Inorganic Chemistry

Article

pubs.acs.org/IC

Zirconium-Mediated Synthesis of Arsaalkene Compounds from Arsines and Isocyanides

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Supporting Information

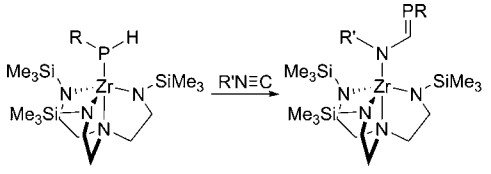
ABSTRACT: An atom-economical synthesis of arsaalkenes via a net coupling of aryl arsines with aryl or alkyl isocyanides at zirconium is presented. Reaction of zirconium arsenido complexes $(N_3N)ZrAsHAr$ [$N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$; Ar = Ph, (**2**) Mes (**3**)] with aryl and alkyl isocyanides yields arsaalkene products of the general form $(N_3N)Zr[NRC(H)=As(Ar)]$. Two examples (**5**: R = Mes, Ar = Ph; **6**: R = CH_2Ph, Ar = Mes) were structurally characterized. Observation of intermediates in the reaction and structural characterization of the previously reported 1,1-insertion product benzylisocyanide with $(N_3N)ZrAsPh_2$ (**8**), $(N_3N)Zr[\eta^2\text{-}C(PPh_2)=NCH_2Ph]$ (**9**), support the mechanistic hypothesis that these reactions occur via 1,1-insertion followed by rearrangement.

INTRODUCTION

It is well-known that the development of low valent organoarsenic chemistry has lagged behind that for phosphorus.[1] In some instances, this lag has been attributed to less developed synthetic methods associated with the heavier congener.[2] More commonly, the reduced stability of arsenic−carbon multiple bonds as compared to their phosphorus counterparts has hampered development.[1a] However, the tremendous reaction chemistry exhibited by phosphaalkenes[3] as well as their application in materials science[4] argues for continued exploration of arsaalkenes and potential applications.

Principal synthetic methods that produce phosphaalkenes also apply to the preparation of arsaalkenes.[3c,d] These common methods include condensation reactions, 1,2-elimination of typically HCl, and 1,3-silyl migration.[1a] The drawback to all of these methods is the amount of waste generated, but in some cases, syntheses are dependent on the presence of specific functional groups or exhibit limited functional group tolerance.

Recently, we have established a general synthetic route to phosphaalkenes by reaction of zirconium phosphide complexes, derived from primary phosphines, with isocyanides (eq 1).[5]

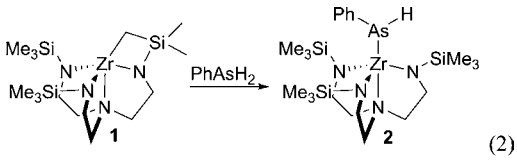


(1)

The tolerance of the phosphaalkene synthesis toward isocyanide substitution and the ability to use aryl and alkyl phosphines argue that this method may have yet broader promise, including the synthesis of arsaalkenes. Herein, expansion of that reactivity to a synthesis of arsaalkenes is presented. Metal-mediated syntheses of multiple bonds in the main group are rare,[1c,3c,6] and expansion of methods that produce E−E multiply bonded species may represent a new paradigm in inorganic synthesis.

RESULTS AND DISCUSSION

It has been established that $[\kappa^5\text{-}N,N,N,N,C\text{-}(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (**1**) is a convenient precursor to Zr−E bonds by E−H activation.[7] Indeed this is also true for arsines, and $(N_3N)ZrAsHPh$ (**2**) was prepared by reaction of **1** with 1 equiv of phenylarsine and isolated as analytically pure yellow crystals in 76% yield (eq 2).



(2)

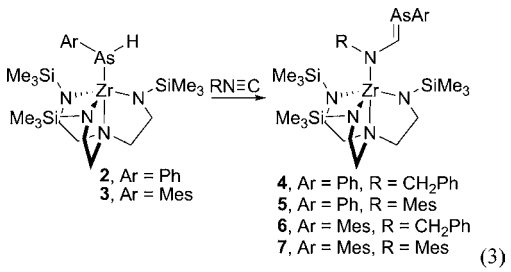
The spectroscopic data for **2** mimic those of the previously reported primary arsenido complex $(N_3N)ZrAsHMes$ (**3**, Mes = 2,4,6-trimethylphenyl)[8] and are similar to those of other zirconium complexes featuring terminal arsenido ligands.[9] The diagnostic spectroscopic features of **2** include an arsenido proton resonance at δ 3.42 in the ^{1}H NMR spectrum and ν_{AsH} = 2061 cm^{-1} in the infrared.

Both arsenido complexes **2** and **3** react readily with aryl and alkyl isocyanides to give analytically pure arsaalkene products, $(N_3N)Zr[N(R)CH=AsAr]$, that can be isolated in good to

Received: May 14, 2013
Published: June 7, 2013

   dx.doi.org/10.1021/ic4012058 | Inorg. Chem. 2013, 52, 7811−7816

excellent yields (eq 3, Table 1). The reaction of arsenido complexes with isocyanide proceeded smoothly to product, in



(3)

Table 1. Selected Spectroscopic Data for Arsaalkene Products 4–7[a]

cmpd	yield (%)	R	R′	As=C*H* (δ)	As=*C* (δ)
4	86	Ph	CH_2Ph	11.46	251.4
5	97	Ph	Mes	11.54	214.3
6	78	Mes	CH_2Ph	10.95	273.5
7	82	Mes	Mes	11.01	262.2

[a] ^{1}H and ^{13}C NMR spectroscopic data collected in benzene-d_6 solution.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (N_3N)Zr[N(Mes)CH=AsPh] (5) and (N_3N)Zr[N(CH_2Ph)CH=AsMes] (6)

	5	6
	Bonds Length	
Zr–N(1)	2.089(3)	2.0831(14)
Zr–N(2)	2.072(3)	2.1016(13)
Zr–N(3)	2.064(3)	2.0824(14)
Zr–N(4)	2.517(3)	2.4467(14)
Zr–N(5)	2.194(3)	2.1629(13)
As–C(16)	1.845(4)	1.8419(16)
As–R[a]	1.966(4)	1.9735(16)
N(5)–C(16)	1.359(5)	1.347(2)
	Bond Angles	
As–C(16)–N(5)	113.2(2)	127.5(1)
H(1)–C(16)–N(5)	134.0(2)	114.5(1)
As–C(16)–H(16)	112.8(3)	118.0(1)
C–As–C(16)[b]	95.28(1)	97.7(7)

[a] Substituent at arsenic, C(21) for **5** and C(22) for **6**. [b] The "R–As–C angle" where R is the arsenic substituent.

most cases, at ambient temperature. As a precaution, reactions were performed in the absence of light. However, it was shown for these examples, that similar yields to those noted can be obtained under ambient lighting.

The indicative spectroscopic features for these compounds include arsaalkene ^{1}H NMR and ^{13}C NMR resonances (Table 1). The benzyl-substituted products **4** and **6** exhibit arsaalkene resonances downfield as compared to those of the mesityl-substituted derivatives **5** and **7** in the respective ^{1}H NMR spectra, while the reverse trend is observed in the ^{13}C NMR spectra. These trends suggest that the electronic influence of the nitrogen substituent is likely the dominant factor in these chemical shifts rather than ring current at the mesityl substituent. In all instances, the ^{13}C NMR resonances are consistent with reported arsaalkenes.[1,6a]

Solid state structures of two arsaalkene derivatives, **5** and **6**, were determined by X-ray diffraction studies using crystals grown from concentrated ethereal solutions cooled to −30 °C. The compounds are as highly similar as is visually evident in Figure 1 and are isostructural based on comparison of metrical parameters (Table 2). The As=C bond length for both compounds is short (Table 2), as anticipated, and the values fit neatly within the range of structurally characterized examples of arsaalkenes.[1,6a] Of course arsenic substitution has substantial effect on As=C bond length (i.e., normal vs inverse demand). The As=C bonds of compounds **5** and **6** are similar to other examples of monoamine substituted arsaalkenes including Cp*Fe(CO)$_2$As=C(Ph)NMe (As=C = 1.84.9 (7) Å),[10] but these bonds are still longer than the theoretical As–C π-bond length of 1.79.[11]

As expected from steric arguments, the arsenic substituent is syn to the crystallographically located arsaalkene hydrogen atom. In both examples, the R–As–C angle is acute within the range of structurally characterized arsaalkenes (Table 2). For **6**, this angle is slightly more obtuse than that for **5**, which may be a result of the steric demands of the mesityl substituent on arsenic. There has not been a great deal of comment in the literature regarding the R–As–C angle, which varies over not less than 22° for reported examples.[1a] However, it has been suggested for a variety of other multiply bonded systems that a shallow R–E–E′ angle is consistent with greater s-character of the lone pair at E.[1c]

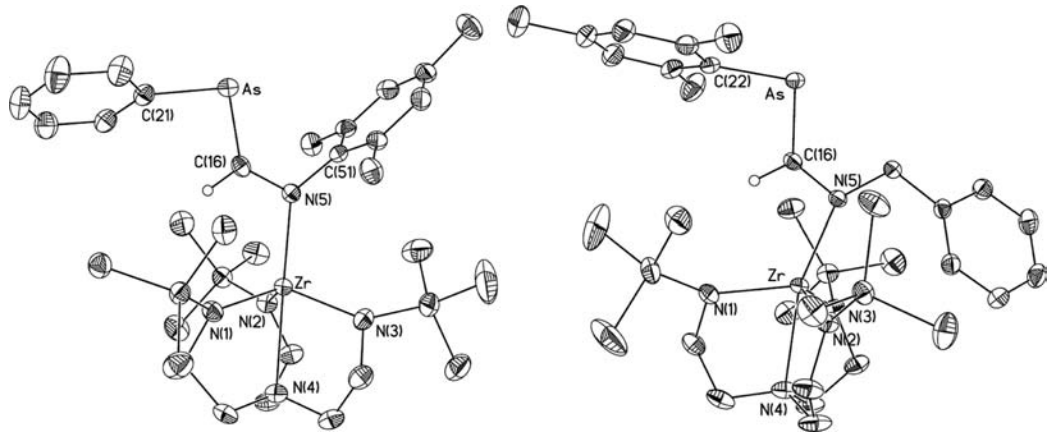


Figure 1. Molecular structure of (N_3N)Zr[N(Mes)CH=AsPh] (**5**, left) and (N_3N)Zr[N(CH_2Ph)CH=AsMes]·Et_2O (**6**, right), with thermal ellipsoids drawn at the 50% level. Hydrogen atoms, except those located on C(16), as well as solvent of crystallization for **6** are omitted for clarity.

dx.doi.org/10.1021/ic4012058 | Inorg. Chem. 2013, 52, 7811–7816

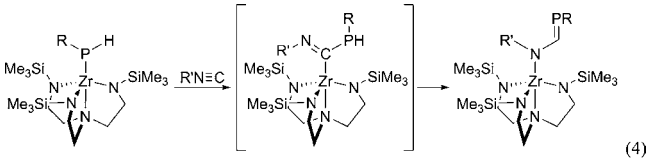
Perhaps the most striking feature of the solid state structures of arsaalkene compounds **5** and **6** are that neither the As lone pair nor As=C bond are associated with zirconium. This stands in contrast with the known bonding modes of arsaalkene ligands,[1a] yet the lack of interaction is consistent with highly related phosphaalkene complexes prepared analogously.[5] This behavior may be these less a function of these ligands and more of the (N_3N)Zr platform, for which six-coordinate examples are limited and involve stronger donors. For example, phosphine-substituted iminato ligands bind exclusively in an η^1 fashion, whereas phosphaguanidinate ligands bind in an η^2 fashion but only through the nitrogen atoms.[12]

Complete conversion to product **5** required mild heating to 40 °C for approximately 20 min. Observation of the reaction of **2** with mesitylisocyanide by ^{1}H NMR spectroscopy in benzene-d_6 solution revealed an intermediate with a new arsenic proton resonance at δ 5.50 that is tentatively assigned as the 1,1-insertion product based on the relative similarity of the arsenido proton chemical shift to that of related phosphine-substituted iminoacyl compounds.[5] Formation of **5** is qualitatively slower than generation of the intermediate, but sufficient concentrations of the intermediate could not be generated for more thorough characterization. All efforts to isolate such intermediates in any reaction of **2** or **3** with isocyanide failed.

Reaction of *tert*-butylisocyanide with arsenido complex **3** gave a mixture of products that is analytically the simple combination of the two reagents (Anal. Calcd for $C_{29}H_{60}N_5AsSi_3Zr$: C, 47.76; H, 8.29; N, 9.60. Found: C, 47.86; H, 8.08; N, 9.31). Observation of the mixture by ^{1}H NMR spectroscopy revealed a resonance at δ 10.92 that accounted for all of the arsenic proton by mass balance. In the ^{13}C NMR spectrum however, strong evidence for two products is given by resonances at δ 265.5 and δ 142.8, where the former is coupled to the aforementioned proton and the latter is not via an ^{1}H-^{13}C HMQC experiment. The ^{1}H NMR data suggest that neither compound is a 1,1-insertion product, and the reaction may produce a mixture of the desired arsaalkene product (N_3N)Zr[N(^{t}Bu)CH=AsMes] and the arsaamidinate compound (N_3N)Zr[N(^{t}Bu)=C(H)AsMes], which is the tautomer of the arsaalkene. Current data prohibits assignment of a binding mode for the proposed ^{t}BuN=C(H)AsMes$^-$ ligand, and the rich variety of binding for the phosphorus derivative of these amidinate congeners suggests a range of options are possible.[13] Exclusive formation of the phospha-formamidinate product (N_3N)Zr[*N,P*:η^2-N(^{t}Bu)=C(H)PPh] (i.e., the phosphaalkene tautomer) was seen in the reaction of *tert*-butylisocyanide with (N_3N)ZrPHPh, suggesting unique reactivity associated with this particular isocyanide substrate.[5b] Efforts to separate the two species failed, and subjecting the reaction to more forcing conditions only resulted in eventual decomposition.

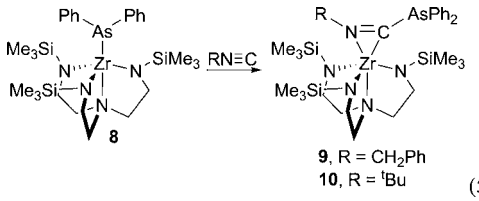
The reaction of **2** with benzylisocyanide proceeded to product **4** at ambient temperature without observation of an intermediate by ^{1}H NMR spectroscopy in benzene-d_6 solution. In the reaction of (N_3N)ZrPHPh with benzylisocyanide, the 1,1-insertion product was isolated prior to formation of the phosphaalkene (eq 4).[5a] That no intermediate is observed in the reaction of arsenido derivative **2**, an exact analogue to (N_3N)ZrPHPh, with benzylisocyanide suggests that rearrangement to form phosphaalkenes is slower than that to form arsaalkenes.

It has been proposed that the relative sluggishness of arsenic to undergo 1,3-silyl migration to form arsaalkenes as compared



to the same reaction to form phosphaalkenes is a result of the increased size of arsenic.[1a] Of course, the pivotal migration herein is a 1,2-H shift, but the reverse of the trend seen for 1,3-silyl migration is intriguing and suggests that atomic size may not be the only factor governing the rate of migration. These apparent disparities invite further study of migration reactions between phosphorus and arsenic.

Despite the inability to isolate a 1,1-insertion intermediate, some evidence to support this mechanistic hypothesis comes from the reaction of secondary phosphines with isocyanides. As previously reported, (N_3N)ZrAsPh$_2$ (**8**) reacts with benzylisocyanide to give the 1,1-insertion product (N_3N)Zr[C(AsPh$_2$)-N=(CH$_2$Ph)] (**9**). This is a general transformation. For example, reaction of *tert*-butylisocyanide with **8** affords analytically pure, yellow crystals of (N_3N)Zr[C(AsPh$_2$)-N=(C^{t}Bu)] (**10**) in 76% yield (eq 5). Compound **10** was



characterized by the usual suite of techniques and gave similar spectroscopic data to that of **9** and the products of related insertion reactions involving phosphido derivatives.[5,8]

In the course of this study, single crystals of **9** were obtained by cooling an ethereal solution to −30 °C for extended periods. The molecular structure of **9** reveals an η^2-bound iminoacyl ligand, consistent with the infrared data (Figure 2). The bond lengths are particularly important here. For **9**, As−C(16) =

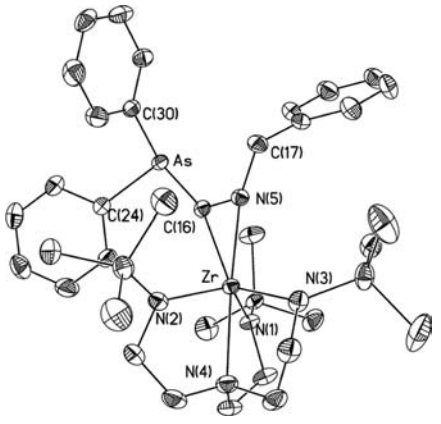


Figure 2. Molecular structure of (N_3N)Zr[C(AsPh$_2$)N=(CH$_2$Ph)] (**9**) with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−N(1) = 2.1218(1), Zr−N(2) = 2.0923(2), Zr−N(3) = 2.4703(1), Zr−N(4) = 2.2466(1), Zr−N(5) = 2.1186(1), C(16)−N(5) = 1.285(1), Zr−C(16) = 2.2840(2), C(16)−As = 1.974(2), Zr−C(16)−N(5) = 71.94(9), Zr−N(5)−C(16) = 75.14(9), C(16)−Zr−N(5) = 32.93(5), N(2)−C(16)−As = 128.7(1).

dx.doi.org/10.1021/ic4012058 | *Inorg. Chem.* 2013, 52, 7811−7816

1.974(2) Å as well as the angles about arsenic are inconsistent with As−C multiple bond character while C(16)−N(5) = 1.285(1) Å is consistent with an imine functionality.

Isocyanide 1,1-insertion reactions with group 4 arsenido complexes are known. The first example was reaction of phenylisocyanide with $Cp'_2HfCl[As(SiMe_3)_2]$ as reported by Hey-Hawkins.[9b] The structural similarities of that hafnium compound and **9** are high. More important, the prevalence of these 1,1-insertion reactions argue for their intermediacy in the formation of arsaalkenes at primary arsenido complexes.

CONCLUSIONS

Insertion of isocyanides into Zr−As bonds yields iminoacyl products that are unstable with respect to rearrangement to afford arsaalkene products for primary arsenide ligands. This stands in contrast to literature examples of isocyanide insertion into Zr−As bonds that yield stable iminoacyl products for secondary arsines. Indeed this is a second example in which zirconium arsenide chemistry significantly changes between primary and secondary arsines. These observations imply that rich reaction chemistry of M−As bonds may yet be available upon further exploration. This reaction type, a net coupling of arsines with isocyanides at zirconium, appears to be a general transformation based on the examples provided and may represent the basis for new, metal-mediated synthetic strategies to multiple bonding in the main group.

EXPERIMENTAL DETAILS

Reactions were performed under a purified nitrogen atmosphere using dry, oxygen-free solvents in an M. Braun glovebox or by standard Schlenk techniques. Celite-454 was heated to a temperature above 180 °C under dynamic vacuum for at least 8 h. Benzene-d_6 was purchased then degassed and dried over NaK alloy. Elemental analyses were performed on an Elementar microCube. NMR spectra were recorded with either a Bruker Avance III, Bruker ARX, or Varian 500 MHz spectrometer in benzene-d_6 and are reported with reference to residual solvent resonances (δ = 7.16 and 128.0) unless otherwise noted. Infrared spectra were collected on a Bruker Alpha FT-IR with an ATR plate or a Perkin-Elmer System 2000 FT-IR spectrometer at a resolution of 1 cm^{-1} with KBr plates.

Compounds **1**, **3**, and **8**, and **9** were prepared using the literature procedures.[7,8] Mesitylisocyanide was prepared according to the literature procedure for phenylisocyanide substituting 2,4,6-trimethylaniline.[14] Diphenylarsine and mesitylarsine were prepared according to literature procedure.[8] Phenylarsine was prepared using a modified version of that in the literature.[15] All other chemicals were obtained from commercial suppliers and dried or purified by conventional means.

(N_3N)ZrPhAsH (2). A −30 °C, 5 mL ethereal solution of $PhAsH_2$ (197 mg, 1.28 mmol) was added dropwise to a 5 mL ethereal solution of **1** (605 mg, 1.34 mmol) at −30 °C. The colorless solution was stirred and allowed to warm to ambient temperature over 16.5 h. The resulting red solution was filtered through Celite, concentrated to ∼2 mL, and then cooled to −30 °C for 24 h to afford yellow crystals (587 mg, 0.972 mmol, 76%). ^{1}H (500 MHz): δ 7.91 (t, J = 7.05 Hz, C_6H_5, 1 H); 7.79 (d, J = 7.09 Hz, C_6H_5, 2 H); 7.11 (t, J = 7.44 Hz, C_6H_5, 2 H); 3.42 (s, AsH_2, 1 H); 3.17 (t, J = 5.00 Hz, CH_2, 6 H); 2.09 (t, J = 5.00 Hz, CH_2, 6 H); 0.27 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 134.9 (s, C_6H_5); 128.5 (s, C_6H_5), 126.5 (s, C_6H_5), 123.9 (s, C_6H_5); 63.6 (s, CH_2); 47.5 (s, CH_2); 0.9 (s, CH_3). IR 2061 (ν_{AsH}) cm^{-1}. Anal. Calcd for $C_{21}H_{45}N_4AsSi_3Zr$: C, 41.76; H, 7.51; N, 9.28. Found: C, 41.41; H, 7.72; N, 9.23.

(N_3N)Zr[N(CH_2Ph)CH=AsPh] (4). A 2 mL ethereal solution of benzylisocyanide (25 mg, 0.212 mmol) was added dropwise to a 5 mL ethereal solution of **2** (125 mg, 0.207 mmol) cooled to −30 °C in the dark and stirred for 2 h at ambient temperature. The resulting solution was filtered and then concentrated until incipient crystallization under reduced pressure. After gentle warming to redissolve the solids, the solution was cooled to −30 °C for several days to afford orange crystals (128 mg, 0.178 mmol, 86%). ^{1}H (500 MHz): δ 11.46 (s, As=CH, 1 H), 7.93 (t, C_6H_5, 2 H), 7.53 (d, C_6H_5, 2 H), 7.24 (t, C_6H_5, 2 H), 7.19 (t, C_6H_5, 2 H), 7.08 (t, C_6H_5, 2 H), 5.15 (s, CH_2, 2 H), 3.17 (t, CH_2, 6 H), 2.25 (t, CH_2, 6 H), 0.15 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 251.4 (s, As=C); 134.3 (s, C_6H_5), 133.3, (s, C_6H_5), 126.9 (s, C_6H_5), 126.2 (s, C_6H_5), 64.2 (s, CH_2), 59.4 (s, CH_2), 46.7 (s, CH_2), 1.24 (s, CH_3). IR 3051 w, 2948 m, 2887 w, 2845 m, 1642 w, 1574 w, 1475 w, 1451 w, 1330 m, 1299 w, 1242 s, 1183 m, 1155 w, 1103 m, 1051 m, 1019 m, 996 s, 925 m, 825 s, 785 m, 744 m, 731 s, 689 m, 641 m, 622 m, 561 m, 456 m, 430 m, 408 m. Anal. Calcd for $C_{29}H_{52}N_5AsSi_3Zr$: C, 48.30; H, 7.27; N, 9.71. Found: C, 47.92; H, 7.36; N, 9.44.

(N_3N)Zr[N(Mes)CH=AsPh] (5). A 2 mL ethereal solution of mesitylisocyanide (41 mg, 0.282 mmol) was added dropwise to a 5 mL ethereal solution of **2** (170 mg, 0.281 mmol) cooled to −30 °C in the dark. The resultant red-orange solution was heated to 40 °C for 20 min, filtered, then concentrated until incipient crystallization under reduced pressure. After gentle warming to redissolve the solids, the solution was cooled to −30 °C for several days to afford orange crystals. Analytically pure material was given by dissolving the crystals in benzene followed by filtration of the solution though Celite and lyophylization, presumed to remove ether trapped in crystallization, to afford a red-orange powder (205 mg, 0.274 mmol, 97%). ^{1}H (500 MHz): δ 11.54 (s, As=CH, 1 H), 7.98 (d, C_6H_5, 2 H); 7.24 (t, C_6H_5, 2 H), 7.13 (m, obscured by solvent), 6.92 (s, $C_6Me_3H_2$, 2 H), 3.19 (t, CH_2, 2 H), 2.63 (s, o-CH_3, 6 H), 2.26 (t, CH_2, 6 H), 2.17 (s, p-CH_3, 3 H), 0.17 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 214.3 (s, As=CH), 141.2 (s, Ar), 138.3 (s, Ar), 134.1 (s, Ar), 131.5 (s, Ar), 131.4 (s, Ar), 129.3 (s, Ar), 128.4 (s, Ar), 68.4 (s, CH_2); 49.5 (s, CH_2), 23.9 (s, o-CH_3), 23.8 (s, o-CH_3), 13.8 (s, p-CH_3), 0.08 (s, CH_3). One aryl resonance was not observed, presumably obscured by solvent. IR: 3059 w, 2949 w, 2893 w, 2850 w, 1476 w, 1395 w, 1348 w, 1309 w, 1246 m, 1183 w, 1146 w, 1125 m, 925 m, 891 m, 830 s, 782 s, 733 s, 674 m, 539 m, 471 m, 435 m. Anal. Calcd for $C_{31}H_{56}N_5AsSi_3Zr$: C, 49.70; H, 7.53; N, 9.35. Found: C, 50.30; H, 8.23; N, 9.00.

(N_3N)Zr[N(CH_2Ph)CH=AsMes] (6). A 2 mL solution of benzylisocyanide (21 mg, 0.178 mmol) was cooled to −30 °C and added to a 4 mL ethereal solution of **3** (112 mg, 0.174 mmol) at −30 °C in the dark. The reaction mixture was stirred in the dark while warming to ambient temperature over 4 h. The resulting orange solution was then filtered and concentrated to ∼2 mL before being cooled to −30 °C for several days to afford orange-yellow crystals (103 mg, 0.136 mmol, 78%). ^{1}H (500 MHz): δ 10.95 (s, As=CH, 1 H), 7.60 (d, C_6H_6,2 H), 7.50 (t, C_6H_6, 2 H), 7.12 (d, C_6H_6, 2 H), 6.94 (s, $C_6Me_3H_2$, 2 H), 5.20 (s, CH_2, 2 H), 3.11 (t, CH_2, 2 H), 2.68 (s, CH_3, 6 H), 2.34 (s, CH_3, 3 H), 2.25 (t, CH_2, 6 H), 0.11 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 273.53 (s, As=C), 140.0 (s, Ar); 135.5 (s, Ar), 135.0 (s, Ar), 134.8 (s, Ar), 131.6 (s, Ar), 129.1 (s, Ar), 128.3 (s, Ar), 65.0 (s, CH_2); 64.1 (s, CH_2), 46.6 (s, CH_2), 25.0 (s, o-CH_3), 20.0 (s, p-CH_3), 1.2 (s, CH_3). One aryl resonance was not observed, presumably obscured by solvent. IR: 3062 w, 2955 w, 2873 w, 1565 w, 1471 w, 1340 w, 1322 w, 1303 w, 1244 m, 1183 w, 1148 w, 1115 m, 925 m, 875 m, 828 s, 782 s, 732 s, 679 m, 531 m. Anal. Calcd for $C_{32}H_{58}N_5AsSi_3Zr$: C, 50.36; H, 7.66; N, 9.18. Found: C, 50.51; H, 7.84; N, 9.02.

(N_3N)Zr[N(Mes)CH=AsMes] (7). A 2 mL solution of mesitylisocyanide (16 mg, 0.110 mmol) was cooled and added to a 3 mL ethereal solution of **3** (68 mg, 0.105 mmol) at −30 °C in the dark. The reaction mixture was stirred in the dark while warming to ambient temperature over 5 h. The resulting yellow solution was then filtered and concentrated to ∼2 mL before being cooled to −30 °C for 2 d to afford yellow crystals (69 mg, 0.087 mmol, 82%). ^{1}H (500 MHz): δ 11.01 (s, As=CH, 1 H); 6.96 (s, $C_6Me_3H_2$, 2 H), 6.73 (s, $C_6Me_3H_2$, 2 H), 3.21 (t, CH_2, 2 H), 2.76 (s, CH_3, 6 H), 2.71 (s, CH_3, 6 H), 2.34 (s, CH_3, 3 H), 2.22 (t, CH_2, 2 H); 2.17 (s, CH_3, 3 H), 0.13 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 262.2 (s, As=C) 144.6 (s, $C_6Me_3H_2$), 143.2 (s, $C_6Me_3H_2$), 138.7 (s, $C_6Me_3H_2$), 137.1 (s, $C_6Me_3H_2$), 134.5

dx.doi.org/10.1021/ic4012058 | Inorg. Chem. 2013, 52, 7811−7816

Table 3. Crystal Data and Structure Refinement Parameters for Compounds 5, 6, and 9

	5	6	9
formula	$C_{31}H_{56}AsN_5Si_3Zr$	$C_{34}H_{63}AsN_5Si_3ZrO_{0.5}$	$C_{35}H_{56}AsN_5Si_3Zr$
M	749.22	800.30	797.26
crystal syst.	monoclinic	triclinic	monoclinic
a/Å	10.2583(1)	11.3755(6)	11.3035(5)
b/Å	21.351(3)	12.1971(6)	19.5564(9)
c/Å	17.623(2)	16.5256(8)	19.0860(9)
α/deg	90	84.972(1)	90
β/deg	90.998(2)	72.278(1)	106.078(1)
γ/deg	90	70.593(1)	90
V/Å^3	3859.4(9)	2059.76(18)	4054.0(3)
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Z	4	2	4
θ range/deg	2.20 to 23.98	1.29 to 28.33	1.52 to 29.20
μ/mm^{-1}	1.255	1.181	1.199
N	33524	27250	55579
N_{ind}	6025	10195	10961
R_{int}	0.0463	0.0229	0.0381
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0406	0.0261	0.0283
$wR_2{}^b$ ($I > 2\sigma(I)$)	0.1038	0.0640	0.0635
$\Delta\rho_{max}$/e Å^3	1.518	1.077	0.540
$\Delta\rho_{min}$/e Å^3	−0.610	−0.553	−0.483
GoF on R_1	1.063	1.077	1.020

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

(s, $C_6Me_3H_2$), 131.0 (s, $C_6Me_3H_2$), 129.3 (s, $C_6Me_3H_2$), 128.0 (s, $C_6Me_3H_2$), 65.3 (s, CH_2), 46.4 (s, CH_2), 26.9 (s, *o*-CH_3), 24.7 (s, *o*-CH_3), 20.9 (s, *p*-CH_3), 20.7 (s, *p*-CH_3), 0.99 (s, CH_3). IR: 3045 w, 2943 m, 2884 w, 1576 w, 1473 w, 1456 w, 1328 m, 1298 w, 1238 s, 1183 m, 1158 w, 1101 m, 1048 m, 925 m, 867 s, 781 m, 739 m, 730 s, 684 m. Anal. Calcd for $C_{34}H_{62}N_5AsSi_3Zr$: C, 51.61; H, 7.90; N, 8.85. Found: C, 51.74; H, 7.76; N, 8.58.

$(N_3N)Zr[C(AsPh_2)═N^tBu]$ (10). A 2 mL ethereal solution of *tert*-butylisocyanide (13 mg, 0.155 mmol) was added to a 5 mL ethereal solution of **8** (104 mg, 0.153 mmol) cooled to −30 °C. After 3 h stirring at ambient temperature, the yellow solution was filtered through a bed of Celite then cooled to −30 °C. After 5 d, yellow crystals formed and were collected by filtration and dried (89 mg, 0.116 mmol, 76%). ^{1}H (500 MHz): δ 7.56 (d, C_6H_5, 4 H), 7.34 (t, C_6H_5, 4 H), 7.10 (t, C_6H_5, 2 H), 3.31 (t, CH_2, 6 H), 2.43 (t, CH_2, 6 H), 1.16 (s, CH_3, 9 H); 0.42 (s, CH_3, 27 H). ^{13}C{^{1}H} (125.8 MHz): δ 145.2 (s, C═N); 136.1 (s, C_6H_5); 129.9 (s, C_6H_5); 129.8 (s, C_6H_5); 128.5 (s, C_6H_5); 62.64 (s, CH_2); 48.9 (s, CH_2); 33.5 (s, $C(CH_3)_3$), 30.3 (s, CH_3), 3.6 (s, CH_3). IR (Nujol): 2924 w, 2116 w, 1614 s (ν_{CN}), 1583 m, 1461 m, 1377 s, 1089 m, 1018 m, 950 m, 909 w, 837 m, 734 s, 690 m. Anal. Calcd. for $C_{34}H_{60}N_5AsSi_3Zr$: C, 50.36; H, 7.66; N, 9.18. Found: C, 49.98; H, 7.38; N, 8.91.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (MoKα, λ = 0.71073 Å) at set temperature of 125 K. Suitable crystals of each compounds **5**, **6**, and **9** were mounted in a nylon loop under Paratone-N cryoprotectant oil. Direct methods and standard difference map techniques were used for solution structure followed by refinement using full-matrix least-squares procedures on F^2 via SHELXTL (version 6.14).[16] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. The hydrogen atoms on the arsaalkene carbon atom of each **5** and **6**, H(1), were located in the Fourier difference map and refined semifreely using a distance restraint. Crystallographic data for compounds **5**, **6**, and **9** can be found in Table 3.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for complexes **5**, **6**, and **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation (NSF, CHE-0747612 to R.W.). The NSF also provided X-ray crystallographic (CHE-0521237 to J.M.T. and CHE-1039436 to R.W.) and NMR (CHE-1126265) facilities.

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