

The solid-state structure of bis(pentafluorophenyl)zinc

Yimin Sun, Warren E. Piers, and Masood Parvez

Abstract: Using the published method of Wiedenbruch, bis(pentafluorophenyl)zinc, **1**, was prepared from anhydrous ZnCl_2 and 2 equiv. of LiC_6F_5 in diethyl ether. Base-free **1** was obtained in 60–65% yield by repeated distillation of the initially formed bis(diethyl) ether adduct of **1**. The X-ray quality crystals of **1** were obtained from benzene solution. The molecular structure of **1** revealed a near linear geometry for the two-coordinate zinc center ($\text{C}(1)\text{-Zn-C}(7) = 172.6(2)^\circ$), typical of monomeric ZnR_2 derivatives. In the crystal structure, stacking interactions between C_6F_5 rings on adjacent molecules is a dominant motif, with ring centroid to ring centroid distances of 3.503 and 3.563 Å observed. A weak intermolecular $\text{C-F}\cdots\text{Zn}$ interaction between F(2) and an adjacent zinc center, as judged by the close contact of 2.849(2) Å, also appears to be an important aspect of the crystal structure. Compound **1** is an effective but nonselective C_6F_5 transfer agent to BCl_3 ; **1**: monoclinic, space group $P2_1/n$, $a = 11.902(2)$ Å, $b = 7.732(2)$ Å, $c = 13.735(2)$ Å, $\beta = 110.58(1)^\circ$, $V = 1183.4(4)$ Å³, $Z = 4$, $R = 0.048$, $R_w = 0.069$.

Key words: organozinc complex, pentafluorophenyl transfer agent.

Résumé : En faisant appel à la méthode non publiée de Wiedenbruch, on a préparé le bis(pentafluorophényl)zinc, **1**, à partir du ZnCl_2 et de deux équivalents de LiC_6F_5 dans l'éther. On a obtenu le composé **1** sous la forme de base libre avec un rendement de 60 à 65% en procédant à la distillation répétée de l'adduit formé initialement du composé **1** avec deux molécules d'éther. À partir d'une solution de benzène, on a obtenu des cristaux de **1** pouvant être utilisés pour études par diffraction des rayons X. La structure moléculaire du composé **1** révèle que ce composé présente une géométrie pratiquement linéaire pour le zinc central bicoordiné ($\text{C}(1)\text{-Zn-C}(7) = 172,62(2)^\circ$) typique de dérivés ZnR_2 monomères. Dans la structure cristalline, les interactions d'empilement entre les noyaux C_6F_5 de molécules adjacentes correspondent au motif dominant et on observe des distances 3,503 et de 3,563 Å entre les centroïdes de noyaux. Il semble qu'une faible interaction intermoléculaire $\text{C-F}\cdots\text{Zn}$ entre F(2) et le zinc central adjacent, détectée par un contact de 2,849(2) Å, correspond à un aspect important de la structure. Le composé **1** est un agent de transfert efficace, mais non sélectif, de C_6F_5 vers le BCl_3 . Le composé est monoclinique, groupe d'espace $P2_1/n$, avec $a = 11,902(2)$ Å, $b = 7,732(2)$ Å et $c = 13,735(2)$ Å, $\beta = 110,58(1)^\circ$, $V = 1183,4(4)$ Å³, $Z = 4$, $R = 0,048$ et $R_w = 0,069$.

Mots clés : complexe organozincique, agent de transfert de pentafluorophényle.

[Traduit par la rédaction]

Introduction

The increasing commercial importance of $\text{B}(\text{C}_6\text{F}_5)_3$ (**1**) has stimulated interest in other perfluorinated boranes (**2**). The robust nature of the $\text{B}-\text{C}_6\text{F}_5$ bond and the heightened Lewis acidity, which the C_6F_5 group confers upon the boron center, contributes to the utility of these compounds. Increasingly, bis(pentafluorophenyl) boranes of general formula $\text{X}[\text{B}(\text{C}_6\text{F}_5)_2]_n$ are finding utility as catalysts or reagents in organic synthesis ($\text{X} = \text{OH}$, $n = 1$ (**3**); $\text{X} = \text{H}$, $n = 1$ (**4**)) and as alternative co-catalysts in homogeneous olefin polymerization ($\text{X} = t\text{-C}_4\text{H}_9\text{CH}_2\text{CH}$, $n = 2$ (**5**)).

The syntheses of such compounds is not, however,

straightforward at this point. For example, the borane $\text{HB}(\text{C}_6\text{F}_5)_2$ and the boronic acid $\text{HOB}(\text{C}_6\text{F}_5)_2$ both rely on the chloroborane $\text{ClB}(\text{C}_6\text{F}_5)_2$ as a starting material. While a reliable published procedure for the preparation of this compound exists (**6**), it is not ideal in that it depends on the organotin compound $\text{Me}_2\text{Sn}(\text{C}_6\text{F}_5)_2$ as a reagent capable of selectively delivering two C_6F_5 groups to BCl_3 . The tedious procedures necessary for separating Me_2SnCl_2 completely from the chloroborane product and concerns around the handling of this volatile organotin by-product have led us to explore other reagents for C_6F_5 transfer to boron. While testing the known compound bis(pentafluorophenyl)zinc, **1**, as a possible reagent for preparing $\text{ClB}(\text{C}_6\text{F}_5)_2$, we obtained its molecular structure, which had not previously been determined.

Results and discussion

To our knowledge, four routes to $\text{Zn}(\text{C}_6\text{F}_5)_2$, **1**, have been published (eqs. [1]–[4]). The original preparation of **1** utilized the Grignard reagent BrMgC_6F_5 for introducing the pentafluorophenyl groups to ZnCl_2 , by refluxing in toluene for 2 h after an initial contact of the reagents in diethyl ether solution

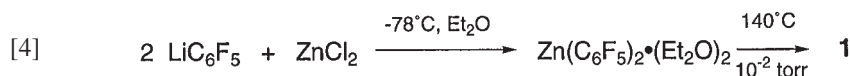
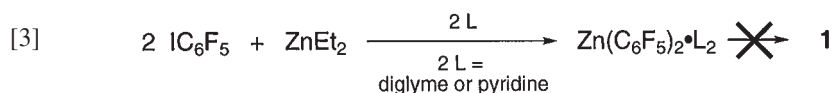
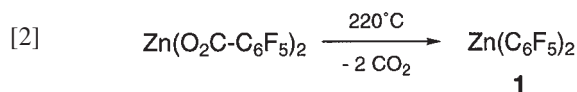
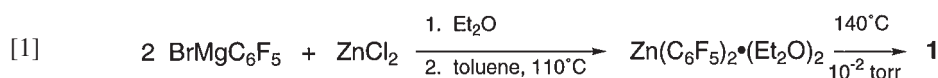
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Y. Sun, W.E. Piers,¹ and M. Parvez. Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, AB T2N 1N4, Canada.

¹ Fellow of the Alfred P. Sloan Foundation, 1996–1998.

Author to whom correspondence may be addressed.

Telephone: (403) 220-5746. Fax: (403) 289-9488. E-mail: wpiers@chem.ucalgary.ca.



(7). The crude product mixture contained the ether adduct of **1**, which was isolated base-free by distillation of $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot (\text{Et}_2\text{O})_2$ under high vacuum at 140°C , resulting in a 15% yield of $\text{Zn}(\text{C}_6\text{F}_5)_2$. However, significant amounts of an unidentified colorless liquid by-product was also produced in this reaction.

In our hands, this procedure produced very little $\text{Zn}(\text{C}_6\text{F}_5)_2$ but large amounts of the liquid by-product, which we identified as an isomeric mixture of the Diels–Alder products formed upon reaction with tetrafluorobenzene and toluene.² It is not clear which species in the reaction mixture is the source of tetrafluorobenzene but, given the thermal stability of **1** itself, it is likely to be an intermediate in this process or perhaps BrMgC_6F_5 . In a second route to **1**, loss of CO_2 from the dicarboxylate compound $\text{Zn}(\text{O}_2\text{CC}_6\text{F}_5)_2$ (eq. [2]) provides the driving force for relatively clean formation of **1** directly (8). Third, eq. [3] represents a relatively safe route to pentafluorophenyl zinc derivatives, but the bases employed in the published procedure (9) are not easy to remove; for our purposes, we must have base free **1**.

Despite the potential hazards associated with the more reactive reagent pentafluorophenyllithium, we turned to the fourth procedure, also developed by Weidenbruch (8), which produces **1** much more cleanly (eq. [4]). A diethyl ether solution of ZnCl_2 was added to in situ generated $\text{C}_6\text{F}_5\text{Li}$, and the resulting mixture was allowed to warm slowly to room temperature. Work-up led to base-free **1**, which gave a ^{19}F NMR spectrum essentially identical to that reported, with no trace of the Diels–Alder by-product in evidence. For larger scale preparations (>2 g), multiple distillations were required to fully remove the diethyl ether, which was judged complete when the distillate was a free-flowing powder as opposed to the oily white solid characteristic of **1** contaminated with its ether adduct.

While a few Lewis base adducts $\mathbf{1} \cdot \text{L}_2$ have been structurally characterized ($\text{L} = \text{THF}$ (10); tetramethyltetrazene (11)), that of base free **1** has not. We therefore obtained X-ray quality crystals of **1** and evaluated its solid-state structure; an ORTEP diagram is shown in Fig. 1, while metrical parameters are given in Table 1, and atomic coordinates are given in Table 2. Two coordinate organozinc compounds are typically

monomeric with linear geometries (12), and most of those whose structures have been determined bear this out (13). The exception is diphenylzinc (13a), which is dimeric in the solid state by virtue of an interaction between an ipso carbon of one σ -bound phenyl group and the zinc center of another $\text{Zn}(\text{C}_6\text{H}_5)_2$ unit. This interaction was rationalized as being akin to an electrophilic attack on the zinc phenyl group by an adjacent Lewis acidic zinc center. This feature is not replicated in the structure of perfluoro diphenylzinc, **1**, presumably because the C_6F_5 groups are much less susceptible to electrophilic attack even though the zinc centers must also be more powerful electrophiles.

Thus, in contrast to its perproteo cousin, **1** behaves like most other ZnR_2 derivatives and is monomeric in the solid state with with C(1)–Zn–C(7) approaching ideal linearity at $172.6(2)^\circ$. The Zn–C bonds in **1** are typical of ZnR_2 compounds, which range from 1.93–1.95 Å in compounds where R is not sterically bulky. These lengths are slightly shorter than those found in four coordinate $\text{Zn}(\text{C}_6\text{F}_5)_2 \cdot \text{L}_2$ compounds (cf. Zn–C lengths of 1.999(4) and 2.102(3) Å in $\text{Zn}(\text{C}_6\text{F}_5)_2(\text{THF})_2$ (10). The two C_6F_5 rings in **1** are almost orthogonal to one another, with an angle between the planes of the aromatic rings of $76.7(2)^\circ$. This compares to 67.1° for the same parameter in $\text{Zn}[2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_3]_2$ (13c).

In addition to alleviating intramolecular steric interactions between the C_6F_5 rings, the orthogonality of the C_6F_5 rings in **1** allows for intramolecular stacking interactions between rings on adjacent molecules in the crystal structure of the compound. These stacking interactions engender a layered structure in the crystal; Fig. 2 shows a chemical 3-D representation of the molecular arrangement in the crystal looking down on a portion of one layer (A) and from the side (B). The distances between the centroids of each C_6F_5 ring and its stacking partner are 3.503 and 3.563 Å, similar to the ring separations observed in stacking interactions between phenyl and pentafluorophenyl rings (14). Between the layers, a weak interaction between one of the meta fluorines, F(2), and a Zn center of an adjacent molecule may be present, as judged by the intermolecular separation of 2.849(2) Å. Although this is at the long end of the range (2.532(6)–2.733(6) Å) of previously observed intramolecular C–F...Zn interactions (15), the intermolecular nature of the contact here might be expected to be slightly longer. Furthermore, the distance is within the sum of the van der

² D.J. Parks and W.E. Piers. Unpublished results.

Fig. 1. An ORTEP drawing of $\text{Zn}(\text{C}_6\text{F}_5)_2$, **1** (thermal ellipsoid probability = 50%).

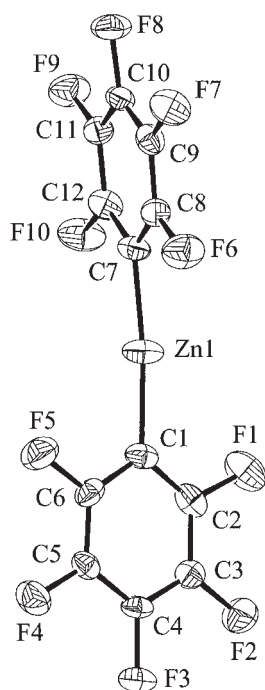
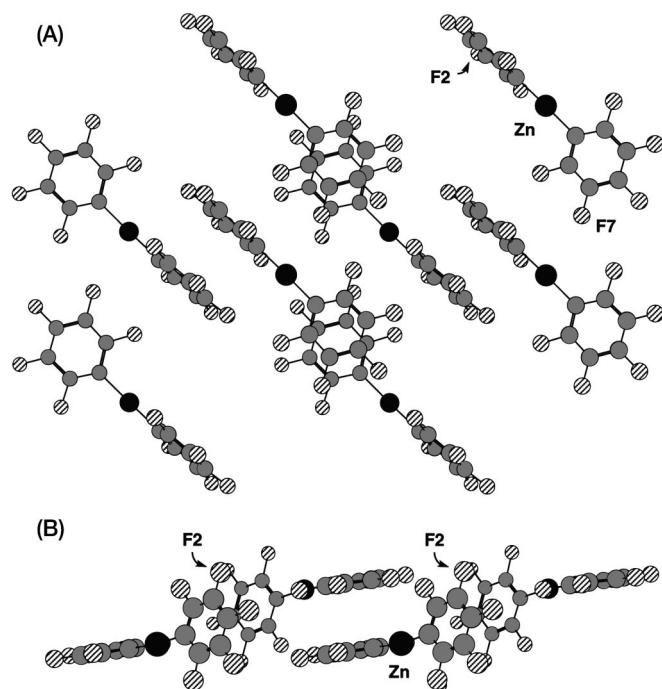


Fig. 2. Two views of the molecular arrangement of $\text{Zn}(\text{C}_6\text{F}_5)_2$ molecules in the crystal structure of **1**. (A) View looking down on one of the layers of stacked $\text{Zn}(\text{C}_6\text{F}_5)_2$ molecules. (B) Side view of layer shown in A.



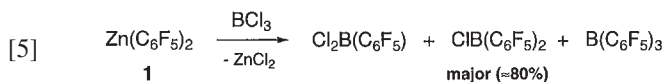
Waals radii(16) for fluorine (1.50–1.60 Å) and zinc (1.40 Å). The fact that the slight bend in the C(1)–Zn–C(7) angle is oriented away from the C(3)–F(2) vector is further evidence in favor of this interaction. The tendency of ZnR_2 complexes to

Table 1. Bond distances and angles for $\text{Zn}(\text{C}_6\text{F}_5)_2$, **1**.

Bond lengths (Å)			
Zn(1)—C(1)	1.930(4)	C(1)—C(2)	1.382(5)
Zn(1)—C(7)	1.926(4)	C(1)—C(6)	1.379(5)
F(1)—C(2)	1.358(4)	C(2)—C(3)	1.370(5)
F(2)—C(3)	1.343(4)	C(3)—C(4)	1.384(5)
F(3)—C(4)	1.340(4)	C(4)—C(5)	1.371(5)
F(4)—C(5)	1.347(4)	C(5)—C(6)	1.364(5)
F(5)—C(6)	1.360(4)	C(7)—C(8)	1.385(5)
F(6)—C(8)	1.361(4)	C(7)—C(12)	1.370(5)
F(7)—C(9)	1.344(4)	C(8)—C(9)	1.367(5)
F(8)—C(10)	1.339(4)	C(9)—C(10)	1.378(5)
F(9)—C(11)	1.344(4)	C(10)—C(11)	1.371(5)
F(10)—C(12)	1.354(4)	C(11)—C(12)	1.378(5)
Bond angles (°)			
C(1)—Zn(1)—C(7)	172.6(2)	Zn(1)—C(7)—C(8)	121.5(3)
Zn(1)—C(1)—C(2)	126.2(3)	Zn(1)—C(7)—C(12)	123.8(3)
Zn(1)—C(1)—C(6)	119.2(3)	C(8)—C(7)—C(12)	114.7(3)
C(2)—C(1)—C(6)	114.6(3)	F(6)—C(8)—C(7)	119.1(3)
F(1)—C(2)—C(1)	120.0(3)	F(6)—C(8)—C(9)	116.9(4)
F(1)—C(2)—C(3)	116.4(3)	C(7)—C(8)—C(9)	123.9(4)
C(1)—C(2)—C(3)	123.6(3)	F(7)—C(9)—C(8)	121.4(3)
F(2)—C(3)—C(2)	122.1(3)	F(7)—C(9)—C(10)	119.8(3)
F(2)—C(3)—C(4)	118.9(3)	C(8)—C(9)—C(10)	118.8(4)
C(2)—C(3)—C(4)	119.0(3)	F(8)—C(10)—C(9)	120.0(3)
F(3)—C(4)—C(3)	120.1(3)	F(8)—C(10)—C(11)	120.1(3)
F(3)—C(4)—C(5)	120.3(3)	C(9)—C(10)—C(11)	119.8(3)
C(3)—C(4)—C(5)	119.6(3)	F(9)—C(11)—C(10)	119.5(3)
F(4)—C(5)—C(4)	119.6(3)	F(9)—C(11)—C(12)	121.6(4)
F(4)—C(5)—C(6)	121.4(3)	C(10)—C(11)—C(12)	118.9(3)
C(4)—C(5)—C(6)	119.0(3)	F(10)—C(12)—C(7)	119.1(3)
F(5)—C(6)—C(1)	118.7(3)	F(10)—C(12)—C(11)	117.1(3)
F(5)—C(6)—C(5)	117.0(3)	C(7)—C(12)—C(11)	123.8(4)
C(1)—C(6)—C(5)	124.3(3)		

coordinate Lewis bases is thus partially satisfied in the crystal structure of “base free” **1** through this intermolecular contact.³

As expected, **1** rapidly reacts with Lewis bases to form **1**-L₂ adducts in toluene solution. For example, the known adducts of diethyl ether (8, 10) and THF (10) can be generated quantitatively upon treatment with these solvents. Base free, **1** is an efficient C_6F_5 transfer agent, although it does not react selectively with BCl_3 (eq. [5]). Unfortunately, inseparable mixtures of $\text{Cl}_2\text{B}(\text{C}_6\text{F}_5)$, $\text{ClB}(\text{C}_6\text{F}_5)_2$, and $\text{B}(\text{C}_6\text{F}_5)_3$ were formed when **1** was reacted with 1 equiv. of BCl_3 under various conditions, a similar situation to that observed in the reaction of $\text{C}_6\text{F}_5\text{Li}$ with BCl_3 . Thus, **1** is too reactive to be a suitable reagent for selective formation of $\text{ClB}(\text{C}_6\text{F}_5)_2$; however, it has promise as a C_6F_5 transfer agent to compounds of general formula RBCl_2 . We will report on its utility in this capacity in due course.



³ The second closest contact between the zinc centers and a fluorine atom is that of meta fluorine F(7) at 3.200(3) Å. This interaction occurs within the layers mentioned in the text; however, due to the rather large separation, caution must be employed in interpreting this interaction as the second incipient zinc/base interaction.

Table 2. Atomic coordinates x , y , z and B_{eq} for $\text{Zn}(\text{C}_6\text{F}_5)_2$, **1**.

Atom	x	y	z	B_{eq}^a
Zn(1)	0.15686(4)	0.12335(6)	0.89789(4)	3.33(1)
F(1)	0.2482(2)	-0.1429(3)	0.7609(2)	4.30(6)
F(2)	0.4394(2)	-0.3549(3)	0.8233(2)	3.77(6)
F(3)	0.5844(2)	-0.3629(3)	1.0255(2)	3.16(5)
F(4)	0.5285(2)	-0.1749(3)	1.1691(2)	3.62(5)
F(5)	0.3401(2)	0.0414(3)	1.1082(2)	3.81(6)
F(6)	0.1779(2)	0.5214(3)	0.9004(2)	4.08(6)
F(7)	0.0128(2)	0.7687(3)	0.8797(2)	3.89(6)
F(8)	-0.2165(2)	0.6805(3)	0.8550(2)	3.71(6)
F(9)	-0.2816(2)	0.3437(3)	0.8438(2)	3.97(6)
F(10)	-0.1162(2)	0.0942(3)	0.8647(2)	4.21(6)
C(1)	0.2857(3)	-0.0434(5)	0.9330(3)	2.54(8)
C(2)	0.3156(3)	-0.1471(5)	0.8638(3)	2.63(8)
C(3)	0.4127(3)	-0.2559(5)	0.8925(3)	2.48(8)
C(4)	0.4857(3)	-0.2637(4)	0.9962(3)	2.26(8)
C(5)	0.4581(3)	-0.1662(5)	1.0681(3)	2.29(8)
C(6)	0.3612(3)	-0.0585(5)	1.0350(3)	2.45(8)
C(7)	0.0360(3)	0.2976(5)	0.8817(3)	2.54(8)
C(8)	0.0628(3)	0.4722(5)	0.8836(3)	2.66(9)
C(9)	-0.0189(3)	0.6011(5)	0.8744(3)	2.40(8)
C(10)	-0.1357(3)	0.5569(5)	0.8606(3)	2.43(8)
C(11)	-0.1676(3)	0.3860(5)	0.8568(3)	2.60(8)
C(12)	-0.0815(3)	0.2613(5)	0.8667(3)	2.73(9)

$$^a B_{\text{eq}} = (8/3)\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha].$$

Experimental

General procedures have been presented in detail elsewhere (17). Pentafluorobromobenzene and zinc dichloride were purchased from Aldrich Chemicals. The former was used without further purification, while the latter was rendered completely anhydrous by refluxing in dry dioxane along with zinc dust. The suspension was filtered hot and cooled; the resulting crystalline ZnCl_2 -dioxane adduct was isolated by filtration and exposed to high vacuum at 110°C for several hours to liberate the coordinated dioxane.

Preparation of **1**

A procedure similar to that reported earlier by Sartori and Weidenbruch (8) was employed to generate $\mathbf{1}\cdot(\text{OEt}_2)_2$. (CAUTION! Do not allow solutions of $\text{C}_6\text{F}_5\text{Li}$ to warm above -40°C ; spontaneous elimination of LiF is possible above this temperature.) The only modification involved quenching the reaction with a small amount of methanol ($\approx 1\text{--}2\%$) to ensure that no $\text{C}_6\text{F}_5\text{Li}$ remained for the workup procedure. For smaller scale reactions ($\approx 0.5\text{--}1.0$ g), distillation of $\mathbf{1}\cdot(\text{OEt}_2)_2$ at 140°C and high vacuum was sufficient to completely remove the ether. For larger scale preparations (>2 g), multiple distillations were required to generate pure **1**. This was most conveniently accomplished by repeatedly subliming the material in a long glass tube. Loss of the oily appearance of the sublimate signalled the complete removal of ether. The material thus obtained had essentially identical ^{19}F NMR data as that reported previously for **1** by Weidenbruch et al. (10).

X-ray determination of **1**

A suitable crystal was affixed to a glass fiber with epoxy resin and mounted onto a Rigaku AFC6S diffractometer. A

Table 3. Summary of data collection and structure refinement details for $\text{Zn}(\text{C}_6\text{F}_5)_2$, **1**.

Formula	$\text{ZnC}_{12}\text{F}_{10}$
fw	399.50
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a , Å	11.902(2)
b , Å	7.732(2)
c , Å	13.735(2)
β , °	110.58(1)
V , Å ³	1183.4(4)
Z	4
d_{calc} , mg m ⁻³	2.242
$F(000)$	768
μ , cm ⁻¹	22.02
T , °C	-103
Crystal dimensions, mm ³	$0.45 \times 0.40 \times 0.13$
Rel. transmission factors	0.71–1.0000
Scan type	$\omega - 2\theta$
Scan range, deg	$1.68 + 0.34 \tan \theta$
Scan speed, deg/min	16.0
2θ (max), deg	55.1
Unique reflections	2940
Reflections with $I > 3\sigma I$	1655
No. of variables	209
R	0.048
R_w	0.069
gof	1.72
Max. Δ/σ (final cycle)	0.00
Residual density, e/Å ³	-0.46–0.52

summary of data collection, reduction, and refinement parameters are given in Table 3. Measurements were made at 103°C using graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.39° with a take-off angle of 6.0° . For data collection, the weak reflections ($I < 10\sigma(I)$) were rescanned, and the counts were accumulated to ensure good counting statistics. No decay correction was required. The data were corrected for Lorentz, polarization, and for absorption correction by ψ scans of a few reflections (18). A correction for secondary extinction was also applied (coefficient = 5.11673×10^{-6}) (19). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4(F_o)^2]^{-1}$ and the p -factor was 0.0200. The final cycle of full-matrix least-squares refinement converged with unweighted ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) and weighted ($R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$) agreement factors of 0.048 and 0.069, respectively. All calculations were performed using the TEXAN⁴ crystallographic software package of Molecular Structure Corporation. Anisotropic thermal parameters along with a full listing of torsion angles and nonbonded contacts to 3.60 Å are available as supplementary material.⁵

⁴ Crystal structure analysis package, Molecular Structure Corporation, 1985 and 1992.

⁵ Supplementary material may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

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References

1. (a) A.G. Massey and A.J. Park. *J. Organomet. Chem.* **2**, 245 (1964); (b) W.E. Piers and T. Chivers. *Chem. Soc. Rev.* 345 (1997).
2. Y.-X. Chen, C.L. Stern, S. Yang, and T.J. Marks. *J. Am. Chem. Soc.* **118**, 12 451 (1996).
3. K. Ishihara, H. Kurihara, and H. Yamamoto. *J. Org. Chem.* **62**, 5664 (1997).
4. D.J. Parks, R.E.v.H. Spence, and W.E. Piers. *Angew. Chem. Int. Ed. Engl.* **34**, 809 (1995).
5. L. Jia, X. Yang, C. Stern, and T. J. Marks. *Organometallics*, **13**, 3755 (1994).
6. R.D. Chambers and T. Chivers. *J. Chem. Soc.* 3933 (1965).
7. J.G. Noltes and J.W.G. Vanden Hurk. *J. Organomet. Chem.* **1**, 377 (1964).
8. P. Sartori and M. Weidenbruch. *Chem. Ber.* **100**, 3016 (1967).
9. H. Lange and D. Naumann. *J. Fluorine Chem.* **26**, 435 (1984).
10. M. Weidenbruch, M. Herrndorf, A. Schäfer, S. Pohl, and W. Saak. *J. Organomet. Chem.* **361**, 139 (1989).
11. V.W. Day, D.H. Campbell, and C.J. Michejda. *J. Chem. Soc. Chem. Commun.* 118 (1975).
12. J. Boersma. *In Comprehensive organometallic chemistry*. Vol. 2. Edited by G. Wilkinson. Pergamon, Oxford, U.K. 1982. p. 823.
13. (a) P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, and A.L. Spek. *Organometallics*, **9**, 2243 (1990), and refs. therein; (b) M. Westerhausen, B. Rademacher, and W. Pohl. *J. Organomet. Chem.* **421**, 175 (1991); (c) S. Brooker, N. Bertel, D. Stalke, M. Noltemeyer, H.W. Roesky, G.M. Sheldrick, and F.T. Edelman. *Organometallics*, **11**, 192 (1992).
14. G.W. Coates, A.R. Dunn, L.M. Henling, D.A. Dougherty, and R.H. Grubbs. *Angew. Chem. Int. Ed. Engl.* **36**, 248 (1997), and refs. therein; J.H. Williams. *Acc. Chem. Res.* **26**, 593 (1993).
15. H. Plenio. *Chem. Rev.* **97**, 3363 (1997).
16. A. Bondi. *J. Phys. Chem.* **68**, 441 (1964).
17. Y. Sun, R.E.v.H. Spence, W.E. Piers, M. Parvez, and G.P.A. Yap. *J. Am. Chem. Soc.* **119**, 5132 (1997).
18. A.C.T. North, D.C. Phillips, and F.S. Matthews. *Acta Cryst.* **A24**, 351 (1968).
19. W. H. Zachariasen. *Acta Crystallogr. Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **A24**, 212 (1968).