group parameters and derived crystallographic coordinates for the $B_{11}CH_{12}^-$ anion, and Tables SIV, SV, and SVI, magnetic susceptibility data for $Fe(TPP)(CuIm)_2{\cdot}2toluene$, $[Fe(TPP)(NiIm)_2]B_{11}CH_{12}{\cdot}5THF$, and $[Fe(TPP)(CuIm_2)]B_{11}CH_{12}{\cdot}5THF$, respectively (11 pages). Ordering information is given on any current masthead page.

Organometallic Vapor Phase Epitaxy of InP Layers Using the New Precursor Methylcyclopentadienylindium

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An important application of organometallic vapor phase epitaxy (OMVPE) is the growth of thin, monocrystalline layers of III–V semiconductor materials such as GaAs and InP for electronic and optoelectronic devices.[1-3] Basically the OMVPE growth of such III–V materials involves the thermal decomposition, in the gas phase, of a group III alkyl such as $In(CH_3)_3$ and a group V hydride such as PH_3 for the growth of InP (eq 1).

$$In(CH_3)_3 + PH_3 \xrightarrow[600-700\ ^\circ C]{H_2} InP + 3\ CH_4 \qquad (1)$$

OMVPE is chemically and technologically complicated, and the nature of the chemical reactions that occur in the gas phase and at the gas–solid interface is only poorly understood.

Some of the many problems encountered in epitaxial growth are the incorporation of residual carbon from the organometallic precursor[4] and unwanted prereactions or side reactions of group III and V compounds in the gas phase.[5,6] The effects of these side reactions in OMVPE are especially pronounced in the growth of In- and P-containing semiconductors,[2,7] and for a long time they prevented the growth of high quality InP by OMVPE. In these side reactions, the adduct **1** is in chemical equilibrium with $In(CH_3)_3$ and PH_3; **1** may also decompose, with elimination of CH_4, to produce the polymeric compound **2** (eq 2). The polymeric compound **2** may be, at least partially, responsible for the incorporation of carbon in the growing layer.

$$n In(CH_3)_3 + n PH_3 \rightleftarrows \underset{\mathbf{1}}{n(CH_3)_3In{-}PH_3} \xrightarrow{-2nCH_4} \underset{\mathbf{2}}{\{(CH_3)In{-}PH\}_n} \qquad (2)$$

Several procedures have been suggested in literature[3,5,8-11] that diminish the deleterious effects of these side reactions in OMVPE. However, none of them removes the true cause of these side reactions: the Lewis acid character of the III alkyl and the Lewis base properties of the V hydride.

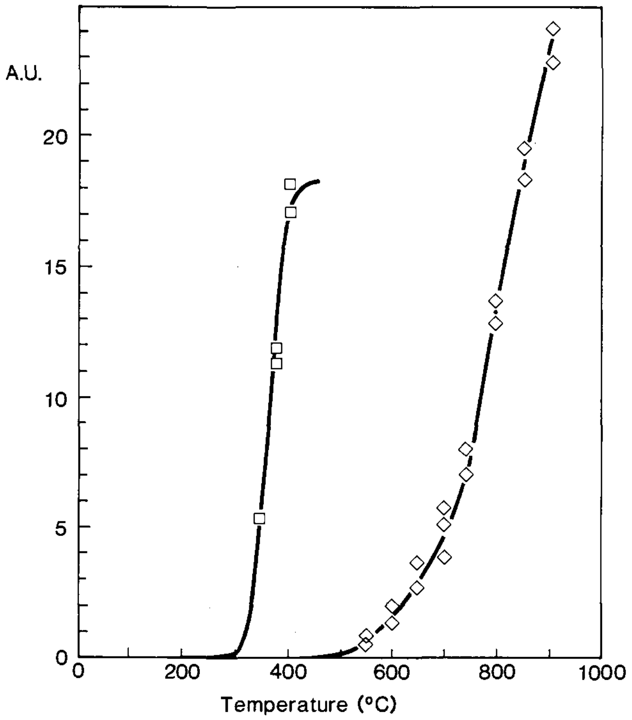

Figure 1. Thermal decomposition of $(CH_3C_5H_4)In$ (◇) and $(CH_3)_3In$ (□) in H_2 atmosphere. The amount of In metal deposited per unit time, normalized for the area of the substrate, is expressed as a rate in arbitrary units.

Table I. Vapor Pressure of CpIn Compounds and In Alkyls

indium compd	P_v (Pa) at 20 °C	P_v (Pa) at 40 °C
$(C_5H_5)In$	12	36
$(CH_3C_5H_4)In$	53	236
$(CH_3CH_2C_5H_4)In$	28	52
$(CH_3)_3In^a$	236	1040
$(CH_3CH_2)_3In^a$	13	145

[a] From ref 10.

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This paper reports on our approach to alleviate the problems associated with the side reactions and the incorporation of carbon. We focussed our attention on the monovalent η^5-$(C_5H_5)In$ (CpIn) and related compounds. By their chemical nature these compounds have no tendency to form adducts. CpIn shows weak Lewis base properties,[12,13] and theoretical studies indicate the presence of a lone pair on indium.[14] Reactions with Lewis bases such as phosphines are not to be expected. Since the Cp moiety is a stable fragment in itself, no degradation of this unit leading to the incorporation of carbon atoms in the growing layer is expected.[15] The parent compound η^5-$(C_5H_5)In$ is a high-melting polymeric solid with a low vapor pressure (Table I), despite the essentially covalent character[16] of the metal–ligand bonding in the compound.

Our investigations showed that the closely related η^5-$(CH_3C_5H_4)In$ (MeCpIn) and η^5-$(CH_3CH_2C_5H_4)In$ (EtCpIn) have much higher vapor pressures[17,18] (Table I). The synthesis of CpIn and MeCpIn has been described in literature,[13,19] the liquid EtCpIn is a new compound.[20,21] As expected, ^{31}P and ^{13}C NMR showed that no adducts are formed between these CpIn-type compounds and various phosphines.

Our initial studies were directed toward determining the thermal stability of MeCpIn, as a typical example of these CpIn-type precursors, as compared to $In(CH_3)_3$. We monitored the decomposition of the indium compounds as a function of temperature by passing their vapors, in H_2, over a heated Si substrate and determining the rate of indium metal deposition onto the substrate (Figure 1). The mol fractions of $In(CH_3)_3$ and MeCpIn in these experiments were 1.6×10^{-4} and 2.7×10^{-4}, respectively. The maximum deposition rate from $In(CH_3)_3$ was reached at 400 °C.[22] Much to our surprise MeCpIn showed a remarkable thermal stability in a H_2 atmosphere. Only at temperatures as high as 550 °C was deposition of indium metal from MeCpIn observed. At higher temperatures the rate of deposition increases, and even at 900 °C the maximum deposition rate has not yet been reached. However, in the temperature range of 600–700 °C the rate of deposition is sufficiently high to be useful. Analysis of the organic products of the thermal decomposition of MeCpIn by GC/MS showed that the isomers of methylcyclopentadiene and smaller amounts of cyclopentadiene,[23] 1,3-cyclohexadiene, and benzene are formed. This indicates a homolytic fission of the indium–ligand bond and rearrangement of the resulting organic radical.

Table II. Carrier Concentration (n) and Mobility (μ)[a] in OMVPE Grown InP Using MeCpIn and $In(CH_3)_3$

	n (293 K) cm^{-3}	n (77 K) cm^{-3}	μ (293 K) $cm^2 \cdot V^{-1} \cdot s^{-1}$	μ (77 K) $cm^2 \cdot V^{-1} \cdot s^{-1}$
$(CH_3C_5H_4)In$	1.7×10^{16}	9.4×10^{15}	2820	12250
$(CH_3)_3In$	3.3×10^{14}	3×10^{14}	5160[b]	119000[b]
$(CH_3)_3In$	2×10^{15}		3660[c]	30000[c]

[a] Layer thickness 2 μm. [b] Highest mobility reported[25] for atmospheric pressure OMVPE of InP. [c] Typical, every day value for mobility in InP.

These results encouraged us to use MeCpIn in the growth of epitaxial InP layers at atmospheric pressure. In a representative experiment the evaporator containing MeCpIn was thermostated at 40 °C. H_2 was used as a carrier gas ($[O_2]$ and $[H_2O] < 0.01$ ppm). PH_3 was used as a phosphorus source. The mol fraction of the reactants in the gas phase was adjusted to be 3×10^{-3} for PH_3 and 9×10^{-5} for MeCpIn. The gas mixture was passed over ⟨100⟩ InP substrates kept at 675 °C. Layer thicknesses were determined by stylus-profilometry (DEKTAK). The growth rate at 675 °C was 1.0 $\mu m \cdot h^{-1}$, corresponding to one atomic layer per second. Much higher rates can be reached by increasing the concentrations of the reactants in the gas phase. Under similar conditions the deposition rate on InP using $In(CH_3)_3$ as a source is 3.0 $\mu m \cdot h^{-1}$. As was expected, no prereactions or unwanted side reactions were observed by using the new MeCpIn precursor. The morphology of the grown layer was examined by using optical Nomarski interference microscopy. Usually the layers showed specular reflection. Investigation of the InP layers by double crystal X-ray diffraction and by RBS channeling technique showed that the layers were perfectly single crystalline. The line width of the ⟨004⟩ reflection in the double crystal measurements was only 11 arc s. The carbon concentration in the layers was below the detection limit of SIMS measurements, i.e., below 2×10^{17} $atoms \cdot cm^{-3}$. The electronic properties of the grown layers were determined of a 2-μm thick layer, grown on semi-insulating InP substrate. CV profiling showed a background carrier concentration of 1.5×10^{16} cm^{-3} so that the total impurity concentration is around 10 ppm at most. Hall–van der Pauw measurements on the same layer showed comparable figures for the background impurities: 1.7×10^{16} cm^{-3} at 293 K and 9.4×10^{15} cm^{-3} at 77 K. Electron mobilities were determined to be 2820 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at 293 K and 12250 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at 77 K. Both the background carrier concentration and the electron mobilities that we obtained by using MeCpIn are somewhat inferior to what can be achieved by using the standard so-called "electronic grade" $In(CH_3)_3$ (see Table II). However, these $In(CH_3)_3$ samples have been prepared and purified by specially developed procedures to obtain this "electronic grade" purity.[24] Impurities are usually below the 0.1 ppm level. Analysis of our sample MeCpIn by atomic absorption and emission techniques (flameless AAS and ICP) showed that several impurities, such as Fe, Ge, Si, Na, Pt, Zn, and Li are present at levels ranging from 1 to 6 ppm. Therefore we are currently working on procedures to obtain higher purity MeCpIn, which will certainly reduce the background carrier concentration in the epitaxial layer.

Summarizing, we state that our results clearly illustrate that MeCpIn is a very promising precursor for OMVPE of InP layers because it shows no deleterious side reactions due to its inertness toward Lewis bases such as phosphines and because no carbon is incorporated in the grown layers due to the stability of the Cp unit. In general, the MeCp ligand may be a useful ligand for the development of other volatile organometallic precursors for OMVPE of various layers.

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(20) EtCpH was prepared according to Hausweiler[21] and converted into its Li salt immediately after preparation. The synthesis was performed by using the procedure for MeCpIn, except for the final purification by sublimation, which was replaced by a distillation, since EtCpIn is a mobile liquid (mp around 10 °C). MeCpIn was prepared without encountering any difficulty on a 0.5 mol scale (80 g); EtCpIn was prepared on 0.25 mol scale. The chemical yields are usually >80%.

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Supplementary Material Available: Figures of the Nomarski microscopy, the double crystal X-ray diffraction, and the RBS channeling experiments (6 pages). Ordering information is given on any current masthead page.

α-Hydroxy Esters as Chiral Reagents: Asymmetric Synthesis of 2-Arylpropionic Acids

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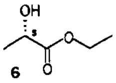
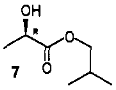
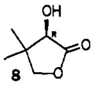
The 2-arylpropionic acids are a class of non-steroidal antiinflammatory agents that have remained an area of intense study.[1] Often only one enantiomer is biologically active. Therefore, the asymmetric synthesis of this class of compounds has received considerable attention. While many approaches have been developed, the majority lack simplicity and high stereoselectivity.[2] We wish to report an exciting find in the asymmetric transformation[3] of racemic 2-arylpropionic acids to either their *S* or *R* enantiomers by tertiary amine mediated addition of the chiral alcohols, (*S*)-ethyl lactate (**6**), (*R*)-isobutyl lactate (**7**), or the α-hydroxylactone, (*R*)-pantolactone (**8**), to the respective arylmethylketenes providing 2-arylpropionate esters in 94–99% diastereomeric excesses (de's). This communication describes the unprecedented use of simple, readily available chiral alcohols for highly diastereoselective protonations.

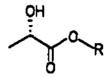
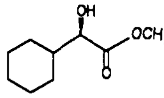
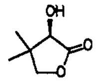
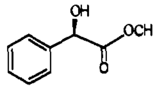
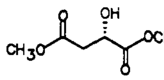
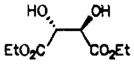
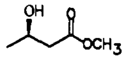
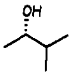
Addition of a chiral alcohol or amine to a ketene was reported as early as 1919 (de < 35%).[4] Recent advances by Ruechardt[5] and Bellucci[6] brought diastereomeric excesses above 80% but required alcohols of limited availability. Naturally occurring α-hydroxy esters and lactones are a readily available source of chirality. They have received little attention as chiral reagents,[7]

Table I[a]

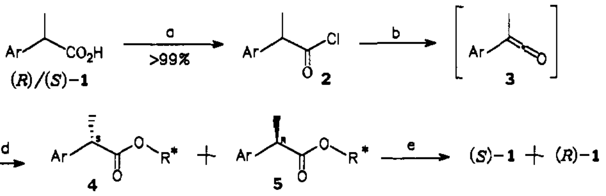
R*OH	ratio of diastereomers	% yield (**4** + **5**)	ratio of enantiomers (*S*)-**1**/(*R*)-**1**	% overall yield (*S*)-**1** + (*R*)-**1**
 **6**	97:3 *S*,*S*/*R*,*S*	92	94.5:5.5	89
 **7**	97:3 *R*,*R*/*S*,*R*	96	5.5:94.5	83
 **8**	>99:1 *R*,*R*/*S*,*R*	90	0.5:99.5	86

[a] Ar = *p*-isobutylphenyl.

Table II

entry	alcohol	ratio of diastereomers	ratio of enantiomers *S*/*R*
			
1	R = Me	95:5	93.5:6.5
2	R = Et	95:5	93:7
3	R = *i*-Pr	95:5	93:7
4	R = benzyl	95:5	91.5:8.5
5			5:95
6			0.5:99.5
7			34:66
8			80:20
9			11:89
10			67:33	34:66
11			46:54

Scheme I[a]



[a] (a) $SOCl_2$ (110 mol %), DMF (5 mol %), heptane or toluene, 50–55 °C; (b) trimethylamine or dimethylethylamine (300 mol %), 25 °C; (c) R*OH (120 mol %), same solvent (0.2 M) as (a), −78 °C; (d) 3-(dimethylamino)propylamine (5–10 mol %), 25 °C or acetic acid–H_2O, 70 °C; (e) acetic acid–2 N HCl, 85 °C, or LiOH, heptane–acetonitrile–water, 5 °C.

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