CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600429

Catalytic P−H Activation by Ti and Zr Catalysts

Jason D. Masuda, Aaron J. Hoskin, Todd W. Graham, Chad Beddie, Maria C. Fermin, Nola Etkin, and Douglas W. Stephan*[a]

Abstract: Catalytic dehydrocoupling of phosphines was investigated using the anionic zirconocene trihydride salts [Cp*$_2$Zr(μ-H)$_3$Li]$_3$ (**1a**) or [Cp*$_2$Zr(μ-H)$_3$K(thf)$_4$] (**1b**), and the metallocycles [CpTi(NP*t*Bu$_3$)(CH$_2$)$_4$] (**6**) and [Cp*M(NP*t*Bu$_3$)(CH$_2$)$_4$] (M = Ti **20**, Zr **21**) as catalyst precursors. Dehydrocoupling of primary phosphines RPH$_2$ (R = Ph, C$_6$H$_2$Me$_3$, Cy, C$_{10}$H$_7$) gave both dehydrocoupled dimers RP(H)P(H)R or cyclic oligophosphines (RP)$_n$ ($n = 4$, 5) while reaction of *t*Bu$_3$C$_6$H$_2$PH$_2$ gave the phosphaindoline *t*Bu$_2$(Me$_2$CCH$_2$)C$_6$H$_2$PH (**9**). Stoichiometric reactions of these catalyst precursors with primary phosphines afforded [Cp*$_2$Zr((PR)$_2$)H][K(thf)$_4$] (R = Ph **2**, Cy **3**, C$_6$H$_2$Me$_3$ **4**), [Cp*$_2$Zr((PPh)$_3$)H][K(thf)$_4$] (**5**), [CpTi(NP*t*Bu$_3$)(PPh$_3$)] (**7**) and [CpTi(NP*t*Bu$_3$)(μ-PHPh)]$_2$ (**8**), while reaction of **6** with (C$_6$H$_2$*t*Bu$_3$)PH$_2$ in the presence of PMe$_3$ afforded [CpTi(NP*t*Bu$_3$)(PMe$_3$)(P(C$_6$H$_2$*t*Bu$_3$)] (**10**). The secondary phosphines Ph$_2$PH and (PhHPCH$_2$)$_2$CH$_2$ also undergo dehydrocoupling affording (Ph$_2$P)$_2$ and (PhPCH$_2$)$_2$CH$_2$. The bisphosphines (CH$_2$PH$_2$)$_2$ and C$_6$H$_4$(PH$_2$)$_2$ are dehydrocoupled to give (PCH$_2$CH$_2$PH)$_2$ (**12**) and (C$_6$H$_4$P(PH))$_2$ (**13**) while prolonged reaction of **13** gave (C$_6$H$_4$P$_2$)$_8$ (**14**). The analogous bisphosphine Me$_2$C$_6$H$_4$(PH)$_2$ (**17**) was prepared and dehydrocoupling catalysis afforded (Me$_2$C$_6$H$_2$P(PH))$_2$ (**18**) and subsequently [(Me$_2$C$_6$H$_2$P$_2$)$_2$(μ-Me$_2$C$_6$H$_2$P$_2$)]$_2$ (**19**). Stoichiometric reactions with these bisphosphines gave [Cp*$_2$Zr(H)(PH)$_2$C$_6$H$_4$][Li(thf)$_4$] (**22**), [CpTi(NP*t*Bu$_3$)(PH)$_2$C$_6$H$_4$]$_2$ (**23**) and [Cp*Ti(NP*t*Bu$_3$)(PH)$_2$C$_6$H$_4$] (**24**). Mechanistic implications are discussed.

Keywords: heterogeneous catalysis · P–H activation · polyphosphines · titanium · zirconium

Introduction

The development and synthetic application of organometallic reagents and catalysts to organic chemistry has been the subject of exceptional advances over the last 25 years. The recent awarding of Nobel Prizes in 2001 to Sharpless,[1,2] Noyori,[3–6] and Knowles[7] and in 2005 to Chauvin,[8,9] Grubbs[10–20] and Schrock[21–28] for the development of catalytic methods in organic synthesis are clear indicators of the impact of organometallic chemistry. A parallel area, ripe for similar impact, involves the application of the concepts of organometallic chemistry to main group synthesis and materials chemistry. This area, coined "inorganometallics", has drawn some recent attention.[29] Much of the work to date has involved stoichiometric transformations nonetheless some catalytic processes have been uncovered. For example, catalytic dehydrocoupling has been successfully applied to prepare Si- and Sn-based oligomers and polymers from the corresponding silanes and stannanes.[30–33]

Within the broad range of inorganometallic systems, our interest has focused on transition metal–pnictogenide chemistry. During the 1990s we reported a number of studies of the stoichiometric chemistry of highly reactive zirconocene phosphinidene complexes (Zr=PR). Parallel studies have examined the reactivity of Zr−P single bonds. Much of this chemistry has been reviewed.[34] More recently, Mindiola and co-workers have probed Ti–phosphinidenes supported by diketiminato ligands.[35] These earlier studies established propensity of early metals to mediate P−P bond formation via activation of P−H bonds and suggested the potential for catalytic dehydrocoupling of phosphines. To this end, we communicated the catalytic formation of cyclic oligophosphines utilitizing a zirconocene–trihydride species as the catalyst precursor.[36] We subsequently communicated that catalytic oligomerization of bidentate phosphines afforded routes to novel P$_4$ and P$_{16}$ derivatives.[37,38] In a similar fashion, Harrod and co-workers[39,40] showed that titanocene derivatives can act as catalysts for this process. Brookhart and

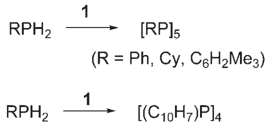
---

[a] Dr. J. D. Masuda, Dr. A. J. Hoskin, v T. W. Graham, Dr. C. Beddie, Dr. M. C. Fermin, Dr. N. Etkin, Prof. Dr. D. W. Stephan
Department of Chemistry & Biochemistry
University of Windsor, Windsor ON N9B 3P4 (Canada)
Fax: (+1) 519-973-7098
E-mail: stephan@uwindsor.ca

co-workers described the use of Rh-based catalysts for the dehydrocoupling of phosphines.[41] In a very recent paper, Waterman and Tilley[42] have reported the use of zirconocene and hafnocene complexes to effect the catalytic dehydrocoupling of stibines to give oligostibines of formulae $(ArSb)_n$ ($n = 2, 4$). In this paper we detail our work with the previously reported Zr catalyst as well as new Ti- and Zr–phosphinimide-based catalysts for dehydrocoupling of a range of mono- and bidentate, primary and secondary phosphines. Stoichiometric reactions of phosphines with the Zr and Ti catalyst precursors are also probed in an effort to garner some mechanistic information.

Results and Discussion

Dehydrocoupling of primary phosphines: We have previously communicated that the anionic zirconocene trihydride salts $[Cp^*_2Zr(\mu\text{-}H)_3Li]_3$ (**1a**) and $[Cp^*_2Zr(\mu\text{-}H)_3K(thf)_4]$ (**1b**) catalyze the dehydrocoupling of the primary phosphines $PhPH_2$, $CyPH_2$ and $Me_3C_6H_2PH_2$ upon heating to 80 °C for four days to give the cyclic oligophosphines $(RP)_5$ (Scheme 1, Table 1).[36] The analogous reaction of the naphthylphosphine $(C_{10}H_7)PH_2$ afforded the symmetric tetramer $(C_{10}H_7P)_4$ formulated on the basis of ^{31}P NMR and the mass-spectral data.



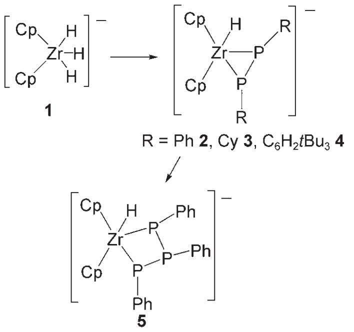
Scheme 1. Catalytic dehydrocoupling of primary phosphines by **1**.

Table 1. Catalysis using the catalysts precursor **1**, **2**, **6** and **7**.

Cat. (mol %)	Substrate	t	T [°C]	Yield major product [%][a]
1 (1)	$PhPH_2$	4d	80	92 $(PhP)_5$
1 (1)	$CyPH_2$	4d	80	85 $(CyP)_5$
1 (1)	$Me_3C_6H_2PH_2$	56 h	80	95 $(Me_3C_6H_2P)_5$
1 (1)	$(C_{10}H_7)PH_2$	7d	100	80 $((C_{10}H_7)P)_4$
1 (10)	Ph_2PH	24 h	95	87 $(Ph_2P)_2$
1 (3)	$(PhHPCH_2)_2CH_2$	36 h	25	$(PhPCH_2)_2CH_2$
2 (1)	$PhPH_2$	9 d	110	41 $(PhP)_5$[b]
2 (10)	$Me_3C_6H_2PH_2$	10 d	120	10 $(Me_3C_6H_2PH)_2$
2 (10)	$i\text{-}Pr_3C_6H_2PH_2$	10 d	120	5 $(iPr_3C_6H_2PH)_2$
2 (5)	Ph_2PH	7 d	75	50 $(Ph_2P)_2$
2 (5)	Et_2PH	7 d	75	10 $(Et_2P)_2$
2 (5)	$Ph_3C_6H_2PH_2$	20 h	75	30 $(Ph_3C_6H_2PH)_2$
2 (5)	$tBu_3C_6H_2PH_2$	2 h	75	100 $(tBu_2(Me_2CCH_2)C_6H_2PH)$
2 (5)	$tBu_3C_6H_2N_3$	4 d	115	100 $(tBu_2(Me_2CCH_2)C_6H_2NH)$
1 (3)	$H_2PCH_2CH_2PH_2$	72 h	25	87 $(C_2H_4P(PH))_2$
2 (5)	$C_6H_4(PH_2)_2$	18 h	75	100 $(C_6H_4P(PH))_2$
2 (5)	$C_6H_4(PH_2)_2$	48 h	75	75 $(C_6H_4P(PH))_2$
6 (5)	$C_6H_4(PH_2)_2$	14 d	75	95 $(C_6H_4P(PH))_2$
7 (5)	$C_6H_4(PH_2)_2$	14 d	75	30 $(C_6H_4P(PH))_2$
2 (5)	$C_6H_4(PH_2)_2$	4 d	90	100 $(C_6H_4P(PH))_2$
2 (5)	$Me_2C_6H_2(PH_2)_2$	7 d	90	65 $(Me_2C_6H_2P(PH))_2$
2 (5)	$Me_2C_6H_2(PH_2)_2$	7 d	120	35 $[(Me_2C_6H_2P_2)_2(\mu\text{-}Me_2C_6H_2P_2)]_2$

[a] Yields reported were determined by NMR spectroscopy. [b] Other yields and products 22 % $(PhPH)_2$, 4 % $(PhP)_6$, trace $(PhP)_4$.

Stoichiometric reactions of **1b** with these primary phosphines were studied in order to ascertain mechanistic information. Two equivalents of $PhPH_2$ react with **1b** to cleanly generate a new species **2** that gave rise to $^{31}P\{^1H\}$ and ^{31}P NMR spectra consisting of doublets at δ −49.2 and −89.1 ppm with $J_{P,P}$ coupling of 335 Hz. The lower field half of this pattern also showed a $J_{P,H}$ coupling constant of 41 Hz, while the ^{1}H NMR spectrum of showed the corresponding resonance at δ −2.34 ppm. These data as well as elemental analysis were consistent with the formulation of **2** as $[Cp^*_2Zr((PPh)_2)H][K(thf)_4]$ (Scheme 2). In the same vein, the related compounds $[Cp^*_2Zr((PCy)_2)H][K(thf)_4]$ (**3**) and $[Cp^*_2Zr((P(C_6H_2Me_3))_2)H][K(thf)_4]$ (**4**) were isolated. All attempts to isolate crystals of these species were unsuccessful, although this anion is presumed to be isostructural to the known isoelectronic Ta–hydride complex $[Cp_2Ta((PPh)_2)H]$.[43]



Scheme 2. Stoichiometric reactions of primary phosphines with **1**.

Reaction of **2** with an additional equivalent of $PPhH_2$ leads to the clean conversion to a new species **5**. This species exhibited a clean ABC pattern in the $^{31}P\{^1H\}$ NMR spectrum with resonances at δ −17.3, −35.0, and −60.5 ppm. The central resonance also exhibits a P–H coupling of 71 Hz. A resonance attributable to a Zr–hydride was also observed in the ^{1}H NMR spectrum at δ −2.57 ppm. These data together with elemental analysis are consistent with the formulation of **5** as $[Cp^*_2Zr((PPh)_3)H][K(thf)_4]$ (Scheme 2). The analogous products derived from $CyPH_2$ and $(C_6H_2Me_3)PH_2$ were not observed at 25 °C while at elevated temperatures only the polyphosphines $(PR)_5$ were observed. Similarly, addition of more $PhPH_2$ to **2** resulted in no further reaction at 25 °C, while $(PPh)_5$ was formed at elevated temperatures. The isolation of **2**--**5** suggests a mechanism for P–P bond formation involving sequential reaction of phosphine to yield Zr–P intermediates with concomitant loss of H_2. It is also noteworthy that addition of LiH to sample of independently prepared $[Cp^*_2Zr(PPh)_3]$ affords a species which catalyzes the formation of the oligophosphines, further supporting the notion that **5** is an intermediate in the catalytic cycle. The proposition of the initial formation of a terminal

Zr–phosphinidene species is supported by the previous isolation and characterization of $[Cp^*_2Zr(P(C_6H_2tBu_3)H][K(thf)_2]$[44] while the ZrP_2 and ZrP_3 species are observed directly in the present systems. The completion of the catalytic cycle remains unclear. One possibility is thermolysis drives reductive elimination liberating polyphosphine and generating a Zr^{II}–hydride species which oxidatively adds phosphine. Whether this occurs after further insertion of phosphine or not remains unknown. An alternative mechanism could involve elimination of $(PPh)_3$ which is known to undergo thermolysis to $(PPh)_5$.

The species $[CpTi(NPtBu_3)(CH_2)_4]$ (**6**) was also shown to act as a catalyst for dehydrocoupling, albeit slower than **1**. Heating $PhPH_2$ to 110 °C for nine days in the presence of **6**, resulted in the catalytic dehydroupling giving $(PhP)_5$ in 41 % yield while also generating several other minor products including $(PhPH)_2$, $(PhP)_6$ and $(PhP)_4$. ^{31}P NMR spectra of the reaction mixtures (Figure 1) showed resonances at δ −65.1 and −68.4 ppm that were assigned to *meso* and racemic $(PhPH)_2$.[40,45,46] In addition, a series of minor peaks located between δ −35 and −70 ppm have been tentatively assigned to Ph(H)PP(Ph)P(Ph)P(H)Ph and higher oligomers $Ph(H)P(PPh)_nP(H)Ph$.[46,47] Literature precedent has shown disproportionation of $(PhPH)_2$ affords $PhPH_2$, cyclic oligomers $(RP)_n$ and $Ph(H)P(PPh)_nP(H)Ph$ (predominantly $n=3$).[46] Upon prolonged heating three additional signals appeared which were assigned to $(PPh)_4$,[48] $(PPh)_5$[49] and $(PPh)_6$.[48] By integration, $(PPh)_5$ is the major product although it is also known that $(PPh)_4$ and $(PPh)_6$ disproportionate to $(PPh)_5$ upon heating.[50] In comparison, the analogous dehydrocoupling catalyzed by a Rh species yields $(PhPH)_2$ in 56 % yield on heating to 150 °C for 26 h.[41]

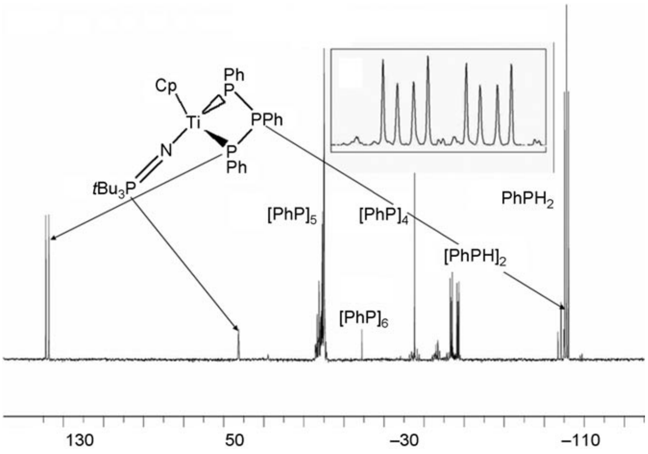
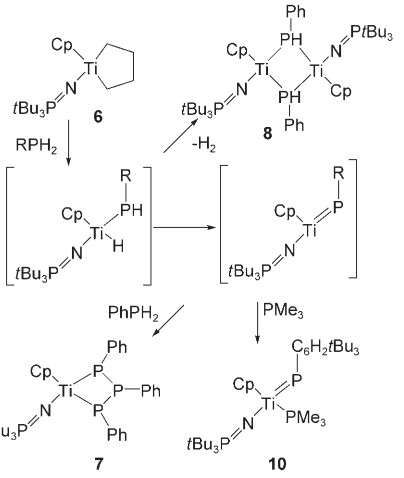


Figure 1. ^{31}P NMR spectra of the dehydrocoupling of $PhPH_2$ catalysis reaction mixture using **6** as the catalyst. Inset: expansion of *meso* and racemic $[PhPH]_2$.

In addition to the dehydrocoupling products, the ^{31}P NMR spectra of the above $PhPH_2$ reaction mixtures showed resonances including a doublet at δ 136.6 ppm and triplet at −119.9 ppm with a $J_{P,H}$ coupling constant of 304 Hz and a singlet at δ 41.0 ppm, all of which were attributed to species $[CpTi(NPtBu_3)(PPh)_3]$ (**7**) (Scheme 3). This species was prepared directly via reaction of **6** with three equivalents of $PhPH_2$ at 110 °C. The resonances attributable to the $(PPh)_3$ fragment were analogous to those reported for $[Cp_2Zr(PPh)_3]$,[51] $[Cp^*_2Zr(PPh)_3]$[52] and $[Cp_2Ti(PPh)_3]$.[53,54] The species **7** was also obtained in the reaction of $[CpTi(NPtBu_3)Cl_2]$ with PhPHLi, albeit in low yield. It is noteworthy that heating 5 mol % of **6** with $PhPH_2$ initiated further dehydrocoupling reaction, suggesting the role of **7** as a catalytic intermediate analogous to that described above for **2**.



Scheme 3. Stoichiometric reactions of primary phosphines with **6**.

The single crystal X-ray structure of **7** confirmed this formulation (Figure 2). The Ti–N and P–N distances were found to be 1.790(5) and 1.597(5) Å, respectively, while the Ti-N-P angle was 173.8(3)°, typical of Ti–phosphinimide complexes.[55] The Ti–P distances were determined to be 2.476(2) and 2.482(2) Å. The Ti–P distances are significantly shorter than the Zr–P and Hf–P distances seen in $[Cp_2Zr(PPh)_3]$, $[Cp_2Zr(PCy)_3]$, $[Cp^*_2Zr(PPh)_3]$,[51] and $[Cp_2Hf(PPh)_3]$.[56] As a result the P-Ti-P bite angle of 92.76(6)° in **2** is significantly larger than the corresponding angles of 89.3(2), 90.4(2) and 87.7(2)°, seen in $[Cp_2Zr(PPh)_3]$, $[Cp_2Zr(PCy)_3]$, and $[Cp^*_2Zr(PPh)_3]$, respectively.[51] The transannular Ti–P distance is 2.991(2) Å while the P–P distances were 2.203(2) and 2.213(3) Å. This also gives rise to a P-P-P angle of 108.74(9)°.

Attempts were made to garner further mechanistic information from additional stoichiometric reactions of $PhPH_2$ and **6**. Reaction of these reagents in a 1:1 ratio resulted in the formation of the Ti^{III} dimer $[CpTi(NPtBu_3)(\mu\text{-}PHPh)]_2$ (**8**) albeit in rather low yields (Scheme 3). While the small yield precluded detailed spectroscopic and magnetic studies of **8**, an X-ray crystallographic examination for **8** confirmed the formulation (Figure 3). In the solid state the Ti_2P_2 core is approximately planar with Ti–P distances of 2.4871(14) and 2.5009(16) Å and P-Ti-P and Ti-P-Ti angles of 88.02(5) and 91.98(5)°, respectively. The Ti–N and P–N distances are 1.836(3) and 1.595(3) Å while the P-N-Ti angle is 168.5(2)°.

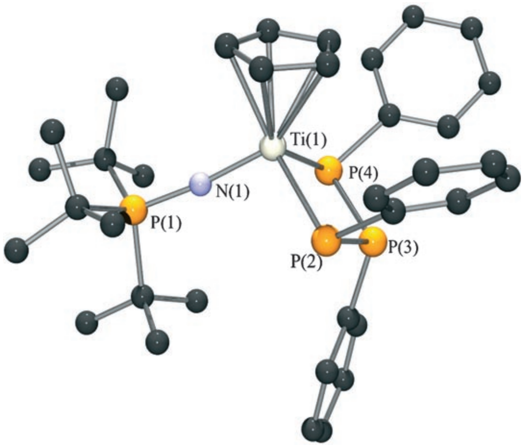


Figure 2. POV-ray drawing of the structure of **7**; Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, N: blue, P: orange, C: black; Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.790(5), Ti(1)–P(4) 2.476(2), Ti(1)–P(2) 2.482(2), Ti(1)–P(3) 2.991(2), P(1)–N(1) 1.597(5), P(2)–P(3) 2.203(2), P(3)–P(4) 2.213(3), N(1)-Ti(1)-P(4) 98.92(15), N(1)-Ti(1)-P(2) 101.24(16), P(4)-Ti(1)-P(2) 92.76(6), N(1)-Ti(1)-P(3) 107.64(15), P(2)-P(3)-P(4) 108.74(9), P(1)-N(1)-Ti(1) 173.8(3).

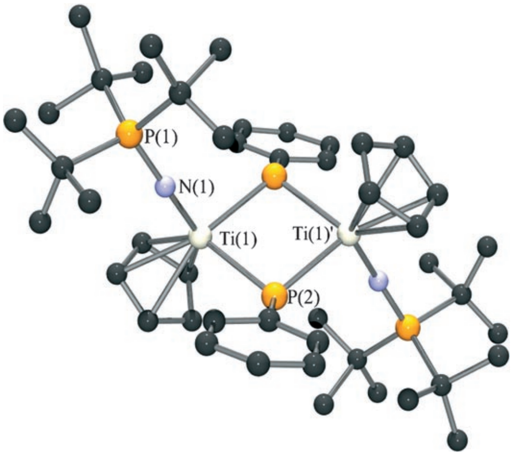
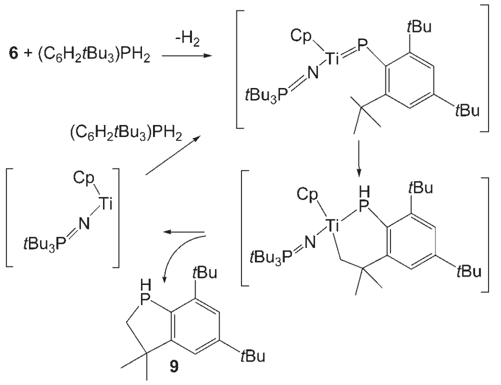


Figure 3. POV-ray drawing of the dimeric structure of **8**; Hydrogen atoms are omitted for clarity. Color scheme: Ti: wheat, N: blue, P: orange, C: black; Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.836(3), Ti(1)–P(2) 2.4871(14), Ti(1)–P(2) 2.5009(16), P(1)–N(1) 1.595(3), N(1)-Ti(1)-P(2) 104.38(10), N(1)-Ti(1)-P(2) 108.16(11), P(2)-Ti(1)-P(2)' 88.02(5), Ti(1)-P(2)-Ti(1)' 91.98(5), P(1)-N(1)-Ti(1) 168.5(2).

This Ti–N distance is slightly longer than that described for **7**, while the P–N distance is slightly shorter. These perturbations are consistent with the change in oxidation state of Ti.

The isolation of **7** and **8** has mechanistic implications. Oxidative addition of $PhPH_2$ to the Ti^{II}-synthon **6** is expected to yield a transient phosphide–hydride species [CpTiH(NP*t*Bu$_3$)(PPhH)] which can either reductively dimerize to give **8** or eliminate H_2 to generate a reactive phosphinidene which reacts with excess phosphine, prompting P–P bond formation and yielding **7**. This proposition is similar to that previously illustrated for related zirconocene chemistry.[57]

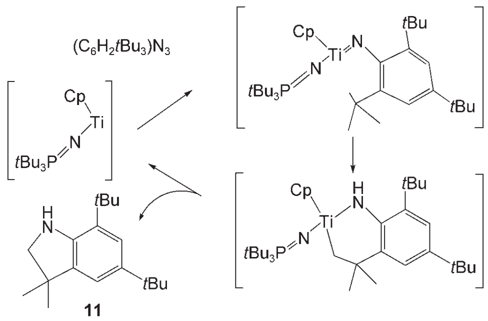
Sterically demanding phosphines react even slower. For example, after ten days at 120 °C, $Me_3C_6H_2PH_2$ and *i*Pr$_3$C$_6$H$_2$PH$_2$ were converted to $(RPH)_2$ in only 10 and 5% yield, respectively; in these cases the known cyclic oligomers $(RP)_n$ ($n=3, 4, 5$)[36,58,59] were not detected. In stark contrast, catalytic reactions of the even bulkier phosphine *t*Bu$_3$C$_6$H$_2$PH$_2$ using 5 mol% of **6** resulted in rapid and clean growth of a new signal at −79.1 ppm with a P–H coupling of 175 Hz in the ^{31}P NMR spectrum with completion of the reaction in only 2 h at 115 °C. This species was identified as phosphaindoline *t*Bu$_2$(Me$_2$CCH$_2$)C$_6$H$_2$PH (**9**) by comparison to literature data (Scheme 4).[41,60] This product has been previously prepared in a stoichiometric synthesis.[60] The species [(CH$_2$P*i*Pr$_2$)$_2$Rh(η_3-benzyl)][61] has been shown to catalyze the formation of **9** from *t*Bu$_3$C$_6$H$_2$PH$_2$ in 90% yield after 72 h at 25 °C using a 10 mol% catalyst loading. Similarly, [Cp*Rh(CH$_2$=CHTMS)$_2$][41] also gave **9** in 93% yield after 4 h at 145 °C using 2 mol% catalyst.



Scheme 4. Proposed mechanism of the catalytic formation of **9**.

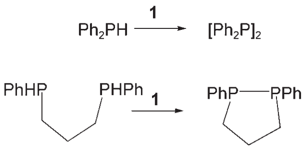
Reaction of **6** with one equivalent of the primary phosphine *t*Bu$_3$C$_6$H$_2$PH$_2$ in the presence of PMe$_3$ afforded the isolation of the species **10** in 50% yield (Scheme 3). ^{31}P NMR resonances for **10** were observed at δ 769.9, 35.3 and −10.3 ppm and assigned to a terminal Ti–phosphinidene fragment, the phosphinimide ligand and coordinated PMe$_3$, respectively. These data together with the ^1H and $^{13}C\{^1H\}$ spectra were consistent with the formulation of **10** as [CpTi(NP*t*Bu$_3$)(PMe$_3$)(P(C$_6$H$_2$*t*Bu$_3$)] (Scheme 3). While this could not be confirmed crystallographically, these data were consistent with that reported for Zr–phosphinidene[62] and more recently (Nacnac)Ti–phosphinidenes.[35] The stoichiometric synthesis of **10** suggests that a phosphinidene species is an intermediate in the catalytic formation of **9** (Scheme 4). In the absence of intervening PMe$_3$, C-H addition of an *ortho-tert*-butyl group would give the Ti metallocycle [CpTi(NP*t*Bu$_3$)(P(C$_6$H$_2$*t*Bu$_2$(CMe$_2$CH$_2$))]. Such a species would be analogous to the zirconocene derivative Cp$_2$Zr(P(C$_6$H$_2$Me$_2$(CH$_2$)) that has been isolated and characterized.[62] In the case of the present Ti species, steric crowding must drive reductive elimination to give **9** and regenerate the Ti^{II} species which reacts further with phosphine.

Attempts to effect the analogous reaction with the amine ($tBu_3C_6H_2NH_2$) showed no reaction even on heating 120 °C for several days. However, reaction of $tBu_3C_6H_2N_3$ with 5 mol % **6** for four days at 115 °C gave indoline **11** in quantitative yield by ^{1}H NMR spectroscopy.[63] A mechanism similar to that suggested for the formation of **9** is envisioned (Scheme 5). Although it appears that the amine $tBu_3C_6H_2NH_2$ fails to undergo oxidative addition to the Ti^{II} synthon, the azide does react with **6** generating a transient Ti–imide which presumably undergoes C–H activation to yield a transient metallocycle. Reductive elimination yields the indoline and releases an Ti^{II} catalyst for further with the azide. Attempts to effect similar ring formations with 2-$tBuC_6H_4N_3$ showed no reaction suggesting that steric crowding is essential for tandem E-H and C–H bond activations affording **9** and **11**.



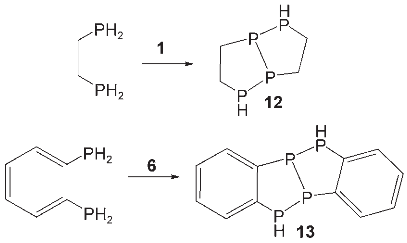
Scheme 5. Proposed mechanism of the catalytic formation of **11**.

Dehydrocoupling of secondary phosphines: Secondary phosphines also undergo catalytic dehydrocoupling reactions in the presence of **1** or **6** (Table 1). For example, treatment of Ph_2PH with 10 mol % **1** at 95 °C for 24 h gave 87 % yield of $(Ph_2P)_2$ while heating Ph_2PH with 5 mol % **6** in toluene for seven days at 75 °C gave approximately 50 % conversion to the diphosphine $(Ph_2P)_2$. The formation of this mixture of products stands in contrast to the previously reported Rh-catalyst system, [Cp*Rh($H_2CC(H)SiMe_3$)], that gave 63 % conversion of Ph_2PH to $(Ph_2P)_2$ after 27 h at 70 °C with 7.8 mol % catalyst loading.[41] In a similar fashion, 3 mol % of **1** was shown to catalyze the dehydrocoupling of $(PhHPCH_2)_2CH_2$ to give the 5-membered ring product diphenyldiphospholane $(PhPCH_2)_2CH_2$ in 36 h at 25 °C (Scheme 6, Table 1). ^{31}P NMR spectra of this reaction product showed only one resonance at δ −4.5 ppm, consistent with the formation of an enantiomeric mixture of one diastereomer of $(PhPCH_2)_2CH_2$.[64,65] Efforts to obtain X-ray quality crystals of this product were unsuccessful.



Scheme 6. Catalytic dehydrocoupling of secondary phosphines by **1**.

Dehydrocoupling of bisphosphines: Bisphosphines also undergo dehydrocoupling reactions and afford interesting oligomers. For example, we have previous reported that the dehydrocoupling of bisphosphine, $(CH_2PH_2)_2$ was catalyzed by **1a** in 72 h at 25 °C to give a 87 % isolated yield of the product **12** (Scheme 7). The $^{31}P\{^1H\}$ NMR spectrum of **12** shows two resonances at δ −22.5 and −65.4 ppm, each with second-order coupling. Simulation of the $^{31}P\{^1H\}$ NMR spectrum confirmed the interpretation as an AA′BB′ spin system, with one and two bond P–P coupling constants of J = 237, 186 and 20 Hz, respectively. These data are in good agreement with those reported by Baudler et al. who prepared **12** in 30–55 % yield via stoichiometric reductive coupling strategies.[66] We have previously communicated an X-ray diffraction study of **12** confirming the formulation as $(PCH_2CH_2PH)_2$ (Figure 4a).[38]



Scheme 7. Catalytic dehydrocoupling of **12** and **13**.

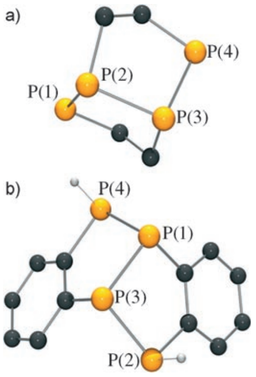


Figure 4. POV-ray drawing of the structure of a) **12**,[38] b) **13**; hydrogen atoms except P–H atoms are omitted for clarity. Color scheme: P: orange, C: black; Selected bond lengths [Å] and angles [°] for **13**: P(1)–P(4) 2.1952(7), P(1)–P(3) 2.2085(7), P(4)-P(1)-P(3) 96.19(3), P(2)-P(3)-P(1) 96.35(3).

In a similar fashion, **6** also behaves as a catalyst to effect the dehydrocoupling of bisphosphines. Reaction of $C_6H_4(PH_2)_2$ with 5 mol % **6** gave a 75 % yield of the dehydrocoupled dimer $(C_6H_4P(PH))_2$ (**13**) (Scheme 7) after 48 h at 75 °C. The $^{31}P\{^1H\}$ spectrum of **13** is also an AA′BB′ spin system, with resonances centered at δ −4.2 ppm and

−48.6 ppm (Figure 5). The coupling constants were obtained by simulation and agreed with literature data.[67] Single crystals of **13** were grown from a toluene solution. The single crystal diffraction of **13** (Figure 4b) showed a structure reminiscent of **12** reported by Hoskin et al.[38] The dimeric nature of **13** gives rise to two five-membered rings, in which the P atoms adopt a zig-zag arrangement The P–P distances are 2.1952(7) and 2.2085(7) Å while the P-P-P angles average 96.27(4)°. The dihedral angle between the aryl ring planes is 88.6°. The hydrogen atoms were located and refined and are found to adopt a *trans* disposition.

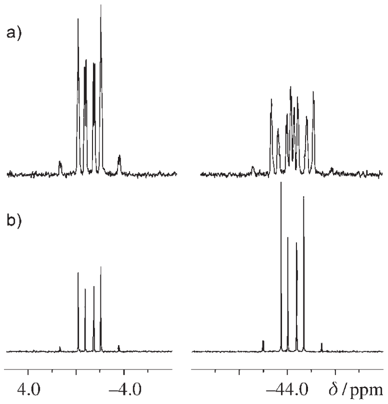


Figure 5. a) ^{31}P NMR and b) $^{31}P\{^1H\}$ spectra of **13**.

Further heating of the reaction mixtures of **6** and C_6H_4-$(PH_2)_2$ for an additional six days resulted in the complete consumption of **13** affording the new dehydrocoupled product **14**. The species **14** gave rise to two extremely broad ^{31}P NMR signals ranging from δ 34 to 17 ppm and 15 to −3 ppm, identical to $(C_6H_4P_2)_8$,[37] the P_{16} macrocyclic species (Figure 6) obtained by the catalytic dehydrocoupling of $C_6H_4(PH_2)_2$ using **1a** as the catalyst.[37] X-ray crystals were also obtained from the present catalysis and the identity of the product **14** was confirmed via preliminary crystallographic analysis. However, powder X-ray diffraction of the bulk reaction product showed the product is not uniformly microcrystalline **14** (Figure 7). This suggests the presence of other dehydrocoupling oligomers.

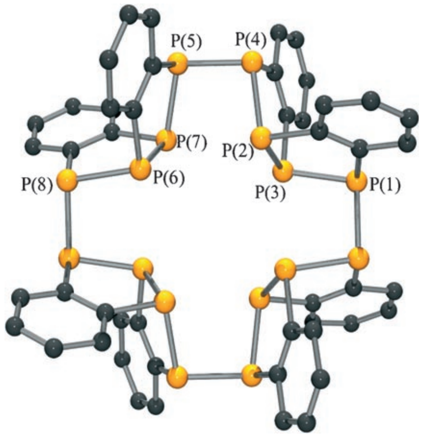


Figure 6. POV-ray drawing of the structure of **14**; hydrogen atoms are omitted for clarity. Color scheme: P: orange, C: black.[37]

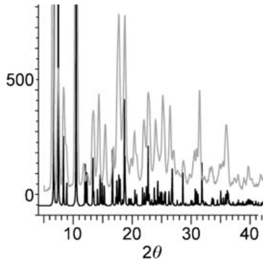


Figure 7. Experimentally observed powder X-ray diffraction plot (counts vs 2θ) for the bulk product of dehydrocoupling of $C_6H_4(PH_2)_2$ in red and the PXRD pattern calculated for **14** in black.

In an effort to improve on the solubility of the P_{16} oligomer **14**, the synthesis of a substituted analogue was undertaken. To this end $((MeO)_2PO)_2C_2$ (**15**) was prepared by literature method of Seyferth and co-workers.[68] This was converted via a [4+2] cycloaddition of dimethylbutadiene to $Me_2C_6H_4((MeO)_2PO)_2$ (**16**)[69,70] and reduced to $Me_2C_6H_4(PH)_2$ **17**. During our work, the synthesis of **17** was reported in the literature.[71] The formulation of **17** was confirmed crystallographically (Figure 8) although a twofold disorder precludes a discussion of the metric parameters.

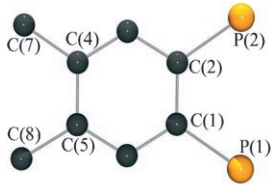
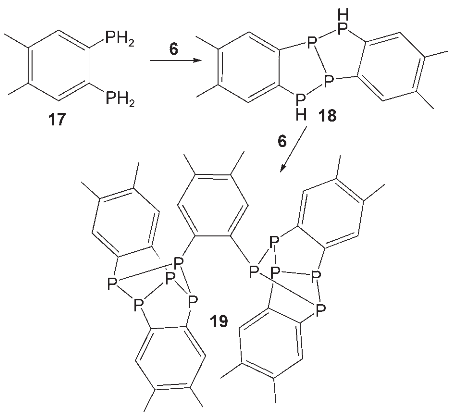


Figure 8. POV-ray drawing of the structure of **18**; Hydrogen atoms are omitted for clarity. Color scheme: P: orange, C: black. One of the form of the twofold disorder is shown.

Reaction of **17** with 5 mol % **6** in toluene at 90 °C for seven days gave the corresponding dehydrocoupled product **18**. The ^{31}P NMR spectrum reveals the signals of the AA′BB′ spin system at δ 1.85 and −45.4 ppm similar to that described for **13**. These data support the formulation of **18** as $(Me_2C_6H_2P(PH))_2$ (Scheme 8). Heating at 120 °C for one week, this reaction mixture gives a faint yellow colored crystalline highly insoluble solid **19**. Fortunately, single crystals were obtained from the reaction mixture and single crystal X-ray diffraction revealed that **19** is formulated as $[(Me_2C_6H_2P_2)_2(\mu\text{-}Me_2C_6H_2P_2)]_2$ (Scheme 8). This molecule consists of two P_5 rings bridged by a central P_2 fragment (Figure 9). The P–P bond lengths range from 2.1891(9) to 2.2716(9) Å, similar to the P–P bond length seen in white phosphorus (2.21(2) Å).[72] The P-P-P bond angles range from 92.54(3) to 103.98(3)°. It is noteworthy that in contrast to **14**, powder X-ray diffraction of a bulk sample of **19**



Scheme 8. Catalytic dehydrocoupling of **18** and **19**.

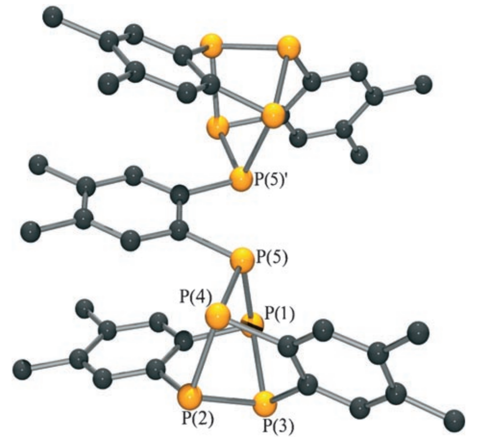


Figure 9. POV-ray drawing of the structure of **19**; Hydrogen atoms are omitted for clarity. Color scheme: P: orange, C: black; Selected bond lengths [Å] and angles [°]: P(1)−P(3) 2.2305(9), P(1)−P(5) 2.2716(9), P(2)−P(3) 2.1891(9), P(2)−P(4) 2.2546(9), P(4)−P(5) 2.2017(8), P(3)-P(1)-P(5) 101.73(3), P(3)-P(2)-P(4) 92.54(3), P(2)-P(3)-P(1) 93.70(3), P(5)-P(4)-P(2) 103.98(3), P(4)-P(5)-P(1) 99.90(3).

showed the product to be a uniform, microcrystalline material (Figure 10).

The related Ti and Zr complexes [Cp*M(NP*t*Bu$_3$)(CH$_2$)$_4$] (M = Ti **20**, Zr **21**) were also tested as catalysts for dehydrocoupling of $C_6H_4(PH_2)_2$. These tests revealed that steric congestion presumably a result of the pentamethylcyclopentadienyl ligand slowed the reaction significantly as **6** gave **13** quantitatively in 18 h, while **20** gave 95 % conversion in 14 days. Use of the corresponding Zr catalyst **21** resulted in a much less effective conversion giving only a 30 % yield of **13** in 14 days.

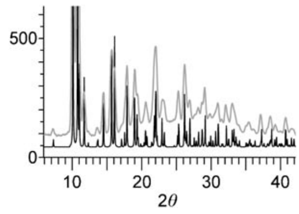


Figure 10. Experimentally observed powder X-ray diffraction plot (counts vs 2θ) for the bulk product of dehydrocoupling of $Me_2C_6H_2(PH_2)_2$ in red and the PXRD pattern calculated for **19** in black.

Stoichiometric reactions with these bisphosphines were also examined. A 1:1 reaction of **1a** with $C_6H_4(PH_2)_2$ gave green crystals of a new species **22**. $^{31}P\{^1H\}$ NMR spectral data of **22** showed two sets of doublets at δ −34.6 and −37.7 ppm with P–P coupling constants of J = 25 and 215 Hz. The former resonance also exhibited P–H coupling of 168 Hz (Figure 11). The latter resonance also exhibits and additional P–H couplings of 22 Hz. The ^{1}H NMR spectrum showed a doublet of multiplets at δ 2.03 ppm with a P–H coupling of J = 74 Hz attributable to a Zr–hydride. In addition, the ^{1}H NMR spectrum showed two sets of resonances at δ 2.78 and 2.35 ppm attributable to P–H fragments. These resonances exhibited couplings attributable to one-bond P−H, four bond P−H, three-bond H–H couplings. These spectroscopic data together support the formulation of **22** as [Cp*$_2$Zr(H)(PH)$_2$C$_6$H$_4$][Li(thf)$_4$] (Scheme 9) although attempts to obtain elemental analysis data were precluded by the extreme air sensitivity of **22**. Nonetheless the salt formulation of **22** was confirmed by a crystallographic study (Figure 12). The anion of **22** reveals Zr–P distances of 2.680(5) and 2.764(6) Å while a P-Zr-P angle of 68.29(18)°. The longer Zr–P distance is observed for the P atom adjacent the Zr–hydride. These distances are typical of those reported for a variety of Zr–P species.[34]

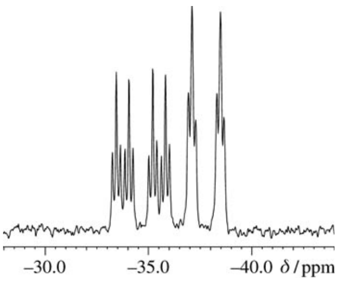
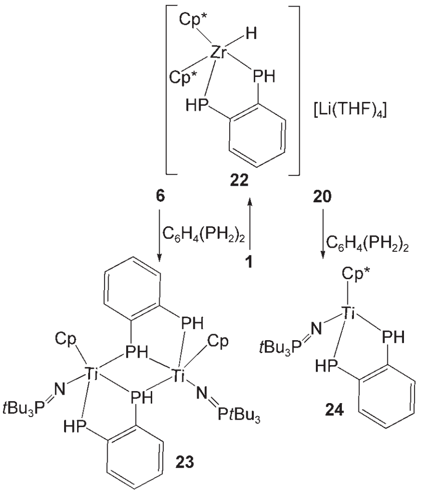


Figure 11. a) ^{31}P NMR and b) $^{31}P\{^1H\}$ spectra of **22**.



Scheme 9. Synthesis of compounds **22**–**24**.

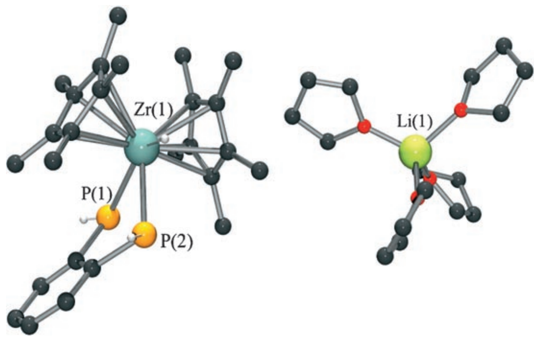


Figure 12. POV-ray drawing of the structure of **22**; Hydrogen atoms except the hydride are omitted for clarity. Color scheme: P: orange, C: black; Selected bond lengths [Å] and angles [°]: Zr(1)–P(2) 2.680(5), Zr(1)–P(1) 2.764(6), P(2)-Zr(1)-P(1) 68.29(18).

In a related stoichiometric reaction, **6** reacted with C_6H_4-$(PH_2)_2$ to give a new product **23**. The $^{31}P\{^1H\}$ NMR spectrum of **23** reveals a singlet at 36.3 ppm, typical of a titanium-bound phosphinimide, as well as two other singlets at δ −18.7 and −72.2 ppm. The corresponding ^{31}P spectrum showed the signals at −18.7 and −72.2 ppm as doublets with P–P couplings of $J = 157$ and 236 Hz, respectively. These signals are reminiscent of those seen for the *meso* (−72.2 ppm) and racemic (−18.7 ppm) $[Cp_2Zr(PH)_2C_6H_4]$ reported by Hey et al.[73] The ^1H NMR spectrum of **23** showed two doublets attributable to P–H bonds at δ 4.13 and 5.39 ppm. A NOESY spectrum showed correlation between the phosphinimide *t*Bu groups and the doublet at 5.39 ppm. A second, less intense cross peak was related to the doublet at 4.13 ppm. These data suggest that one of the P–H units is closer to the phosphinimide implying a dimeric structure in solution. This view was also supported by the fact that addition of pyridine to a solution of **23** failed split the dimer. Single crystal X-ray diffraction confirmed that **23** is in fact a dimer in the solid state of formula $[CpTi(NPtBu_3)(PH)_2C_6H_4]_2$ (Scheme 9, Figure 13). The dimeric nature of **23** arises from one of the two P atoms of a chelate on a Ti center bridging to a second Ti center. In the solid state this geometry dictates a *cisoid* orientation of the Cp ligands. The phosphinimide linkages are typical of Ti^{IV} complexes with Ti–N and P–N distances averaging 1.816(6) and 1.588(5) Å, respectively, with P-N-Ti angles approaching linearity at 176.0(3) and 175.6(3)°. The terminal Ti–P distances were found to be 2.584(2) and 2.581(2) Å, while the bridging Ti–P distances are 2.6339(19), 2.6551(19), 2.6398(19), and 2.644(2) Å. The Ti_2P_2 core is slightly puckered with an angle between the TiP_2 planes of 17.7°. The angles at Ti within this core are 63.72(6) and 63.79(5)° while the corresponding angles at P are 114.35(7) and 113.80(7)°. The chelate P-Ti-P angles are 71.18(6) and 70.74(6)°.

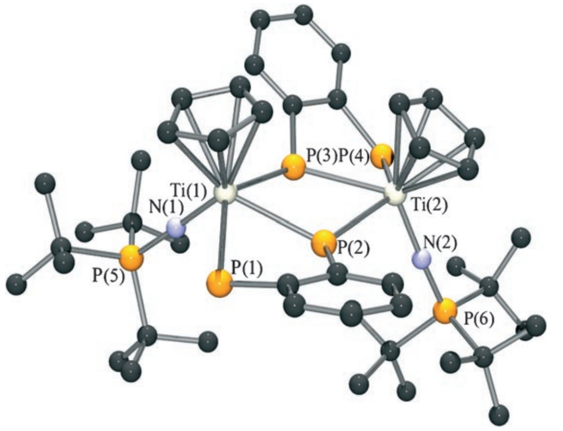


Figure 13. POV-ray drawing of the structure of **23**; Hydrogen atoms are omitted for clarity. Color scheme: P: orange, C: black; Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.807(5), Ti(1)–P(1) 2.584(2), Ti(1)–P(2) 2.6339(19), Ti(1)–P(3) 2.6551(19), Ti(2)–N(2) 1.825(5), Ti(2)–P(4) 2.581(2), Ti(2)–P(3) 2.6398(19), Ti(2)–P(2) 2.644(2), P(5)–N(1) 1.595(5), P(6)–N(2) 1.580(5), N(1)-Ti(1)-P(2) 115.89(15), P(1)-Ti(1)-P(2) 71.18(6), N(1)-Ti(1)-P(3) 96.02(16), P(1)-Ti(1)-P(3) 132.11(7), P(2)-Ti(1)-P(3) 63.72(6), N(2)-Ti(2)-P(4) 89.23(16), N(2)-Ti(2)-P(3) 120.05(16), P(4)-Ti(2)-P(3) 70.74(6), N(2)-Ti(2)-P(2) 97.11(16), P(4)-Ti(2)-P(2) 130.62(7), P(3)-Ti(2)-P(2) 63.79(5), Ti(1)-P(2)-Ti(2) 114.35(7), Ti(2)-P(3)-Ti(1) 113.80(7), P(5)-N(1)-Ti(1) 176.0(3), P(6)-N(2)-Ti(2) 175.6(3).

In the analogous stoichiometric reaction of $C_6H_4(PH_2)_2$ with **20**, the resulting product **24** exhibits a singlet at δ 41.9 and a doublet at 34.9 ppm ($^1J_{P,H} = 179$ Hz) in the ^{31}P NMR spectrum. The corresponding ^1H NMR spectrum contains resonances attributable to the Cp* and phosphinimide ligands as well as a doublet at 4.67 ppm ($^1J_{P,H} = 179$ Hz) consistent with P–H fragments. Single crystal X-ray diffraction revealed that in contrast to **23** the species **24** is a monomer with formulation $[Cp^*Ti(NPtBu_3)(PH)_2C_6H_4]$ (Scheme 9, Figure 14). The pseudo tetrahedral geometry about Ti gives arise to Ti–P distances of 2.4998(9) and 2.5046(9) Å. The chelate P-Ti-P angle of 81.18(3)° is significantly larger than that seen in **23**, presumably a result of reduced steric congestion. The phosphinimide fragment is again typical of Ti^{IV} species with a Ti–N and P–N distances of 1.812(2) and 1.600(2) Å, respectively, with a P-N-Ti angle of 176.20(14)°. The P-bound hydrogen atoms were located and adopt a

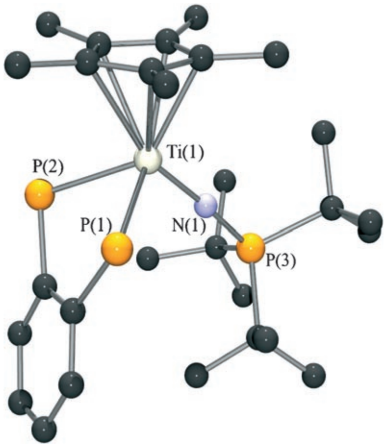


Figure 14. POV-ray drawing of the structure of **24**; Hydrogen atoms are omitted for clarity. Color scheme: P: orange, C: black; Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.812(2), Ti(1)–P(2) 2.4998(9), Ti(1)–P(1) 2.5046(9), P(3)–N(1) 1.600(2), P(2)-Ti(1)-P(1) 81.18(3), P(3)-N(1)-Ti(1) 176.20(14).

meso configuration as the aryl ring is bent towards the phosphinimide *t*Bu groups with C_{ipso}-P-Ti angles of 98.12(9) and 97.71(9)° and away from the Cp* ligand. Attempts to effect a crossover between dimeric **23** and monomeric **24** showed no exchange in toluene.

The isolation of these complexes **23** and **24** are consistent with the expected complexation which initiates the catalytic process, however, attempts to garner further insight via addition of excess phosphine were uninformative. In the case where catalysis is mediated by **1** the isolation of **22** also represents the initial complexation product. However, in this case we have previously communicated the spectroscopic observation of $[Cp^*Zr((HP)_2C_6H_4)_2]^-$ and the isolation of the minor crystalline product $[Cp^*Zr(P_2C_6H_4)_2]_2^{2-}$. As these species could not be isolated in bulk, it remains unclear whether these species are reaction intermediates or byproducts.

In summary, we have shown that Zr and Ti species can mediate the catalytic dehydrocoupling of phosphines to give a variety of oligophosphines. While products of stoichiometric reactions provide some insight into the initiation of dehydrocoupling, a full understanding of the mechanism of this process continues to be a target of research efforts. In addition, we are currently seeking new, more active catalysts as well as developing applications for the resulting oligomers.

Experimental Section

General data: All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glove box. Solvents were purified employing a Grubbs'-type solvent purification system manufactured by Innovative Technology. Deuterated solvents were purified using the appropriate techniques. All organic reagents were purified by conventional methods. ^{1}H, ^{31}P, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance-300 and 500 spectrometers. All NMR spectra were recorded in C_6D_6 at 25 °C, unless otherwise noted. For ^{1}H and ^{13}C{^{1}H} NMR spectra, trace amounts of protonated solvents were used as internal references and chemical shifts are reported relative to $SiMe_4$. For ^{31}P, ^{31}P{^{1}H} NMR spectroscopy, 85 % H_3PO_4 was used an external reference. Chemical shifts are reported in ppm and coupling constants are reported in Hz. In some cases, spectral simulations were performed with the software PANIC. Combustion analyses were done in house employing a Perkin Elmer CHN Analyzer. $PhPH_2$, Ph_2PH, Et_2PH and $C_2H_4(PH_2)_2$ were purchased from either the Aldrich Chemical Company or the Strem Chemical Co. $Me_3C_6H_2PH_2$,[74] iPr$_3C_6H_2Br$,[75] iPr$_3C_6H_2PH_2$,[76] tBu$_3C_6H_2PH_2$,[77] tBu$_3C_6H_2N_3$,[78] tBuC$_6H_4N_3$,[78] $Ph_3C_6H_2Br$,[79] $Ph_3C_6H_2PH_2$[76] $[Cp^*_2Zr(\mu\text{-}H)_3Li]_3$ (**1a**),[80] $[Cp^*_2Zr(\mu\text{-}H)_3K(thf)_4]$ (**1b**),[36] [CpTi(NP*t*Bu$_3$)(CH$_2$)$_4$] (**6**)[81] and [Cp*Ti(NP*t*Bu$_3$)(CH$_2$)$_4$] (**20**)[81] were prepared by literature methods.

General conditions for catalytic dehydrocoupling of phosphines: These reactions were performed in a similar fashion and thus the general procedure is described. Temperatures and times are tabulated in Table 1. An NMR tube fitted with a Teflon stopcock was charged with phosphine and 0.01–0.10 molar equivalents of **6** in [D$_8$]toluene (0.6 mL). The initially light brown solution changed to dark brown with evolution of gas. The solution was heated for 4–12 days at 90 °C and the reaction monitored by ^{31}P NMR spectroscopy. The products were identified by comparison of the chemical shifts to literature data. Reaction mixtures were transferred to vials and evacuated to dryness. In some cases the products were isolated by recrystallization after dissolution in hot toluene and filtration through Celite. Products: **(PPh)$_5$**: ^{1}H NMR ([D$_8$]THF): δ = 7.37 (m, 2H, Ph), 7.03 (d, 1H, Ph), 6.85 (m, 2H, Ph); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 141.1 (d, $^{3}J_{P,C}=14$ Hz), 134.5 (d, $^{4}J_{P,C}=23$ Hz), 127.8, 127.3; ^{31}P{^{1}H} NMR (THF): δ = −5 (br m); HRMS: m/z: 541.1265 [M+H$^+$; X-ray unit cell parameters: orthorhombic, $a=9.75$, $b=10.16$, $c=27.53$ Å; elemental analysis calcd (%) for C_6H_5P: C 66.7, H 4.7; found: C 66.6, H 4.7.

(PC$_6$H$_2$Me$_3$)$_5$: ^{1}H NMR ([D$_8$]THF): δ = 6.93 (m, 2H, $^{4}J_{P,H}=18$ Hz, Ar), 1.76 (s, 3H, Me), 1.67 (s, 6H, Me); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 143.5 (d, $^{3}J_{P,C}=18$ Hz), 139.1, 136.7 (d, $^{1}J_{P,C}=28$ Hz), 123.8, 23.3, 21.3; ^{31}P{^{1}H} NMR (THF): δ = −2 (br m); elemental analysis calcd (%) for $C_9H_{11}P$: C 72.0, H 7.9; found: C 71.8, H 7.4.

(PCy)$_5$: ^{1}H NMR ([D$_8$]THF): δ = 3.11 (m, 1H, $^{2}J_{H,P}=3$ Hz), 1.45 (m, 4H, CH), 1.44 (m, 4H, CH), 1.13 (br m, 2H, CH); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 51.8 (d, $^{1}J_{P,C}=17$ Hz), 38.1, 26.8 (d, $^{2}J_{P,C}=24$ Hz), 25.6; ^{31}P{^{1}H} NMR (THF): δ = −15 (br m); elemental analysis calcd (%) for $C_6H_{11}P$: C 63.1, H 9.7; found: C 63.0, H 9.7.

(C$_{10}$H$_7$P)$_4$: ^{31}P{^{1}H} NMR (THF): δ = −63.0; EIMS: m/z: 632.

[Cp*$_2$Zr((PR)$_2$)H][K(thf)$_4$] (R = Ph 2, Cy 3, C$_6$H$_2$Me$_3$ 4) and [Cp*$_2$Zr((PPh)$_3$)H][K(thf)$_4$] (5): These compounds were prepared in a similar fashion and thus only one preparation is detailed. Two equivalents of $PhPH_2$ (0.019 g, 0.110 mmol) were added to a THF solution (5 mL) of **1b** (0.037 g, 0.055 mmol). The reaction was stirred for 4 h and monitored by ^{31}P NMR spectroscopy. The solution was concentrated and the product precipitated with hexanes to give **2** (0.040 g, 82 %). ^{1}H NMR ([D$_8$]THF): δ = 8.14 (br m, 4H, Ph), 7.81 (br m, 4H, Ph), 7.12 (br m, 2H, Ph), 3.59 (br s, 16H, THF), 2.08 (s, 30H, Me), 1.54 (br s, 16H, THF), −2.34 (d, 1H, $^{2}J_{P,H}=41$ Hz, ZrH); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 130.0, 128.5, 127.1, 121.7 (d, $^{1}J_{P,C}=6$ Hz), 111.8, 67.5, 25.5, 12.5; ^{31}P NMR (THF): δ = −49.2 (dd, $^{1}J_{P,P}=335$, $^{2}J_{P,H}=41$ Hz), −89.2 (d, $^{1}J_{P,P}=335$ Hz); elemental analysis calcd (%) for $C_{48}H_{73}KP_2O_4Zr$: C 63.54, H 8.22; found: C 63.50, H 8.09.

Compound 3: ^{1}H NMR ([D$_8$]THF): δ = 3.64 (br m, 16H, THF), 2.30 (s, 30H, Me), 1.89, 1.88, 1.73 (br m, 22H), 1.51 (br m, 16H, THF), −2.29 (d, 1H, $^{2}J_{P,H}=28$ Hz, ZrH); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 109.8, 67.6, 35.9 (d, $^{2}J_{P,C}=29$ Hz), 27.3, 27.2, 26.9, 25.5, 13.1; ^{31}P NMR (THF): −23.6 (dd, $^{1}J_{P,P}=340$, $^{2}J_{P,H}=28$ Hz), −66.3 (d, $^{1}J_{P,P}=340$); elemental analysis calcd (%) for $C_{48}H_{85}KP_2O_4Zr$: C 62.8, H 9.3; found: C 62.5, H 9.3.

Compound 4: ^{1}H NMR ([D$_8$]THF): δ = 7.43 (s, 4H, Ar), 3.65 (br m, 16H, THF), 1.98 (s, 30H, Me), 2.02 (br s, 18H, Me), 1.51 (br m, 16H, THF), −2.40 (d, 1H, $^{2}J_{P,H}=32$ Hz); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 134.7, 1.34.6, 134.4, 134.2, 117.7, 67.5, 25.6, 22.9, 20.7, 12.5; ^{31}P NMR (THF): δ = −55.8 (dd, $^{1}J_{P,P}=348$, $^{2}J_{P,H}=32$ Hz), −87.1 (d, $^{1}J_{P,P}=348$ Hz); elemental analysis calcd (%) for $C_{54}H_{85}KP_2O_4Zr$; C 65.5, H 8.7; found: C 65.3, H 8.6.

Compound 5: ^{1}H NMR ([D$_8$]THF): δ = 8.01 (br m, 6H, Ph), 7.69 (br m, 6H, Ph), 7.15 (br m, 3H, Ph), 3.51 (br m, 16H, THF), 1.82 (s, 15H, Me), 1.08 (s, 15H, Me), 1.50 (br m, 16H, THF), −2.57 (d, 1H, $^{2}J_{P,H}=71$ Hz, ZrH); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 127.8, 127.5, 126.2, 120.1, 112.8, 107.0, 67.0, 25.0, 13.7, 13.6; ^{31}P NMR ([D$_8$]THF): δ = −35.0 (ddd, $^{2}J_{P,P}=172$, $^{1}J_{P,P}=182$, $^{2}J_{P,H}=71$ Hz), −17.3 (dd, $^{2}J_{P,P}=172$, $^{1}J_{P,P}=149$ Hz), −60.5 (dd, $^{1}J_{P,P}=149$, $^{1}J_{P,P}=182$ Hz); elemental analysis calcd (%) for $C_{54}H_{78}KP_3O_4Zr$: C 63.9, H 7.8; found: C 63.8, H 7.7.

[CpTi(NP*t*Bu$_3$)(PPh)$_3$] (7): Three equivalents of $PhPH_2$ (64 mg, 0.584 mmol) were added to a sealed glass vessel fitted with a Teflon stopcock containing **6** (75 mg, 0.195 mmol) in toluene (2 mL). The solution was heated for 5 h at 110 °C resulting in a red colored solution. Upon cooling a copious amount of red solid precipitated. The solvent was decanted and the solids were dissolved in hot toluene (7 mL). Upon cooling to room temperature the solution was layered with pentane (5 mL) and cooled to −35 °C for three days giving red block-like crystals. Crystals were isolated by decantation and washed with cold pentane (3 × 5 mL) giving the title compound (30 mg, 23 %). ^{1}H NMR: δ = 8.66 (br s, 2H, Ph), 7.86 (br s, 4H, Ph), 7.00–7.21 (m, 9H, Ph), 5.76 (s, 5H, Cp), 1.03 (d, 27H, $^{3}J_{P,H}=13$ Hz, *t*Bu); ^{13}C{^{1}H} NMR (partial): δ = 133.5–133.9 (br m), 129.7–130.0 (br m), 128.1–128.6 (m, obscured by C_6D_6), 126.3, 126.0, 112.4 (s, Cp), 41.7 (d, P-C, $^{1}J_{P,C}=70$ Hz), 30.0 (s, Me); ^{31}P NMR: δ = 135.1 (d, PPP, $^{1}J_{P,P}=303$ Hz), 40.0 (s, NP), −120.6 (t, $^{1}J_{P,P}=303$ Hz, TiP); elemental analysis calcd (%) for $C_{35}H_{47}NP_4Ti$: C 64.3, H 7.3, N 2.1; found: C 64.6, H 7.7, N 2.2.

[CpTi(NPtBu$_3$)(μ-PHPh)]$_2$ (8): $PhPH_2$ (30 μL) in pentane (3 mL) was added dropwise at −80 °C to **6** (2 mg, 0.26 mmol) in pentane (5 mL). The solution was warmed to room temperature and stirred for 20 min and then the solvent was removed in vacuo. Brown X-ray quality crystals were obtained from a concentrated benzene solution upon prolonged standing (ca. two weeks). Yield: 42 mg, 25 %. elemental analysis calcd (%) for $C_{50}H_{76}N_2P_4Ti_2$: C 63.2, H 8.5, N 3.2; found: C 59.1, H 8.7, N 3.4.

Catalytic synthesis of (tBu$_2$(Me$_2$CCH$_2$)C$_6$H$_2$PH) (9): In a Teflon capped 5 mm NMR tube, tBu$_3$C$_6$H$_2$PH$_2$ (50 mg, 0.180 mmol) was combined with **6** (5 mol %, 8.98 μmol, 3.5 mg) dissolved in [D$_8$]toluene (0.6 mL). The sealed NMR tube was heated to 75 °C for 2 h after which complete conversion to phosphaindoline (**8**) was ascertained by ^{1}H and ^{31}P NMR.

[CpTi(NPtBu$_3$)(PMe$_3$)(P(C$_6$H$_2$$tBu_3$)] (10): PMe_3 (500 μL, 4.830 mmol) was added to a solution of (620 mg, 1.609 mmol) of **6** in pentane (5 mL). The mixture was stirred for 5 min and the flask was then evacuated briefly to remove ethylene, and then back-filled with nitrogen. The evacuation/back-fill procedure was repeated twice, with a 5 min interval of stirring at atmospheric pressure between the cycles. A solution of (C$_6$H$_2$$tBu_3$)PH$_2$ (380 mg, 1.608 mmol) in pentane (5 mL) was then added dropwise at −80 °C; the mixture was warmed slowly to room temperature and then stirred overnight. After concentrating to precipitation, the mixture was cooled to −35 °C overnight and the black solid was collected and dried in vacuo (540 mg, 50 %). ^{1}H NMR: δ = 7.76 (s, 2H, Ar), 5.73 (d, $^{3}J_{P,H}=2$ Hz, Cp), 1.71 (s, 18H, tBu), 1.63 (s, 9H, tBu), 1.44 (d, $^{3}J_{P,H}=13$ Hz, tBu), 1.10 (d, $^{2}J_{P,H}=6$ Hz, Me); ^{13}C{^{1}H} NMR: δ = 144.4, 141.8, 120.5, 107.8, 41.6 (d, $^{1}J_{P,C}=50$ Hz), 33.6, 32.5, 32.5, 30.8; ^{31}P{^{1}H} NMR: δ = 769.9 (s, TiPAr), 35.3 (s, NP), −10.3 (s, PMe$_3$); elemental analysis calcd (%) for $C_{46}H_{70}NP_3Ti$: C 66.9, H 10.4, N 2.1; found: C 66.7, H 10.3, N 2.0.

Catalytic synthesis (tBu$_2$(Me$_2$CCH$_2$)C$_6$H$_2$NH) (11): In a Teflon capped 5 mm NMR tube, tBu$_3$C$_6$H$_2$N$_3$ (50 mg, 0.174 mmol) was combined with **6** (5 mol %, 8.70 μmol, 3.4 mg) dissolved in [D$_8$]toluene (0.6 mL). The sealed NMR tube was heated to 115 °C for 4 d after which complete conversion to indoline **9** was ascertained by ^{1}H NMR.

(PCH$_2$CH$_2$PH)$_2$ (12): Compound **1a** (0.1 g, 0.27 mmol) was dissolved in THF (3 mL) and $(CH_2PH_2)_2$ (1 g, 10.6 mmol) was added, with stirring. The colorless solution became green, then aquamarine and finally blue, over a period of 30 min. The reaction mixture was stirred for a period of 72 h, until it became colorless. Solvent was removed in vacuo leaving a white solid, which was dissolved in hexane, filtered, and placed in a freezer (−35 °C). Colorless X-ray quality crystals (0.86 g, 87 %) of **12** precipitated from solution, over 24 h. ^{1}H NMR ([D$_8$]THF): δ = 3.65 (dt, 2H, $^{1}J_{P,H}=330$, $^{3}J_{H,H}=10$ Hz, PH), 2.43 (m, 2H, CH$_2$), 1.87 (m, 2H, CH$_2$), 1.14 (m, 2H, CH$_2$), 0.74 (m, 2H, CH$_2$); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 38.4, 30.7; ^{31}P NMR: δ = −22.5 (dd, $^{1}J_{P,P}=237$, $^{1}J_{P,P}=186$, $^{2}J_{PP}=20$ Hz, P), −65.4 ($^{1}J_{P,H}=237$, $^{1}J_{P,P}=186$, $^{2}J_{P,P}=20$ Hz, PH); elemental analysis calcd (%) for $C_4H_{10}P_4$: C 26.4, H 5.5; found: C 26.2, H 5.4.

(C$_6$H$_4$P(PH))$_2$ (13), (C$_6$H$_4$P$_2$)$_8$ (14) and (Me$_2$C$_6$H$_2$P(PH))$_2$ (18): These compounds were prepared in a similar fashion and thus one preparation is detailed. Temperatures, times, and yields are tabulated in Table 1. In a sealed NMR tube, $C_6H_4(PH_2)_2$ (350 mg, 2.46 mmol) was combined with 0.05 molar equivalents of **1** (0.123 mmol, 47 mg) in [D$_8$]toluene (0.6 mL). The initially light brown solution changed to dark brown with evolution of gas. Heating the solution for 4 d at 90 °C gave nearly quantitative conversion by ^{31}P NMR. The mixture was transferred to a vial and evacuated to dryness. The tan colored solid was dissolved in a minimum of hot toluene and filtered through Celite. Removal of toluene gave **13** as an analytically pure powder (275 mg, 80 %). ^{1}H NMR ([D$_8$]toluene): δ = 7.53 (br s, 2H, Ar), 7.10 (m, 2H, Ar), 6.79 (m, 2H, Ar), 6.61 (m, 2H, Ar), 4.65 (dd, 2H, $^{1}J_{P,H}=209$, $^{2}J_{P,H}=8$ Hz, Ar); ^{13}C{^{1}H} NMR: δ = 136.9 ($^{1}J_{P,C}=12$ Hz, Ph), 136.4 ($^{1}J_{P,C}=38$ Hz), 132.7, 130.3; elemental analysis calcd (%) for $C_{12}H_{10}P_4$: C 61.4, H 9.0; found: C 61.2, H 9.0.

Compound 14: ^{1}H NMR (CDCl$_3$): δ = 7.69 (1H, Ph), 7.43 (1H, Ph), 7.27 (1H, Ph), 7.21 (1H, Ph); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 128.6 ($^{1}J_{P,C}=41$, $^{1}J_{P,C}=38$ Hz), 127.0, 125.3, 123.7 ($^{1}J_{P,C}=28$ Hz); ^{31}P{^{1}H} NMR: δ = −0.98 (dd, $^{1}J_{P,P}=156$, $^{2}J_{P,P}=70$ Hz), −44.0 (dd, $^{1}J_{P,P}=156$, $^{2}J_{P,P}=70$ Hz);[67] ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 38.4 (br m), −4.7 (br m); elemental analysis calcd (%) for $C_6H_4P_2$: C 52.2, H 2.9; found: C 52.0, H 2.9.

Compound 18: ^{1}H NMR: δ = 7.40–7.58 (m, 4H, Ar), 4.85 (d of m, 2H, $^{1}J_{P,H}=203$, P-H), 1.76 (s, 6H, Me), 1.64 (s, 6H, Me); ^{13}C{^{1}H} NMR: δ = 147.6 (br m), 137.8, 136.6, 134.3, 133.9, 131.3 (br m), 19.3, 19.0; ^{31}P{^{1}H} NMR: δ = 1.85 (m, $^{3}J_{P,P}=7$, $^{1}J_{P,P}=229$, $^{3}J_{P,P}=1$, $^{1}J_{P,P}=257$ Hz), −45.4. (m, $^{3}J_{P,P}=7$, $^{1}J_{P,P}=229$, $^{3}J_{P,P}=1$, $^{1}J_{P,P}=257$ Hz); elemental analysis calcd (%) for $C_{16}H_{18}P_4$: C 57.5, H 5.4; found: C 57.9, H 5.2.

((MeO)$_2$PO)$_2$C$_2$ (15): Prepared according to literature procedure.[68] ^{1}H NMR (CDCl$_3$): δ = 3.70–3.82 (m, 12H, MeO); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 87.6 (dd, $^{1}J_{P,C}=269$, $^{2}J_{P,C}=40$ Hz), 54.0; ^{31}P{^{1}H} NMR (CDCl$_3$): δ = −6.8.

Me$_2$C$_6$H$_4$((MeO)$_2$PO)$_2$ (16): Prepared according to literature procedure[69,70] in quantitative yield. ^{1}H NMR ([D$_6$]acetone): δ = 3.72–3.75 (m, 12H, MeO), 2.94 (br s, 4H, CH$_2$), 1.64 (s, 6H, Me); ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 139.9 (d, $^{1}J_{P,C}=188$ Hz), 122.9, 53.5, 38.0 (d, $^{2}J_{P,C}=13$ Hz), 37.8 (d, $^{2}J_{P,C}=13$ Hz), 18.4; ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 17.2.

Me$_2$C$_6$H$_2$(PH$_2$)$_2$ (17): Prepared in a similar manner as the parent 1,2-diphosphinobenzene from **16**.[82] During our work, the synthesis of **17** was reported in the literature.[71] NMR data were consistent with the published data.[71]

Catalytic synthesis of [(Me$_2$C$_6$H$_2$P$_2$)$_2$(μ-Me$_2$C$_6$H$_2$P$_2$)]$_2$ (19): In a sealed NMR tube, $Me_2C_6H_2(PH_2)_2$ (100 mg, 0.588 mmol) was combined with 0.05 molar equivalents of **6** (0.0294 mmol, 11 mg) in [D$_8$]toluene (0.6 mL). The initially light brown solution changed to dark brown with evolution of gas. After heating the solution for one week at 120 °C, a large amount of light yellow crystals were deposited. The crystals were removed from the NMR tube and exhaustively washed with toluene and then pentane. Upon drying in vacuo, the title compound was isolated (34 mg, 35 %). The insolubility of **19** precluded characterization by NMR methods. Elemental analysis calcd (%) for $C_{40}H_{50}P_{10}$: C 57.9, H 4.9; found: C 57.9, H 5.2.

[Cp*Zr(NPtBu$_3$)(CH$_2$)$_4$] (21): [Cp*Zr(NP(tBu)$_3$)Cl$_2$] (0.742 g, 1.44 mmol), Mg metal (246 mg, 10.11 mmol) and THF (25 mL) were added to a sealed reaction vessel equipped with a Teflon stopcock. The mixture was then freeze-pump-thaw degassed three times and 1 atm of ethylene was added at −78 °C. The mixture was allowed to warm to room temperature over 2.5 h after which additional ethylene was added. After stirring overnight the THF was removed and the solids were extracted pentane (3×10 mL). Removal of pentane gave a crude solid (643 mg). Recrystallization from Et$_2$O gave a brown compound (247 mg, 34 %). ^{1}H NMR: δ = 2.62 (m, 2H, ZrCH$_2$), 2.16 (m, 2H, ZrCH$_2$), 2.10 (s, 15H, Cp*), 1.37 (m, 2H, CH$_2$CH$_2$), 1.30 (d, $^{3}J_{P,H}=25$ Hz, 27H, tBu), 0.87 (m, 2H, CH$_2$CH$_2$); ^{13}C{^{1}H} NMR: δ = 117.4, 48.5, 41.1 (d, $^{1}J_{P,C}=47$ Hz), 30.3, 29.4, 12.1; ^{31}P{^{1}H} NMR: δ = 34.0; elemental analysis calcd (%) for $C_{22}H_{50}NPZr$: C 62.6, H 10.1, N 2.8; found: C 63.0, H 10.2, N 2.7.

[Cp*$_2$Zr(H)(PH)$_2$C$_6$H$_4$][Li(thf)$_4$] (22): $C_6H_4(PH_2)_2$ (38 mg, 0.269 mmol) in THF (5 mL) was added to a stirred mixture of **1a** (100 mg, 0.269 mmol) in THF (5 mL). The mixture immediately turned green along with vigorous evolution of gas (H$_2$). The mixture was stirred for 2 h and filtered through Celite. The THF solution was then layered with pentane and after 2 d plate-like crystals were isolated by filtration (74 mg, 55 %). ^{1}H NMR ([D$_8$]THF) (partial): δ = 6.85 (br s, 1H, Ar), 6.68 (br s, 1H, Ar), 6.05 (m, 2H, Ar), 2.78 (dddd, 1H, $^{1}J_{P,H}=215$, $^{3}J_{P,H}=19$, $^{3}J_{H,H}=11$, $^{4}J_{P,H}=2$ Hz, PH), 2.36 (dd, 1H, $^{1}J_{P,H}=168$, $^{3}J_{P,H}=23$ Hz, PH), 2.03 (m, 1H, ZrH), 1.79 (s, 30H, Cp*); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 131.4, 127.5, 119.6 (d, $^{1}J_{P,C}=63$), 110.3, 13.0; ^{31}P NMR ([D$_8$]THF): −34.6 (dddd, $^{1}J_{P,H}=214$, $^{2}J_{P,H}=74$, $^{2}J_{P,P}=25$, $^{3}J_{P,H}=19$ Hz), −37.7 (ddd, $^{1}J_{P,H}=168$, $^{2}J_{P,P}=25$, $^{3}J_{P,H}=23$ Hz). Due to the highly reactive nature of this product, reliable elemental analysis data were not obtained.

[CpTi(NPtBu$_3$)(PH)$_2$C$_6$H$_4$]$_2$ (23): One equivalent of 1,2-diphosphinobenzene (46 mg) was added to a vial containing a stirring solution of **2** (125 mg, 0.324 mmol) in pentane (5 mL). The solution immediately turned from yellow to red with evolution of gas and after stirring for 30 min, a red precipitate formed. The solids were separated from the solvent by decantation and washed with pentane (3×3 mL). The solid was dried in vacuo yielding a red powder (115 mg, 76%). ^{1}H NMR: δ = 7.79 (d, 2H, $^3J_{H,H}$=7 Hz, Ar), 7.44 (brs, 2H, Ar), 7.0 (t, 2H, $^3J_{H,H}$=7 Hz, Ar), 6.86 (t, 2H, $^3J_{H,H}$=7 Hz, Ar), 6.30 (s, 5H, Cp), 5.39 (d, 1H, $^1J_{P,H}$=236 Hz, PH), 4.13 (dm, 1H, $^1J_{PH}$=157 Hz, PH), 1.27 (d, 27H, $^3J_{P,H}$=13 Hz, *t*Bu); ^{13}C{^{1}H} NMR (partial): δ = 132.7, 130.5, 129.7, 128.9, 128.7, 128.1–128.6 (m, obscured by C_6D_6), 127.6, 122.0, 108.0 (s, Cp), 41.0 (d, $^1J_{P,C}$=45 Hz, PC), 23.0 (s, Me); ^{31}P NMR: δ = 36.3 (s, NP), −18.7 (d, $^1J_{P,H}$=157 Hz), −72.2 (d, $^1J_{P,H}$=236 Hz); elemental analysis calcd (%) for $C_{51}H_{88}N_2P_6Ti_2$: C 60.6, H 8.8, N 2.8; found: C 60.5, H 9.2, N 2.7.

[Cp*Ti(NP*t*Bu$_3$)(PH)$_2$C$_6$H$_4$] (24): One equivalent of 1,2-diphosphinobenzene (31 mg) in pentane (5 mL) was added to a vial containing a stirring solution of **6** (100 mg, 0.220 mmol) in pentane (5 mL). The solution immediately turned from yellow to green. After stirring overnight a green precipitate formed which was washed with pentane (3×5 mL) and dried under vacuum to give a green powder (89 mg, 60%). ^{1}H NMR: δ = 7.58 (m, 2H, Ar), 7.01 (m, 2H, Ar), 4.67 (d, 2H, $^1J_{P,H}$=179 Hz, PH), 2.06 (s, 15H, Cp*), 1.24 (d, 27H, $^3J_{P,H}$=13 Hz, *t*Bu); ^{13}C{^{1}H} NMR (partial): δ = 135.9, (d, $^1J_{P,C}$=26 Hz, P-C$_{ipso}$), 125.8, 122.4, 42.1 (d, $^1J_{P,C}$=44 Hz, PC), 30.0, 12.7; ^{31}P NMR: δ = 41.9 (s, NP), 34.9 (d, (PH)$_2$C$_6$H$_4$, $^1J_{P,H}$=179 Hz); elemental analysis calcd (%) for $C_{28}H_{48}NP_3Ti$: C 62.3, H 9.0, N 2.6; found: C 62.5, H 9.2, N 2.7.

X-ray data collection and reduction: Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1448 frames with 10 second exposure times ($4.5° < 2\theta < 45$–$50.0°$). The observed extinctions were consistent with the space groups in each case (Table 2). The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set employing the SADABS routine.[83] In the case of **22**, the R_{int} value suggests only a poor quality crystals were accessible. The subsequent solution and refinement was performed using the SHELXTL solution package.[84]

Structure solution and refinement: Non-hydrogen atomic scattering factors were taken from the literature tabulations.[85] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine.[84] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on *F*, minimizing the function $\omega\ (F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. In the case of compound **1** the methyl group of toluene was modeled by a 50:50 two-site disorder. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

CCDC-604041–604048 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support from NSERC of Canada is gratefully acknowledged. J.D.M. is also grateful for the award of an Ontario Graduate Scholarship. Sharonna Greenberg is thanked for assistance with editing.

[1] T. Katsuki, K. B. Sharpless, *J. Am. Chem. Soc.* **1980**, *102*, 5974–5976.
[2] E. N. Jacobsen, I. Marko, W. S. Mungall, G. Schröder, K. B. Sharpless, *J. Am. Chem. Soc.* **1988**, *110*, 1968–1970.
[3] A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934.
[4] T. Ohta, H. Takaya, R. Noyori, *Inorg. Chem.* **1988**, *27*, 566–569.
[5] M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutagawa, T. Otha, H. Takaya, R. Noyori, *J. Am. Chem. Soc.* **1988**, *110*, 629–631.
[6] T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 2675–2676.
[7] W. S. Knowles, *Acc. Chem. Res.* **1983**, *16*, 106–112.
[8] J.-L. Hérisson, Y. Chauvin, *Makromol. Chem.* **1971**, *141*, 161–176.
[9] J.-P. Soufflet, D. Commereuc, Y. Chauvin, C. R. Hebd, *C. R. Seances Acad. Sci. Ser. C* **1973**, *276*, 169–171.

Table 2. Crystallographic data.

	7	**8**·2 C_6H_6	**15**	**16**	**18**	**22**	**23**·0.5 C_5H_{12}	**24**
formula	$C_{35}H_{47}NPTi$	$C_{32}H_{47}NPTi$	C_8H_8P	$C_{12}H_{10}P$	$C_{40}H_{40}P_{10}$	$C_{42}H_{69}LiO_4PZr$	$C_{48.50}H_{82}N_2P_6Ti$	$C_{28}H_{48}NP_3Ti$
F_w	653.52	1111.10	166.08	278.08	830.42	798.07	974.78	539.48
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P(2)_1/c$	$P\bar{1}$	$P(2)_1/n$	$P(2)_1/c$	$C2/c$	$P(2)_1/c$	$P(2)_1/n$	$P(2)_1/c$
a [Å]	10.528(3)	10.312(6)	6.681(6)	10.3018(4)	18.0674(13)	15.368(8)	14.2133(18)	10.5648(16)
b [Å]	16.699(6)	11.433(7)	8.219(7)	13.0208(5)	9.3530(7)	14.040(8)	13.5829(17)	17.871(3)
c [Å]	19.952(8)	14.360(8)	17.527(15)	9.7272(4)	25.1572(18)	21.000(11)	29.320(4)	16.436(3)
α [°]		74.119(10)						
β [°]	94.93(4)	80.461(12)	94.565(9)	103.5670(10)	103.1250(10)	94.475(8)	91.859(2)	106.084(2)
γ [°]		82.038(12)						
V [Å^3]	3495(2)	1598.0(16)	959.3(14)	1268.38(9)	4140.1(5)	4517(4)	5657.5(12)	2981.8(8)
Z	4	1	4	4	4	4	4	4
ρ_{calcd} [g cm^{-1}]	1.242	1.155	1.150	1.456	1.332	1.173	1.144	1.202
μ [mm^{-1}]	0.452	0.388	0.382	0.563	0.443	0.350	0.483	0.464
data collected	16386	6827	8837	6110	19403	33871	48698	28482
R(int)	0.0881	0.0241	0.0313	0.0142	0.0315	0.2875	0.0881	0.0424
data $F_o^2 > 3\sigma(F_o^2)$	6023	4536	1680	1817	3641	5905	8857	5249
variables	370	329	108	153	231	367	534	320
R	0.0775	0.0599	0.0763	0.0252	0.0367	0.0990	0.0839	0.0421
Rw	0.1631	0.1658	0.2465	0.0689	0.0907	0.2394	0.1989	0.1065
GOF	0.970	0.977	1.361	1.011	1.049	0.991	1.103	1.011

[10] R. H. Grubbs, T. K. Brunck, *J. Am. Chem. Soc.* **1972**, *94*, 2538–2540.
[11] B. M. Novak, R. H. Grubbs, *J. Am. Chem. Soc.* **1988**, *110*, 960–961.
[12] S. T. Nguyen, L.K. Johnsson, R. H. Grubbs, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975.
[13] Z. Wu, S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 5503–5511.
[14] S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858–9859.
[15] G. C. Fu, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1993**, *115*, 9856–9857.
[16] P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem.* **1995**, *107*, 2179–2181; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041.
[17] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.
[18] M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250.
[19] R. H. Grubbs, *Handbook of Metathesis*, Wiley-VCH, New York, **2003**.
[20] S. J. Miller, H. E. Blackwell, R. H. Grubbs, *J. Am. Chem. Soc.* **1996**, *118*, 9606–9614.
[21] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796–6797.
[22] C. D. Wood, S. J. McLain, R. R. Schrock, *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.
[23] R. R. Schrock, S. M. Rocklage, J. H. Wengrovius, G. Rupprecht, J. Fellmann, *J. Mol. Catal.* **1980**, *8*, 73–83.
[24] S. M. Rocklage, J. D. Fellman, G. A. Rupprecht, L. W. Messerle, R. R. Schrock, *J. Am. Chem. Soc.* **1981**, *103*, 1440–1447.
[25] J. S. Murdzek, R. R. Schrock, *Organometallics* **1987**, *6*, 1373–1374.
[26] R. R. Schrock, S. A. Krouse, K. Knoll, J. Feldman, J. S. Murdzek, D. C. Yang, *J. Mol. Catal.* **1988**, *46*, 243–253.
[27] R. R. Schrock, J. S. Murdzek, G. C. Barzan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.
[28] G. C. Bazan, J. H. Oskam, H.-N. Cho, L. Y. Park, R. R. Schrock, *J. Am. Chem. Soc.* **1991**, *113*, 6899–6907.
[29] T. P. Fehlner, *Inorganometallics*, Plenum Press, New York, **1992**.
[30] F. Gauvin, J. F. Harrod, H. G. Woo, *Adv. Organomet. Chem.* **1998**, *42*, 363–405.
[31] J. Y. Corey, *Adv. Organomet. Chem.* **2004**, *51*, 1–52.
[32] T. D. Tilley, *Comments Inorg. Chem.* **1990**, *10*, 37–51.
[33] T. D. Tilley, *Acc. Chem. Res.* **1993**, *26*, 22–29.
[34] D. W. Stephan, *Angew. Chem.* **2000**, *112*, 322–338; *Angew. Chem. Int. Ed.* **2000**, *39*, 315–329.
[35] F. Basuli, J. Tomaszewski, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2003**, *125*, 10170–10171.
[36] M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 12645–12646.
[37] N. Etkin, M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, *119*, 2954–2955.
[38] A. J. Hoskin, D. W. Stephan, *Angew. Chem.* **2001**, *113*, 1917–1919; *Angew. Chem. Int. Ed.* **2001**, *40*, 1865–1867.
[39] R. Shu, L. Hao, J. F. Harrod, H.-G. Woo, E. Samuel, *J. Am. Chem. Soc.* **1998**, *120*, 12988–12989.
[40] S. Xin, H. G. Woo, J. F. Harrod, E. Samuel, A.-M. Lebuis, *J. Am. Chem. Soc.* **1997**, *119*, 5307–5313.
[41] V. P. W. Bohm, M. Brookhart, *Angew. Chem.* **2001**, *113*, 4832–4834; *Angew. Chem. Int. Ed.* **2001**, *40*, 4694–4696.
[42] R. Waterman, T. D. Tilley, *Angew. Chem.* **2006**, *118*, 2992–2995; *Angew. Chem. Int. Ed.* **2006**, *45*, 2926–2929.
[43] N. Etkin, M. T. Benson, S. Courtenay, M. J. McGlinchey, A. D. Bain, D. W. Stephan, *Organometallics* **1997**, *16*, 3504–3510.
[44] M. C. Fermin, J. Ho, D. W. Stephan, *Organometallics* **1995**, *14*, 4247–4256.
[45] J. P. Albrand, J. B. Robert, *J. Chem. Soc. Chem. Commun.* **1976**, 876–877.
[46] M. Baudler, B. Carlsohn, D. Koch, P. K. Medda, *Chem. Ber.* **1978**, *111*, 1210–1216.
[47] M. Baudler, D. Koch, B. Carlsohn, *Chem. Ber.* **1978**, *111*, 1217–1220.
[48] M. Baudler, B. Carlsohn, W. Boehm, G. Reuschenbach, *Z. Naturforsch. B* **1976**, *31*, 558–564.
[49] P. R. Hoffman, K. G. Caulton, *Inorg. Chem.* **1975**, *14*, 1997–1999.
[50] M. Baudler, J. Hahn, E. Clef, *Z. Naturforsch. B* **1984**, *39*, 438–444.
[51] J. Ho, T. L. Breen, A. Ozarowski, D. W. Stephan, *Inorg. Chem.* **1994**, *33*, 865–870.
[52] Z. Hou, D. W. Stephan, *Organometallics* **1993**, *12*, 3158–3167.
[53] H. Koepf, R. Voigtlaender, *Chem. Ber.* **1981**, *114*, 2731–2743.
[54] K. Issleib, G. Wille, F. Krech, *Angew. Chem.* **1972**, *84*, 582; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 527.
[55] D. W. Stephan, *Organometallics* **2005**, *24*, 2548–2560.
[56] E. Hey, S. G. Bott, J. L. Atwood, *Chem. Ber.* **1988**, *121*, 561–563.
[57] J. Ho, D. W. Stephan, *Organometallics* **1991**, *10*, 3001–3003.
[58] C. Couret, J. Escudie, H. Ranaivonjatovo, J. Satge, *Organometallics* **1986**, *5*, 113–117.
[59] C. N. Smit, T. A. van der Knaap, F. Bickelhaupt, *Tetrahedron Lett.* **1983**, *24*, 2031–2034.
[60] A. H. Cowley, M. Pakulski, *Tetrahedron Lett.* **1984**, *25*, 2125–2126.
[61] M. Stradiotto, K. L. Fujdala, T. D. Tilley, *Helv. Chim. Acta* **2001**, *84*, 2958–2970.
[62] Z. Hou, T. L. Breen, D. W. Stephan, *Organometallics* **1993**, *12*, 3158–3167.
[63] Y. Inagaki, T. Hosogai, R. Okazaki, N. Inamoto, *Bull. Chem. Soc. Jap.* **1980**, *53*, 205–209.
[64] T. Kauffmann, E. Antfang, J. Olbrich, *Tetrahedron Lett.* **1984**, *25*, 1963–1966.
[65] T. Kauffmann, E. Antfang, J. Olbrich, *Chem. Ber.* **1985**, *118*, 1022–1030.
[66] M. Baudler, S. Esat, *Chem. Ber.* **1983**, *116*, 2711–2713.
[67] K. Issleib, H. Schmidt, E. Leissring, *J. Organomet. Chem.* **1987**, *330*, 17–24.
[68] D. Seyferth, J. D. H. Paetsch, *J. Org. Chem.* **1969**, *34*, 1483–1484.
[69] A. I. Senderikhin, A. V. Dogadina, B. I. Ionin, A. A. Petrov, *Z. Obsh. Khimii* **1989**, *59*, 2141–2142.
[70] A. I. Senderikhin, A. V. Dogadina, B. I. Ionin, A. A. Petrov, *Z. Obsh. Khimii* **1988**, *58*, 1662–1663.
[71] S. N. Tverdomed, A. V. Dogadina, B. I. Ionin, *Russ. J. Gen. Chem.* **2003**, *73*, 319–320.
[72] R. C. Weast, *Handbook of Chemistry and Physics*, 54th ed, **1974**, p. 2436.
[73] E. Hey, *J. Organomet. Chem.* **1989**, *378*, 375–385.
[74] T. Oshikawa, M. Yamashita, *Chem. Ind.* **1985**, 126–127.
[75] A. R. Miller, D. Y. Curtin, *J. Am. Chem. Soc.* **1976**, *98*, 1860–1865.
[76] Y. Van den Winkel, H. M. M. Bastiaans, F. Bickelhaupt, *J. Organomet. Chem.* **1991**, *405*, 183–194.
[77] A. H. Cowley, N. C. Norman, M. Pakulski, *Inorg. Synth.* **1990**, *27*, 235–240.
[78] J. P. Anselme, W. Fischer, *Tetrahedron* **1969**, *25*, 855–856.
[79] E. P. Kohler, L. W. Blanchard Jr., *J. Am. Chem. Soc.* **1935**, *57*, 367–371.
[80] N. Etkin, A. J. Hoskin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, *119*, 11420–11424.
[81] T. W. Graham, J. Kickham, S. Courtenay, P. Wei, D. W. Stephan, *Organometallics* **2004**, *23*, 3309–3318.
[82] E. P. Kyba, S. T. Liu, R. L. Harris, *Organometallics* **1983**, *2*, 1877–1879.
[83] Bruker AXS Inc, Madison, WI, USA, **2003**.
[84] G. M. Sheldrick, SHELXTL, Bruker AXS Inc., Madison, WI, USA, **2000**.
[85] D. T. Cromer, J. T. Waber, *Int. Tables X-Ray Crystallogr.* **1974**, *4*, 71–147.

Received: March 29, 2006