and hydrogen halides (HY) to yield the oxidative-addition products $[Ir(dppe)_2H_2]X$ and $[Ir(dppe)_2H(Y)]X$.[3] This ability of d^8 iridium(I) species to undergo oxidative addition prompted our present study of the reactions of $[Ir(dppe)_2]Cl$ and $[Ir(CO)(dppe)_2]Cl$ with derivatives of decaborane.

RESULTS AND DISCUSSION

The four-co-ordinate complex $[Ir(dppe)_2]Cl$ was found to react with $B_{10}H_{13}X$ (X = H or 6-Cl) to give the oxidative-addition products $[Ir^{III}Cl(dppe)_2H][B_{10}H_{12}X]$. The five-co-ordinate complex $[Ir(CO)(dppe)_2]Cl$ reacted with $[NEt_3H][B_{10}H_{13}]$, in methanol solution, giving both $[Ir^{I}(CO)(dppe)_2][B_{10}H_{13}]$ and $[Ir^{III}(dppe)_2H_2][B_9H_{14}]$; the latter was obtained, in small yield, as a result of carrying out the reaction in methanol:

$$[B_{10}H_{13}]^- + 3MeOH \longrightarrow [B_9H_{14}]^- + 2\{H\} + B(OMe)_3$$

The i.r. spectra of $[Ir^{III}Cl(dppe)_2H][B_{10}H_{12}X]$ differed only in the B–H terminal stretching absorptions. For X = H, the B–H terminal absorption occurred at 2 500 cm^{-1}, whereas for X = Cl it occurred at 2 520 cm^{-1}. In both cases the B–H–B absorption appeared as a very weak peak at 2 000 cm^{-1}, and the Ir–H absorption as a weak band at 2 200 cm^{-1}. The i.r. spectrum of $[Ir^{I}(CO)(dppe)_2][B_{10}H_{13}]$ showed the CO stretching absorption as an intense peak at 1 920 cm^{-1}, and the B–H terminal stretching absorption appeared as a strong band at 2 490 cm^{-1}. The main features of the i.r. spectrum of $[Ir^{III}(dppe)_2H_2][B_9H_{14}]$ were strong bands at 2 500 and 2 075 cm^{-1}, due to B–H terminal stretching and Ir–H stretching respectively.

The 36.43-MHz ^{31}P-$\{^1H\}$ n.m.r. spectrum of the $[IrCl(dppe)_2H]^+$ cation, for both the $[B_{10}H_{13}]^-$ and $[B_{10}H_{12}(Cl\text{-}6)]^-$ anions, consisted of a singlet at $\delta = -120.9$ p.p.m. The spectrum obtained for $[Ir^{I}(CO)(dppe)_2][B_{10}H_{13}]$ was a singlet at $\delta = -116$ p.p.m., and that obtained for $[Ir^{III}(dppe)_2H_2][B_9H_{14}]$ was an A_2X_2 spectrum, consisting of two triplets J(P–Ir–P) = 8.3 Hz at $\delta = -109.2$ and -120.8 p.p.m., of equal areas. These spectra all agree with those previously reported for these cations.[5,6] The spectrum obtained for $[Ir(dppe)_2H_2]^+$ clearly indicates *cis* geometry about the iridium atom; however, recently reported work on the $[IrCl(dppe)_2H]^+$ cation suggests that the ^{31}P-$\{^1H\}$ n.m.r. spectrum may comprise a singlet due to stereochemical non-rigidity, rather than as a consequence of *trans* geometry.[5,6]

The 28.87-MHz ^{11}B n.m.r. spectra of both $[Ir^{III}Cl(dppe)_2H][B_{10}H_{13}]$ and $[Ir^{I}(CO)(dppe)_2][B_{10}H_{13}]$ are very similar, and are consistent with the presence of $[B_{10}H_{13}]^-$ in these compounds.[9,10] The $[IrCl(dppe)_2H]^+$ salt consists of three doublets, relative areas 2 : 6 : 2, and $\delta = +6.4$, -4.8, and -35.3 p.p.m. respectively; the peaks of the $[Ir(CO)(dppe)_2]^+$ salt appear at $\delta = +7.1$, -4.7, and -35.1 p.p.m. On proton decoupling, these doublets collapse to singlets.

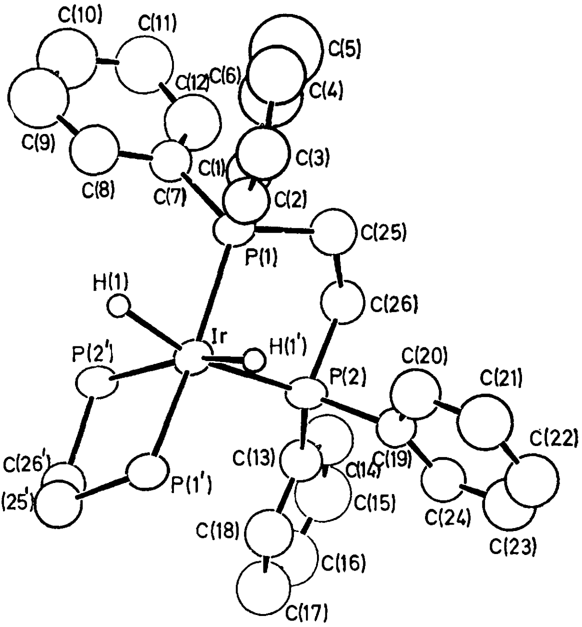
The ^{11}B n.m.r. spectrum of $[Ir^{III}Cl(dppe)_2H][B_{10}H_{12}Cl]$ consisted of a broad singlet at $\delta = +27.8$ p.p.m., a very broad singlet at -3.9 p.p.m., and two broad doublets at -26.9 and -43.7 p.p.m., of relative area *ca.* 1 : 7 : 1 : 1. In the ^{11}B-$\{^1H\}$ n.m.r. spectrum, the doublets were collapsed to singlets, and the most intense peak narrowed significantly. These spectra can be explained in terms of a $[B_{10}H_{12}(Cl\text{-}6)]^-$ anion, the broad peak at $\delta = +27.8$ p.p.m. arising from the boron atom joined to the chlorine atom at position 6. The remaining boron-atom resonances are encompassed in the broad large peak at $\delta = -3.9$ p.p.m.

The ^{11}B n.m.r. spectrum of $[Ir^{III}(dppe)_2H_2][B_9H_{14}]$ comprised three doublets at $\delta = -7.7$, -20.8, and -22.9 p.p.m., all of equal area. On ^1H-decoupling, these collapsed to singlets. These are very similar to the spectra previously reported for $[B_9H_{14}]^-$, and their structural implications are now well established.[11,12]

The formation of the complexes $[Ir^{III}Cl(dppe)_2H]$-

$[B_{10}H_{12}X]$ appears to proceed by the abstraction of a hydrogen atom, from $B_{10}H_{13}X$, by the four-co-ordinate $[Ir(dppe)_2]^+$; then, instead of the residue of the borane moiety taking part in the oxidative addition, the chlorine anion enters the co-ordination sphere of the iridium atom, giving $[IrCl(dppe)_2H]^+$ and leaving $[B_{10}H_{12}X]^-$ as the counter ion.

The formation of $[Ir^{III}(dppe)_2H_2][B_9H_{14}]$ was alluded to earlier. The compound was the subject of an *X*-ray study, to determine whether the structure of the $[B_9H_{14}]^-$ anion was the same as that described for $Cs[B_9H_{14}]$,[11] or if it adopted the alternative possible structure, as in the adduct $MeCN{\cdot}B_9H_{13}$.[13] It was found that the $[B_9H_{14}]^-$ anion was grossly disordered. However, the structure of the cation (which has not previously been determined) was solved and is now described.



The structure of the cation $[Ir(dppe)_2H_2]^+$

The cation, $[Ir(dppe)_2H_2]^+$, was found to lie on a two-fold axis, and to have the predicted *cis* configuration, as illustrated in the Figure. The important interatomic distances and angles are shown in Table 1, and it can be seen from this that the values of the Ir–P distances fall within the expected ranges.[14] There are, however, significant differences between the Ir–P bond lengths *trans* to the hydride ligands, and those *trans* to the phosphine ligands; those *trans* to the hydride ligands are *ca.* 0.05 Å longer than those *trans* to phosphorus. The strong *trans*-lengthening influence of the hydride ligand is well established,[15] and it is of interest to ascertain the extent of this effect. The structure of the ortho-metallated complex $[IrH\{PPh_2(o\text{-}C_6H_4)\}_2(PPh_3)]$ shows that the Ir–P bond *trans* to the hydride ligand is significantly longer than the Ir–P bonds *trans* to the σ-C atoms, although how the effects of ring strain in the Ir–C–C–P ring affect this is not known.[16] The *trans*-lengthening effect of a σ-bound boron atom is also known to be greater than that of a σ-bound carbon atom,[17,18] so it appears that the *trans*-lengthening effects of a hydride ligand, and that of a σ-bound boron atom, may be similar.

TABLE 1

Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses

(*i*) Distances from the iridium atom			
Ir–P(1)	2.315(8)	Ir–H(1)	1.77
Ir–P(2)	2.371(7)		
(*ii*) Phosphorus–carbon distances			
P(1)–C(1)	1.81(3)	P(2)–C(13)	1.83(3)
P(1)–C(7)	1.82(2)	P(2)–C(19)	1.82(2)
P(1)–C(25)	1.85(3)	P(2)–C(26)	1.83(3)
(*iii*) Other distances			
C(25)–C(26)	1.53(4)		
C–C(Ph)	1.29(4)—1.49(4);	average C–C(Ph)	1.37
C–H(Ph)	0.86—1.25;	average C–H(Ph)	1.08
C–H (methylene)	0.89—1.08;	average C–H (methylene)	1.03
(*iv*) Angles at the iridium atom			
P(1)–Ir–P(2)	86.2(2)	P(2)–Ir–P(2′)	97.3(2)
P(1)–Ir–H(1)	80	P(1)–Ir–P(1′)	161.0(2)
P(2)–Ir–H(1)	165	P(1)–Ir–H(1′)	88
		P(1)–Ir–P(2′)	106.6(2)
(*v*) Iridium–phosphorus–carbon angles			
Ir–P(1)–C(1)	115.9(8)	Ir–P(2)–C(13)	122.4(8)
Ir–P(1)–C(7)	118.6(7)	Ir–P(2)–C(19)	120.8(8)
Ir–P(1)–C(25)	107.2(8)	Ir–P(2)–C(26)	105.8(8)
(*vi*) Other angles			
P(1)–C(25)–C(26)	112.2(6)	P(2)–C(26)–C(25)	111.8(6)

EXPERIMENTAL

All reactions were carried out at room temperature, under an atmosphere of nitrogen. Reagents were obtained from commercial sources, or made by standard literature methods. All solvents were purified immediately prior to use.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. N.m.r. spectra were obtained on a Bruker HFX4 spectrometer modified for use in the Fourier-transform mode by Bruker Datasystem BNC12. The deuterium lock was provided by the solvent. Chemical shifts are quoted using the convention that a resonance to high frequency (low field) of the standard is positive. The standards were $SiMe_4$ for ^1H, $OEt_2{\cdot}BF_3$ for ^{11}B, and $P(OMe)_3$ for ^{31}P spectra.

Reactions of $[Ir(dppe)_2]Cl$.—*With* $B_{10}H_{14}$. A solution of $[Ir(dppe)_2]Cl$ (0.52 g, 0.51 mmol) in chloroform (40 cm^3), was added to $B_{10}H_{14}$ (0.06 g, 0.49 mmol) and the mixture stirred for 4 h, during which time the colour of the solution changed from red to pale yellow. The volume of the filtrate was reduced to 5 cm^3 and diethyl ether (40 cm^3) was added with vigorous stirring to precipitate the product. The resulting off-white precipitate was purified by dissolving it in chloroform (5 cm^3) and reprecipitating with diethyl ether to give $[Ir^{III}Cl(dppe)_2H][B_{10}H_{13}]$ (0.41 g, 73%). Analytical data for this, and other products, are presented in Table 2.

With $B_{10}H_{13}(Cl\text{-}6)$. A solution of $[Ir(dppe)_2]Cl$ (0.52 g, 0.51 mmol) in chloroform (40 cm^3) was added to $B_{10}H_{13}(Cl\text{-}6)$ (0.08 g, 0.51 mmol) and the mixture stirred for 2 h. The isolation procedure was identical to that for $[Ir^{III}Cl(dppe)_2H][B_{10}H_{13}]$, and yielded $[Ir^{III}Cl(dppe)_2H][B_{10}H_{12}Cl]$ as an off-white powder (0.45 g, 74.5% yield).

TABLE 2

Complex	Analytical data (wt.%) *				
	C	H	B	Cl	P
$[IrCl(dppe)_2H][B_{10}H_{12}Cl]$	51.9	5.4	8.8	5.9	10.3
	(52.8)	(5.2)	(9.2)	(6.0)	(10.5)
$[IrCl(dppe)_2H][B_{10}H_{13}]$	53.0	5.6	9.0	3.2	10.5
	(54.4)	(5.4)	(9.4)	(3.1)	(10.8)
$[Ir(CO)(dppe)_2][B_{10}H_{13}]$	56.0	6.0	9.0		10.6
	(56.0)	(5.4)	(9.5)		(10.9)
$[Ir(dppe)_2H_2][B_9H_{14}]$	56.3	5.8	9.3		10.8
	(56.6)	(5.9)	(8.8)		(11.3)

* Theoretical values in parentheses.

Reaction of $[Ir(CO)(dppe)_2]Cl$ *with* $[NEt_3H][B_{10}H_{13}]$.—The salt $[NEt_3H][B_{10}H_{13}]$ (0.11 g, 0.49 mmol) was added to a solution of $[Ir(CO)(dppe)_2]Cl$ (0.52 g, 0.49 mmol) in methanol (40 cm^3). A pale yellow precipitate rapidly formed, the mixture was stirred for 15 min and then filtered. The precipitate was washed with methanol (10 cm^3), benzene (20 cm^3), and then purified by dissolving it in chloroform (5 cm^3) and reprecipitating it by addition of diethyl ether (40 cm^3) to give $[Ir^I(CO)(dppe)_2][B_{10}H_{13}]$ as a yellow powder (0.35 g, 62% yield). On allowing the filtrate to stand for 5 d, a second product, $[Ir(dppe)_2H_2][B_9H_{14}]$, crystallized as pale yellow needles, which were filtered off and washed with cold methanol (0.66 g, 11% yield).

Crystal Data.—$C_{52}H_{64}B_9IrP_4$, $M = 1\,102.4$, Orthorhombic, $a = 15.456(4)$, $b = 23.936(4)$, $c = 28.529(7)$ Å, $U = 10\,554(4)$ Å^3, $Z = 8$, $D_c = 1.387$ g cm^{-3}, $F(000) = 4\,464$, space group *Ccca* (no. 68), Mo-K_α radiation, graphite monochromatized, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 25.89$ cm^{-1}.

Structure Determination.—The compound was recrystallized from methanol as pale yellow needles. The crystal used was a fragment of dimensions *ca.* 0.5 × 0.4 × 0.3 mm.

Measurements were made on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections with $5 < 2\theta < 50°$ were measured in the θ—2θ scan mode using scans from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$. The structure analysis used the 2 053 independent reflections having $I \geqslant 3\sigma(I)$ where $\sigma(I)$ is the standard deviation derived from counting statistics; a further 3 120 reflections were excluded as ' unobserved '. This large number of unobserved reflections was later found to be due to the disorder in the structure.

Iridium, phosphorus, and carbon atoms were located from Patterson and electron-density syntheses with the iridium atom on a two-fold axis at ($\frac{1}{4}$, 0, 0.172 6). The borane anion appeared as an approximately spherical region of electron density about a two-fold axis ($\frac{1}{2}$, $\frac{1}{4}$, z). Within this region 11 individual broad peaks of height 0.91—1.49 e Å^{-3} were resolved, but they did not conform to a chemically plausible structure and we concluded that the anion was disordered.

Block-diagonal least-squares refinement of co-ordinates for iridium, phosphorus, and carbon atoms, anisotropic thermal parameters for iridium and phosphorus atoms and isotropic thermal parameters for carbon atoms led to convergence with $R = 0.071$ and $R' = 0.090$. The data were then corrected for the effects of absorption and continued refinement (as above) converged with $R = 0.068$ and $R' = 0.085$. At this stage a further attempt to locate individual boron atoms of the disordered anion was unsuccessful.

Hydrogen atoms of the cation were located by running three difference-Fourier syntheses based upon different $[(\sin\theta)/\lambda]$ cut-offs of data,[19] respectively those 1 170 data with $(\sin\theta)/\lambda \leqslant 0.45$, those 898 data with $(\sin\theta)/\lambda \leqslant 0.4$, and those 450 data with $(\sin\theta)/\lambda \leqslant 0.3$. The hydrogen atoms of the cation were apparent at their expected positions in each of the three difference maps and the co-ordinates of each differed only slightly. Preliminary bond-length calculations showed that the hydrogen positions in the $(\sin\theta)/\lambda \leqslant 0.45$ map gave the smallest scatter of C–H distances (0.88—1.21 Å). The 25 hydrogen atoms in the asymmetric unit of the cation appeared in this difference map among a total of 48 peaks (other than those associated with the borane anion) of height $\geqslant 0.25$ e Å^{-3}. Peak heights were in the range 0.25—0.66 e Å^{-3}. These hydrogen atoms were included as fixed contributions with isotropic temperature factors of 0.06 Å^2. Further refinement of iridium, phosphorus, and carbon atoms led to convergence at $R = 0.065$, and $R' = 0.081$.

Atomic scattering factors were calculated using the analytical approximation and coefficients tabulated in ref. 20. Final atomic co-ordinates and estimated standard deviations are listed in Table 3. Observed and calculated structure-factor amplitudes, hydrogen-atom parameters, and thermal parameters are listed in Supplementary Publication No. SUP 22522 (16 pp.).* The molecular structure and atom numbering of non-hydrogen atoms are shown in the Figure.

TABLE 3

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Ir(1)	$\frac{1}{4}$	0	0.172 6(1)
P(1)	0.302 0(4)	0.089 3(3)	0.186 0(2)
P(2)	0.364 3(4)	−0.008 9(2)	0.117 6(2)
C(1)	0.329 1(16)	0.105 6(9)	0 246 0(9)
C(2)	0.329 9(17)	0.070 0(10)	0.280 0(9)
C(3)	0.357 5(18)	0.084 1(11)	0.328 8(11)
C(4)	0.375 7(20)	0.140 0(12)	0.333 3(12)
C(5)	0.381 3(27)	0.174 0(17)	0.294 5(14)
C(6)	0.356 7(22)	0.159 2(13)	0.252 7(13)
C(7)	0.232 4(15)	0.148 4(8)	0.172 9(8)
C(8)	0.152 4(18)	0.152 0(11)	0.191 5(9)
C(9)	0.092 7(22)	0.195 3(13)	0.186 4(11)
C(10)	0.120 8(22)	0.235 7(13)	0.157 8(11)
C(11)	0.201 2(19)	0.237 5(13)	0.134 8(11)
C(12)	0.253 1(33)	0.189 3(10)	0.141 8(9)
C(13)	0.346 8(17)	−0.033 7(9)	0.057 7(8)
C(14)	0.370 5(15)	−0.003 2(16)	0.018 9(8)
C(15)	0.357 2(20)	−0.025 0(11)	−0.024 6(11)
C(16)	0.318 1(20)	−0.069 4(12)	−0.029 6(11)
C(17)	0.293 0(17)	−0.106 0(11)	0.006 9(11)
C(18)	0.308 6(17)	−0.085 4(11)	0.053 9(9)
C(19)	0.464 0(15)	−0.045 2(9)	0.133 1(8)
C(20)	0.493 6(19)	−0.040 3(10)	0.177 5(10)
C(21)	0.570 7(19)	−0.070 7(12)	0.192 4(10)
C(22)	0.614 4(19)	−0.102 7(11)	0.159 8(10
C(23)	0.582 5(19)	−0.101 2(12)	0.116 6(10)
C(24)	0.509 2(17)	−0.073 8(10)	0.101 7(8)
C(25)	0.405 4(17)	0.095 7(10)	0.154 1(9)
C(26)	0.406 0(17)	0.061 7(10)	0.108 7(8)

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REFERENCES

[1] A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Comm.*, 1966, 589.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

[2] W. Heiber and V. Frey, *Chem. Ber.*, 1966, **99**, 2607.

[3] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 1966, **88**, 5324.

[4] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and K. A. Taylor, *Chem. Comm.*, 1966, 906.

[5] K. G. Caulton and J. S. Miller, *J. Amer. Chem. Soc.*, 1975, **97**, 1067.

[6] M. J. Hopkinson and J. F. Nixon, *J. Organometallic Chem.*, 1978, **148**, 201.

[7] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.

[8] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335.

[9] J. Q. Chambers, A. D. Norman, M. R. Bickell, and S. H. Cadle, *J. Amer. Chem. Soc.*, 1968, **90**, 6056.

[10] A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3671.

[11] N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Comm.*, 1970, 505; N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J.C.S. Dalton*, 1972, 986.

[12] P. C. Keller, *Inorg. Chem.*, 1970, **9**, 75.

[13] F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, 1961, **35**, 1335.

[14] M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1974, **13**, 1418 and refs. therein.

[15] J. C. Green and M. L. H. Green, ' Comprehensive Inorganic Chemistry,' Pergamon, Oxford, 1973, ch. 48.

[16] G. Del Piero, G. Perego, A. Zazzetta, and M. Cesari, *Cryst. Struct. Comm.*, 1974, **3**, 725.

[17] M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, and S. S. Wreford, *J. Amer. Chem. Soc.*, 1974, **96**, 4042.

[18] M. R. Churchill and J. J. Hackbarth, *Inorg. Chem.*, 1975, **14**, 2047.

[19] S. J. Laplaca and J. A. Ibers, *Acta Cryst.*, 1965, **18**, 511.

[20] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
