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A general synthesis of phosphaalkenes at zirconium with liberation of phosphaformamides†

Andrew J. Roering,‡[a] L. Taylor Elrod,§[a] Justin K. Pagano,[a] Sarah L. Guillot,[a] Stephanie M. Chan,[a] Joseph M. Tanski[b] and Rory Waterman*[a]

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A general, atom-economical method for the synthesis of phosphaalkenes is reported *via* the net coupling of primary alkyl or aryl phosphines with aryl or alkyl isocyanides at zirconium. The phosphorus-containing ligand can be liberated as the phosphaformamide from zirconium by reaction with an organic electrophile.

Introduction

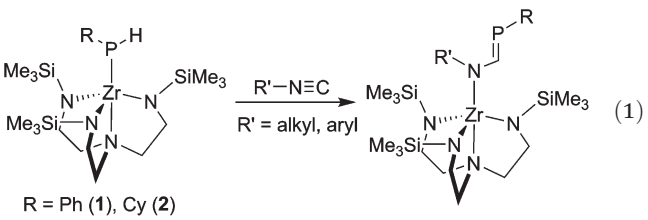
After decades of interest, molecules containing P═C bonds, phosphaalkenes, have retained continual prominence within the chemical and materials science communities.[1] The P═C moiety displays heightened reaction chemistry, parallel to that of alkenes,[2] which engenders phosphaalkenes unique importance as pivotal components in electronically intriguing materials,[3] key molecular precursors in the preparation of organophosphines,[4] and the structural basis for new classes of transition-metal ligands.[3c,5]

Unlike alkenes, which are fundamental products of the petrochemical industry, phosphaalkenes must be prepared synthetically. Effective methods for the preparation of these molecules are well known, and these can be roughly divided into condensation, typified by the phospha-Peterson reaction, and elimination routes.[4b,d,6] It must be noted that reactions of metal phosphinidene complexes are an interesting organometallic addition to that suite.[7] While these methods are effective, they are costly in terms of chemical waste and the compatibility of some functionalities with synthetic conditions. For example, the phospha-Peterson reaction was limited to aryl phosphines until only recently.[8] Moreover, the high purity demanded by current applications leads to significant loss in purification steps. Thus, continued development and application of phosphaalkene chemistry depends upon new and efficient synthetic methods. This report outlines a broad method for the synthesis of phosphaalkenes at zirconium *via* insertion into Zr–P bonds followed by rearrangement, a reaction initially reported as a synthetic peculiarity.[9] As part of this now general transformation, these phosphorus-containing ligands can be liberated from zirconium as phosphaformamides by reaction with an organic electrophile.

Results and discussion

Phosphaalkene synthesis

A family of zirconium–phosphaalkene complexes were synthesized by reaction of zirconium phosphide complexes, prepared from primary phopshines,[10] with a series of isocyanides (eqn (1)).



(1)

This set of reactions was intended to establish the generality of the reaction in that both phenyl and cyclohexyl (*i.e.*, aryl and alkyl) phosphido complexes as well as aryl and alkyl isocyanides are able to undergo facile P═C bond formation at zirconium (Table 1). Additionally, the use of 2-chlorotolylisocyanide begins to establish functional group tolerance in this chemistry. Reactions proceeded cleanly and gave products in high isolated yields. For example, treatment of (**1**) with aryl isocyanides (eqn (1), R′ = phenyl, 2,6-ClMeC$_6$H$_3$) resulted in the formation of phosphaalkene products (N$_3$N)Zr[N(Ph)C(H) =

[a]*Department of Chemistry, University of Vermont, Cook Physical Sciences Building, Burlington, VT 05405, USA. E-mail: rory.waterman@uvm.edu; Fax: +1 802 656-8705; Tel: +1 802 656-0278*

[b]*Department of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA*

†Electronic supplementary information (ESI) available: Variable temperature NMR data for **7** (pdf) as well as crystallographic data. CCDC 900053 (**6**), 900054 (**8**), 900055 (**7**), 900056 (**12**), and 900057 (**15**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32322b

‡Current address: Department of Chemistry and Biochemistry, University of San Diego, San Diego, CA 92110, USA.

§Current address: Department of Chemistry, Brown University, Providence, RI 02906, USA.

Table 1 Reaction conditions to form phosphaalkene complexes illustrated in eqn (1)

Entry	*R*/cmpd	*R*′	Temp [°C]	Yield [%]
1	Ph (**1**)	Ph	25	92
2	Ph (**1**)	Ar[a]	25	80
3	Ph (**1**)	Mes	100	86
4	Ph (**1**)	^{t}Bu	90	84
5	Ph (**1**)	Cy	80	89
6	Cy (**2**)	Ar[a]	100	50
7[b]	Ph (**1**)	CH_2Ph	25	78

[a] Ar = 2,6-$ClMeC_6H_3$. [b] Reported in ref. 9.

Table 2 Selected ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR data (δ) with coupling constants (Hz) in benzene-d_6 of phosphaalkenes moieties

Cmpd.	^{1}H(J_{PH})	^{13}C(J_{PC})	^{31}P
(N_3N)ZrN(Ph)C(H)=PPh (**3**)	10.09(6)	190.0(45)	108.1
(N_3N)ZrN(Ar)C(H)=PPh (**4**)[a]	10.29(13)	194.4[c]	100.4
(N_3N)ZrN(Mes)C(H)=PPh (**5**)	10.38(12)	195.1(53)	95.2
(N_3N)ZrN(^{t}Bu)C(H)PPh (**6**)[b]	10.10(9)	187.1(29)	0.484[c]
(N_3N)ZrN(Cy)C(H)=PPh (**7**)	9.90(9)	189.9(54)	87.9
(N_3N)ZrN(Ar)C(H)=PCy (**8**)[a]	10.16(14)	189.9(54)	120.0
(N_3N)ZrN(CH_2Ph)C(H)=PPh (**9**)[d]	10.29[c]	193.1(56)	91.9

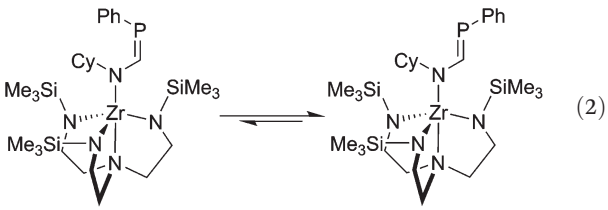
[a] Ar = 2,6-$ClMeC_6H_3$. [b] NMR spectra collected in toluene-d_8. [c] Broad resonance. [d] Reported in ref. 9.

P(Ph)] (**3**) and (N_3N)Zr[N(2,6-$ClMeC_6H_3$)C(H) = P(Ph)] (**4**) in good to excellent yields of 92 and 80% respectively (Table 1, entries 1 and 2). Both reactions occurred at ambient temperature, similar to the previously reported example (Table 1, entry 7). Compounds **3** and **4** have pseudo-C_{3v}-symmetry with respect to the ligand backbone as well as diagnostic ^{1}H NMR spectroscopic features of the P=C(H) moiety with resonances as doublets at δ 10.09 and 10.29 with J_{PH} = 6 and 13 Hz, respectively (Table 2).

Reaction of mesityl isocyanide with **1** at ambient temperature was ineffective, whereas conducting the reaction at 100 °C resulted in good yields of the phosphaalkene product (Table 1, entry 3). Similar to other zirconium phosphaalkenes compounds, the phosphaalkene hydrogen atom was observed downfield at δ 10.38 as a doublet with J_{PH} = 12 Hz by ^{1}H NMR spectroscopy (Table 2, entry 3). The need for increased heat to afford the phosphaalkene product is rationalized by the steric bulk of the mesityl group of the isocyanide.

The use of alkyl isocyanides have also been shown to provide P=C bonds in moderate to good yields (Table 1, entries 4, 5, 7). Unlike simple aryl derivatives, reaction of alkyl isocyanides with **1** required heating to afford phosphaalkene products. The ^{1}H NMR spectra of (N_3N)Zr[(^{t}Bu)NC=P(Ph)] (**6**) and (N_3N)Zr[(Cy)NC=P(Ph)] (**7**) yielded resonances at δ 10.10 and 9.90, respectively, as doublets with J_{PH} = 9 Hz for both complexes. These chemical shifts are notably upfield relative to those for the aryl derivatives. The ^{13}C NMR spectra of **6** and **7** provide phosphaalkene carbon atom resonances at δ 187.1 and 189.9, respectively, which are also shifted upfield as compared to the respective aryl derivatives.

The ^{1}H NMR spectrum of **7** displayed broad peaks in the ^{1}H NMR spectrum at ambient temperature suggesting a dynamic process occurring on the NMR timescale. To investigate this, a variable-temperature NMR study was undertaken. Cooling toluene-d_8 solution of **7** to less than 278 K resulted in the appearance of a new resonance near the phosphaalkene proton. This behavior is implicit of an *E*/*Z* isomerization of the phosphaalkene (eqn (2)). The coupling constants for each resonance, 12 Hz and 5 Hz, respectively, allow an assignment of the δ 10.04 resonance as the *E* isomer with the resonance at δ 9.62 as the *Z* isomer based on the magnitude of coupling constants for other phosphaalkene compounds.[4b] The existence of both isomers at low temperature demonstrates a relatively low activation barrier, which was calculated to be 9.50(6) kcal mol^{-1}.[11]



(2)

These reactions are also successful for alkyl-substituted phosphines. Reaction of **2** with (2,6-$ClMeC_6H_3$)N≡C at 100 °C resulted in the formation of phosphaalkene product (N_3N)Zr-[N(Ar)C(H)=PCy] (**8**) in moderate yield (Table 1, entry 6). NMR spectroscopic data (^{1}H, ^{13}C, and ^{31}P) of **8** were similar to the aryl products (Table 2). Monitoring the reaction by ^{1}H and ^{31}P NMR spectroscopy in benzene-d_6 solution showed high conversion (>90%) to **8**. The lower than typical isolated yield may be a consequence of product lipophilicity.

Structural characterization

Solid-state structures, determined by X-ray crystallography, aid in confirming the identification and further understanding of these complexes. Cooling concentrated ethereal solutions of **7** or **8** at −30 °C for extended periods resulted in X-ray quality crystals. The molecular structures of compounds **7** and **8**, shown in Fig. 1 and 2, respectively, are highlighted by short P–C bonds confirming the spectroscopic indications of P–C π-bonding. Also observed for both structures are relatively long Zr–N bonds for the phosphaalkene ligand as compared to those of amido (N_3N)ZrNRR′ derivatives, suggestive of limited ligand-to-metal π-donation.[10] These nitrogen atoms are planar and likely involved in a delocalized π-system with the phosphaalkene as has been seen for other amine-substituted phosphaalkenes.[12]

The solid-state structure of **6** provides insight into its particular ^{31}P NMR chemical shift (Table 2). Unlike the related phosphaalkene compounds that have been characterized, complex **6**, which features both a long P–C bond and a short C–N bond, contains a phosphaformamidinate moiety rather than a phosphaalkene (Fig. 3). Additional support comes from

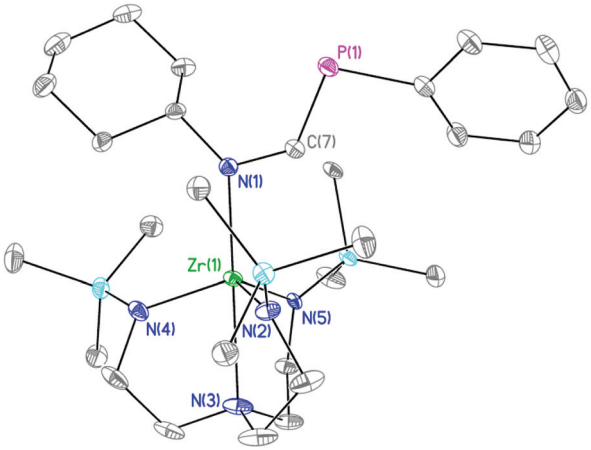


Fig. 1 Molecular structure of **7** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N(1) = 2.1740(7), Zr–N(2) = 2.0959(8), Zr–N(3) = 2.4725(8), Zr–N(4) = 2.0649(8), Zr–N(5) = 2.0990(9), N(1)–C(7) = 1.3497(11), C(7)–P(1) = 1.7234(9), C(7)–P(1)–C(1) = 100.96(4), P(1)–C(7)–N(1) = 128.96(6).

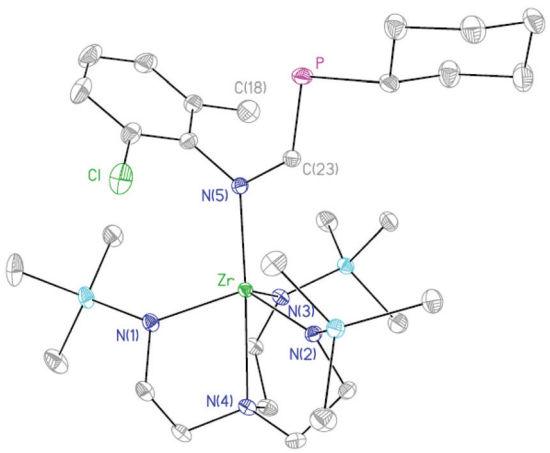


Fig. 2 Molecular structure of **8** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N(1) = 2.2067(1), Zr–N(2) = 2.085(1), Zr–N(3) = 2.070(1), Zr–N(4) = 2.536(1), Zr–N(5) = 2.200(1), C(23)–P(1) = 1.708(2), C(23)–N(5) = 1.372(2), P–C(23)–N(5) = 128.80(11), C(23)–P–C(24) = 99.17(7).

the bond angles around phosphorus, where the sum of the angles indicates that phosphorus is pyramidal ($\sum\angle \sim 309°$). A direct comparison of the solid state structure of **6** can be made with a phosphaguanidate complex $(N_3N)Zr[N,N:\eta^2\text{-}(^iPrN)_2C(PPh_2)]$.[13] Complex **6**, $(N_3N)Zr[N,P:\eta^2\text{-}N(^tBu)=C(H)PPh]$, is the tautomer of the sought phosphaalkene complex $(N_3N)Zr[N(^tBu)C(H)=PPh]$. At present, it is unclear why this tautomerization is facile while the cyclohexyl derivative **7** is isolated as the phosphaalkene complex. This apparent tautomerization merits further investigation.

The structures of the phosphaalkene complexes are unusual in that neither the phosphorus lone pair nor the double bond of the P=C moiety are associated with the zirconium center. For phosphaguanidate complexes of the

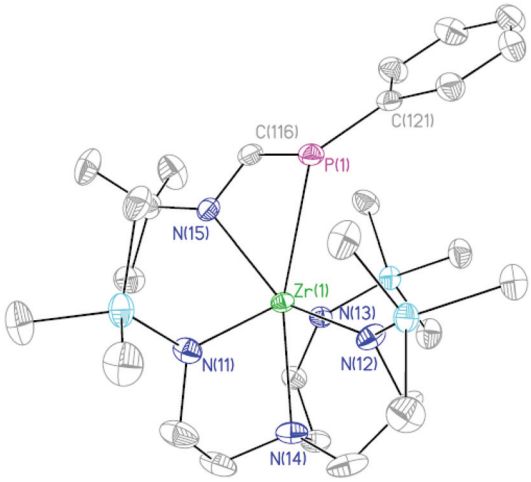


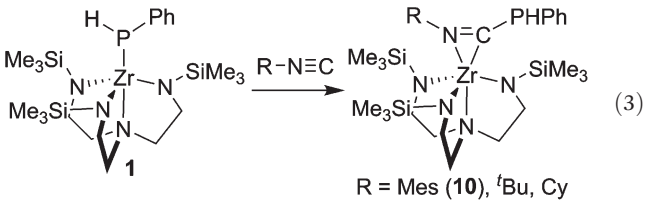
Fig. 3 Molecular structure of **6** with thermal ellipsoids drawn at the 50% level. One of two independent molecules in the unit cell are shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N(11) = 2.1156(13), Zr–N(12) = 2.1320(12), Zr–N(13) = 2.0997(12), Zr–N(14) = 2.4498(12), Zr–N(15) = 2.3745(12), Zr–P(1) = 2.8014(4), C(116)–P(1) = 1.8222(2), N(15)–C(116) = 1.304(2), N(15)–C(116)–P(1) = 115.22(11), C(116)–P(1)–C(121) = 105.81(7).

Table 3 Selected ^{1}H and ^{31}P NMR data (δ) from 1,1-insertion products

Cmpd.	^{1}H P*H*Ph (J_{PH})	^{31}P
$(N_3N)Zr[C(PHPh)=NMes]$ (**10**)	5.91 (266 Hz)	−27.7
$(N_3N)Zr[C(PHPh)=N^tBu]$	6.16 (258 Hz)	−48.7
$(N_3N)Zr[C(PHPh)=NCy]$	6.33 (261 Hz)	−49.9

triamidoamine zirconium fragment, η^2 bonding is observed.[14] Furthermore, the structure of **6** also displays η^2 bonding (*vide supra*). Therefore, these compounds are unique in that they are the only metal compounds with a phosphaalkene-containing ligand to not have an interaction of the P=C moiety with the metal.

The mechanism of phosphaalkene formation is hypothesized to occur through a rearrangement of a phosphine-substituted iminato complex, the 1,1-insertion product of $(N_3N)ZrPHR$ with R′N≡C. Support for this mechanism was garnered *via* stoichiometric reactions of phosphido complexes with isocyanide reagents. Reaction of **1** with MesN≡C resulted in the isolation of $(N_3N)Zr[\eta^2\text{-}C(PHPh)=N(Mes)]$ (**10**) as yellow microcrystals in 67% yield (eqn (3)). The ^{1}H NMR spectrum of **10** shows pseudo-C_{3v}-symmetry with respect to the ligand backbone. Key observations in establishing the identity of **10** spectroscopically are a phosphine proton resonance in the ^{1}H NMR spectrum at δ 5.91 as a doublet with J_{PH} = 266 Hz and an imine resonance at δ 266.9 as a doublet with J_{PC} = 101 Hz in the ^{13}C NMR spectrum (Table 3). All data for **10** are consistent with that for related insertion products.[9,15] Compound **10** is not stable for extended periods. Efforts to grow X-ray quality crystals would frequently result in the isolation of **5**. Heating solutions of **10** gave **5** in quantitative yield.



(3)

Though reaction with many isocyanide reagents resulted in the formation of phosphaalkene products (*vide supra*), the use of mesityl isocyanide afforded the only isolable 1,1-insertion product. For example, in the reaction of **1** with *tert*-butyl or cyclohexyl isocyanide resulted intermediate complexes consistent with 1,1-insertion products were identified as observed by ^{1}H and ^{31}P NMR spectroscopy in benzene-d_6 solution (Table 3). Unfortunately, efforts to isolate these products prior to rearrangement failed and only products **6** and **7** were isolated, respectively.

That $(N_3N)Zr[\eta^2\text{-}C(PHPh)\text{=}N^tBu]$ was observed in solution en route to formation of phosphaformamidinate **6** suggests that these 1,1-insertion products are a common intermediate. Thus, **6** may represent a deviation from the rearrangement reaction that would produce a phosphaalkene rather than **6**, the apparent product of tautomerization of a phosphaalkene complex. That **6** might be a local minimum was tested: Solutions of **6** in benzene-d_6 were heated to 100 °C for extended periods, but no alternative products were formed and **6** remained unreacted. The energetics of these tautomers are of further interest.

Additional support for a 1,1-insertion product as an intermediate came from a secondary phosphide complex $(N_3N)ZrPPh_2$ (**11**). Reaction of **11** with one equiv. of benzylisocyanide resulted in formation of $(N_3N)Zr[\eta^2\text{-}C(PPh_2)\text{=}NCH_2Ph]$ (**12**) as analytically pure orange crystals in 81% yield. The key spectroscopic observations in the assignment of the compound include a ^{31}P NMR resonance at δ 2.94 and ν_{CN} = 1694 cm^{-1} in the infrared.

Single crystals of **12** were grown from ethereal solution, and the molecular structure is presented in Fig. 4. The compound features an η^2-iminoacyl ligand with Zr–N(5) = 2.232(1) Å, which is intermediate in distance between those for the amido and amine nitrogen donor atoms of the triamidoamine ligand in these complexes. This bond length is consistent with a metal–nitrogen σ-bond and, as expected, no π-donation. There is nothing exceptional about the diphenylphosphide substituent with P–C(18) = 2.293(2) Å.

Heating solutions of **12** in benzene-d_6 for extended periods at temperatures as high as 100 °C resulted in no change prior to decomposition to a complex mixture of unidentifiable products. That little clean chemistry happened without exceeding the stability of the compound suggests that the migration of a phenyl substituent is not favorable. At this point, it is unclear if the resultant phosphaalkene complex is unstable with a relatively bulky substituent at carbon or if the barrier is significantly higher for phenyl migration.

It is important to note that the 1,1-insertion of an isocyanide into a zirconium–phosphorus bond was originally reported by Hey-Hawkins.[15] No mention is made of further reactivity of the η^2-iminoacyl product in that report, but the results herein suggest that the secondary phosphide substituent, $P(SiMe_3)_2$, would be reticent to the rearrangement that is facile for primary phosphines (*vide infra*).

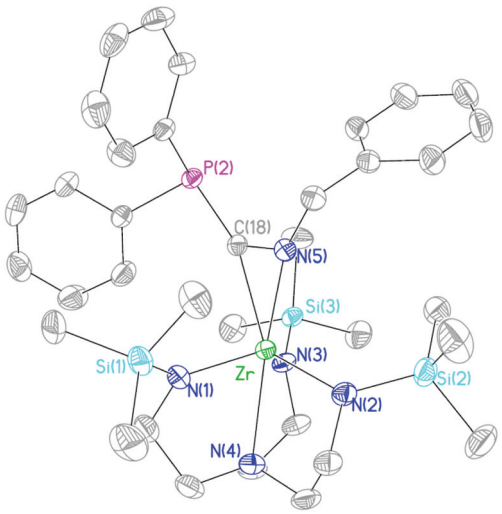


Fig. 4 Molecular structure of **12** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–N(1) = 2.093(1), Zr–N(2) = 2.121(1), Zr–N(3) = 2.127(1), Zr–N(4) = 2.475(1) Zr, N(5) = 2.232(1), Zr–C(18) = 2.293(2), P(2)–C(18) = 1.817(2), C(18)–P(2)–C(25) = 100.74(7), C(18)–P(2)–C(31) = 109.71(7), C(25)–P(2)–C(31) = 102.22(7).

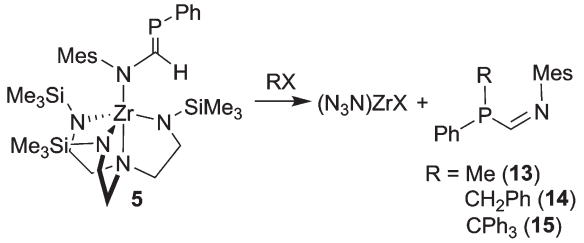
Reaction with electrophiles

These zirconium-bound phosphaalkene complexes react with electrophiles to release the phosphorus-containing fragment and generate $(N_3N)ZrX$ byproducts (eqn (4)). Reaction of **5** with one equiv. of methyliodide afforded $(N_3N)ZrI$ and Mes(Me)N=C(H)PPh (**13**). The phosphaformamidine **13** was purified by flash silica chromatography. These products can also be separated by fractional crystallization from non-polar solvents such as pentane, but several crystallization steps are required. The ^{1}H NMR spectrum of **13** reveals an imine proton at δ 8.19 as a doublet with J_{PH} = 44 Hz, an upfield shift from that of **3**, and the ^{31}P NMR spectrum of **13** shows a singlet at δ 22.3. Key to the assignment of the phosphaformamidine, J_{PC} = 14.1 Hz was measured for the imine carbon in the $^{13}C\{^{1}H\}$ NMR spectrum. In a similar reaction, the addition of methyl triflate to **3** results in the formation of compound **13** as well as a product presumed to be $(N_3N)ZrOTf$. The ^{1}H and ^{31}P NMR spectra of the organophosphorus product from these separate reactions are identical.

Other organic electrophiles are also successful in liberating a phosphaformamide products. For example, reaction of **5** with benzylbromide in benzene solution resulted in the formation of $(N_3N)ZrBr$ and MesN=CP(CH_2Ph)Ph (**14**). Compound **14** was isolated by passing the crude reaction mixture through silica, though isolated yields of **14** were low (<10%). The ^{1}H NMR spectra of **14** shows an imine proton at δ 8.20 as

a doublet with J_{PH} = 44 Hz. The NMR spectra and coupling constants of **14** are similar to that of complex **13**.

Definitive assignment of the phosphaformamide product resulted from the reaction of a more crystalline electrophile. Treatment of **5** with tritylchloride in diethylether at ambient temperature resulted in the formation of the phosphaformamide, MesN=CP(Ph)(CPh_3) (**15**), and (N_3N)ZrCl. Compound **15** was passed the crude reaction mixture through a short path of silica and crystallized to analytical purity from Et_2O in 81% yield. The imine proton of **15** can be found at δ 8.48 as a doublet with J_{PH} = 36 Hz in the ^{1}H NMR spectrum.



(4)

Compound **15** was subject to an X-ray crystallography study. Crystals of **15** were obtained by cooling a concentrated ethereal solution at −30 °C for extended periods. The solid state structure of **15** is highlighted by the short C=N bond length of 1.264(2) Å, which is well within range of typical C=N bonds (Fig. 5). The X-ray study also reveals a pyramidal, sp^3 hybridized geometry, around phosphorus (Σ ∠307°).

Two reasonable pathways may explain why reactions of electrophiles with the zirconium phosphaalkene complexes produce phosphaformamides rather than phosphamidines. One possibility is that phosphaamidine products are formed initially, then these products tautomerize to the phosphaformamide. This seems unlikely because there are known phosphamidines ($R_2NC(H)$=PR'),[16] and these are stable molecules. The second possibility is that the electrophile reacts with phosphorus before nitrogen to give the phosphaformamide directly.

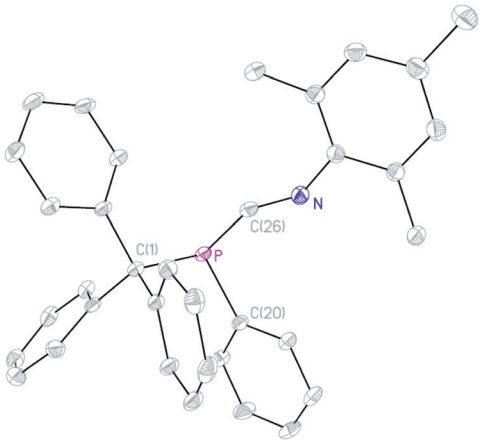


Fig. 5 Molecular structure of **15** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–P = 1.930(2), C(20)–P = 1.825(2), C(26)–P = 1.832(2), C(26)–N = 1.264(2), C(1)–P–C(20) = 103.48(7), C(20)–P–C(26) = 103.60(7), P–C(26)–N = 120.43(13).

Such a reaction pathway is more satisfying because the phosphaalkene phosphorus is considerably less sterically encumbered than is nitrogen.

A catalytic variant of this reaction, where the organophosphorus fragment is lost by cyclometalation of a trimethylsilyl substituent, may select for the phosphaamidine (P=C) product over the phosphaformamide. Unfortunately, efforts to make this reaction catalytic have been unsuccessful. Multiple equivalents of starting phosphine and isocyanide are consumed, but complex mixtures of products, some apparently arising from reaction of P=C bonds with starting materials, are observed. The implication is that conditions to promote product liberation are in competition with undesired reactions of starting materials. Though ligand-to-metal π-donation appears to be attenuated in these phosphaalkene complexes (*vide supra*), the Zr–N bond is still likely to be strong,[10] which is known to pose a challenge for promoting product liberation over alternative reaction pathways.[17]

Concluding remarks

In summary, insertion reactions of isocyanides into terminal zirconium primary phosphido complexes is a mild and general route to phosphaalkene products. This process appears to occur *via* a 1,1-insertion of the isocyanide into the Zr–P bond followed by a rearrangement. Liberation of the phosphaformamide products from the metal can be accomplished by reaction with organic electrophiles, which were confirmed by structural characterization of the trityl derivative, **15**.

This insertion and rearrangement represents a new, general alternative in phosphaalkene syntheses and provides phosphaalkene products in perhaps the most atom economical route to be seen. There have been no observations to suggest this reaction should be unique to zirconium or isocyanides, but primary phosphines appear to be key in the rearrangement process. Thus, alternative metals and reagents are currently under exploration.

Experimental section

General considerations

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glove box or standard Schlenk techniques. Benzene-d_6 was purchased from Cambridge Isotope Laboratory then degassed and dried over NaK alloy. Celite-454 was heated to a temperature greater than 180 °C under dynamic vacuum for at least 8 h. Elemental analyses were performed on an Elementar microcube. NMR spectra were recorded with either a Bruker AXR or Varian 500 MHz spectrometer in benzene-d_6 or toluene-d_8 and are reported with reference to residual solvent resonances (δ 7.16 and δ 128.0 for benzene-d_6 or 2.09 for toluene-d_8) or external 85% H_3PO_4 (0.00). Infrared spectra were collected on a Perkin Elmer System 2000 FT-IR spectrometer or

Bruker Alpha FT-IR with an ATR plate at a resolution of 1 cm^{-1}. GCMS spectra were collected on a Varian Saturn 2100T gas chromatograph-mass spectrometer. Starting materials $(N_3N)ZrPHPh$ (**1**), $(N_3N)ZrPHCy$ (**2**), and $(N_3N)ZrPPh_2$ (**11**) were prepared by a reported syntheses.[10] Phenylisocyanide was prepared from a literature route.[18] Mesitylisocyanide was prepared as a light brown solid by an analogous procedure from 2,4,6-trimethylaniline. The light brown solid was sublimed at 40 °C under vacuum to afford mesitylisocyanide as a colorless crystalline solid. All other reagents and solvents were obtained from commercial sources and dried by conventional means.

Phosphaalkene syntheses

$(N_3N)Zr[N(Ph)C(H)=PPh]$ (3). A 50 mL round bottom flask was charged with **1** (100 mg, 0.178 mmol) and *ca.* 5 mL benzene solvent. To the flask was added a 2 mL benzene solution of PhN≡C (18 mg, 0.178 mmol). An instant color change from yellow to pale yellow was observed, and the solution was stirred at ambient temperature for 2 h. The flask was then placed in the freezer, and the benzene was lyophilized under reduced pressure yielding brown microcrystals of the title compound (109 mg, 0.163 mmol, 92%). ^1H (500.1 MHz): δ 10.09 (d, J_{PH} = 6 Hz, C*H*, 1 H) 7.84 (t, C_6H_5, 2 H), 7.39 (d, C_6H_5, 2 H), 7.24 (t, C_6H_5, 2 H), 7.17 (t, C_6H_5, 2 H), 7.06 (t, C_6H_5, 1 H), 6.95 (t, C_6H_5, 1 H), 3.28 (t, CH_2, 6 H), 2.37 (t, CH_2, 6 H), 0.12 (s, CH_3, 27 H). $^{13}C\{^1H\}$ (125.8 MHz): δ 190.0 (d, $J_{P=C}$ = 45 Hz, P=*C*), 150.6 (d, J_{PC} = 6 Hz, C_6H_6), 133.1 (d, J_{PC} = 14.5 Hz, C_6H_6), 129.1 (s, C_6H_6), 2 resonances missing and assumed to be under the benzene-d_6 solvent peak, 127.1 (s, C_6H_6), 124.5 (s, C_6H_6), 123.8 (s, C_6H_6), 63.6 (s, CH_2), 47.7 (s, CH_2), 1.65 (s, CH_3). $^{31}P\{^1H\}$ (202.4 MHz): δ 108.1 (s). IR (KBr, Nujol): 2405 w, 2098 w, 1937 w, 1585 s, 1377 s, 1344 m, 1242 s, 1151 s, 1047s, 1021 s, 928 s, 893 m. Anal Calcd for $C_{28}H_{50}N_5PSi_3Zr$: C, 50.71; H, 7.60; N, 10.56. Found: C, 50.41; H, 7.29; N, 10.43.

$(N_3N)Zr[N(2\text{-}Cl\text{-}6\text{-}MeC_6H_3)C(H)=PPh]$ (4). A 50 mL round bottom flask was charged with **1** (50 mg, 0.089 mmol) and *ca.* 5 mL benzene solvent. To the flask, a 2 mL benzene solution of 2-chloro-6-methylphenylisocyanide (13 mg, 0.089 mmol) was added. The color of the solution changes from yellow to light red after ~1 min. The solution was allowed to stir for 8 h at ambient temperature at which time the benzene was lyophilized under reduced pressure yielding colorless microcrystals of the title compound (51 mg, 0.071 mmol, 80%). ^1H (500.1 MHz): δ 10.29 (d, J_{PH} = 13 Hz, C*H*, 1 H), 7.87 (t, Ar, 2 H), 7.26 (d, Ar, 1 H), 7.19 (t, Ar, 2 H), 7.07 (t, Ar, 1 H), 6.95 (d, Ar, 1 H), 6.78 (t, Ar, 1 H), 3.20 (t, CH_2, 6 H), 2.61 (s, CH_3, 3 H), 2.28 (t, CH_2, 6 H), 0.11 (s, CH_3, 27 H). $^{13}C\{^1H\}$ (125.8 MHz): δ 194.4 (br s, *C*=P), 146.6 (d, J_{PC} = 7 Hz, Ar), 144.8 (d,), 136.1 (s, Ar), 133.0 (s, Ar), 132.9 (s, Ar), 131.3 (s, Ar), 130.0 (s, Ar), 128.6 (s, Ar), 126.4 (s, Ar), 126.2 (s, Ar). $^{31}P\{^1H\}$ (202.4 MHz): δ 100.4 (s). IR (KBr, Nujol): 1581 w, 1462 s, 1260 s, 1160 s, 1040 s, 925 s, 836 s, 786 s, 736 m, 679 w. Anal Calcd for $C_{29}H_{51}ClN_5PSi_3Zr$: C, 48.94; H, 7.22; N, 9.84. Found: C, 48.88; H, 7.53; N, 9.99.

$(N_3N)Zr[N(Mes)C(H)=PPh]$ (5). A PTFE-valved Schlenk tube was charged with **1** (100 mg, 0.178 mmol), mesityl isocyanide (26 mg, 0.178 mmol), and 4 mL benzene solvent. The yellow solution was placed in a 100 °C oil bath and stirred for 12 h. The flask was then brought into the glove-box, and the benzene was lyophilized under reduced pressure. The crude mixture was purified by washing the solid with hexanes leaving colorless microcrystals (108 mg, 0.153 mmol, 86%). ^1H (500.1 MHz): δ 10.38 (d, J_{PH} = 12 Hz, C*H*, 1 H) 7.88 (t, C_6H_5, 2 H), 7.23 (m, C_6H_5, 2 H), 7.08 (m, C_6H_5, 1 H), 6.91 (s, C_9H_{11}, 2 H), 3.20 (t, CH_2, 6 H), 2.61 (s, CH_3, C_9H_{11}, 6 H), 2.27 (t, CH_2, 6 H), 2.18 (s, CH_3, C_9H_{11}, 3 H), 0.045 (br s, CH_3, 27 H). $^{13}C\{^1H\}$ (125.8 MHz): δ 195.1 (d, J_{PC} = 53 Hz, *C*=P), 146.3 (s, C_6H_5), 145.9 (s, C_6H_5), 145.6 (d, J_{PC} = 7 Hz, C_6H_5), 135.3 (s, Ar), 133.5 (s, Ar), 133.3 (s, Ar), 133.2 (s, Ar), 130.6 (s, Ar), 126.3 (s, Ar), 3 resonances missing and assumed to be under the benzene-d_6 solvent peak, 65.3 (s, CH_2), 46.4 (s, CH_2), 20.9 (s, C_9H_{11}), 20.8 (C_9H_{11}), 1.1 (s, CH_3). $^{31}P\{^1H\}$ (202.4 MHz): δ 95.2 (s). IR (KBr, Nujol): 2944 w, 2888 w, 2848 w, 1365 m, 1245 s, 1031 s, 926 s, 828 s, 781 s, 731 s, 675 m, 545 m. Anal Calcd for $C_{31}H_{56}N_5PSi_3Zr$: C, 52.79; H, 8.00; N, 9.93. Found: C, 52.56; H, 8.19; N, 10.09.

$(N_3N)ZrN(C_4H_9)=C(H)PPh$ (6). A PTFE-valved Schlenk tube was charged with **1** (100 mg, 0.178 mmol), *tert*-butyl isocyanide (14.9 mg, 0.178 mmol), and *ca.* 3 mL benzene solvent. The solution was heated to 90 °C for 2.5 h. The tube was then brought into the glovebox, and the benzene was lyophilized under reduced pressure to yield yellow microcrystals of the titled compound (96 mg, 0.149 mmol, 84%). All NMR spectroscopy of this compound was performed in toluene-d_8 and at 273 K. ^1H (500.1 MHz): δ 10.10 (d, J_{PH} = 8.5 Hz, C*H*, 1 H), 7.87 (t, C_6H_5, 2 H), 7.34 (d, C_6H_5 2 H), 7.17 (t, C_6H_5, 1 H), 3.36 (bs, CH_2, 6 H), 2.48 (bs, CH_2, 6 H), 1.43 (s, CH_3, 9 H), 0.44 (s, CH_3, 27 H). $^{13}C\{^1H\}$ (125.8 MHz): δ 187.1 (d, J_{PC} = 29 Hz, *C*–P), 132.0 (s, C_6H_5), 125.9 (s, C_6H_5), 1 resonance missing and assumed to be under the toluene-d_8 solvent peak, 61.6 (bs, CH_2), 59.4 (s, CH_3), 48.0 (s, *C*), 30.8 (bs, CH_2), 2.16 (bs, CH_3). $^{31}P\{^1H\}$ (202.4 MHz): δ 0.484 (s, *C*–P). IR (KBr, Nujol): 1463 s, 1363 s, 1240 s, 1142 w, 1037 m, 945 w, 827 w, 733 w, 721 s. Anal Calcd for $C_{26}H_{54}N_5PSi_3Zr$: C, 48.55; H, 8.46; N, 10.89. Found: C, 48.67; H, 8.59; N, 10.72.

$(N_3N)Zr[N(Cy)C(H)=PPh]$ (7). A PTFE-valved Schlenk tube was charged with **1** (100 mg, 0.178 mmol), CyN≡C (19.5 mg, 0.178 mmol) and *ca.* 4 mL benzene solvent. The resulting pale-yellow solution was heated in an oil bath at 80 °C for 3 h. The tube was then brought into the glove box and the benzene was lyophilized under reduced pressure to afford compound **7** as colorless microcrystals (106 mg, 0.158 mmol, 89%). ^1H (500.1 MHz, toluene-d_8): 9.90 (d, J_{PH} = 8.6 Hz, 1 H, C*H*), 7.80 (t, C_6H_5, 2 H), 7.19 (t, C_6H_5, 2 H), 7.05 (m, C_6H_5, 1 H), 3.67 (m, C_6H_{10}, 1 H), 3.21 (t, CH_2, 6 H), 2.37 (t, CH_2, 6 H), 1.80 (m, C_6H_{10}, 2 H), 1.62 (m, C_6H_{10}, 3 H), 1.37 (m, C_6H_{10}, 3 H), 1.23 (m, C_6H_{10}, 2 H), 0.17 (s, CH_3, 27 H). $^{31}P\{^1H\}$ (202.4 MHz): δ 87.9 (s). IR (KBr, Nujol): 2360 m, 1461 s, 1377 s, 1245 s, 1043 s, 936 s, 836 s, 783 s. Anal Calcd for $C_{29}H_{51}ClN_5PSi_3Zr$: C, 50.25; H, 8.43; N, 10.46. Found: C, 50.39; H, 8.62; N, 10.36.

(N_3N)Zr[N(2-Cl-6-MeC_6H_3)C(H)=PCy] (8). A PTFE-valved Schlenk tube was charged with **2** (100 mg, 0.176 mmol), 2-chloro-6-methylphenylisocyanide (26.7 mg, 0.176 mmol), and *ca.* 5 mL benzene solvent. The resulting pale yellow solution was heated at 100 °C for 18 h. The tube was then brought into the glovebox and the benzene was lyophilized under reduced pressure. The crude mixture was taken up in minimal Et_2O and filtered through Celite. The solution was concentrated under reduced pressure until incipient crystallization. The solution was allowed to warm to room temperature to redissolve the solid, and the solution was cooled to −30 °C yielding yellow microcrystals of **8** (63 mg, 0.0878 mmol, 50%). ^{1}H (500.1 MHz): δ 10.16 (d, J_{PH} = 14 Hz, C*H*, 1 H), 7.23 (d, Ar, 1 H), 6.92 (d, Ar, 1 H), 6.75 (t, Ar, 1 H), 3.23 (t, CH_2, 6 H), 2.57 (s, CH_3, 3 H), 2.32 (t, CH_2, 6 H), 2.11 (m, C_6H_{11}, 2 H), 1.80 (m, C_6H_{11}, 2 H), 1.57 (m, C_6H_{11}, 3 H), 1.42 (m, C_6H_{11}, 2 H), 1.22 (m, C_6H_{11}, 2 H), 0.121 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 189.9 (d, J_{PC} = 54 Hz, *C*=P), 130.1 (s, Ar), 2 resonances missing and assumed to be under the benzene-d_6 solvent peak, 126.3 (s, Ar), 65.2 (s, *C*H_2), 46.2 (s, *C*H_2), 35.4 (d, J_{PC} = 12 Hz), 27.8 (s, C_6H_{11}), 26.4 (s, C_6H_{11}), 20.9 (s, C_6H_{11}), 1.30 (s, *C*H_3). ^{31}P{^{1}H} (202.4 MHz): δ 120.0 (s). IR (KBr, Nujol): 2362 m, 1462 s, 1376 s, 1260 w, 1158 w, 1041 w, 926 m, 836 m, 722 s. Anal Calcd for $C_{29}H_{57}ClN_5PSi_3Zr$: C, 48.53; H, 8.01; N, 9.76. Found: C, 48.72; H, 8.32; N, 10.05.

1,1-Insertion reactions

(N_3N)Zr[C(PHPh)=N(Mes)] (10). A scintillation vial was charged with **1** (50 mg, 0.0893 mmol) and *ca.* 2 mL Et_2O solvent and the solution was cooled to −30 °C. A cold, 2 mL Et_2O solution of MesN≡C (13 mg, 0.0893 mmol) was added dropwise to the solution of (N_3N)ZrPHPh. The resulting colorless solution was allowed to stir for 10 min as the solution warmed to ambient temperature where upon Et_2O was evaporated under reduced pressure. The resulting solid was extracted into minimal Et_2O and filtered through Celite and cooled to −30 °C where the product was collected as yellow microcrystals (43 mg, 0.0598 mmol, 67% yield). ^{1}H (500.1 MHz): δ 6.84 (m, Mes, 2 H), 5.91 (d, J_{PH} = 266 Hz, P*H*, 1 H), 3.26 (t, CH_2, 6 H), 2.48 (t, CH_2, 6 H), 2.07 (s, CH_3, 6 H), 0.167 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 266.4 (d, J_{PC} = 101 Hz, N=*C*), 149.8 (d, J_{PC} = 15 Hz, C_6H_6), 135.1 (d, Ar), 134.6 (s, Ar), 134.4 (s, Ar), 131.3 (s, Ar), 3 resonances assumed to be under the solvent peak, 64.6 (s, *C*H_2), 46.7 (s, *C*H_2), 20.8 (s, C_9H_{11}), 20.1 (s, C_9H_{11}), 2.2 (s, *C*H_3). ^{31}P{^{1}H} (202.4 MHz): δ −27.7 (s).

(N_3N)Zr[C(PPh_2)=NCH_2Ph] (12). A 3 mL Et_2O solution of **11** (50 mg, 0.079 mmol) was cooled to −30 °C, and to that solution was added a cold 1 mL Et_2O solution of benzyl isocyanide (9.2 mg, 0.079 mmol). After 1 h, resulting light orange solution was dried under reduced pressure. The residue was dissolved in Et_2O, and the solution was filtered then concentrated under reduced pressure and cooled to −30 °C for several days. Light orange crystals were collected in several crops and dried under reduced pressure (48 mg, 0.064 mmol, 81%). ^{1}H (500 MHz): δ 8.00 (t, C_6H_5, 4 H), 7.44 (d, C_6H_5, 2 H, J = 7.4 Hz), 7.23 (m, C_6H_5, 6 H), 7.20 (m, C_6H_5, 3 H), 5.11 (s, CH_2, 2 H), 3.47 (t, CH_2, 6 H), 2.64 (t, CH_2, 6H), 0.188 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 144.9 (d, *C*=N, J_{PC} = 38.6 Hz), 128.9 (s, C_6H_5), 128.8 (s, C_6H_5), 128.7 (s, C_6H_5), 128.6 (s, C_6H_5), 136.5 (d, C_6H_5, J_{PC} = 10.8 Hz), 135.9 (d, C_6H_5, J_{PC} = 10.8 Hz), 129.5 (s, C_6H_5), 61.3 (s, *C*H_2), 47.8 (s, *C*H_2), 1.9 (s, *C*H_3). ^{31}P{^{1}H} (202.4 MHz): δ 2.96 (s). IR (KBr, Nujol): 1694 s (ν_{CN},), 1584 w, 1461 s, 1378 m, 1245 m, 1054 s, 940 s, 910 w, 832 s, 792 m, 698 m, 574 w cm^{-1}. Anal Calcd for $C_{35}H_{56}N_5PSi_3Zr$: C, 55.80; H, 7.49; N, 9.30. Found: C, 55.61; H, 7.34; N, 9.01.

Liberation of phosphaformamides

(Mes)(Me)NC(H)=PPh (13). *Method 1*. A 50 mL round bottom flask was charged with **5** (75 mg, 0.106 mmol), Methyliodide (15.1 mg, 0.106 mmol) and 3 mL Et_2O solvent. The reaction was stirred at ambient temperature for 2 h where the solvent was evaporated under reduced pressure. The residual solid was dissolved in hexanes and filtered through a plug of silica (~0.075 mg) and dried to afford the title compound as an oil (19 mg, 0.072 mmol, 68%). ^{1}H (500.1 MHz): δ 8.19 (d, J_{PH} = 45 Hz, C*H*, 1 H), 7.47 (t, C_6H_5, 2 H), 7.08 (m, C_6H_5, 2 H), 6.74 (s, C_6H_2, 2 H), 2.15 (s, C_6H_2, 3 H), 2.04 (s, C_6H_2, 6 H), 1.56 (d, J_{PH} = 3 Hz, CH_3). ^{13}C NMR (125.8 MHz) δ 176.5 (d, J_{PC} = 14.1 Hz, *C*=P), 136.1 (s, Ar), 136.0 (s, Ar), 133.8 (d, J_{PC} = 19.1 Hz, C_6H_5) 129.4 (s, Ar), 129.3 (s, Ar), 129.2 (s, Ar), 1 aromatic resonance assumed under solvent peak, 126.7 (s, Ar), 21.1 (s, CH_3), 18.7 (s, CH_3), 9.2 (s, N–CH_3). ^{31}P{^{1}H} (202.4 MHz): δ −22.3.

Method 2. A 50 mL round bottom flask was charged with **5** (98.5 mg, 0.140 mmol), methyl triflate (22.1 mg, 0.140 mmol), and 3 mL benzene solvent. The reaction was stirred at ambient temperature for 4 h, then the benzene was lyophilized. The residue was dissolved in hexanes, and the solution was filtered through a plug of silica. The solution was then concentrated under reduced pressure and cooled to −30 °C for several days. **13** (mg, 0.078 mmol, 57%) was obtained as an off-white solid. Spectroscopic data for this compound is identical to that from Method 1. MS (CI (benzene)): 270 $[M + H]^+$.

(Mes)N=C(H)P(CH_2Ph)(Ph) (14). A PTFE-valved Schlenk tube was charged with **5** (75 mg, 0.106 mmol), $PhCH_2Br$ (18 mg, 0.106 mmol), and 5 mL benzene solvent. The mixture was heated to 80 °C for 2 h. The solution was then flashed through a plug of silica and the benzene was then lyophilized to afford the title product as a pale yellow oil (29 mg, 0.083 mmol, 78%). ^{1}H (500.1 MHz): δ 8.21 (d, J_{PH} = 44 Hz, C*H*, 1 H), 7.47 (m, C_6H_5, 7 H), 7.11–7.01 (m, C_6H_5, 3 H), 6.77 (s, C_6H_2, 2 H), 3.78 (d, J_{PH} = 14 Hz, CH_2, 1 H), 3.33 (dd J_{PH} = 14 Hz, J_{HH} = 4 Hz, CH_2, 1 H), 2.16 (s, CH_3, 3 H), 2.10 (s, CH_3, 6 H). ^{13}C{^{1}H} (125.8 MHz): δ 175.0 (d, J_{PC} = 16.0 Hz, *C*=N), 135.3 (d, J_{PC} = 19.8 Hz, C_6H_5), 133.3 (s, C_6H_2), 130.2 (s, C_6H_2), 130.1 (s, C_6H_2), 129.5 (s, C_6H_5), 128.9 (s, C_6H_5), 2 aromatic resonances assumed to be under solvent peak, 126.7 (d, J_{PC} = 32.8 Hz, CH_2), 23.3 (s, CH_3), 21.2 (s, CH_3). ^{31}P{^{1}H} (202.4 MHz): δ −6.67. MS (CI(benzene)): 346 $[M + H]^+$.

(Mes)N=C(H)P(Ph)(CPh_3) (15). A 50 mL round bottom flask was charged with **5** (100 mg 0.141 mmol) and tritylchloride (39 mg, 0.141 mmol) and 5 mL of diethylether. The reaction is

Table 4 Crystal data and structure refinement parameters for compounds **6**, **7**, **8**, **12** and **15**

	6	**7**	**8**	**12**	**15**
Formula	$C_{26}H_{54}N_5PSi_3Zr$	$C_{28}H_{56}N_5PSi_3Zr$	$C_{29}H_{57}ClN_5PSi_3Zr$	$C_{35}H_{56}N_5PSi_3Zr$	$C_{35}H_{32}NP$
M	643.20	669.24	717.71	753.31	497.59
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Color	Colorless	Yellow	Colorless	Yellow	Colorless
a/Å	20.806(1)	10.1609(10)	10.6702(4)	11.2901(9)	9.3521(9)
b/Å	19.687(1)	20.3994(19)	11.2128(4)	19.5468(16)	9.9508(9)
c/Å	18.640(1)	16.9631(16)	16.7109(6)	18.9804(16)	29.528(3)
α/°	90	90	83.704(1)	90	90
β/°	115.838(1)	91.791(2)	72.392(1)	105.424(1)	94.906(1)
γ/°	90	90	78.761(1)	90	90
V/Å^3	6871.7(6)	3514.3(6)	1866.4(1)	4037.8(6)	2737.9(4)
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	8	4	2	4	4
θ range/°	1.60 to 30.57	1.56 to 32.20	1.85 to 30.51	2.17 to 27.45	2.16 to 30.57
μ/mm^{-1}	0.494	0.483	0.531	0.430	0.124
N	110 878	65 436	30 223	46 730	42 804
N_{ind}	21 007	12 205	11 282	9248	8388
R_{int}	0.0410	0.0474	0.0286	0.0474	0.0703
R_1[a] ($I > 2\sigma(I)$)	0.0289	0.0626	0.0297	0.0362	0.0543
wR_2[b] ($I > 2\sigma(I)$)	0.0651	0.1380	0.1294	0.0724	0.1380
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^3	0.463; −0.313	5.358; −1.010	0.710; −0.323	0.359; −0.397	5.358; −1.010
GoF on R_1	1.011	1.083	1.029	1.017	1.083

[a] $R_1 = ||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

allowed to stir at ambient temperature for 8 h, then the solution is filtered through a plug of silica followed by 4 mL of diethylether. The solution was then concentrated to ~2 mL and cooled to −30 °C to give crystals of 13 in three crops (61 mg, 120 mmol, 81%). ^{1}H (500.1 MHz): δ 8.47 (d, J_{PH} = 36 Hz, C*H*, 1 H), 7.55 (m, C_6H_5, 2 H), 7.34 (m, C_6H_5, 6 H), 7.12–6.89 (m, C_6H_5, 12 H), 6.69 (s, C_6H_2, 2 H), 2.10 (s, CH_3, 3 H), 2.01 (s, CH_3, 6 H). $^{13}C\{^1H\}$ (125.8 MHz) δ 173.3 (d, J_{PC} = 12.7 Hz, *C*═N), 151.7 (s, Ar), 145.6 (s, Ar), 145.5 (s, Ar), 133.6 (d, J_{PC} = 56.1 Hz, C_6H_5), 130.8 (d, J_{PC} = 10.6 Hz, *C*(C_6H_5)), 129.6 (s, Ar), 3 aromatic resonances assumed to be under solvent peak, 127.8 (s, Ar), 127.0 (s, Ar), 126.7 (s, Ar), 23.3 (s, CH_3), 21.1 (s, CH_3). $^{31}P\{^1H\}$ (202.4 MHz): δ 20.6. Anal. Calcd for $C_{35}H_{32}NP$: C, 84.48; H, 6.48; N, 2.81. Found: C, 84.77; H, 6.72; N, 2.81.

X-ray crystallography

X-Ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometers (MoKα, λ = 0.71073 Å) at 125 K. A suitable crystal of compounds were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least squares procedures on F2 with SHELXTL (version 6.14).[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. The solution of structure 7 exhibited disorder and a trimethylsilyl substituent was modeled. Despite some unusual parameters, a second independent data set collected on a different sample yielded the same molecular structure. Crystal data and refinement details are presented in Table 4.

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