Pergamon

Tetrahedron: *Asymmetry* 11 (2000) 4877–4883

TETRAHEDRON:
ASYMMETRY

Synthesis, isolation and structural characterization of optically active planar chiral cyclomercurated ferrocenylimines

Yangjie Wu,[a,]* Xiuling Cui,[a] Ning Zhou,[a] Maoping Song,[a] Hongying Yun,[a] Chenxia Du[b] and Yu Zhu[b]

[a]*Department of Chemistry, Zhengzhou University, Zhengzhou 450052, PR China*
[b]*Henan Provincial Laboratory of Applied Chemistry, Zhengzhou University, Zhengzhou 450052, PR China*

Received 2 October 2000; accepted 27 November 2000

Abstract

Asymmetric cyclomercuration of chiral ferrocenylimines (+)-(*R*)-**2** and (–)-(*S*)-**2** with mercuric acetate and subsequent treatment by lithium chloride gave two different pairs of diastereomeric cyclomercurated ferrocenylimines. The four enantiomerically pure compounds with both planar and central chirality were isolated from the two pairs by thin layer chromatography. The structures and absolute configurations of these complexes were determined by single-crystal X-ray analysis and characterized by IR, ^{1}H NMR, specific rotation and elemental analysis. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

During the last two decades, 1,2-disubstituted chiral ferrocene derivatives have been of great interest as a result of their useful application in areas such as organic synthesis, material science, and particularly in asymmetric catalysis.[1] This research has led to a general strategy which, as its key step, involves synthesis of chiral *ortho*-metallated ferrocene precursors bearing *ortho*-directing auxiliary groups with stereogenic centers.

Consequently, the resulting ferrocenes are diastereomers containing elements of both planar and central chirality. Recently, we have reported on the synthesis of optically active 1,2-disubstituted cyclomercurated ferrocenylimines by transmetallation reaction of the planar chiral cyclopalladated ferrocenylketimines with metallic mercury, and employed them as transmetallating reagents to synthesize the optically active cyclostannated ferrocenylimines,[2] so that the chiral *ortho*-mercurated ferrocenylimines can be used as precursors of other optically active organometallics which are usually difficult to synthesize. To the best of our knowledge, so far

---

* Corresponding author. Fax: +86-371-7979408; e-mail: wyj@mail.zzu.edu.cn

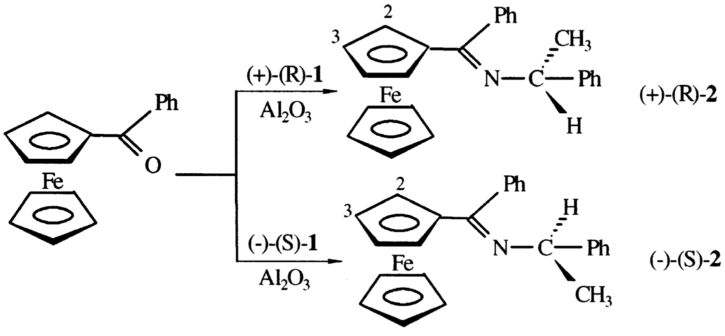
PII: S0957-4166(00)00478-X

no reports have been published dealing with direct mercuration of chiral ferrocenylimines. Synthesis and isolation of these kinds of compounds are very important for understanding the stereochemistry of similar reactions. Herein, we report on the direct *ortho*-mercuration of chiral ferrocenylimines and the determination of their absolute configurations by X-ray diffraction.

2. Results and discussion

2.1. Synthesis of chiral ferrocenylimines

Ferrocenylimines (*R*)-**2** and (*S*)-**2** were prepared by condensation of benzoylferrocene with (+)-(*R*)-α-phenylethylamine [(+)-(*R*)-**1**] and (−)-(*S*)-α-phenylethylamine [(−)-(*S*)-**1**], respectively, in dry toluene and in the presence of freshly activated Al_2O_3 (Scheme 1). The products (*R*)-**2** and (*S*)-**2** were characterized by elemental analyses, IR and ^{1}H NMR spectra.

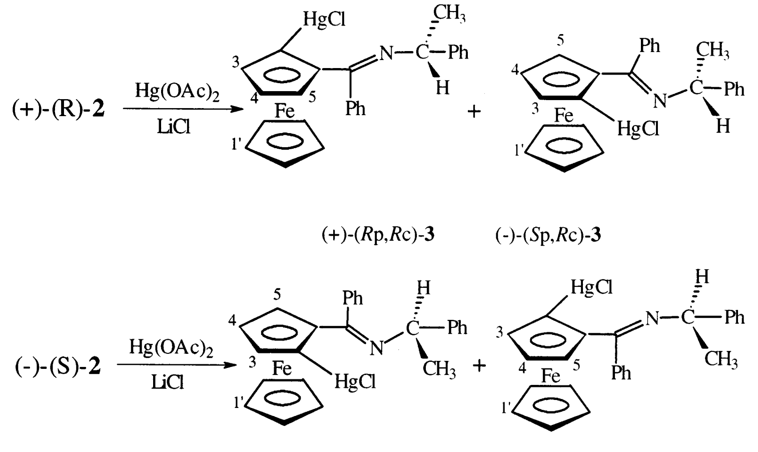


Scheme 1.

2.2. Cyclomercuration of ferrocenylimines (R)-2 and (S)-2

Cyclomercuration of (*R*)-**2** with mercuric acetate and subsequent treatment by lithium chloride at room temperature gave a pair of diastereomeric cyclomercurated products (*R*p,*R*c)-**3** and (*S*p,*R*c)-**3**. Asymmetric cyclomercuration of (*S*)-**2** by the same procedure gave another pair of diastereomers (*S*p,*S*c)-**3** and (*R*p,*S*c)-**3** (Scheme 2). The four enantiomerically pure compounds were isolated from the two pairs by preparative silica gel chromatography eluting with methylene chloride and petroleum ether (60–90°C), since the diastereomers (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3** exhibited a higher R_f value than those of the diastereomers (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3**, respectively. All of the compounds **3** were characterized by elemental analysis, IR and ^{1}H NMR spectra. The structures and absolute configurations of the four stereoisomers of compounds **3** were determined by X-ray diffraction.

The IR spectra of the C=N bond showed absorption at 1608 cm^{-1} for (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3**, and at 1603 cm^{-1} for (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3**, which were shifted to lower energy by 4 to 9 cm^{-1} in comparison with the unmercurated parent compounds **2**, indicating the presence of intramolecular N→Hg coordination.[3] The IR spectra of compounds **2** and **3** showed absorption at ca. 1000 and 1100 cm^{-1}, indicating an unsubstituted Cp ring in both compounds.[4] The ^{1}H NMR spectra of compound **3** showed that the ratio of its diastereomers was nearly 1:1 when the ^{1}H NMR spectra of the crude products were recorded prior to separation of



(+)-(*R*p,*R*c)-**3** (-)-(*S*p,*R*c)-**3**

(-)-(*S*p,*S*c)-**3** (+)-(*R*p,*S*c)-**3**

Scheme 2.

diastereomers. The chemical shifts for unsubstituted cyclopentadienyl protons and methylidyne protons of enantiomeric isomers (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3** were 4.00 and 4.61 ppm, respectively, but those of (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3** were 4.22 and 4.68 ppm, respectively. The chemical shifts for methylidyne proton shifted downfield by 0.18 ppm in enantiomeric isomers (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3**, and by 0.25 ppm in enantiomeric isomers (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3** in comparison with the starting materials **2**, exhibiting δ at 4.43 ppm for both stereoisomers. These results are attributed to the effect of intramolecular N→Hg coordination. Moreover, the signals of substituted cyclopentadienyl protons H-3, H-4 and H-5 in (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3** were 4.40, 4.43 and 4.04 ppm, respectively, and those in (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3** were 4.38, 4.47 and 4.00 ppm, respectively.

*2.3. Molecular structures and absolute configurations of (*R*p,*R*c)-**3**, (*S*p,*S*c)-**3**, (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3***

X-Ray analysis established the absolute planar chiralities of the ferrocenyl moieties on the basis of the (+)-(*R*)-phenylethylamine, (−)-(*S*)-phenylethylamine, by which the absolute configurations of (*R*p,*R*c)-**3**, (*S*p,*S*c)-**3**, (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3** were determined. (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3**, (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3** are two pairs of enantiomeric isomers, respectively. The single crystal and molecular structures of (*R*p,*R*c)-**3** and (*S*p,*R*c)-**3** are shown in Figs. 1 and 2, respectively. In all cases, the mercury atom in the metallocycle was in a slightly distorted square-planar coordination environment. The dihedral angles between the substituted Cp rings and the chelate cycle were 3.2° for (*R*p,*R*c)-**3**, 5.5° for (*S*p,*S*c)-**3**, 3.2° for (*S*p,*R*c)-**3** and 3.1° for (*R*p,*S*c)-**3**. The cyclopentadienyl rings were nearly parallel to each other (dihedral angle: 1.9° for (*R*p,*R*c)-**3**, 1.7° for (*S*p,*S*c)-**3**, 2.9° for (*S*p,*R*c)-**3** and 2.4° for (*R*p,*S*c)-**3**). The distances between N and Hg [2.774 Å for (*R*p,*R*c)-**3**, 2.741 Å for (*S*p,*S*c)-**3**, 2.757 Å for (*S*p,*R*c)-**3** and 2.763 Å for (*R*p,*S*c)-**3**] were shorter than the sum of the Van der Waals radii of N and Hg (3.05–3.15 Å),[5] which indicated a notable coordination between N and Hg. All the observed differences of crystal data between the enantiomeric isomers are within the experimental error range allowed by crystallography.

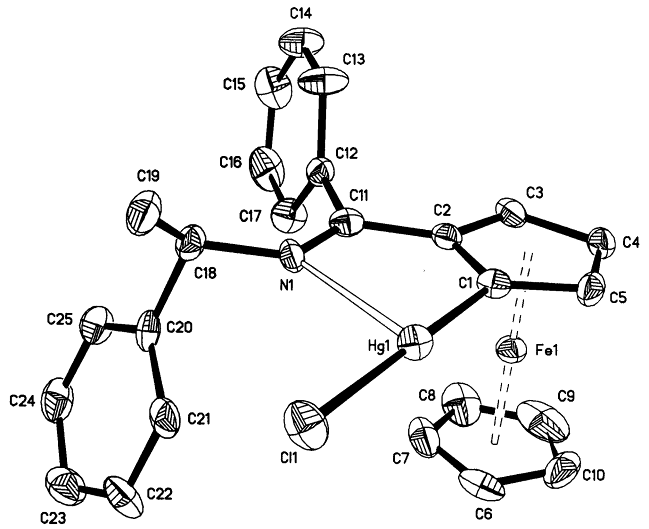


Figure 1. Perspective view of complex (*R*p,*R*c)-**3**. Selected bond distances (Å) and angles (°) are: Hg(1)–N(1), 2.774; Hg(1)–C(1), 2.017(8); C(1)–Hg(1)–Cl(1), 175.9(2); Hg(1)–C(1)–C(2), 119.7(7); C(1)–C(2)–C(11), 124.8(8); C(2)–C(11)–N(1), 117.8(7)

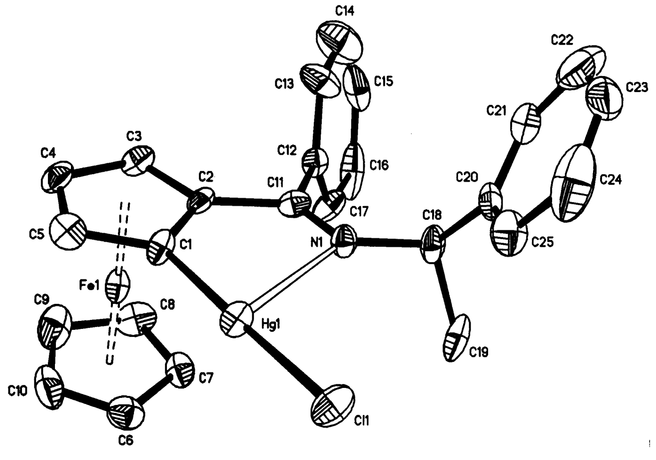


Figure 2. Perspective view of complex (*S*p,*R*c)-**3**. Selected bond distances (Å) and angles (°) are: Hg(1)–N(1), 2.757; Hg(1)–C(1), 2.016(12); C(1)–Hg(1)–Cl(1), 177.3(2); Hg(1)–C(1)–C(2), 121.3(9); C(1)–C(2)–C(11), 121.8(11); C(2)–C(11)–N(1), 119.4(11)

3. Experimental

3.1. Materials and instruments

Melting points were measured on a WC-1 apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer by using $CDCl_3$ as the solvent and TMS as an internal standard; all *J* values were in Hz. IR spectra were recorded on a Perkin–Elmer FTIR 1750 spectrophotometer. Preparative TLC was performed on dry silica gel plates developed with dichloromethane/petroleum ether. Optical rotations at 5890 Å were determined by Perkin–Elmer 341 polarimeter at 22°C.

3.2. Synthesis of chiral ferrocenylimines

Benzoylferrocene and a slight excess of (+)-(*R*)-α-phenylethylamine or (–)-(*S*)-α-phenylethylamine were refluxed in anhydrous toluene in the presence of activated alumina for about 10 hours and then filtered. The filtrate was evaporated to dryness in vacuo. Both of the optically active ferrocenylimines **2** were obtained as red oil. Characterization data for (+)-(*R*)-**2**: red oil, yield 96%, $[\alpha]_D^{22}=+151.6$ (*c* 0.6, CH_2Cl_2); IR (KBr pellet): 3080, 1612, 1445, 1102, 1000, 818 cm^{-1}. ^1H NMR (selected data): δ 4.29 (bs, 2H, H-3), 4.34 (bs, 2H, H-2); 4.12 (s, 5H, unsubstituted Cp-ring); 4.43 (q, 1H, *J*=6.4 Hz, *CH*); 1.42 (d, 3H, *J*=6.4 Hz, CH_3). Anal. calcd for $C_{25}H_{23}NFe$: C, 76.34; H, 5.89; N, 3.56. Found: C, 76.67; H, 6.03; N, 3.44. For (–)-(*S*)-**2**: red oil, yield 90%, $[\alpha]_D^{22}=-150.3$ (*c* 0.8, CH_2Cl_2); IR (KBr pellet): 3080, 1612, 1445, 1102, 1000, 819 cm^{-1}. ^1H NMR (selected data): δ 4.28 (bs, 2H, H-3), 4.34 (bs, 2H, H-2); 4.12 (s, 5H, unsubstituted Cp-ring); 4.43 (q, 1H, *J*=6.4 Hz, *CH*); 1.42 (d, 3H, *J*=6.4 Hz, CH_3). Found: C, 76.12; H, 6.08; N, 3.56.

3.3. Cyclomercuration of chiral ferrocenylimines

Details of the mercuration reaction were similar to those described previously.[6] Asymmetric cyclomercuration of (*R*)-**2** gave a mixture of diastereomeric cyclomercurated products. The mixture of diastereomers was purified by preparative silica gel plate chromatography, eluted with 1:1 (v/v) methylene chloride and petroleum ether (60–90°C). The first band contained (*R*p,*R*c)-**3**. The second band contained (*S*p,*R*c)-**3**. The third band contained a very small amount of the other mercurated product, which was not isolated for further investigation. The pure diastereomers of (*S*p,*S*c)-**3** and (*R*p,*S*c)-**3** were obtained according to the above-mentioned procedure and using (*S*)-**2** as the starting material. New compounds were characterized as follows.

3.3.1. (R*p*,R*c*)-*{HgCl(η⁵-C₅H₅)Fe[(η⁵-C₅H₃CPh=NCH(CH₃)(C₆H₅)]} (+)-(*R*p*,R*c*)-**3***

Orange red crystals, yield 22%; mp 132–133°C, $[\alpha]_D^{22}=+493.0$ (*c* 1.06, CH_2Cl_2). IR (KBr pellet): 3081, 3023, 2978, 2921, 1608, 1594, 1494, 1431, 1104, 1000, 770, 699 cm^{-1}. ^1H NMR (selected data): δ 4.40 (bs, 1H, H-3), 4.43 (bs, 1H, H-4), 4.04 (bs, 1H, H-5), 4.00 (s, 5H, H-1′), 4.61 (q, 1H, *J*=6.4 Hz, *CH*), 1.52 (d, 3H, *J*=6.4 Hz, CH_3). Anal. calcd for $C_{25}H_{22}ClFeHgN$: C, 47.78; H, 3.53; N, 2.23. Found: C, 47.78; H, 3.57; N, 2.20.

3.3.2. (S*p*,R*c*)-*{HgCl(η⁵-C₅H₅)Fe[(η⁵-C₅H₃CPh=NCH(CH₃)(C₆H₅)]} (–)-(*S*p*,R*c*)-**3***

Orange red crystals, yield 20%; mp 102–103°C, $[\alpha]_D^{22}=-661.4$ (*c* 1.01, CH_2Cl_2). IR (KBr pellet): 3081, 3024, 2957, 2923, 1603, 1592, 1491, 1430, 1106, 1001, 771, 702 cm^{-1}. ^1H NMR (selected data): δ 4.38 (d, 1H, *J*=2.4 Hz, H-3), 4.46 (t, 1H, *J*=2.4 Hz, H-4), 4.00 (d, 1H, *J*=2.4 Hz, H-5), 4.22 (s, 5H, H-1′), 4.68 (q, 1H, *J*=6.4 Hz, *CH*), 1.61 (d, 3H, *J*=6.4 Hz, CH_3). Found: C, 47.66; H, 3.38; N, 2.15.

3.3.3. (S*p*,S*c*)-{HgCl(η^5-C_5H_5)Fe{(η^5-C_5H_3CPh=NCH(CH_3)(C_6H_5)} (−)-(S*p*,S*c*)-**3**

Orange red crystals, yield 16%; mp 132–133°C, $[\alpha]_D^{22} = -493.5$ (*c* 1.07, CH_2Cl_2). IR (KBr pellet): 3080, 3023, 2978, 2921, 1608, 1595, 1492, 1431, 1104, 1000, 770, 700 cm^{-1}. ^1H NMR (selected data): δ 4.40 (d, 1H, $J=2.0$ Hz, H-3), 4.43 (t, 1H, $J=2.0$ Hz, H-4), 4.03 (d, 1H, $J=2.0$ Hz, H-5), 4.00 (s, 5H, H-1′), 4.61 (q, 1H, $J=6.4$ Hz, *CH*), 1.52 (d, 3H, $J=6.4$ Hz, CH_3). Found: C, 47.94; H, 3.55; N, 2.27.

3.3.4. (R*p*,S*c*)-{HgCl(η^5-C_5H_5)Fe[(η^5-C_5H_3CPh=NCH(CH_3)(C_6H_5)]} (+)-(R*p*,S*c*)-**3**

Orange red crystals, yield 12%; mp 102–103°C, $[\alpha]_D^{22} = +660.1$ (*c* 1.06, CH_2Cl_2). IR (KBr pellet): 3080, 3028, 2963, 2922, 1603, 1591, 1492, 1431, 1104, 1000, 769, 703 cm^{-1}. ^1H NMR (selected data): δ 4.38 (d, 1H, $J=2.0$ Hz, H-3), 4.47 (t, 1H, $J=2.0$ Hz, H-4), 4.00 (d, 1H, $J=2.0$ Hz, H-5), 4.22 (s, 5H, H-1′), 4.68 (q, 1H, $J=6.4$ Hz, *CH*), 1.61 (d, 3H, $J=6.4$ Hz, CH_3). Found: C, 47.81; H, 3.64; N, 2.43.

3.4. Crystallographic studies

Crystallographic data for (*R*p,*R*c)-**3**, (*S*p,*S*c)-**3**, (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3** measured on a Rigaku RAXIS-IV imaging plate area detector are summarized in Table 1. The data were collected at 19±1°C using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) ($3.76° < 2\theta < 54.98°$ for (*R*p,*R*c)-**3** and (*S*p,*S*c)-**3**, $3.3° < 2\theta < 55.06°$ for (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3**). The structures were solved by a direct method[7] and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package.[8]

Table 1
Crystal data for (*R*p,*R*c)-**3**, (*S*p,*S*c)-**3**, (*S*p,*R*c)-**3** and (*R*p,*S*c)-**3**[a]

	(*R*p,*R*c)-**3**	(*S*p,*S*c)-**3**	(*S*p,*R*c)-**3**	(*R*p,*S*c)-**3**
Formula	$C_{25}H_{22}ClFeHg$	$C_{25}H_{22}ClFeHg$	$C_{25}H_{22}ClFeHg$	$C_{25}H_{22}ClFeHg$
Fw	628.33	628.33	628.33	628.33
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal size (mm)	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.30	0.35 × 0.30 × 0.20
a (Å)	7.2563(15)	7.2596(15)	7.5177(15)	7.5266(15)
b (Å)	14.402(3)	14.402(3)	16.873(3)	16.903(3)
c (Å)	10.929(2)	10.922(2)	18.014(4)	18.055(4)
V ($Å^3$)	1131.8(4)	1131.2(4)	2285.1(8)	2297.1(8)
Z	2	2	4	4
F(000)	604	604	1208	1208
D_{calcd} g cm^{-3}	1.844	1.845	1.826	1.817
μ(Mo Kα) (mm^{-1})	7.544	7.547	7.473	7.434
R_1	0.0387	0.0509	0.0462	0.0568
R_w	0.0585	0.1221	0.0692	0.1004

[a] All the observed differences of crystal data between the enantiomeric isomers are within the experimental range allowed by crystallography.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Project 29572066) and the Natural Science Foundation of Henan Province for the financial support given to this research.

References

1. (a) *Ferrocenes*; Togni, A.; Hayashi, T., Eds.; VCH: Weinhein, Germany, 1995; (b) Togni, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475; (c) Bolm, C.; Muniz-Fernandez, K.; Seger, A.; Raabe, G.; Gunther, K. *J. Org. Chem.* **1998**, *63*, 7860; (d) Deng, W. P.; Hou, X. L.; Dai, L. X.; Yu, Y. H.; Xia, W. *Chem. Commun.* **2000**, 285.
2. (a) Cui, X. L.; Wu, Y. J.; Du, C. X.; Yang, L. R.; Zhu, Y. *Tetrahedron: Asymmetry* **1999**, *10*, 1255; (b) Wu, Y. J.; Cui, X. L.; Hou, J. J.; Yang, L. R.; Wang, M.; Du, C. X.; Zhu, Y. *Acta Chim. Sin.* **2000**, *58*, 871.
3. Roseenblum, M.; Woodward, R. B. *J. Am. Chem. Soc.* **1958**, *80*, 5443.
4. Kuzmina, L. G.; Bkiy, N. G.; Struchkov, Yu. T. *Usp. Khim.* **1975**, *44*, 134.
5. Grdenic, D. Q. *Rev. Chem. Soc.* **1965**, *19*, 303.
6. Huo, S. Q.; Wu, Y. J.; Zhu, Y.; Yang, L. *J. Organomet. Chem.* **1994**, *470*, 17.
7. SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.
8. teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.