

# Novel chiral compounds of Group 13 metals: the X-ray crystal structures of $[(S)\text{-}2\text{-methylbutyl}]_2\text{MP}^i\text{Bu}_2$ ( $M = \text{Ga}$ or $\text{In}$ )

M. Azad Malik, Stephen W. Haggata, Majid Motevalli, Paul O'Brien<sup>\*1</sup>

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

Received 7 February 1996

## Abstract

A series of novel chiral organometallic compounds has been synthesised and characterised by NMR, FT-IR and mass spectrometry. The X-ray crystal structures of the dimeric compounds  $[(C_5H_{11})_2MP^iBu_2]_2$  ( $M = \text{Ga}, \text{In}$ ;  $C_5H_{11} = (S)\text{-}2\text{-methylbutyl}$ ) are reported.

Keywords: MOCVD; III/V; Pnictide

## 1. Introduction

There have been several recent reports concerning the preparation of single-source molecular precursors of the type  $R_2MER'_2$  ( $M = \text{Al}, \text{Ga}, \text{In}$ ;  $E = \text{pnictide}$ ) for the deposition of III/V materials [1–3] by MOCVD. The original examples of these compounds were described by Cowley and Jones [4], and Bradley, Faktor and coworkers [5]. In the present work a chiral substituent has been introduced into compounds of this type, and a series of compounds  $[R_2MPR'_2]_2$  ( $R = (S)\text{-}2\text{-methylbutyl}$ ;  $M = \text{Ga}, \text{In}$ ;  $R' = \text{Bu}, \text{Ph}$ ) has been synthesised and characterised.

## 2. Experimental

The majority of compounds described are extremely sensitive to oxygen and/or moisture. All operations were performed in an atmosphere of oxygen free nitrogen, or argon, using Schlenk-type glass apparatus. All solvents were distilled under nitrogen from sodium benzophenone ketyl.

### 2.1. Chemicals

(*S*)-1-bromo-2-methylbutane, magnesium turnings, gallium(III) trichloride, indium(III) trichloride, <sup>n</sup>BuLi,

HPPH<sub>2</sub> and HP<sup>i</sup>Bu<sub>2</sub> were all purchased from Aldrich Chem. Co. Ltd.

### 2.2. Physical measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker WH250 Fourier transform spectrometer with TMS as a reference. <sup>31</sup>P{<sup>1</sup>H} spectra obtained were referenced to 85% H<sub>3</sub>PO<sub>4</sub>. Infra-red spectra were recorded between CsI plates with a Perkin-Elmer 1720 X FT-IR spectrometer using mineral oil (Nujol) mulls where necessary; mass spectra were obtained using an AEI MS902 spectrometer, only the principal peaks are reported.

### 2.3. Crystallography

Measurements were made on a sample mounted in a glass capillary with an Enraf-Nonius CAD4 diffractometer operating in the  $\omega$ -2 $\theta$  scan mode with graphite-monochromated Mo K $\alpha$  radiation as described previously [6]. The structures were solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods [7] with scattering factors calculated by using the data from Ref. [8]. All non-hydrogen atoms were refined with anisotropic displacement factors; hydrogen atoms were geometrically ideally positioned and refined according to the riding model using isotropic displacement parameters. Crystal data and the details of the intensity measurements and refinement for compounds **2** and **5** are given in Table 1. Atomic coordinates are given in Table 2. Selected bond lengths and angles for compounds **2** and **5** are given in Table 3.

<sup>\*</sup> Corresponding author.

<sup>1</sup> Present address: Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AZ, UK.

Table 1  
Crystal data, intensity measurements and structure refinement

	2	5
Formula	C <sub>36</sub> H <sub>80</sub> Ga <sub>2</sub> P <sub>2</sub>	C <sub>36</sub> H <sub>80</sub> In <sub>2</sub> P <sub>2</sub>
M	714.38	804.58
T(K)	293(2)	293(2)
Crystal size (mm <sup>3</sup> )	0.31 × 0.15 × 0.25	0.18 × 0.14 × 0.19
Crystal system	Monoclinic	Orthorhombic
Space group	C2	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	21.476(2)	10.860(1)
b (Å)	20.800(2)	18.223(2)
c (Å)	15.948(1)	23.740(2)
α (°)	90	90
β (°)	92.56(10)	90
γ (°)	90	90
V (Å <sup>3</sup> )	6671.6(1)	4265.6(7)
Z	6	4
D <sub>c</sub> (g cm <sup>-3</sup> )	1.067	1.253
μ (mm <sup>-1</sup> )	1.303	1.176
F(000)	2328	1696
θ <sub>min</sub> /max	1.90 to 24.96	1.41 to 26.96
Radiation	Mo Kα	Mo Kα
λ (Å)	0.71069	0.71069
Total no. of reflections	6389	5305
No. of unique reflections	6052	5169
No. of observed reflections	2945	2751
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.082	R <sub>1</sub> = 0.0535
R indices (all data)	R <sub>1</sub> = 0.2117, wR <sub>2</sub> = 0.3027	R <sub>1</sub> = 0.1383, wR <sub>2</sub> = 0.1362

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad wR_2 = \frac{[\sum (w(F_o^2 - F_c^2))^2]}{[\sum (w(F_o^2))^2]}^{1/2}$$

$$w = 1/[\sigma(F_o^2) + (0.1761P)^2 + 7.69P], \quad \text{where } P = [\max(F_o^2) + 2F_c^2]/3 \text{ (Compound 2)}$$

$$w = 1/[\sigma(F_o^2)(0.0753P)^2 + 0.00P], \quad \text{where } P = [\max(F_o^2) + 2F_c^2]/3 \text{ (compound 5)}$$

Tables of H atom coordinates, all bond lengths and angles, and anisotropic displacement factor coefficients are included in the supplementary material.

#### 2.4. M(C<sub>5</sub>H<sub>11</sub>)<sub>3</sub> (M = Ga, In)

The synthesis of the trialkylgallium or -indium compounds was carried out using the literature method [9].

#### 2.5. Ga(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>Cl (1)

A solution of Ga(C<sub>5</sub>H<sub>11</sub>)<sub>3</sub> (1.94 g, 6.83 mmol) in petroleum spirits (60–80°C) (40 cm<sup>3</sup>) was added to a solution of GaCl<sub>3</sub> (0.61 g, 3.41 mmol) in petroleum spirits (60–80°C) (40 cm<sup>3</sup>). The flask was equipped with a reflux condenser and the mixture was refluxed overnight at 60°C. Volatile material was removed under vacuum leaving behind the colourless gallium dialkylchloride, yield 1.65 g (97.6%) which was used without purification.

NMR data. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 1.19 [4H, m, Ga(CH<sub>2</sub>)], 1.89 [2H, m, CH], 1.05 [6H, d, HCCCH<sub>3</sub>], 1.38 [4H, m, HCCCH<sub>2</sub>], 0.96 [6H, t, CH<sub>2</sub>CH<sub>3</sub>]. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 32.07 [Ga(CH<sub>2</sub>)], 33.29 [CH], 24.53 [HCCCH<sub>3</sub>], 34.57 [HCCCH<sub>2</sub>], 12.74 [CH<sub>2</sub>CH<sub>3</sub>].

#### 2.6. (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaP'Bu<sub>2</sub> (2)

LiP'Bu<sub>2</sub> was prepared by the addition of HP'Bu<sub>2</sub> (5 g, 33.4 mmol) to a stirred solution of <sup>n</sup>BuLi (14.24 cm<sup>3</sup> of 2.5 M solution in hexanes, 35.6 mmol) diluted further with petroleum spirits (60–80°C, 50 cm<sup>3</sup>, 0°C). The solution was left to stir overnight, concentrated, and then left to crystallise. (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaCl (1) (2.56 g, 10.34 mmol) was dissolved in ether (60 cm<sup>3</sup>) and stirred at 0°C. LiP'Bu<sub>2</sub> (1.57 g, 10.33 mmol) was slowly added and the mixture was allowed to reach ambient temperature. After stirring overnight, the solvent was removed under vacuum leaving a white solid. Petroleum spirits (60–80°C) (30 cm<sup>3</sup>) were added to the solid. After decanting the supernatant, the solution was concentrated and left to crystallise at –25°C. Colourless, triangular shaped crystals formed, yield 3.12 g (84%), m.p. 81°C.

NMR data. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 1.25 [8H, m, Ga(CH<sub>2</sub>)], 2.09 [4H, m, CH], 1.31 [12H, d, HCCCH<sub>3</sub>], 1.66 [8H, m, HCCCH<sub>2</sub>], 1.11 [12H, t, CH<sub>2</sub>CH<sub>3</sub>], 1.51 [36H, dd, <sup>3</sup>J<sub>H-P</sub> = 6.25 Hz, PC(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 30.34 [t, <sup>2</sup>J<sub>C-P</sub> = 7.72 Hz, Ga(CH<sub>2</sub>)], 35.36 [CH], 24.66 [HCCCH<sub>3</sub>], 36.17 [HCCCH<sub>2</sub>], 12.99 [CH<sub>2</sub>CH<sub>3</sub>], 32.43 [d, <sup>1</sup>J<sub>C-P</sub> = 13.19 Hz, PC(CH<sub>3</sub>)<sub>3</sub>], 33.64 [PC(CH<sub>3</sub>)<sub>3</sub>]. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 37.71(s). Mass spectrum (m/z): R<sub>2</sub>M<sub>2</sub>P<sub>2</sub>R', 517 (5.9%), R<sub>2</sub>MPR', 358 (2.8%), R<sup>+</sup> 71 (10.1%), R<sup>+</sup> 57 (76.3%). Major IR bands (cm<sup>-1</sup>): 2952(s), 2901(s), 2872(s), 1460(s), 1376(m), 1365(m), 1261(m), 1141(m), 1081(m), 1019(m), 668(m), 601(m).

#### 2.7. (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaPPh<sub>2</sub> (3)

LiPPh<sub>2</sub> was prepared from the addition of HPPh<sub>2</sub> (5 g, 26.6 mmol) to a stirred solution of <sup>n</sup>BuLi (10.6 cm<sup>3</sup> of 2.5 M solution in hexanes, 26.6 mmol) in ether (50 cm<sup>3</sup>) at 0°C. After stirring overnight the mixture was concentrated and the yellow solid, LiPPh<sub>2</sub>, was obtained by crystallisation at room temperature. (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaCl (5.08 g, 20.4 mmol) was dissolved in diethylether (60 cm<sup>3</sup>) and stirred at 0°C. LiPPh<sub>2</sub> (3.92 g, 20.4 mmol) was added slowly to the stirred solution over half an hour. The mixture was allowed to warm to room temperature and was then stirred for 3 days. The solvent was removed under vacuum and the product was extracted with benzene (40 cm<sup>3</sup>). The solution was filtered and then concentrated. At saturation, pentane

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

Atom	x	y	z	$U_{eq}$
[(C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> GaP <sup>I</sup> Bu <sub>2</sub> ] <sub>2</sub> (2)				
Ga(1)	8748(1)	8583(1)	7388(1)	52(1)
Ga(2)	8167(1)	10109(1)	6445(1)	51(1)
Ga(3)	9529(1)	3972(1)	8944(1)	53(1)
P(1)	8053(1)	8955(1)	6113(2)	51(1)
P(2)	8872(1)	9771(1)	7748(2)	47(1)
P(3)	0	4789(2)	0	48(1)
P(4)	0	3154(2)	0	47(1)
C(1)	7222(4)	8713(5)	6132(7)	59(3)
C(2)	6815(5)	9143(6)	5526(9)	91(5)
C(3)	7093(6)	7999(6)	5948(10)	97(5)
C(4)	6980(5)	8836(6)	7099(7)	80(4)
C(5)	8373(6)	8679(5)	5025(7)	75(4)
C(6)	8500(6)	7943(5)	5017(9)	90(5)
C(7)	9025(6)	9008(6)	4995(7)	82(4)
C(8)	7933(6)	8855(7)	4174(7)	93(5)
C(9)	9671(4)	10156(5)	7629(7)	59(3)
C(10)	10115(5)	10002(6)	8404(7)	74(4)
C(11)	9926(5)	9863(5)	6820(8)	76(4)
C(12)	9615(5)	10861(5)	7504(7)	69(4)
C(13)	8599(5)	9922(4)	8931(7)	62(3)
C(14)	8695(6)	10624(5)	9240(8)	78(4)
C(15)	8949(6)	9467(6)	9577(7)	79(4)
C(16)	7875(5)	9801(6)	8902(8)	82(4)
C(17)	8331(5)	8105(5)	8374(7)	72(4)
C(18)	8004(5)	7461(5)	8184(7)	67(4)
C(21)	8350(7)	7022(6)	7578(8)	97(5)
C(19)	7863(6)	7173(5)	9104(9)	91(5)
C(20)	7527(6)	6522(7)	9055(11)	112(6)
C(22)	9538(5)	8142(6)	7024(9)	81(4)
C(23)	9986(6)	8036(8)	7950(10)	133(5)
C(24)	10668(13)	8173(15)	7814(20)	239(14)
C(25)	10480(7)	7501(6)	7123(8)	110(5)
C(26)	10247(19)	7813(20)	8922(22)	327(21)
C(27)	8629(6)	10662(5)	5584(7)	70(4)
C(28)	8341(6)	10697(5)	4564(7)	64(4)
C(29)	8757(7)	11287(6)	4125(8)	90(5)
C(30)	8542(7)	11360(8)	3108(8)	104(6)
C(31)	7644(6)	10815(9)	4453(9)	109(6)
C(32)	7353(5)	10559(5)	6766(8)	79(4)
C(33)	7449(7)	11278(6)	7036(10)	113(5)
C(34)	7220(12)	11430(11)	7939(17)	192(11)
C(35)	7305(12)	12175(14)	8249(20)	257(14)
C(36)	7833(16)	11921(29)	7208(24)	358(26)
C(37)	10588(5)	5304(5)	9380(7)	59(3)
C(38)	10872(6)	5834(6)	9965(8)	90(4)
C(39)	10265(6)	5623(6)	8533(7)	77(4)
C(40)	11072(5)	4891(6)	9065(7)	69(4)
C(41)	10634(5)	2623(5)	9575(6)	55(3)
C(42)	11046(5)	3056(6)	9002(7)	70(4)
C(43)	10424(5)	2070(5)	8995(8)	69(4)
C(44)	11027(5)	2368(5)	10357(7)	63(3)
C(45)	8599(5)	3915(6)	8833(8)	69(3)
C(46)	8207(5)	4548(6)	8574(8)	73(4)
C(47)	7501(6)	4280(6)	8411(9)	92(5)
C(48)	7043(7)	4819(8)	8100(10)	114(6)
C(49)	8443(5)	4919(6)	7765(8)	81(4)
C(50)	9880(6)	4010(7)	7704(7)	81(4)
C(51)	9603(7)	3355(13)	7129(9)	173(10)
C(52)	10098(7)	3106(6)	6596(8)	102(4)
C(53)	9989(7)	2541(6)	6144(8)	112(5)
C(54)	8980(15)	3474(20)	6816(22)	333(18)

Table 2 (continued)

Atom	x	y	z	$U_{eq}$
[(C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> InP <sup>I</sup> Bu <sub>2</sub> ] <sub>2</sub> (5)				
In(1)	9170(1)	450(1)	9310(1)	34(1)
In(2)	10182(1)	-456(1)	10778(1)	37(1)
P(1)	10523(3)	-717(2)	9684(1)	32(1)
P(2)	8827(3)	727(2)	10405(1)	33(1)
C(1)	12389(11)	-661(6)	9497(5)	32(3)
C(2)	13255(13)	-1209(8)	9830(6)	58(4)
C(3)	12651(14)	-763(8)	8873(5)	60(4)
C(4)	12856(12)	102(7)	9667(6)	42(3)
C(5)	9741(15)	-1614(7)	9415(5)	41(3)
C(6)	8334(13)	-1655(7)	9675(5)	50(4)
C(7)	9591(7)	-1596(8)	8775(6)	63(4)
C(8)	10544(17)	-2294(7)	9597(6)	68(5)
C(9)	9586(15)	1611(7)	10675(5)	48(3)
C(10)	9665(18)	1655(8)	11306(5)	67(5)
C(11)	8901(18)	2297(7)	10466(6)	73(5)
C(12)	11013(15)	1618(8)	10450(6)	61(4)
C(13)	6945(13)	688(7)	10590(5)	46(3)
C(14)	6478(14)	-75(8)	10402(6)	53(4)
C(15)	6703(15)	737(8)	11230(5)	66(5)
C(16)	6082(17)	235(8)	10276(7)	76(5)
C(17)	7263(13)	213(7)	8881(5)	45(3)
C(18)	7112(12)	414(8)	8261(4)	42(3)
C(19)	8056(14)	-34(8)	7896(6)	62(4)
C(20)	5690(13)	374(9)	8027(5)	59(4)
C(21)	4757(14)	946(10)	8270(6)	75(5)
C(22)	10491(14)	1196(8)	8832(5)	53(4)
C(23)	9902(13)	1755(7)	8439(5)	41(3)
C(24)	8840(15)	2234(8)	8723(6)	60(4)
C(25)	11006(14)	2213(7)	8146(5)	52(4)
C(26)	10549(18)	2732(9)	7693(6)	82(5)
C(27)	8772(16)	-1154(7)	11263(5)	55(4)
C(28)	9315(15)	-1738(7)	11668(5)	49(4)
C(29)	8161(16)	-2031(8)	12036(6)	73(5)
C(30)	9987(18)	-2356(8)	11321(8)	79(5)
C(31)	10640(23)	-2951(11)	11686(10)	124(8)
C(32)	12079(14)	-96(9)	11208(6)	61(4)
C(33)	12405(14)	-490(10)	11751(5)	63(4)
C(34)	13110(22)	-1210(11)	11586(10)	133(10)
C(35)	13378(21)	-50(15)	12118(8)	125(10)
C(36)	12715(28)	692(14)	12327(9)	152(12)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

(10 cm<sup>3</sup>) was added slowly. Colourless crystals were obtained from crystallisation at -25°C, although they were solvent dependent and irregular in shape, yield 6.2 g (76%), m.p. 116°C.

NMR data. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 1.06 [8H, m, Ga(CH<sub>2</sub>)], 1.75 [4H, m, CH], 0.82 [12H, d, HCCCH<sub>3</sub>], 1.38 [8H, m, HCCCH<sub>2</sub>], 0.88 [12H, t, CH<sub>2</sub>CH<sub>3</sub>], (7.51, 7.02, 7.02; C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ 25.66 [t, Ga(CH<sub>2</sub>)], 34.50 [CH], 24.62 [HCCCH<sub>3</sub>], 35.47 [HCCCH<sub>2</sub>], 12.90 [CH<sub>2</sub>CH<sub>3</sub>], (34.96(t), 136.33(t), 129.26, 129.07; C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 250 MHz): δ -43.19(s). Mass spectrum (*m/z*): R<sub>4</sub>M<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> 609 (2.4%), R<sub>4</sub>P<sub>2</sub> 370 (25.3%), R<sub>4</sub>PR<sub>2</sub> 327 (0.6%), (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>M<sup>+</sup> 211 (100%), R<sub>4</sub>Ga<sup>+</sup> 142 (2.5%), R<sub>2</sub>P<sup>+</sup> 185 (45.8%), R<sup>+</sup>P<sup>+</sup>

Table 3  
Selected bond lengths (Å) and angles (°)

	$[(C_5H_{11})_2GaP^iBu_2]_2$	$[(C_5H_{11})_2InP^iBu_2]_2$
M(1)–C(22)	2.025(11)	2.20(1)
M(1)–C(17)	2.021(11)	2.18(1)
M(1)–P(1)	2.491(3)	2.664(3)
M(1)–P(2)	2.539(3)	2.669(3)
M(2)–C(27)	2.019(11)	2.21(1)
M(2)–C(32)	2.058(11)	2.23(1)
M(2)–P(1)	2.463(3)	2.660(3)
M(2)–P(2)	2.515(3)	2.686(3)
Ga(3)–C(45)	2.001(10)	
Ga(3)–C(50)	2.032(11)	
Ga(3)–P(3)	2.501(3)	
Ga(3)–P(4)	2.504(2)	
C(22)–M(1)–C(17)	112.2(5)	113.1(4)
C(22)–M(1)–P(1)	114.6(4)	111.7(4)
C(17)–M(1)–P(1)	116.1(3)	115.4(3)
C(22)–M(1)–P(2)	114.7(3)	117.4(4)
C(17)–M(1)–P(2)	111.7(3)	112.5(3)
P(1)–M(1)–P(2)	85.1(9)	83.64(9)
C(27)–M(2)–C(32)	109.7(5)	117.3(5)
C(27)–M(2)–P(1)	118.3(3)	119.1(4)
C(32)–M(2)–P(1)	114.4(3)	113.2(4)
C(27)–M(2)–P(2)	110.9(3)	108.7(4)
C(32)–M(2)–P(2)	115.8(3)	109.4(4)
P(1)–M(2)–P(2)	86.2(9)	83.39(9)
M(2)–P(1)–M(1)	95.6(9)	96.9(1)
M(2)–P(2)–M(1)	93.1(9)	96.2(1)
C(45)–Ga(3)–C(50)	109.7(5)	
C(45)–Ga(3)–P(3)	117.8(3)	
C(50)–Ga(3)–P(3)	113.2(6)	
C(45)–Ga(3)–P(4)	112.6(3)	
C(50)–Ga(3)–P(4)	116.5(4)	
P(3)–Ga(3)–P(4)	85.6(9)	

M = indium or gallium in the general position.

Ga(3) = gallium molecule with  $C_2$  axis.

108 (30.5%),  $R^+$  77 (2.2%),  $R^+$  71 (2.2%). Major IR bands ( $cm^{-1}$ ): 2935(s), 2864(s), 1480(m), 1460(s), 1439(s), 1377(m), 1136(m), 1085(m), 1045(w), 1025(m), 739(s), 695(s), 675(m), 560(m), 508(m), 491(m).

## 2.8. $In(C_5H_{11})_2Cl$ (4)

$C_5H_{11}MgBr$  (46.85  $cm^3$  of 0.397 M solution, 18.60 mmol) was added slowly to a suspension of  $InCl_3$  (2.06 g, 9.30 mmol) in ether (100  $cm^3$ ) at 0°C over 1 h. After stirring overnight, all volatiles were removed leaving a white residue that was extracted with pentane (50  $cm^3$ ). The solution was filtered and pentane removed under vacuum to leave a colourless liquid, yield 2.7 g (99%). The compound was used without purification.

NMR data.  $^1H$  ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  1.57 [4H, m,  $In(CH_2)$ ], 2.06 [2H, m,  $CH$ ], 1.05 [6H, d,  $HCCCH_3$ ], 1.32 [4H, m,  $HCCCH_2$ ], 0.96 [6H, t,  $CH_2CH_3$ ].  $^{13}C$  NMR ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  37.75 [ $In(CH_2)$ ],

35.43 [ $CH$ ], 25.57 [ $HCCCH_3$ ], 34.83 [ $HCCCH_2$ ], 12.87 [ $CH_2CH_3$ ].

## 2.9. $(C_5H_{11})_2InP^iBu_2$ (5)

$(C_5H_{11})_2InCl$  (2.26 g, 7.73 mmol) was dissolved in petroleum spirits (60–80°C) (50  $cm^3$ ) and stirred at 0°C.  $LiP^iBu_2$  (1.14 g, 7.73 mmol) was added to the stirred solution over half an hour. The mixture was allowed to warm to ambient temperature and stirred overnight. The solvent was removed under vacuum leaving behind a white/yellow solid which was extracted with pentane (50  $cm^3$ ). A yellow solid remained undissolved which was probably unreacted  $LiP^iBu_2$ . The supernatant was decanted and the resulting solution concentrated. After 48 h at –25°C, colourless, crystalline, rod-like crystals formed, yield 2.43 g (77%), m.p. 86°C. NMR data.  $^1H$  ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  1.30 [8H, m,  $In(CH_2)$ ], 2.11 [4H, m,  $CH$ ], 1.31 [12H, d,  $HCCCH_3$ ], 1.62 [8H, m,  $HCCCH_2$ ], 1.13 [12H, t,  $CH_2CH_3$ ], 1.48 [36H, dd,  $^3J_{H-P} = 6.25$  Hz,  $PC(CH_3)_3$ ].  $^{13}C$  NMR ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  30.58 [t,  $^2J_{C-P} = 8.24$  Hz,  $In(CH_2)$ ], 35.46 [ $CH$ ], 24.94 [ $HCCCH_3$ ], 35.53 [ $HCCCH_2$ ], 12.36 [ $CH_2CH_3$ ], 31.41 [d,  $^1J_{C-P} = 10.94$  Hz,  $PC(CH_3)_3$ ], 33.14 [ $PC(CH_3)_3$ ].  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  46.02(s). Mass spectrum ( $m/z$ ):  $R_4M_2P_2R'_3$  747 (0.2%),  $R_3M_2P_2R'_4$  733 (5.1%),  $R_3MP_2R'_3$  676 (4.1%),  $R_4M_2PR'_2$  659 (4.1%),  $(C_5H_{11})_2M^+$  257 (100%),  $^{115}In$  115 (71.5%),  $R^+$  71 (4.7%),  $R^+$  57 (20.3%). Major IR bands ( $cm^{-1}$ ): 2922(s), 1457(s), 1376(m), 1364(m), 1261(w), 1019(m), 665(m), 565(w).

## 2.10. $(C_5H_{11})_2InPPh_2$ (6)

$(C_5H_{11})_2InCl$  (3.2 g, 10.9 mmol) was dissolved in ether (50  $cm^3$ ) and stirred at 0°C.  $LiPPh_2$  (2.05 g, 10.9 mmol) was slowly added and the reaction mixture was stirred overnight after reaching room temperature. The solvent was removed and the product extracted with petroleum spirits (60–80°C, 40  $cm^3$ ). The filtrate was concentrated and left to crystallise at –25°C. A pure, colourless, crystalline compound was obtained, yield 4.2 g (87.5%), m.p. 81°C. NMR data.  $^1H$  ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  1.16 [8H, m,  $Ga(CH_2)$ ], 1.72 [4H, m,  $CH$ ], 0.95 [12H, d,  $HCCCH_3$ ], 1.40 [8H, m,  $HCCCH_2$ ], 0.93 [12H, t,  $CH_2CH_3$ ], (7.59, 7.11, 7.11;  $C_6H_5$ ).  $^{13}C$  NMR ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  27.25 [t,  $In(CH_2)$ ], 35.61 [ $CH$ ], 25.49 [ $HCCCH_3$ ], 35.78 [ $HCCCH_2$ ], 13.07 [ $CH_2CH_3$ ], (134.83(t), 135.53(t), 129.48, 128.88;  $C_6H_5$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 25°C, 250 MHz):  $\delta$  –50.72(s). Mass spectrum ( $m/z$ ):  $R_4M_2PR'_2$  731 (0.6%),  $RMP_2R'_2$  403 (1.8%),  $RMPr'_2$  371 (9.3%),  $R'_4P_2$  370 (35.6%),  $R_2M^+$  257 (100%),  $R'_2P^+$  185 (32.5%),  $R^+$  77 (4.7%),  $R^+$  71 (3.5%). Major IR bands ( $cm^{-1}$ ): 2922(s), 2855(s), 1461(s), 1439(s), 1377(m),

1261(m), 1132(s), 1044(m), 1023(m), 742(s), 695(s), 558(m), 489(m).

(M = Ga or In; R = C<sub>5</sub>H<sub>11</sub>, R' = <sup>t</sup>Bu or Ph.)

### 3. Results and discussion

The parent alkyls and chloroalkyls are very sensitive to both oxygen and moisture. The indium compounds are also light sensitive. The compounds MR<sub>3</sub> (M = Ga or In; R = C<sub>5</sub>H<sub>11</sub>) are less pyrophoric, appear to have lower vapour pressures than Me<sub>3</sub>Ga [10] or Me<sub>3</sub>In [11] and are consequently less hazardous to handle. In all compounds the In–CH<sub>2</sub> resonances in the NMR spectra appear at lower field than those for the corresponding Ga–CH<sub>2</sub> resonances, as expected. The differences in the chemical shift for the M–CH<sub>2</sub> protons range from 0.1 ppm in compounds MR<sub>3</sub> to 0.3 ppm in MR<sub>2</sub>Cl. All compounds show a single set of resonances, which indicates the presence of only one species. Compounds **2**, **3**, **5** and **6** are probably dimeric in solution because of carbon–phosphorus splittings observed in the <sup>13</sup>C NMR spectra. The <sup>1</sup>H NMR spectra of (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaP<sup>t</sup>Bu<sub>2</sub> (**2**) and (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>InP<sup>t</sup>Bu<sub>2</sub> (**5**) both give signals in the alkyl region typical of the chiral ligand.

The <sup>13</sup>C NMR spectrum of **5** shows a triplet at δ 30.58 ppm for the In–CH<sub>2</sub> carbon split by two equiva-

lent phosphorus atoms, <sup>2</sup>J<sub>C–P</sub> = 8.24 Hz. The tertiary carbons [(CH<sub>3</sub>)<sub>3</sub>C<sub>a</sub>, (CH<sub>3</sub>)<sub>3</sub>C<sub>b</sub>]P give a bigger splitting and a doublet is seen at δ 31.41 ppm, <sup>1</sup>J<sub>C–P</sub> = 10.94 Hz, suggesting that, in this case, the resonances for the tertiary carbons of the two alkyl substituents on the prochiral phosphorus have identical chemical shifts and overlap completely. <sup>31</sup>P{<sup>1</sup>H} NMR spectra give singlets at δ 37.71 ppm for **2** and δ 46.02 ppm for **5**. This compares well with δ 28.41 ppm for [Me<sub>2</sub>GaP<sup>t</sup>Bu<sub>2</sub>]<sub>2</sub> [12] and δ 39.24 ppm for [Me<sub>2</sub>InP<sup>t</sup>Bu<sub>2</sub>]<sub>2</sub> [12].

The <sup>1</sup>H NMR spectra of (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaPPh<sub>2</sub> (**3**) and (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>InPPh<sub>2</sub> (**6**) give the expected ratio of alkyl to aromatic protons. The <sup>13</sup>C NMR spectra suggest decomposition in both **3** and **6** over a period of time. The δ-CH<sub>2</sub> carbon in **3** gives a triplet at δ 24.06 ppm, <sup>2</sup>J<sub>C–P</sub> = 9.49 Hz, for the δ-C resonance split by the two phosphorus nuclei of the Ga<sub>2</sub>P<sub>2</sub> core. Similar splitting patterns are observed for **3** in the aromatic region. The phosphorus atoms are prochiral and therefore the tertiary carbons in the aromatics, (C<sub>a,b</sub>)P, are inequivalent, producing two doublets with identical coupling constants but slightly different chemical shifts which overlap to give a triplet at δ 134.19 ppm, <sup>1</sup>J = 16.29 Hz. The (C<sub>a,b</sub>)CP carbons have similar splitting patterns. The resonances for the indium analogue **6** are listed in the experimental section.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **6** shows a large singlet at δ –50.72 ppm. This assignment can be

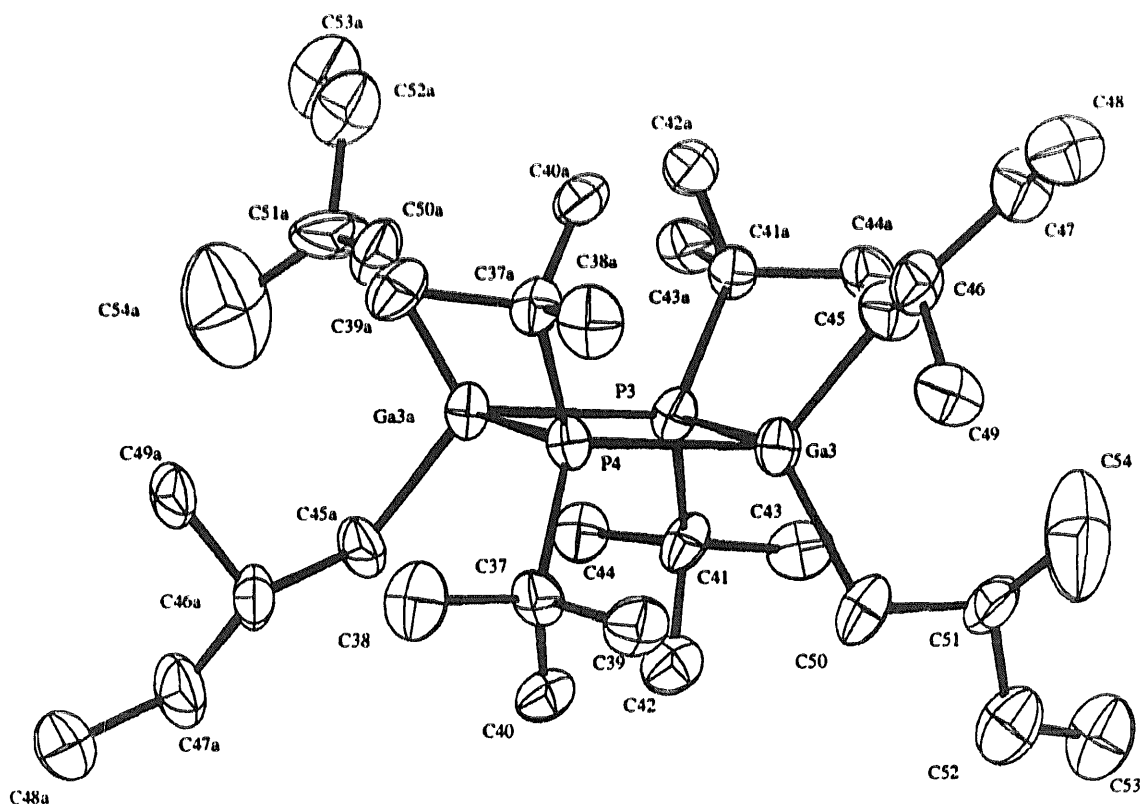


Fig. 1. Molecular structure of [(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>GaP<sup>t</sup>Bu<sub>2</sub>]<sub>2</sub> (**2**) with C<sub>2</sub>-axis and atom numbering scheme.

compared with a similar signal in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum attributed to  $[\text{Me}_2\text{InPPh}_2]_3$  [13] at  $\delta -54.23$  ppm. It is interesting to find that  $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$  [14] has been synthesised and is a trimer in the solid state. However, in solution this compound surprisingly adopts a dimer–monomer equilibrium with signals at  $\delta -49.40$  ppm and  $\delta -29.95$  ppm for a dimer and monomer respectively. The  $^{31}\text{P}\{^1\text{H}\}$  resonance for **3** gives a singlet at  $\delta -43.19$  ppm. Beachley and coworkers [14] have found that a singlet is observed for the dimeric  $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$  species at  $\delta -25.0$  ppm.

### 3.1. Structure of $[(\text{C}_5\text{H}_{11})_2\text{GaP}^i\text{Bu}_2]_2$

The X-ray crystal structure of  $[(\text{C}_5\text{H}_{11})_2\text{GaP}^i\text{Bu}_2]_2$  is presented in Fig. 1. There are two crystallographically independent molecules in an asymmetric unit, one occupying a general position and the other with a  $\text{C}_2$  axis through the bridging phosphorus atoms. Selected bond lengths and angles are given in Table 3. The chiral ligands show high thermal parameters, which reflects significant thermal/positional disorder. In order to accommodate this problem, the final refinement was restrained to yield a satisfactory model. As a consequence of this disorder, no attempt was made to position the hydrogen atoms on the chiral ligand and only the hydrogens of the tert-butyl group were positioned and refined. The chiral-ligand makes the compound non-centrosymmetric; unique in this particular class of compounds.

The  $\text{Ga}_2\text{P}_2$  core is planar in both molecules and not buckled as in  $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$  [14]. The Ga–P bond distances (Table 3) compare well with those of related compounds:  $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$  [14]  $\text{Ga}-\text{P}_{\text{av}} = 2.49(3)$  Å;  $[\text{nBu}_2\text{GaP}^i\text{Bu}_2]_2$  [15]  $\text{Ga}-\text{P}_{\text{av}} = 2.476(5)$  Å;  $[\text{Me}_2\text{GaP}^i\text{Bu}_2]_2$  [12],  $\text{Ga}-\text{P}_{\text{av}} = 2.467(4)$  Å;  $[(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{PPh}_2)_2]_2$  [16],  $\text{Ga}-\text{P}_{\text{av}} = 2.463(9)$  Å; and  $[\text{Me}_2\text{GaP}^i\text{Pr}_2]_3$  [17],  $\text{Ga}-\text{P}_{\text{av}} = 2.436(3)$  Å, but are longer than the Ga–P distance of  $2.36(1)$  Å found in gallium phosphide [14]. The Ga–P–Ga endocyclic obtuse angles are  $95.6(1)^\circ$  and  $93.1(1)^\circ$  and the P–Ga–P angles in the  $\text{Ga}_2\text{P}_2$  core are acute,  $85.1(1)^\circ$  and  $85.6(1)^\circ$ . The C–Ga–C angles  $\text{C}(22)\text{--Ga}(1)\text{--C}(17) = 112.2(5)^\circ$  and  $\text{C}(27)\text{--Ga}(2)\text{--C}(32) = 109.7(5)^\circ$  are larger than the C–Ga–C bond angles in  $[\text{nBu}_2\text{GaP}^i\text{Bu}_2]_2$  [15],  $\text{C}-\text{Ga}-\text{C}_{\text{av}} = 107.0(6)^\circ$ , but considerably less than the C–Ga–C angle found in  $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$  [13],  $\text{C}-\text{Ga}-\text{C}_{\text{av}} = 123.16(8)^\circ$ . The steric hindrance of the substitute influences the degree of distortion away from the ideal tetrahedral angles around the gallium. The chiral ligand is bulky compared with the n-butyl group, forcing the metal to adopt an irregular geometry.

### 3.2. Structure of $[(\text{C}_5\text{H}_{11})_2\text{InP}^i\text{Bu}_2]_2$

The structure of  $[(\text{C}_5\text{H}_{11})_2\text{InP}^i\text{Bu}_2]_2$  is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. In contrast to the gallium analogue, refinement was carried out (full-matrix least-squares) without any restraint. All hydrogen atoms were positioned and in-

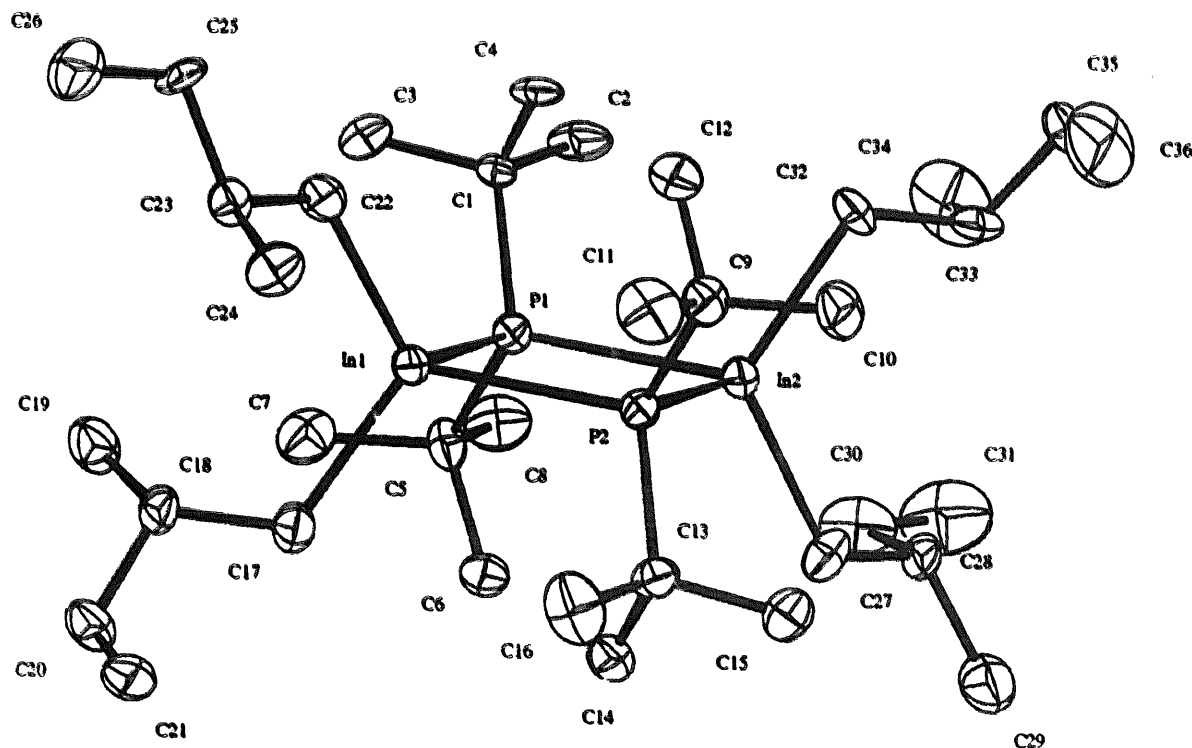


Fig. 2. Molecular structure of  $[(\text{C}_5\text{H}_{11})_2\text{InP}^i\text{Bu}_2]_2$  (**5**) with atom numbering scheme.

cluded in the final refinement (riding model). There is only one molecule in the asymmetric unit of this structure. The central  $\text{In}_2\text{P}_2$  core is planar and the coordination around the metal is close to tetrahedral. The least-square plane calculations of  $\text{In}(1)\text{In}(2)\text{P}(1)\text{P}(2)$  give an average deviation of 0.001 Å from the plane. The In–P bond lengths are  $\text{In}(1)\text{--P}(1) = 2.664(3)$  Å,  $\text{In}(1)\text{--P}(2) = 2.669(3)$  Å,  $\text{In}(2)\text{--P}(1) = 2.660(3)$  Å and  $\text{In}(2)\text{--P}(2) = 2.686(3)$  Å. The calculated average is 2.669 Å, which compares well with the In–P bond distances in  $[\text{Me}_2\text{InP}^t\text{Bu}_2]_2$  [5] of 2.637(4) Å and 2.656(4) Å, in  $[(\text{C}_5\text{H}_{11})_2\text{InP}(\text{C}_6\text{H}_5)_2]_3$  [14] of 2.677(1) Å and 2.699(1) Å, and in  $[\text{Me}_3\text{SiCH}_2]_2\text{InP}(\text{SiMe}_3)_2$  [18],  $\text{In}\text{--P}_{\text{av}} = 2.627(2)$  Å, but is longer when compared with  $[\text{Me}_2\text{InPPh}_2]_3$  [13], 2.593(1) Å and 2.625(2) Å, and indium phosphide [15], 2.541(3) Å. Endocyclic In–P–In bond angles are obtuse,  $\text{In}(2)\text{--P}(1)\text{--In}(1) = 96.86(10)^\circ$ ,  $\text{In}(1)\text{--P}(2)\text{--In}(2) = 96.10(10)^\circ$ . As expected, the P–In–P angles are acute,  $\text{P}(1)\text{--In}(1)\text{--P}(2) = 83.64(9)^\circ$ ,  $\text{P}(1)\text{--In}(2)\text{--P}(2) = 83.39(9)^\circ$ . All the In–C bond distances are similar,  $\text{In}(1)\text{--C}(17) = 2.182(13)$  Å,  $\text{In}(1)\text{--C}(22) = 2.197(13)$  Å,  $\text{In}(2)\text{--C}(27) = 2.209(13)$  Å and  $\text{In}(2)\text{--C}(32) = 2.230(13)$  Å, and longer than the Ga–C distances noted earlier. The tetrahedral geometry at the metal is slightly distorted and therefore the C–In–C bond angles are larger than the tetrahedral angle ( $109.47^\circ$ ),  $\text{C}(27)\text{--In}(2)\text{--C}(32) = 117.3(5)^\circ$ , compared with the C–In–C angle of the dimeric  $[\text{Me}_2\text{InP}^t\text{Bu}_2]_2$  [5]  $108.6(3)^\circ$ .

### Acknowledgements

We thank the I.R.C. at Imperial College, London for an E.P.S.R.C. studentship to SH.

### References

- [1] D.C. Bradley, *Polyhedron*, **13** (1994) 1111.
- [2] P. O'Brien, Precursors for electronic materials, in D.W. Bruce and D. O'Hare (eds.), *Inorganic Materials*, Wiley, Chichester, UK, 1992.
- [3] A.H. Cowley and R.A. Jones, *Polyhedron*, **13** (1994) 1149.
- [4] A.H. Cowley and R.A. Jones, *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 1208.
- [5] K.A. Aitchison, J.D. Julius Backer-Dirks, D.C. Bradley, M.M. Faktor, D.M. Frigo, M.B. Hursthouse, B. Hussain and R.L. Short, *J. Organomet. Chem.*, **366** (1989) 11.
- [6] R.A. Jones, M.B. Hursthouse, K.M. Malik and G. Wilkinson, *J. Am. Chem. Soc.*, **101** (1979) 4128.
- [7] G.M. Sheldrick, SHELX 76, *Program for Crystal Structure Determination*, University of Cambridge, Cambridge, UK, 1979.
- [8] *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, UK, 1974.
- [9] L. Lardicci, P. Salvadori and P. Palagi, *Ann. Chim. Ital.*, **56** (1966) 1043.
- [10] C.A. Kraus and F.E. Toonder, *Proc. N.A.S.*, **19** (1933) 293.
- [11] L.M. Dennis, R.W. Work, E.G. Rochow and E.M. Chamot, *J. Am. Chem. Soc.*, **56** (1934) 1047.
- [12] A.M. Arif, B.L. Benac, A.H. Cowley, R.A. Jones, K.B. Kidd and C.M. Nunn, *New J. Chem.*, **12** (1988) 553.
- [13] J.A.S. Burns, M.D.B. Dillingham, J.B. Hill, K.D. Gripper, W.T. Peggington and G.H. Robinson, *Organometallics*, **13** (1994) 1514.
- [14] M.A. Banks, O.T. Beachley, Jr., L.A. Buttrey, M.R. Churchill and J.C. Fettinger, *Organometallics*, **10** (1991) 1901.
- [15] A.M. Arif, B.L. Benac, A.H. Cowley, R. Geerts, R.A. Jones, K.B. Kidd, and S.T. Schwab, *J. Chem. Soc., Chem. Commun.*, (1986) 1543.
- [16] O.T. Beachley, Jr. and J.D. Maloney, *Organometallics*, **12** (1993) 229.
- [17] A.H. Cowley, R.A. Jones, M.A. Mardones and C.M. Nunn, *Organometallics*, **10** (1991) 1635.
- [18] R.L. Wells, A.T. McPhail and M.F. Self, *Organometallics*, **11** (1992) 221.