Heteroatom Chemistry
Volume 2. Number 1, 1991

Reaction of $(t\text{-BuGaCl}_2)_2$ with Ar′PHLi (Ar′ = 2,4,6-t-$Bu_3C_6H_2$): Preparation of the Chloride-Bridged Dimer $(t\text{-BuGa(Cl)P(H)Ar}')_2$

Alan H. Cowley,* Richard A. Jones, and Miguel A. Mardones
Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

Jerry L. Atwood, and Simon G. Bott
Department of Chemistry, University of Alabama, Tuscaloosa, Alabama 35486, U.S.A.

Received 26 June 1990.

ABSTRACT

The reaction of $(t\text{-BuGaCl}_2)_2$ *with* Ar′P(H)Li (Ar′ = 2,4,6-t-$Bu_3C_6H_2$) *affords the chloride-bridged dimer* $[t\text{-BuGa(Cl)P(H)Ar}']_2$ (**1**). *The structure of* **1** *has been established by X-ray crystallography. Compound* **1**, $C_{44}H_{78}Cl_2Ga_2P_2$, *crystallizes in the monoclinic space group* $P2_1/n$ *with* Z = 2, *a* = 10.468(1), *b* = 14.967(1), *c* = 16.182(2) Å, *and* β = 94.48(1)°. *The reaction of* **1** *with* t-BuLi *is described.*

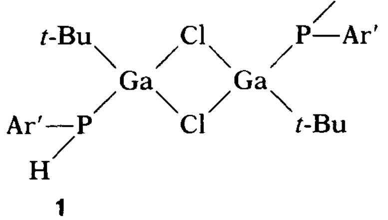
INTRODUCTION

The recent literature reflects a heightened interest in the chemistry of the group 13 and 15 elements. To a large extent, this is due to the search for new precursors to electronic materials [1]. Initial attention has focused on compounds of the general formula $(R_2MER_2')_n$ where R,R′ = alkyl, and M and E represent group 13 and 15 elements respectively. Several compounds of this type have been prepared and structurally characterized and some of them show promise as single source precursors to gallium arsenide and related compound semiconductors [2]. However, more recently our attention has turned to derivatives of the general type $(RMER')_n$. Such compounds represent a potentially new class of semiconductor precursor. Moreover, considerable interest is associated with the rich variety of possible structural forms, which includes analogues of cyclobutadiene, benzene, and cubane, as well as larger polyhedral arrangements. The present manuscript describes our first steps in this direction. Specifically, we describe the synthesis and X-ray crystal structure of the dimer $(t\text{-BuGa(Cl)P(H)Ar}')_2$ (**1**) (Ar′ = 2,4,6-t-$Bu_3C_6H_2$) together with our attempts at dehydrochlorination of **1**.

RESULTS AND DISCUSSION

The reaction of $[t\text{-BuGaCl}_2]_2$ with the phosphide anion $[Ar'PH]^-$ (Ar′ = 2,4,6-t-$Bu_3C_6H_2$), affords the colorless crystalline dimer, $[t\text{-BuGa(Cl)P(H)Ar}']_2$ (**1**) in 54% yield.

$$2\ t\text{-BuGaCl}_2 + 2\ \text{Ar}'\text{P(H)Li} \xrightarrow[-2\text{LiCl}]{}$$



1

The CI mass spectrum of **1** indicated that this compound exists as a dimer in the gas phase. However,

---

*To whom correspondence should be addressed.

1042-7163/91/\$3.50 + .25

a priori it was not possible to predict whether the phosphido or chloro ligands would occupy bridging positions. On the basis of steric bulk, a chloro-bridged dimer would be anticipated. However, in comparable structures such as $[BrGa\{As(CH_2SiMe_3)_2\}_2]_2$ [3] and $[ClGa(Sb\text{-}t\text{-}Bu_2)_2]_2$ [4] the halide ligands have been shown to adopt terminal positions. In $[t\text{-}Bu_2GaP(H)C_5H_9]_2$, the only structurally characterized primary-phosphido gallium dimer, the RPH group occupies a bridging site [5]. The ^{31}P NMR chemical shifts for $[t\text{-}Bu_2GaP(H)C_5H_9]_2$ ($\delta = -90.3$, -94.5 for *cis-trans* isomers) are similar to that for **1**; however, we hesitated to draw a structural conclusion on the basis of this fact alone. Accordingly, a single-crystal X-ray diffraction study of **1** was undertaken. Bond lengths and bond angles are listed in Tables 1 and 2, respectively, and the positional parameters are listed in Table 3.

The solid state of **1** (Figure 1) consists of individual molecules with no short intermolecular contacts. The dimer, which is chloride-bridged, resides on a center of symmetry. The Ga_2Cl_2 core exhibits a slight rhombic distortion (Cl–Ga–Cl′ = 88.91(8); Ga–Cl–Ga′ = 91.09(7)°) and the Ga–Cl distance (2.397(2) Å) is unusually long. The P–C(71) bond length (1.980(8) Å) and P–Ga–C(71) bond angle (137.6(2)Å) are also larger than usual and thus suggestive of steric interactions between the bulky Ar′ and *t*-Bu groups. Note, however, that the Ga–P bond length (2.328(2) Å) is over 0.1 Å shorter than those found in dimers or trimers of empirical composition RR′GaPR″R‴ [1]. The P–H hydrogens were not located in the X-ray study. However, their pres-

TABLE 1 Bond Lengths for **1**

Atoms	*Distance*	*Atoms*	*Distance*
Ga–P	2.328(2)	C(3)–H(3)	1.000
Ga–Cl^a	2.397(2)	C(22)–H(22)A	1.000
P–C(1)	1.865(7)	C(22)–H(22)C	1.000
C(1)–C(6)	1.421(9)	C(23)–H(23)B	1.000
C(2)–C(21)	1.549(9)	C(24)–H(24)A	1.000
C(4)–C(5)	1.39(1)	C(24)–H(24)C	1.000
C(5)–C(6)	1.392(9)	C(62)–H(62)B	1.000
C(21)–C(22)	1.52(1)	C(63)–H(63)A	1.000
C(21)–C(24)	1.54(1)	C(63)–H(63)C	1.000
C(41)–C(42)B	1.43(6)	C(64)–H(64)B	1.000
C(41)–C(43)A	1.74(4)	C(72)–H(72)A	1.000
C(41)–C(44)	1.42(4)	C(72)–H(72)C	1.000
C(41)–C(44)B	1.49(4)	C(73)–H(73)B	1.000
C(61)–C(63)	1.52(1)	C(74)–H(74)A	1.000
C(71)–C(72)	1.50(1)	C(74)–H(74)C	1.000
C(71)–C(74)	1.49(1)	C(5)–H(5)	1.000
Ga–Cl	2.408(2)	C(22)–H(22)B	1.000
Ga–C(71)	1.980(8)	C(23)–H(23)A	1.000
C(1)–C(2)	1.404(9)	C(23)–H(23)C	1.000
C(2)–C(3)	1.373(9)	C(24)–H(24)B	1.000
C(3)–C(4)	1.386(9)	C(62)–H(62)A	1.000
C(4)–C(41)	1.56(1)	C(62)–H(62)C	1.000
C(6)–C(61)	1.56(1)	C(63)–H(63)B	1.000
C(21)–C(23)	1.53(1)	C(64)–H(64)A	1.000
C(41)–C(42)	1.59(2)	C(64)–H(64)C	1.000
C(41)–C(43)	1.65(2)	C(72)–H(72)B	1.000
C(41)–C(43)B	1.41(6)	C(73)–H(73)A	1.000
C(41)–C(44)A	1.68(4)	C(73)–H(73)C	1.000
C(61)–C(62)	1.54(1)	C(74)–H(74)B	1.000
C(61)–C(64)	1.55(1)		
C(71)–C(73)	1.49(1)		

^{a} (x, y, z) → (−x, 1 − y, 2 − z)

TABLE 2 Bond Angles for **1**

Atoms	*Angle*	*Atoms*	*Angle*
Cl′–Ga–Cl	88.91(8)	P–Ga–Cl	105.53(8)
P–Ga–Cl′	103.42(8)	Cl–Ga–C(71)	104.8(3)
Cl′–Ga–C(71)	106.2(3)	P–Ga–C(71)	137.6(2)
Ga–P–C(1)	97.7(2)	Ga′–Cl–Ga	91.09(7)
P–C(1)–C(2)	119.6(5)	P–C(1)–C(6)	120.9(5)
C(2)–C(1)–C(6)	119.2(7)	C(1)–C(2)–C(3)	118.3(7)
C(1)–C(2)–C(21)	125.2(7)	C(3)–C(2)–C(21)	116.4(7)
C(2)–C(3)–C(4)	123.9(7)	C(3)–C(4)–C(5)	115.8(7)
C(3)–C(4)–C(41)	122.2(8)	C(5)–C(4)–C(41)	122.0(8)
C(4)–C(5)–C(6)	123.5(7)	C(1)–C(6)–C(5)	117.4(7)
C(1)–C(6)–C(61)	125.7(7)	C(5)–C(6)–C(61)	116.9(7)
C(2)–C(21)–C(22)	110.1(8)	C(2)–C(21)–C(23)	113.6(7)
C(22)–C(21)–C(23)	109.4(7)	C(2)–C(21)–C(24)	112.0(7)
C(22)–C(21)–C(24)	105.2(8)	C(23)–C(21)–C(24)	106.1(8)
C(4)–C(41)–C(42)	107(1)	C(4)–C(41)–C(42)B	111(2)
C(4)–C(41)–C(43)	107(1)	C(42)–C(41)–C(43)	96(1)
C(4)–C(41)–C(43)A	103(1)	C(43)A–C(41)–C(43)	78(2)
C(42)B–C(41)–C(43)A	110(3)	C(4)–C(41)–C(43)B	107(2)
C(43)B–C(41)–C(43)	126(3)	C(43)B–C(41)–C(43)A	133(3)
C(4)–C(41)–C(44)	115(2)	C(42)–C(41)–C(44)	118(2)
C(43)–C(41)–C(44)	112(2)	C(4)–C(41)–C(44)A	105(2)
C(43)A–C(41)–C(44)A	86(2)	C(42)B–C(41)–C(44)A	135(3)

TABLE 2 (*continued*)

Atoms	*Angle*	*Atoms*	*Angle*
C(4)–C(41)–C(44)B	114(2)	C(42)–C(41)–C(44)B	131(2)
C(44)B–C(41)–C(44)A	108(2)	C(6)–C(61)–C(62)	110.4(7)
C(6)–C(61)–C(63)	112.3(7)	C(62)–C(61)–C(63)	105.0(7)
C(6)–C(61)–C(644)	111.8(7)	C(62)–C(61)–C(64)	111.6(7)
C(63)–C(61)–C(64)	105.5(7)	Ga–C(71)–C(72)	110.9(6)
Ga–C(71)–C(73)	109.7(6)	C(72)–C(71)–C(73)	109.7(9)
Ga–C(71)–C(74)	109.0(6)	C(72)–C(71)–C(74)	107.9(8)
C(73)–C(71)–C(74)	109.6(8)		
C(2)–C(3)–H(3)	118	C(4)–C(3)–H(3)	118
C(4)–C(5)–H(5)	118	C(6)–C(5)–H(5)	118
C(21)–C(22)–H(22)A	109	C(21)–C(22)–H(22)B	110
H(22)B–C(22)–H(22)A	109	C(21)–C(22)–H(22)C	109
H(22)C–C(22)–H(22)A	109	H(22)C–C(22)–H(22)B	109
C(21)–C(23)–H(23)A	109	C(21)–C(23)–H(23)B	109
H(23)B–C(23)–H(23)A	109	C(21)–C(23)–H(23)C	110
H(23)C–C(23)–H(23)A	109	H(23)C–C(23)–H(23)B	109
C(21)–C(24)–H(24)A	110	C(21)–C(24)–H(24)B	109
H(24)B–C(24)–H(24)A	109	C(21)–C(24)–H(24)C	110
H(24)C–C(24)–H(24)A	109	H(24)C–C(24)–H(24)B	109
C(61)–C(62)–H(62)A	109	C(61)–C(62)–H(62)B	109
H(62)B–C(62)–H(62)A	109	C(61)–C(62)–H(62)C	110
H(62)C–C(62)–H(62)A	109	H(62)C–C(62)–H(62)B	109
C(61)–C(63)–H(63)A	110	C(61)–C(63)–H(63)B	110
H(63)B–C(63)–H(63)A	109	C(61)–C(63)–H(63)C	109
H(63)C–C(63)–H(63)A	109	H(63)C–C(63)–H(63)B	109
C(61)–C(64)–H(64)A	110	C(61)–C(64)–H(64)B	109
H(64)B–C(64)–H(64)A	109	C(61)–C(64)–H(64)C	110
H(64)C–C(64)–H(64)A	109	H(64)C–C(64)–H(64)B	109
C(71)–C(72)–H(72)A	110	C(71)–C(72)–H(72)B	109
H(72)B–C(72)–H(72)A	109	C(71)–C(72)–H(72)C	110
H(72)C–C(72)–H(72)A	109	H(72)C–C(72)–H(72)B	109
C(71)–C(73)–H(73)A	110	C(71)–C(73)–H(73)B	110
H(73)B–C(73)–H(73)A	109	C(71)–C(73)–H(73)C	109
H(73)C–C(73)–H(73)A	109	H(73)C–C(73)–H(73)B	109
C(71)–C(74)–H(74)A	110	C(71)–C(74)–H(74)B	110
H(74)B–C(74)–H(74)A	109	C(71)–C(74)–H(74)C	109
H(74)C–C(74)–H(74)A	109	H(74)C–C(74)–H(74)B	109

TABLE 3 Positional Parameters and Their Estimated Standard Deviations for **1**

Atom	*x/a*	*y/b*	*z/c*	*Atom*	*x/a*	*y/b*	*z/c*
Ga	.05237(8)	.52609(6)	.90514(5)	C(43)	.418(2)	.611(2)	.536(1)
Cl	.1460(2)	.4600(1)	1.0313(1)	C(44)	.183(6)	.625(3)	.482(2)
P	.1296(2)	.6720(1)	.9049(1)	C(43)A	.254(5)	.686(3)	.488(2)
C(1)	.1829(7)	.6723(5)	.7977(4)	C(44)A	.121(4)	.564(4)	.502(3)
C(2)	.3048(7)	.6393(5)	.7834(4)	C(42)B	.391(6)	.553(4)	.547(4)
C(3)	.3276(7)	.6149(5)	.7041(4)	C(43)B	.206(6)	.506(4)	.539(4)
C(4)	.2396(8)	.6252(5)	.6362(5)	C(44)B	.327(4)	.656(3)	.495(2)
C(5)	.1289(7)	.6717(5)	.6506(5)	C(61)	−.0234(8)	.7577(6)	.7334(5)
C(6)	.0980(7)	.6982(5)	.7291(4)	C(62)	.0077(9)	.8405(6)	.7881(6)
C(21)	.4191(8)	.6311(7)	.8497(5)	C(63)	−.0707(8)	.7948(7)	.6493(6)
C(22)	.4395(9)	.7187(7)	.8958(6)	C(64)	−.1376(8)	.7041(7)	.7636(6)
C(23)	.4037(9)	.5555(7)	.9121(6)	C(71)	.0297(9)	.4252(6)	.8261(5)
C(24)	.5464(8)	.6127(8)	.8106(6)	C(72)	−.034(1)	.3474(6)	.8647(6)
C(41)	.266(1)	.5900(8)	.5481(6)	C(73)	.1569(9)	.3970(7)	.7995(6)
C(42)	.281(3)	.485(1)	.555(1)	C(74)	−.054(1)	.4546(7)	.7525(6)

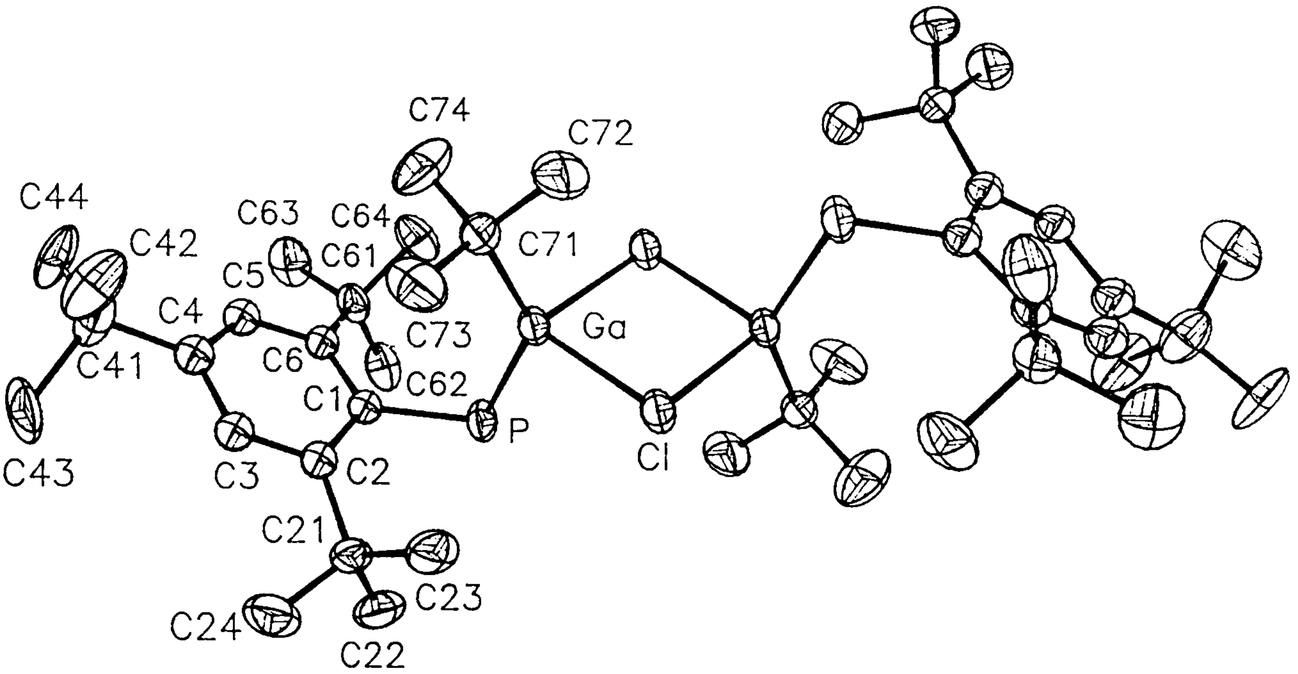


FIGURE 1 Structure of **1** showing the atom numbering scheme.

ence is evident both from NMR data and from the Ga–P–C(1) bond angle of 97.7(2)°.

Given that **1** features a 1,2 arrangement of H and Cl groups, attempts were made at dehydrochlorination. The reaction of **1** with *t*-BuLi resulted in metathesis and formation of the very bulky monomer (*t*-Bu)2GaP(H)Ar′ (**2**). Compound **1** failed to react with DBU or proton sponge, while the reaction of **1** with DABCO resulted in an intractable white precipitate.

EXPERIMENTAL

All experiments were performed by using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were freshly distilled over appropriate drying agents immediately prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a General Electric QE300 instrument operating at 300, 75.48, and 121.5 MHz respectively. ^{1}H and ^{13}C NMR spectra were referenced to Me_4Si (0.0 ppm) and ^{31}P spectra to 85% H_3PO_4, positive values to high frequency. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer and mass spectra on Du Pont Consolidated 21-491 and 21-100 spectrometers (the latter for high-resolution mass spectra, HRMS).

Preparation of [t-*BuGa*(*Cl*)*P*(*H*)*Ar′*]$_2$ (**1**)

The phosphide Ar′PHLi was prepared by adding 6.4 mL of a 1.6 M *n*-BuLi solution to 2.86 g (10.2 mmol) of $Ar'PH_2$ in 30 mL of THF at −78°C. After slow warming to room temperature, the reaction mixture was stirred for 30 min and then added to a cold solution (−78°C) of 2.03 g (10.2 mmol) of [*t*-$BuGaCl_2$]$_2$ [6] in 20 mL of THF. The reaction mixture was allowed to assume ambient temperature and was stirred overnight, following which the solvent and volatiles were removed under vacuum. The resulting residue was extracted with ether and cooled to −20°C resulting in the formation of white needles. Extraction of the residue with toluene followed by crystallization from the concentrated toluene solution afforded a second crop of crystals. The combined yield of product was 2.4 g (54% yield). Colorless crystals suitable for X-ray diffraction were grown from a cold (−20°C) ethereal solution. The mp of **1** is 138–140°C. ^{1}H NMR for **1** (300 MHz, 295 K, THF-d_8, TMS ext.) δ = 1.21 (s, 9H, $(CH_3)_3CGa$), 1.26 (s, 9H, para-$(CH_3)_3C$) 1.56 (s, 18H, ortho-$(CH_3)_3C$), 4.14 (d, ^{1}H, P-H,$^1J_{PH}$ = 207 Hz) 7.37 (s, 2H, arom. H). $^{13}C\{^1H\}$ NMR (75.48 MHz, 295 K, THF-d_8, TMS ext) δ = 28.9 (s, C—Ga), 30.3 (s, $(CH_3)_3CGa$), 31.8 (s, para-$(CH_3)_3C$), 33.7 (broad s, ortho-$(CH_3)_3C$), 35.1 (s, para-$(CH_3)_3C$) 38.7 (s, ortho-$(CH_3)_3C$). ^{31}P NMR (121.5 MHz, 295 K, THF-d_8, 85% H_3PO_4 ext.) δ = −112, d, $^1J_{PH}$ = 207 Hz.

Reaction of **1** *with* t-*BuLi*

A solution of *t*-BuLi (2 mL, 1.7 M) in *n*-hexane was added to a cold (−78°C) solution of **1** (1.5 g, 3.4 mmol) in 30 mL of Et_2O. After slow warming to room temperature, the reaction mixture was stirred for 6 h, following which the solvent and volatiles were removed under vacuum. The light yellow residue was extracted with 80 mL of *n*-hexane, and the resulting solution was filtered and concentrated to a volume of 10 mL. Upon cooling the solution to −20°C, light yellow microcrystalline **2** formed in 57% yield (0.9 g). ^{31}P NMR for **2** (121.5 MHz, 295 K, THF-d_8, 85% H_3PO_4 ext.) $\delta = -132.9$, d, $^1J_{PH} = 198.9$ Hz.

X-ray Structure Analysis of 1

Suitable single crystals of **1** were obtained as described above. Initial lattice parameters were obtained from a least squares fit to 25 reflections, $15° \leq 2\theta \leq 20°$, accurately centered on an Enraf-Nonius CAD-4 automated diffractometer and refined subsequently using higher angle data. Crystal data for **1**: $C_{44}H_{78}C_{12}Ga_2P_2$, $M_r = 879.50$, monoclinic, space group $P2_1/n$, $a = 10.468(1)°$, $b = 14.967(1)$, $c = 16.182(2)$ Å, $\beta = 94.48(1)°$, $U = 2528(2)$ Å^3, $D_c = 1.160$ g cm^{-3}, $Z = 2$, $\lambda(\text{MoK}_\alpha) = 0.71069$ Å, $\mu(\text{MoK}_\alpha) = 12.61$ cm^{-1}. A total of 4720 unique reflections was collected at 25°C using the $\theta/2\theta$ scan mode over the range $2.0° \leq 2\theta \leq 50.0°$. The data set was corrected for Lorentz and polarization effects and for decay (5%). An empirical (ψ-scan) absorption correction was also made. The structure of **1** was solved by Patterson methods using 1928 reflections with $I > 3.0\,\sigma(I)$. Note that, since individual molecules reside over a center of symmetry, disorder is observed in the para-t-Bu group of the 2,4,6-t-$Bu_3C_6H_2$ substituent (over four sites). The final R and R_w values were 0.0463 and 0.0566 respectively.

ACKNOWLEDGMENT

We wish to thank the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

REFERENCES

[1] For a review, see A. H. Cowley and R. A. Jones, *Angew. Chem., Int. Ed. Engl., 28,* 1989, 1208.

[2] A. H. Cowley, B. L. Benac, J. G. Ekerdt, R. A. Jones, K. B. Kidd, J. Y. Lee, J. E. Miller, *J. Am. Chem. Soc., 110,* 1988, 6248; J. E. Miller, K. B. Kidd, A. H. Cowley, R. A. Jones, J. G. Ekerdt, H. J. Gysling, A. A. Wernberg, T. N. Blanton, *Chemistry of Materials, 2,* 1990, 589.

[3] A. P. Purdy, R. L. Wells, A. T. McPhail, C. G. Pitt, *Organometallics 6,* 1987, 2099.

[4] A. R. Barron, A. H. Cowley, R. A. Jones, C. M. Nunn, D. L. Westmoreland, *Polyhedron, 7,* 1988, 77.

[5] D. E. Heaton, R. A. Jones, K. B. Kidd, A. H. Cowley, C. M. Nunn, *Polyhedron, 7,* 1988, 1901.

[6] W. M. Cleaver, A. R. Barron, *Chemtronics, 4,* 1989, 146.