92. Synthesis and X-Ray Crystal Structure of an Optically Pure Tripodal C_3-Symmetric Tritertiary Phosphine Bearing Chirality on Phosphorus

by **Thomas R. Ward*** and **Luigi M. Venanzi**

Laboratorium für Anorganische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstr. 6, CH-8092 Zürich

and **Alberto Albinati** and **Francesca Lianza**

Istituto di Chimica Farmaceutica, Università di Milano, I-20131 Milano

and **Tobias Gerfin** and **Volker Gramlich**

Institut für Kristallographie and Petrographie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Sonneggstr. 5, CH-8092 Zürich

and **Gerardo M. Ramos Tombo**

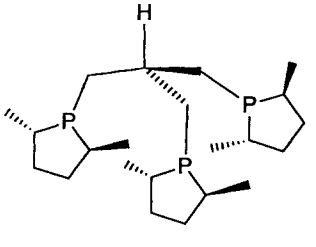
Agricultural Division, *Ciba Geigy AG*, CH-4002 Basel

(6.V.91)

The preparation of the optically pure tritertiary phosphine (*RRR*)-MeSi(CH_2P(*t*-Bu)Ph)$_3$ (**1**) is reported. The route followed involves deprotonation of optically pure (*R*)-P(BH_3)Me(*t*-Bu)Ph (**2**) the reaction of the resulting carbanion with $MeSiCl_3$, followed by removal with morpholine of the BH_3-protecting groups from the tritertiary phosphine-borane **3**. The latter's X-ray crystal structure and that of [Rh(NBD)((*RRR*)-**1**)](OTf) (**4**), are also reported. Furthermore, it is shown that the separation of the racemic phosphine-borane **2** can be conveniently carried out using medium-pressure liquid chromatography with cellulose-triacetate as a chiral stationary phase.

Introduction. – Complexes with terdentate ligands of C_{3v} symmetry, *e.g.* $MeC(CH_2PPh_2)_3$ (Triphos), have been recently studied as catalyst precursors for homogeneously catalyzed reactions such as hydroformylation [1], hydrogenation [2], as well as acetalization [3]. It would, therefore, be of interest to employ chiral ligands of C_3 symmetry in the above catalytic processes. Of particular interest would be reactions involving as catalysts octahedral complexes of the type $[M(S)_3(TRIPOD)]^{z+}$ (S = solvent, TRIPOD = C_3-symmetric ligand), as all coordination sites would be equivalent (see *Fig. 1a*), thus transposing into octahedral systems the properties of C_2-symmetric bidentate ligands in square planar geometries (see *Fig. 1b*) [4] [5].

Optically pure C_3-symmetric phosphine ligands have received increasing attention [16], the most recent contribution being that by *Burk* and *Harlow* who reported the synthesis of the first optically pure C_3-symmetric tripodal phosphine ligand [7] shown below:



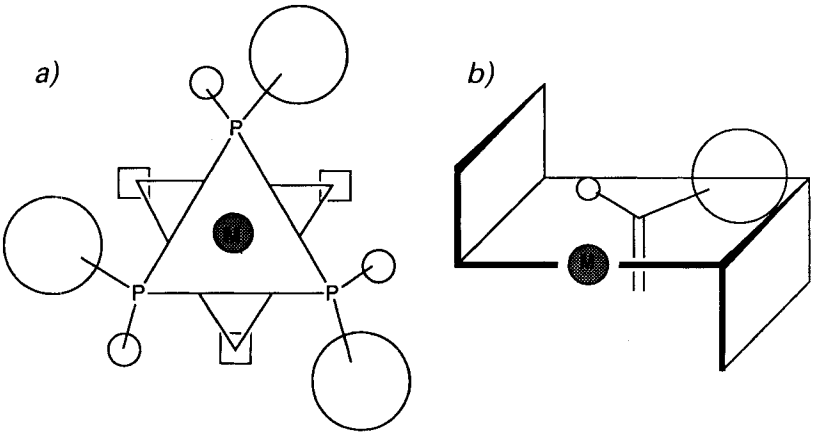


Fig. 1. a) *The* C_3 *model in octahedral geometry*, b) *the* C_2 *model in square-planar geometry*

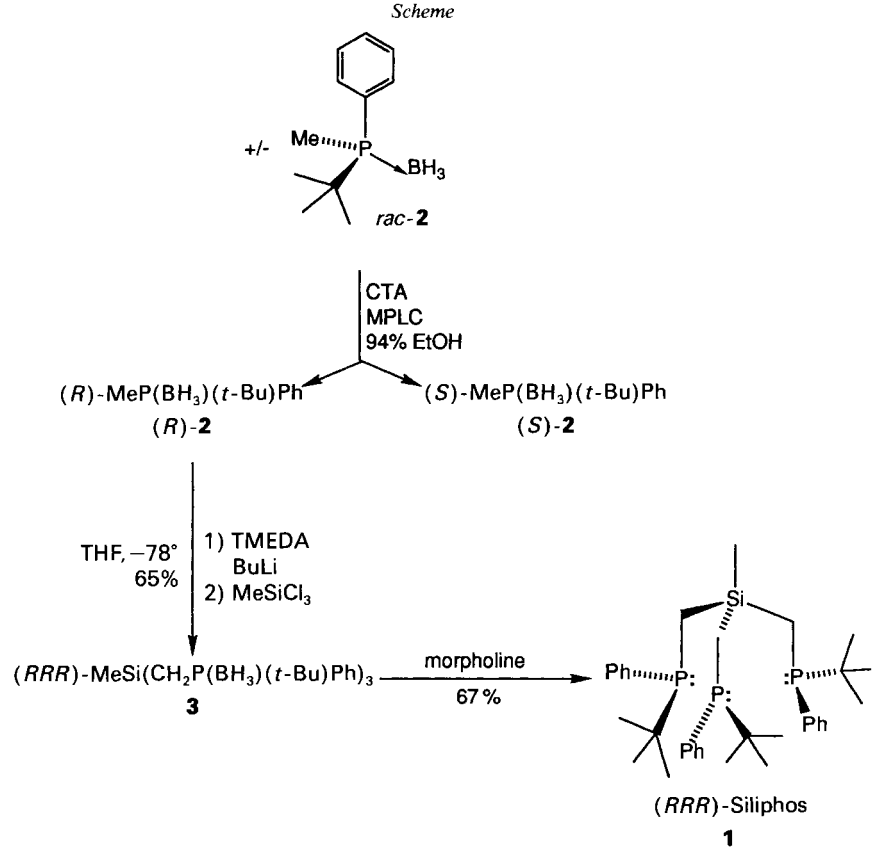
As can be seen, the chirality centers in this ligand are built into the terminal substituents of the P-atoms. We report here the synthesis and characterization of an optically pure C_3-symmetric tripodal phosphine *bearing chirality on the P-atoms* (*RRR*)-$MeSi(CH_2P(t\text{-}Bu)Ph)_3$ ((*RRR*)-Siliphos, **1**).

Results and Discussion. – The major contribution to phosphine synthesis recently published by *Imamoto et al.* [8] as well as the work of *Karsch* and *Appelt* [9] and *Boncella et al.* [10] indicated that the tripodal phosphine (*RRR*)-Siliphos (**1**) could be obtained by the route described in the *Scheme*. This indeed is the case.

The starting material chosen was *rac*-(*tert*-butyl)(methyl)(phenyl)phosphine-borane (**2**) [8]. The separation of the racemate was achieved with medium-pressure liquid chromatography (MPLC) with cellulose-triacetate (CTA) as a chiral stationary phase. Deprotonation of (*R*)-(*tert*-butyl)(methyl)(phenyl)phosphine-borane ((*R*)-**2**) followed by coupling to the electrophilic $MeSiCl_3$, afforded the enantiomerically pure (*RRR*)-Siliphos-borane (**3**) in 65% yield. An X-ray crystal-structure determination of **3** was carried out, and an ORTEP view is presented in *Fig. 2*. Deprotection using morpholine, followed by recrystallization, yielded the free phosphine **1**, in 67% yield, as air-sensitive colourless crystals. The coordination chemistry of this new phosphine is currently being investigated, and we report here the preparation and X-ray crystal structure of the first complex obtained: [Rh(NBD) ((*RRR*)-**1**)](OTf) (**4**; NBD = norbornadiene). The coordination geometry around the Rh-atom (see *Fig. 3*) is best described as distorted square pyramidal, similar to that found in $[Rh(NBD)(Triphos)]^+$ [11]. Although the accuracy of the structural data is low because of disordered norbornadiene and acetone molecules, the overall C_3-symmetry of the 'Rh((*RRR*)-**1**)'-moiety is immediately apparent.

As several other phosphine boranes analogous to **2** undergo selective deprotonation [8], it is likely that this new synthetic route for the preparation of optically pure tritertiary phosphines with C_3 symmetry will be quite general and allow many variations of the terminal P-atoms. We are currently investigating the applicability of this new route for the synthesis of various optically pure C_3-symmetric ligands as well as their use as ligands for enantioselective catalysis.

Scheme



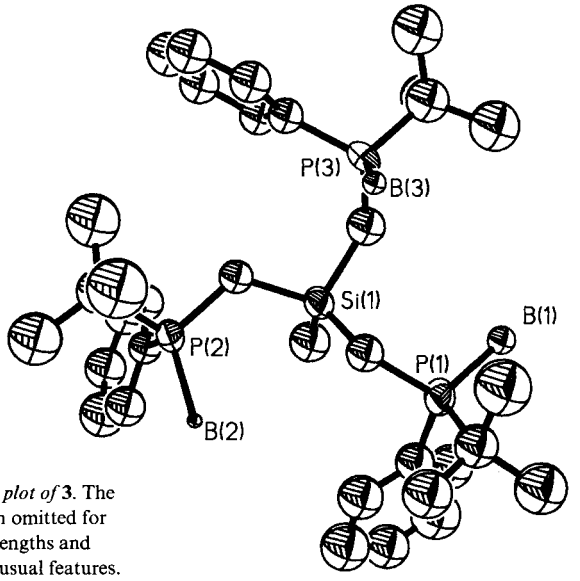


Fig. 2. *An ORTEP plot of* **3**. The H-atoms have been omitted for clarity. The bond lengths and angles show no unusual features.

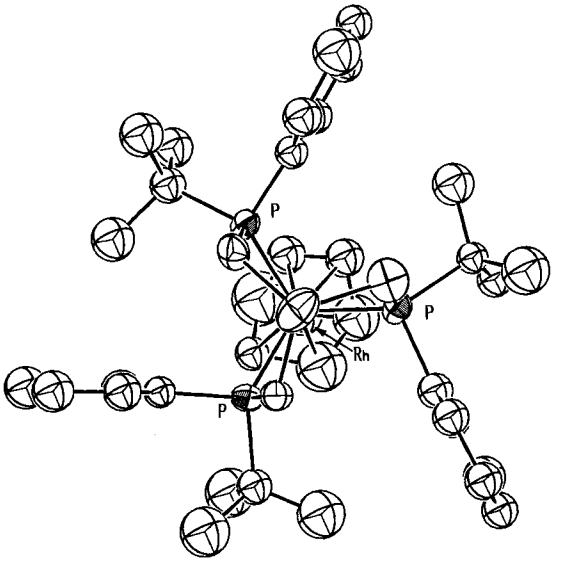


Fig. 3. *An ORTEP plot of cation [Rh(NBD)((RRR)-1)]$^+$ in* **4** *viewed along the pseudo* C_3 *axis.* The H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for one of the two independent molecules in the unit cell: Rh–P(1): 2.489 (8), Rh–P(2): 2.471 (9), Rh–P(3): 2.479(8), Rh–C: 2.21 (9) (average value), Rh-mp1: 2.02(6), Rh-mp2: 2.16 (5) (mp1 and mp2 being the midpoint of the bonds C(5)–C(6) and C(8)–C(9), respectively), P–CH_2): 1.82 (4) (average value), P(1)–Rh–P(2): 92.7 (3), P(1)–Rh–P(3): 92.5 (2), P(2)–Rh–P(3): 94.1 (3), P(1)–Rh-mp1: 141 (3), P(3)–Rh-mp2: 156 (9), P(1)–Rh-mp2: 97 (4), P(3)–Rh-mp1: 91 (3), P(2)-Rh-mp1: 125 (3), P(2)–Rh-mp2: 107 (3).

Finally, it should be emphasized that the separation of racemic phosphine boranes using MPLC with CTA is simple and highly efficient, and this offers a new and valuable tool for the separation of racemic protected monophosphines.

Experimental Part

All operations involving phosphines were performed in deoxygenated solvents under an Ar atmosphere. All reagents and solvents (*purum* or *puriss.* quality) were purchased from *Fluka AG* and were used with no further purification. $[Rh_2Cl_2(NBD)_2]$ was purchased from *Aldrich* (Germany). Optical rotations $[\alpha]_D^{25}$ were determined in 1-dm cells on a *Perkin Elmer 241* polarimeter. The ^{31}P-NMR spectra were recorded on a *Bruker AM-250* operating at 101.21 MHz. A positive sign of the chemical shift denotes a resonance to low field of the external H_3PO_4 reference. The same instrument was used for the ^{1}H-NMR spectra (250.13 MHz) as well as for the ^{13}C-NMR spectra (62.9 MHz).

rac-*P(BH$_3$)Me(*t*-Bu)Ph* (**2**) was prepared as described by *Imamoto et al.* [8]. The pure product (25 g) was loaded on a preparative, custom-designed CTA column. Column diameter: 20 cm, height: 1 m; 17 kg of cellulose-triacetate (*Merck*, 25–40 mesh), flow: 5 l h^{-1}; pressure on column: 0.3 atm at the top, 0.6 atm in the middle, and 1.5 atm at the bottom. UV detection (264 nm). Elution with 94% EtOH separated the enantiomers. After 5.25 h, (*S*)-P(BH_3)(*t*-Bu)PhMe ((*S*)-**2**) was eluted: 11.35 g (91%). M.p.: 53°. $[\alpha]_D^{25} = +8.2$ ($c = 1$, MeOH). A small mixed fraction preceeded enantiomerically pure (*R*)-P(BH_3)(*t*-Bu)PhMe ((*R*)-**2**): 10.72 g (85%) M.p.: 53° ([8]: 52.5–53°). $[\alpha]_D^{25} = -8.2$ ($c = 1$, MeOH). Satisfactory C and H microanalyses were obtained for both enantiomers. (The help of Mr. *K. Auer* was greatly appreciated during enantiomeric separation.)

*(RRR)-MeSi[CH$_2$P(BH$_3$)(*t*-Bu)Ph]$_3$* (**3**). A 2-necked round-bottomed flask was charged with 100 ml of THF and cooled to –78°. BuLi (11.75 ml; 1.6M in hexane, 18.8 mmol) was added, followed by 2.82 ml of TMEDA

(18.8 mmol). The resulting soln. was briefly stirred, and 3.382 g of (*R*)-**2** (17.4 mmol) in THF (30 ml) were added over 30 min to the cooled soln. The resulting pale yellow soln. was stirred at −78° for 7 h. Then, 0.681 ml of $MeSiCl_3$ (5.81 mmol) were added by means of a syringe. The soln. was then allowed to warm up to r.t. and stirred overnight. The resulting red soln. was hydrolysed with 10 ml of 2M HCl, and the product extracted with CH_2Cl_2. The org. layer was washed with a K_2CO_3 soln., dried ($MgSO_4$), and the solvents were evaporated. The crude product was purified by flash chromatography (AcOEt/hexane 1:12). The product was eluted first. The unreacted (*R*)-**2** could be recovered. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a Et_2O soln. containing **3**. Yield: 2.45 g (68%). M.p. 215–217°. $[\alpha]_D^{25} = -56.5$ (*c* = 1, CH_2Cl_2). Satisfactory C and H microanalyses were obtained. ^{1}H-NMR ($CDCl_3$/r.t.): 7.7–7.2 (*m*, 15 arom. H); 1.74 (br. *t*, $^2J(P,H) = {}^2J(H,H) = 14.9$, 3 H, CH_AH_B); 1.65 (*dd*, $^2J(P,H) = 11.0$, 3 H, CH_AH_B); 0.99 (*d*, $^3J(P,H) = 14.1$, 3 CH_3)$_3$C); −1.04 (*s*, $SiCH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$/r.t.): 133.60 (*d*, $^2J(P,C) = 8.0$, C_{ortho}); 131.06 (*d*, $^3J(P,C) = 9.5$, C_{meta}); 128.05 (*s*, C_{para}); 127.95 (*d*, $^1J(P,C) = 49.9$, C_{ipso}); 30.25 (*d*, $^1J(P,C) = 32.0$, $C_{quat.}$); 24.97 (*s*, (CH_3)C); 5.5 (*d*, $^1J(P,C) = 7.0$, PCH_2); −1.2 ($SiCH_3$). $^{31}P\{^1H\}$-NMR ($CDCl_3$/r.t.): 26.83 (br. *s*).

(RRR)-MeSi[CH$_2$P(t-Bu)Ph]$_3$ (**1**). Phosphine-borane **3** (270 mg, 0.434 mmol) was dissolved in 3 ml of degassed morpholine. The soln. was heated to 100° in a closed system for 2 h. The solvent was evaporated *in vacuo*, and the white solid was dissolved in hot MeOH. The soln. was then cooled to −30°, filtered under Ar and afforded 170 mg (67%) of pure **1**. The solid should be stored under Ar as it is very air-sensitive. $[\alpha]_D^{25} = +39.272$ (*c* = 0.55, CH_2Cl_2). ^{1}H-NMR (C_6D_6/r.t.): 7.5–7.0 (*m*, 15 arom. H); 1.31 (*d*, $^2J(H,H) = 14.0$, 3 H, CH_AH_B); 0.98 (*d*, 3 H, CH_AH_B); 0.92 (*d*, $^3J(P,H) = 12$, 3 $(CH_3)_3C$); −0.303 (*s*, $SiCH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$/r.t.): 137.6 (*d*, $^1J(P,C) = 20.1$, C_{ipso}); 134.6 (*d*, $^2J(P,C) = 11.1$, C_{ortho}); 129.0 (*s*, C_{para}); 128.3 (*d*, $^3J(P,C) = 11.9$, C_{meta}); 29.2 (*d*, $^1J(P,C) = 16.8$, $C_{quat.}$); 27.0 (*d*, $^2J(P,C) = 15.2$, (CH_3)C); 6.3 (*dt*, $^1J(P,C) = 35.0$, $^3J(P,C) = 5.3$, PCH_2); 0.2 (*q*, $^2J(P,C) = 3.7$, $SiCH_3$). $^{31}P\{^1H\}$-NMR ($CDCl_3$/r.t.): −5.72 (br. *s*).

*[Rh(NBD)((RRR)-**1**)](OTf)* (**4**). AgOTf (171 mg, 0.668 mmol) was added to a stirred soln. of 154 mg of $[Rh_2Cl_2(NBD)_2]$ (0.334 mmol) in 30 ml degassed acetone. After 15 min, the precipitate was allowed to settle. The pale yellow soln. was reverse-filtered under Ar into a cooled (−78°) 10 ml of acetone suspension of **1** (388 mg, 0.668 mmol). The resulting orange soln. was allowed to warm to r.t. and stirred for 1 h. Finally, it was concentrated under reduced pressure to afford a deep orange solid which was filtered off and dried *in vacuo*. Recrystallization was accomplished by dissolving the crude product (670 mg) in 5 ml of degassed acetone, and overlayered with 30 ml of Et_2O. Slow diffusion afforded 534 mg of crystalline **4** (86%). The crystals were suitable for X-ray diffraction. $[\alpha]_D^{25} = -77.8$ (*c* = 1, CH_2Cl_2). Satisfactory C and H microanalyses were obtained. ^{1}H-NMR ((D$_6$)acetone/r.t.): 7.9–7.45 (*m*, 15 arom. H); 4.67 (br. *s*, 2, bridgehead CH); 4.52 (br. *s*, 2 olefinic CH); 3.89 (br. *s*, 2, olefinic CH); 1.76 (*dd*, $^2J(P,H) = 9.8$, $^2J(H,H) = 14.7$, 3 H, PCH_AH_B); 1.50 (*s*, bridging CH_2); 1.10 (*dd*, $^2J(P,H) = 6.47$, 3 H, PCH_AH_B); 0.76 (*s*, $SiCH_3$); 0.48 (*d*, $^3J(P,H) = 12.9$, 3 $PC(CH_3)_3$). $^{13}C\{^1H\}$-NMR ((D$_6$)acetone/r.t.): 136.5 (br. *s*, C_{ipso}); 132.7 (br. *s*, C_{ortho}); 129.8 (br. *s*, C_{meta}); 128.3 (br. *s*, C_{para}); 62.0 (br. *s*, C_{bridge}); 46.8 (br. *s*, $C_{bridgehead}$); 42.4 (br. *s*, C_{olefin}); 40.1 (br. *s*, C_{olefin}); 26.4 (br. *s*, $(CH_3)_3C$); 23.4 (br. *s*, $C_{quat.}$); 2.3 (br. *s*, PCH_2); −0.6 (br. *s*, $SiCH_3$). $^{31}P\{^1H\}$-NMR ((D$_6$)acetone/r.t.): 1.9 (*d*, $^1J(Rh, P) = 108$).

X-Ray Crystal-Structure Determinations. **3**: *STOE-Picker* four-circle diffractometer; Mo*Kα*; r.t.; $3° \leq 2\Theta \leq 35°$; space group $P2_12_12_1$, orthorhombic, $a = 19.85$ (2) Å, $b = 13.051$ (9) Å, $c = 15.91$ (2) Å; $V = 4119.77$ Å^3; $Z = 4$; 3026 reflections of which 2327 were observed ($I \geq 6\sigma(I)$); solution of the crystal structure with the SHELXTL-Plus System; anisotropic refinement of Si and P, all other atoms were refined isotropically, the calculated position was used for the H-atoms (C–H 0.96 Å); $R = 0.1142$, $R_w = 0.1528$ (185 parameters). More details of the crystal structure determination can be obtained from the authors upon request.

4·2$(CH_3)_2CO$: Monoclinic, $P2_1$, $a = 12.863$ (10) Å, $b = 13.184$ (4) Å, $c = 28.438$ (8) Å; $\beta = 94.89$ (4)°; $V = 4805$ (5) Å^3; $Z = 4$. Data were collected at r.t. on a *CAD4* diffractometer (Mo*Kα*) up to $2\Theta \leq 48°$ using a $\omega/2\Theta$ scan, with variable scan speed to insure constant precision of the collected intensities. 7858 reflections (corrected for absorption: transmission factors in the range 0.9991–0.7646) were collected of which 4934 were considered as observed ($F_0 \geq 3.0\,\sigma(F_o)$) and used for the solution (direct and *Fourier* methods). The structure was refined by full-matrix least squares using anisotropic temp. factors for the Rh-, Si-, P-atoms and for the C-atoms of the Siliphos cage. The NBD ligand is disordered, and it has not been possible to refine a meaningful model for the olefin. Two disordered molecules of acetone were located, and their contribution was included but not refined. The final conventional *R* factor is 0.095 (for the observed reflections). More details of the crystal structure determination can be obtained from the authors upon request.

REFERENCES

[1] G. B. Consiglio, results reported in J. Ott, Dissertation No. 8000, ETH Zürich, 1986; C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, *Organometallics* **1990,** *9,* 226; E. G. Thaler, K. Folting, K. G. Caulton, *J. Am. Chem. Soc.* **1990,** *112,* 2664.

[2] J. Ott, Dissertation No. 8000, ETH-Zürich, 1986; C. Bianchini, A. Meli, F. Laschi, J. A. Ramirez, P. Zanello, A. Vacca, *Inorg. Chem.* **1988,** *27,* 4429.

[3] J. Ott, G. M. Ramos Tombo, B. Schmid, L. M. Venanzi, G. Wang, T. R. Ward, *Tetrahedron Lett.* **1989,** *30,* 6151; *New J. Chem.* **1990,** *14,* 495.

[4] H. B. Kagan, J. Fiaud, in 'Topics in Stereochemistry', Wiley-Interscience, New York, 1978, Vol. 10.

[5] J. K. Whitesell, *Chem. Rev.* **1989,** *89,* 1581; H. B. Kagan, in 'Asymmetric Synthesis', Academic Press, New York, 1985, Vol. 5, Chapt. 1; H. Brunner, *J. Organomet. Chem.* **1986,** *300,* 39.

[6] C. Bolm, W. M. Davis, R. L. Halterman, K. B. Sharpless, *Angew. Chem. Int. Ed.* **1988,** *27,* 835; *Angew. Chem.* **1988,** *100,* 882; C. Bolm, K. B. Sharpless, *Tetrahedron Lett.* **1988,** *29,* 5101; B. Bogdanovic, B. Henc, B. Meister, H. Pauling, G. Wilke, *Angew. Chem. Int. Ed.* **1972,** *11,* 1023; *Angew. Chem.* **1972,** *84,* 1070.

[7] M. J. Burk, R. L. Harlow, *Angew. Chem. Int. Ed.* **1990,** *29,* 1647; *Angew. Chem.* **1990,** *102,* 1511.

[8] T. Imamoto, T. Kusumoto, N. Suzuki, K. Sato, *J. Am. Chem. Soc.* **1985,** *107,* 5301; T. Imamoto, T. Oshiki, T. Onosawa, T. Kusumoto, K. Sato, *ibid.* **1990,** *112,* 5422.

[9] H. H. Karsch, A. Appelt, *Z. Naturforsch., B* **1983,** *38,* 1399.

[10] J. M. Boncella, M. L. H. Green, D. O'Hare, *J. Chem. Soc., Chem. Commun.* **1986,** 618.

[11] F. Bachechi, J. Ott, L. M. Venanzi, *Acta Crystallogr., Sect. C* **1989,** *45,* 724.