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Alternative Reaction Pathways in Domino Reactions of Hydrazinediidozirconium Complexes with Alkynes

Thorsten Gehrmann, Solveig A. Scholl, Julio Lloret Fillol, Hubert Wadepohl, and Lutz H. Gade*[a]

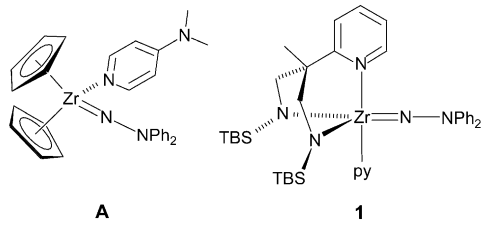
Dedicated to Professor Walter Siebert on the occasion of his 75th birthday

Abstract: Reaction of $[Zr\{(NAr)_2N_{py}\}(NMe_2)_2]$ (Ar = 3,5-xylyl: **2a**, mesityl: **2b**) with one or two molar equivalents of 1,1-diphenylhydrazine gave the mixed amido/hydrazido(1−) complex $[Zr\{(NMes)_2N_{py}\}(HNNPh_2)(NMe_2)]$ (**3**), the bis-hydrazido complex $[Zr\{(NMes)_2N_{py}\}(HNNPh_2)_2]$ (**4**), and, in the presence of excess 4-dimethylaminopyridine (DMAP), hexacoordinate hydrazinediidozirconium complexes $[Zr\{(NXyl)_2N_{py}\}(=NN(Me)Ph)(dmap)_2]$ (**5**) and $[Zr\{(NXyl)_2N_{py}\}(=NNPh_2)(dmap)_2]$ (**6**). The reaction of one equivalent of the zirconium–hydrazinediide $[Zr\{(NTBS)_2N_{py}\}(NNPh_2)(py)]$ (**1**) with disubstituted alkynes at RT for 16 h led to the formation of seven-membered diazazirconacycles **7a**–**7e** in high yields. Similar reactivity was observed by reacting bis-amido complex **2b** with one molar equivalent of the corresponding alkyne and diphenylhydrazine. The formation of the seven-membered zirconacycles implied a key coupling step that involved the alkyne and one of the aryl rings of the diphenylhydrazinediido ligand. In some cases, such as the reaction with 2-butyne, the corresponding metallacycle was only obtained in modest yields (45% for the reaction with 2-butyne) and a second major product, vinylimido complex **9**, was formed in almost equal amounts (42%) by 1,2-amination (formal insertion of the alkyne). The formation of compounds **7a** and **9** followed in part the same sequence of reaction steps and a key intermediate, an azirinido complex, represented a "bifurcation point" in the reaction network. Reaction of 1.2 equivalents of several diarylhydrazines and various substituted alkynes (1 equiv) at ambient temperature (or at 80 °C) in the presence of 10 mol% $[Zr\{(NXyl)_2N_{py}\}(NMe_2)_2]$ (**2a**) gave the corresponding indole derivatives. On the other hand, the replacement of 1,1-diarylhydrazines by 1-methyl-1-phenyl hydrazine led to head-to-head *cis*-1,3-enynes in good yields.

Keywords: alkynes · C–N coupling · domino reactions · indoles · zirconium

Introduction

Transformations of the M=N–NR_2 unit in Group 4 metal–hydrazinediides[1] typically constitute the addition of unsaturated molecules to the highly polar M=N bond and the facile fragmentation of the N–N bond. Both processes may occur sequentially or almost concomitantly and may lead to the combined formation and scission of several chemical bonds in one process, including stoichiometric transformations that involve formal insertions into the N–N bond, as reported by Mountford and co-workers,[2] as well as the titanium catalyzed syntheses of N-heterocycles, as developed by the groups of Odom, Beller, and others.[3–5] The latter syntheses generally involve the catalytic hydrohydrazination of an alkyne and the subsequent transformations of the resulting hydrazones, which may either occur by direct coupling with other unsaturated organic substrates[3] or by a Fischer-type conversion into indoles.[5] Such complex cascades of reaction steps are frequently referred to as "domino reactions" and may provide the key to assembling complex molecules.[6,7] There are relatively few examples of the use of early-transition-metal catalysis, in particular by Group 4 metals, in such transformations. However, the development of synthetic routes to N-heterocycles,[8] as referred to above, merits further research efforts.



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The potential of the M=N–NR_2 unit to undergo combined N–N-bond cleavage and N–C coupling was first demonstrated by Bergman and co-workers in 1991 for $[Cp_2Zr(N_2Ph_2)(dmap)]$ (**A**; DMAP = 4-dimethylaminopyridine).[9] Whilst there is a rapidly growing body of work on the reactivity of

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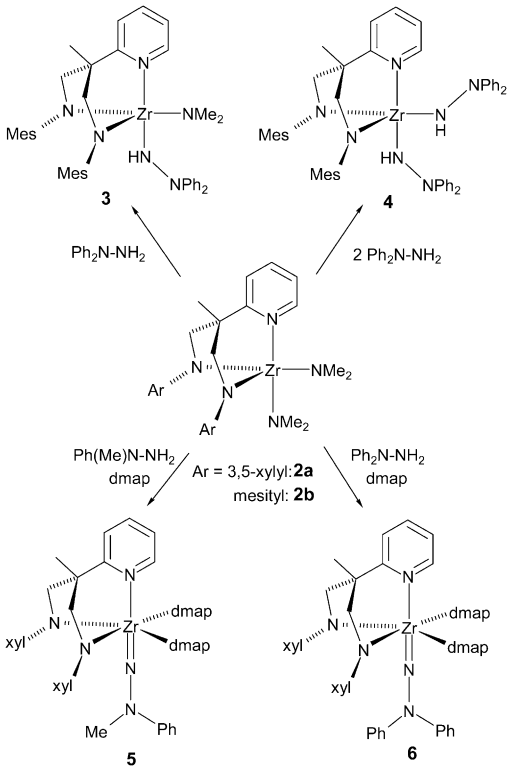
titanium–hydrazides, recent investigations into the chemistry of their heavier Group 4 analogues have primarily focused on the hydrazinediidozirconium complex [Zr{(NTBS)$_2$N$_{py}$}-(NNPh$_2$)(py)] (**1**).[10] This complex has displayed similar stoichiometric and catalytic reactivity towards unsaturated substrates as found for titanium complexes. However, its reactivity towards alkynes appears to be characterized by the absence of a hydrohydrazination step in favor of N–N-bond cleavage before the formation of a hydrazone.[11]

We have recently reported a reaction sequence that offers a route to indoles via a Zr-catalyzed non-Fischer-type pathway.[11] Closer inspection of this sequence revealed the competition of more than one reaction pathway and that subtle structural aspects of the reagent and substrate appeared to determine its outcome. Herein, we provide a detailed account of this class of domino reactions within the coordination sphere of zirconium.

Results and Discussion

Synthesis and structural characterization of hydrazido(1−)-zirconium and hydrazinediido(2−)zirconium complexes: Hydrazinediido analogues of compound **1** were difficult to access from their dichlorozirconium precursors upon replacement of the silylamido units on the tripodal ancillary ligand by the chemically more-robust arylamides. These latter groups were thought to be particularly suitable for the development of catalytic reactions. We used [Zr{(NAr)$_2$N$_{py}$}-(NMe$_2$)$_2$] as the starting material, with 3,5-xylyl (**2a**) and mesityl substituents (**2b**)[12] at the amido N moieties of the supporting ligand (Scheme 1). The reaction of complex **2b** with one or two molar equivalents of 1,1-diphenylhydrazine gave the mixed amido/hydrazido(1−) complex [Zr{(NMes)$_2$N$_{py}$}(HNNPh$_2$)(NMe$_2$)] (**3**) and the bis-hydrazido complex [Zr{(NMes)$_2$N$_{py}$}(HNNPh$_2$)$_2$] (**4**), respectively. For both complexes, thermally induced conversion into their corresponding hydrazinediido compounds was incomplete, even in the presence of additional donors, such as pyridine or DMAP. However, the reaction of the less-sterically shielded *N*-3,5-xylyl-substituted bis-amido complex **2a** with one molar equivalent of diphenyl- or phenylmethylhydrazine in the presence of an excess of DMAP gave the hexacoordinate hydrazinediidozirconium complexes [Zr{(NXyl)$_2$N$_{py}$}(=NN(Me)Ph)(dmap)$_2$] (**5**) and [Zr{(NXyl)$_2$N$_{py}$}(=NNPh$_2$)-(dmap)$_2$] (**6**) in good yields (Scheme 1). Whereas analogues syntheses have been reported in titanium hydrazinediide chemistry,[1d,f] this approach is unprecedented for zirconium.

The detailed structures of complexes **3**, **5**, and **6** were established by X-ray diffraction. The molecular structures of complexes **3** and **6** are shown in Figure 1 (for complex **5**, see the Supporting Information). The coordination geometry of complex **3** is best described as distorted trigonal bipyramidal, with the amido groups of the facial-coordinating tripodal ligand occupying two equatorial positions. The pyridyl fragment of the ligand and the monoanionic hydrazide are coordinated in axial sites. The Zr-N(4)-N(5) angle of



Scheme 1. Synthesis of hydrazido(1−)zirconium complexes **3** and **4**, and hydrazinediido complexes **5** and **6**, starting from the bis-dimethylamido complexes **2a** and **2b**.

131.4(2)° is comparable to that in the monohydrazido complex [Zr{(NTBS)$_2$N$_{py}$}(HNNPh$_2$)Cl] (130.7(4)°) reported previously by our group.[13]

Hydrazinediido complexes **5** and **6** adopted distorted octahedral coordination geometries. In both complexes, the hydrazinediido ligand was in a position *trans* to the pyridyl fragment of the tridentate ligand. In contrast to the hydrazido ligand in compound **3**, the hydrazinediido ligands adopted an essentially linear coordination geometry (Zr-N(4)-N(5) about 176°). A similar arrangement has been reported for a hexacoordinate titanium–hydrazinediido complex by Mountford and co-workers.[14]

As expected for the formally dianionic hydrazinediido ligand, the Zr–N bond was appreciably shorter (about 1.88 Å) than that in hydrazido complex **3** (2.13 Å). The N(4)–N(5) bond lengths (N(4)–N(5) **5**: 1.370(2), **6**: 1.377(4)), as well as the Zr-N(4)-N(5) angles in compounds **5** and **6** (**5**: 175.6(1), **6**: 176.3(2)°), were in good agreement with those reported for other zirconium–hydrazinediides by Bergman and co-workers[9] and ourselves.[10]

Synthesis and structural characterization of diazazirconaheptenyl complexes. One possible reaction pathway of complexes 1 and 2 with alkynes: Reaction of one equivalent of the zirconium–hydrazinediide [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (**1**) with disubstituted alkynes at room temperature for 16 h led to the formation of seven-membered diazazirconacycles **7a–7e** in high yields (Scheme 2). Similar reactivity was ob-

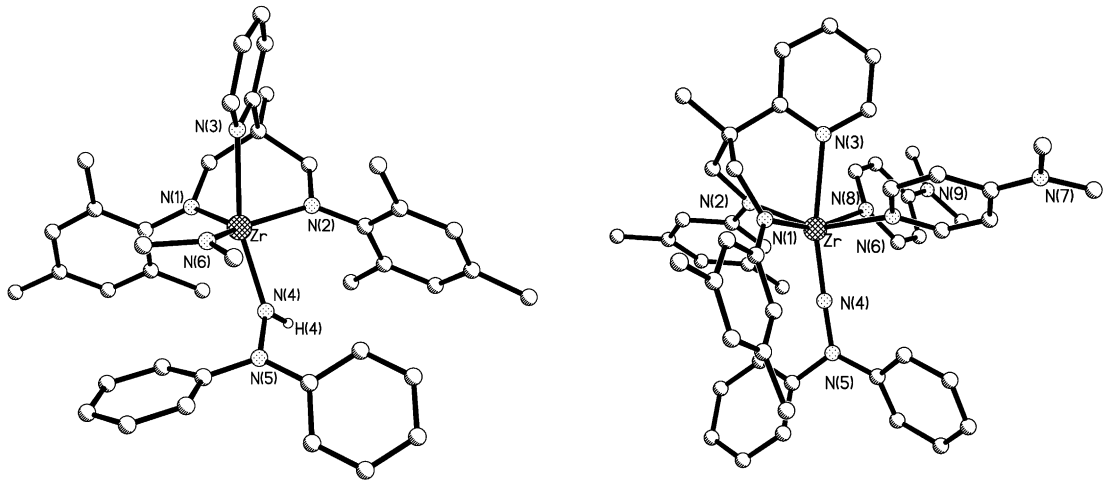
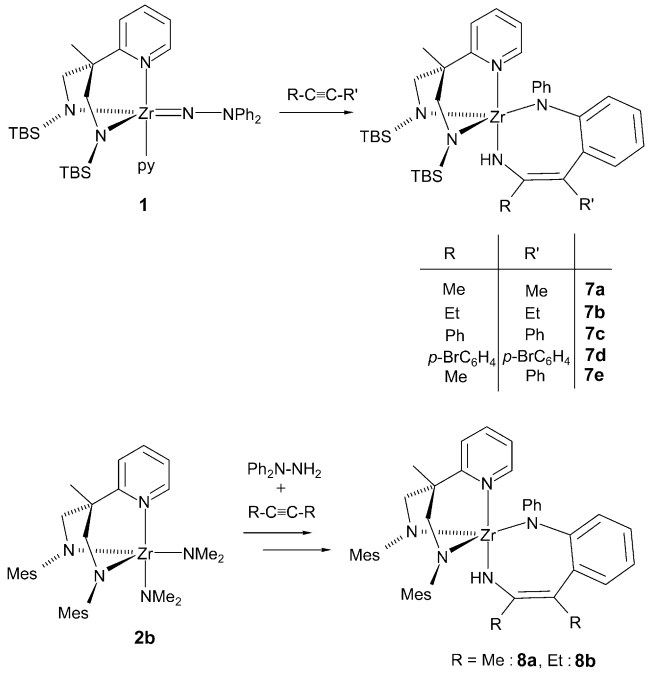


Figure 1. Molecular structures of complexes **3** and **6**. Selected bond lengths [Å] and angles [°] for compound **3**: Zr–N(1)/N(2) 2.051(3)/2.075(3), Zr–N(3) 2.377(3), Zr–N(4) 2.125(3), Zr–N(6) 2.058(3), N(4)–N(5) 1.416(3); N(3)-Zr-N(4) 160.98(9), N(4)-Zr-N(6) 88.37(11), Zr-N(4)-N(5) 131.4(2). Selected bond lengths [Å] and angles [°] for compound **6**: Zr–N(1)/N(2) 2.204(3)/2.194(3), Zr–N(3) 2.444(3), Zr–N(4) 1.885(3), Zr–N(6) 2.410(3), N(4)–N(5) 1.377(4); N(3)-Zr-N(4) 168.0(1), N(4)-Zr-N(6) 95.3(1), Zr-N(4)-N(5) 176.3(2). Selected hydrogen atoms are omitted for clarity.



Scheme 2. Synthesis of diazazirconacycloheptenes **7a**–**7e** and **8a** and **8b**.

served by reacting bis-amido complex **2b** with one molar equivalent of the corresponding alkyne and diphenylhydrazine respectively. In contrast to the *N*-mesityl-substituted complex (**2b**), its 3,5-xylyl-substituted analogue (**2a**) did not form isolable diazazirconaheptenyl complexes, possibly as a result of the less-efficient steric protection of the metallacycle by the ancillary diamido-donor ligand. This property does not rule out its formation, though, as was evident from the reactive behavior of complex **2a** in the catalytic reactions discussed below.

The analytical data and the ^{1}H, ^{13}C, and ^{15}N NMR spectra of compounds **7a**–**7e** and **8a** and **8b** were in agreement with the molecular structures (Scheme 2). In addition to the symmetric alkynes (R−C≡C−R; R = Me, Et, Ph, *p*-BrC_6H_4), the unsymmetrically substituted 1-phenyl-1-propyne was tested, which gave rise to two regioisomers (combined yield: 85%) in a ratio of 65:35 (HNC(Me)/HNC(Ph), by ^{1}H NMR spectroscopy).

The molecular structures of compounds **7b, 7c**, **8a**, and **8b** were established by X-ray diffraction (Figure 1; selected bond lengths and angles are listed in Table 1 and Table 2).

Table 1. Selected bond lengths and angles of complexes **7b** and **7c**.

	7b	**7c**
Bond lengths [Å]		
Zr–N(1)/N(2)	2.0732(14)/2.0483(13)	2.062(4)/2.047(3)
Zr–N(3)	2.3898(15)	2.382(3)
Zr–N(4)	2.0983(15)	2.116(3)
Zr–N(5)	2.1304(15)	2.119(3)
C(1)–N(4)	1.393(2)	1.395(4)
C(1)–C(2)	1.359(2)	1.367(4)
Bond angles [°]		
N(3)-Zr-N(4)	171.30(4)	170.7(1)
N(4)-Zr-N(5)	87.40(5)	85.6(1)
N(4)-C(1)-C(2)	123.7(1)	123.5(3)
Zr-N(4)-C(1)	137.0(1)	136.7(2)
Zr-N(4)-C(1)-C(2)	−44.1(2)	45.7(5)

The four molecular structures were very similar and therefore will be discussed together. The coordination geometry of these complexes was typically distorted trigonal bipyramidal. The amido groups of the facially coordinated tripodal auxiliary ligand occupied two equatorial positions, whereas one axial position was ligated by the neutral pyridyl group. In the chelating bis-amido fragment, which resulted from the metal-induced coupling reaction, the bulky diarylamido unit was bonded at the equatorial position, whereas the

Table 2. Selected bond lengths and angles of complexes **8a**, **8b**, and **8c**. The data for the second independent molecule for compounds **8a** and **8c** are given in square brackets.

	8a	8b	8c
Bond lengths [Å]			
Zr–N(1)	2.055(2) [2.054(2)]	2.061(2)	2.054(3) [2.048(3)]
Zr–N(2)	2.052(2) [2.065(2)]	2.067(2)	2.060(2) [2.054(3)]
Zr–N(3)	2.363(2) [2.357(2)]	2.373(2)	2.355(3) [2.355(3)]
Zr–N(4)	2.112(2) [2.106(2)]	2.111(2)	2.106(4) [2.109(3)]
Zr–N(5)	2.113(2) [2.114(2)]	2.111(2)	2.117(3) [2.113(3)]
C(35)–N(4)	1.388(3) [1.394(3)]	1.397(2)	1.393(5) [1.392(5)]
C(35)–C(34)	1.348(3) [1.350(3)]	1.356(3)	1.346(5) [1.344(6)]
Bond angles [°]			
N(3)-Zr-N(4)	167.51 (7) [160.73(7)]	161.81(6)	160.8(1) [166.5(1)]
N(4)-Zr-N(5)	84.22(7) [84.72(7)]	84.77(7)	84.1(1) [84.4(1)]
N(4)-C(35)-C(34)	123.0(2) [122.3(2)]	123.5(2)	122.8(4) [122.7(4)]
Zr-N(4)-C(35)	135.1(2) [135.3(2)]	135.8(1)	136.1(3) [135.3(3)]
Zr-N(4)-C(35)-C(34)	−34.7(3) [−43.9(3)]	−39.6(3)	40.2(6) [−35.8(6)]

comparatively smaller primary amide occupied the more-crowded axial position. The Zr–N(4) and Zr–N(5) bond lengths in the chelating bis-amide were within the typical range for monoanionic nitrogen ligands bonded to a zirconium(IV) center,[15] and were in good agreement with those reported previously by Bergman and co-workers[9] (2.131(3), 2.120(4) Å). The lengths of the carbon–carbon bonds adjacent to N(4) in the seven-membered diazazirconacycles (C(1)–C(2) in compounds **7b** and **7c**, and C(35)–C(34) in compounds **8a** and **8b**, respectively) were consistent with C=C double bonds (Figure 2). Furthermore, the C(1)–N(4) distances for the silylated ligand (**7b**: 1.3925(19); **7c**: 1.395(4)) and the C(35)–N(4) distances for the arylated ligand (**8a**: 1.388(3) [1.394(3)]; **8b**: 1.397(2)) were slightly shortened compared to a single bond, which may be attributed to the partial planarization at the N(4) atom ($\measuredangle_{Zr\text{-}N(4)\text{-}C(1)}$: **7b**: 137.02(10), **7c**: 136.7(2); $\measuredangle_{Zr\text{-}N(4)\text{-}C(35)}$: **8a**: 135.13(15) [135.26(16)], **8b**: 135.80(14)) caused by N–Zr π-donation, and delocalization of the lone pair into the carbon π-system.

The main difference between the four molecular structures was the way in which the non-planar diazazirconacycles were twisted with respect to the ancillary tripod. This difference was reflected in the Zr-N(4)-C(1)-C(2) and Zr-N(4)-C(35)-C(34) torsion angles, respectively, which were negative (thereby corresponding to an anticlockwise rotation around the N(4)–C bonds) in compounds **7b**, **8a**, and **8b**, but positive in compound **7c**.

The non-planar diazazirconacycloheptenyl units were conformationally stable on the NMR time-scale. In all cases, the ^{1}H NMR spectra displayed two individual sets of signals, which corresponded to the CH_2 groups and the TBDMS (compounds **7a**–**7e**) or mesityl N-substituents (in compounds **8a**, **8b**) of the tripodal diamidopyridyl ligand. The corresponding resonance patterns were also detected in the ^{13}C NMR spectra. No dynamic effects (as evidenced by signal broadening) were observed in the NMR spectra, even at elevated temperatures.

The formation of the seven-membered zirconacycles (**7a**–**7e** and **8a** and **8b**) implied the operation of a key coupling step that involved the alkyne and one of the aryl rings of the diphenylhydrazinediido ligand. To gain an insight into the nature of this intramolecular reaction, we investigated the reactivity of diphenylhydrazine derivatives in

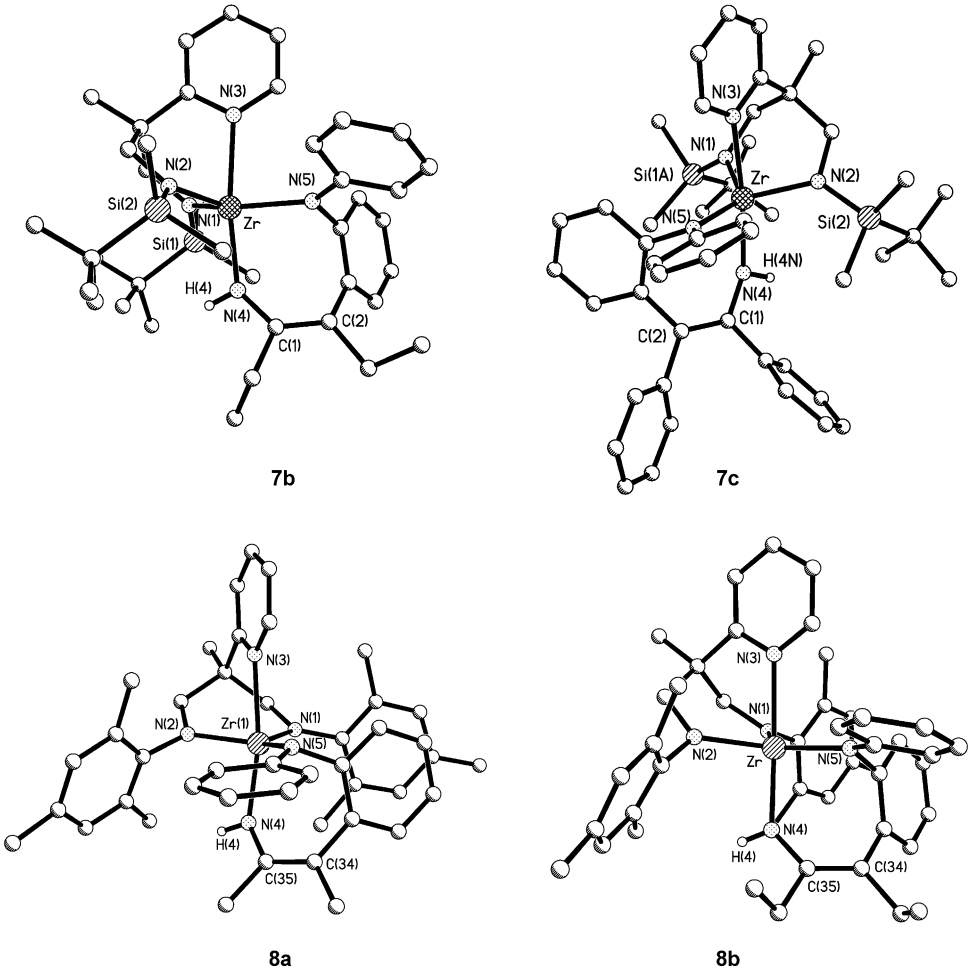
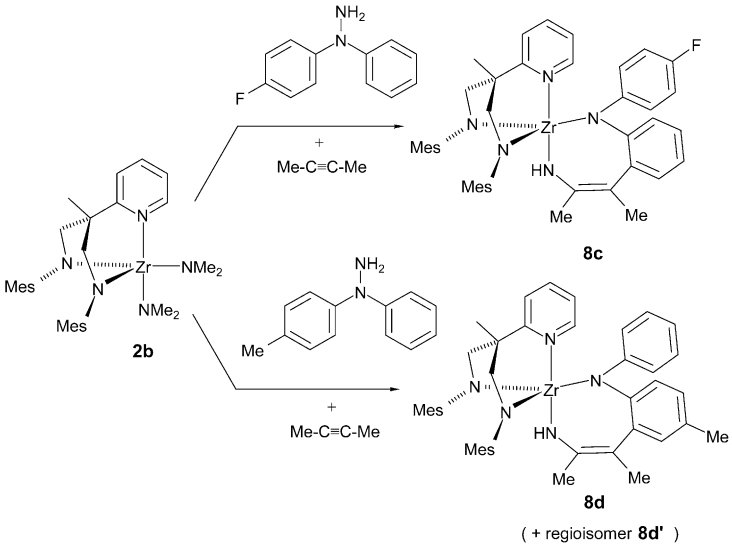


Figure 2. Molecular structures of complexes **7b**, **7c**, **8a**, and **8b** (only one of the two independent molecules of **8a** is shown). H atoms are omitted for clarity (except the N*H* atom). Selected bond lengths and angles are listed in Table 1 and Table 2.



Scheme 3. Synthesis of seven-membered metallacycles **8c** and **8d** by reaction of complex **2b** with butyne and mono-*para*-substituted diphenylhydrazines.

which one of the phenyl rings contained an electron-releasing or -withdrawing substituent. In this context, complex **2b** was reacted with 2-butyne- and 1,1-diphenylhydrazine derivatives, which were *para*-fluoro- or *para*-methyl-substituted on one of the aryl rings (Scheme 3).[16] For the former, only one of the possible metallacyclic products was observed, complex **8c**, which resulted from the coupling of the more-electron-rich unsubstituted aryl ring. Its molecular structure was again established by X-ray diffraction (Figure 3). The measured unit cell contained two stereoisomers that were distinguishable by their torsion angle Zr-N(4)-C(35)-C(34) (+40.2(6)° [−35.8(6)°]).

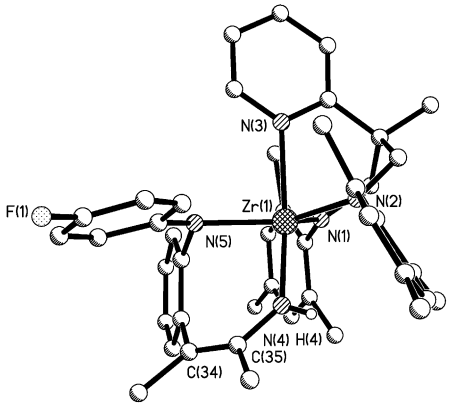
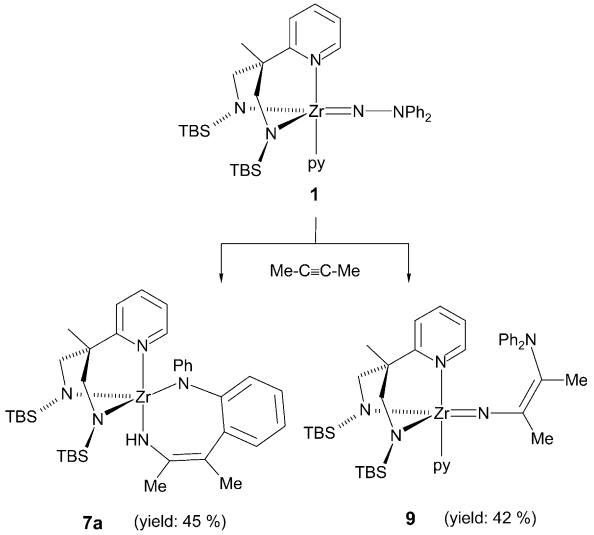


Figure 3. Molecular structure of complex **8c** (only one of the two independent molecules is shown). H atoms are omitted for clarity (except the N*H* atom). Selected bond lengths and angles are listed in Table 2.

A similar reactive pattern was observed in the formation of complex **8d**, in which the major isomer was also formed by attack of the more-electron-rich *p*-methylphenyl ring. In this case, complex **8d** and its regioisomer (**8d'**) were formed in a 5:2 ratio. This general pattern was also confirmed by the catalytic reactions of unsymmetrical diarylhydrazines with alkynes, thereby leading to substituted indoles, which will be discussed in detail below.

Synthesis and structural characterization of a vinylimidozirconium complex: An alternative reaction pathway of complex 1 with an alkyne: Of the reactions of hydrazinediido complex **1** (Scheme 2), the reaction with 2-butyne only gave the corresponding metallacycle (**7a**) in modest yields. In situ ^{1}H NMR studies of the reaction revealed that compound **7a** only accounted for 45% of the converted starting material. A second major product (**9**) was formed in almost equal amounts (42%) along with some unidentified minor components (Scheme 4).



Scheme 4. The two products (**7a** and **9**) formed in almost-equal quantities from the reaction of the hydrazinediidozirconium complex **1** with 2-butyne.

This second major reaction product was the least soluble in hydrocarbon solvents and could be separated as a pure residue after extraction of the product mixture with pentane. The analytical and NMR spectroscopic data of complex **9** were consistent with a vinylimido complex, which would be formed by 1,2-amination (formal insertion of the alkyne), with one coordinated molecule of pyridine. Such a species is analogous to the reaction products reported by Mountford and co-workers in their study of the reactivity of several titanium–hydrazides.[2a,d] To confirm this hypothesis and to establish the structure of compound **9**, single-crystal X-ray analysis was carried out (Figure 4).

The coordination geometry of compound **9** was related to the other molecular structures reported herein. The vinylimido ligand was held in an equatorial position in the distorted trigonal bipyramid, whilst the other coordination sites were occupied by the tripodal spectator ligand and one axially bonded molecule of pyridine. The Zr–N(4) distance (1.911(1) Å) was in the typical range for a zirconium–nitrogen double bond.[17] The C(1)–C(2) bond length of the vinyl

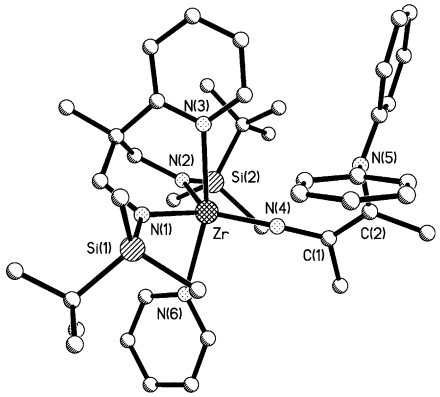


Figure 4. Molecular structure of imido complex **9**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr–N(1) 2.088(1), Zr–N(3) 2.324(1), Zr–N(4) 1.911(1), Zr–N(6) 2.397(1), C(1)–N(4) 1.363(2), C(1)–C(2) 1.360(2); N(3)-Zr-N(4) 98.69(6), N(4)-C(1)-C(2) 126.2(1), Zr-N(4)-C(1) 164.4(1).

substituent (1.360(2) Å) was only insignificantly longer than in the analogous titanium complex reported by Mountford and co-workers (1.352 Å).[2a,d]

As we argue below, the formation of compounds **7a** and **9** follows, in part, the same reaction sequence, and a key intermediate represents a "bifurcation point" in the reaction network. Both reaction pathways have similar selectivity determining activation barriers and the preference of one pathway over the other in a given system is determined by subtle structural aspects. This subtle preference was illustrated by the fact that the reaction of bis-amide **2a**, which contained an N-arylated ancillary tripod ligand, with one molar equivalent of diphenyl hydrazine and 2-butyne quantitatively afforded diazazirconaheptenyl complex **8a**. No vinylimido complex was formed in this reaction.

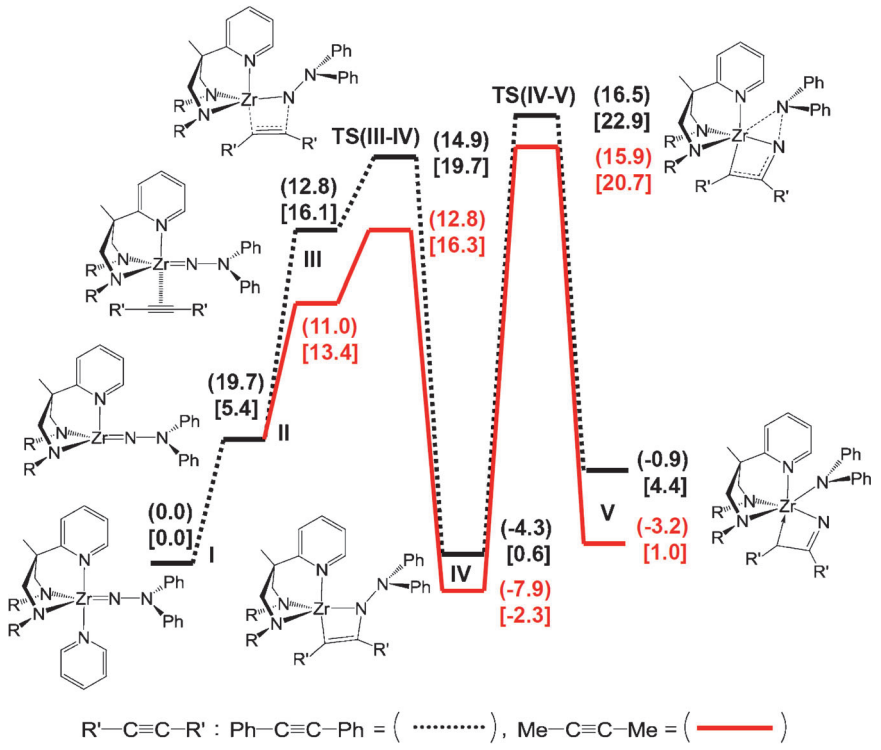
Modeling the reaction profile leading to type-7 metallacycles or type-9 vinylimido complexes: The formation of compounds **7a** and **9** from the same reaction raised the question to what extent these two reaction pathways coincided. A previous mechanistic study had shed some light on the mechanism that led to complexes **7a**–**7e**.[11] That mechanism involved, inter alia, the reaction of the perdeuterated diphenylhydrazinediide, which was also ^{15}N-labeled at the N_α-position, with Et–C≡C–Et to cleanly afford the corresponding metallacycle in which the enamido N atom was fully ^{15}N-labeled and completely deuterated, thus clarifying the origin of the NH group. Crossover experiments and the absence of exchange with solvent hydrogen- or deuterium atoms confirmed the intramolecular nature of this rearrangement. A kinetic study of the reaction of complex **1** with Et–C≡C–Et revealed a pyridine-dissociation pre-equilibrium (the observation of saturation phenomena for high concentrations of alkyne) and a subsequent rate-determining step that was characterized by activation parameters of $\Delta H^{\neq} = 11.5(\pm 0.7)$ kcal mol^{-1} and $\Delta S^{\neq} = -45(\pm 10)$ cal mol^{-1} K^{-1}, and thus a free enthalpy of activation for the rate-determining step of $\Delta G_{275}{}^{\neq} = 24(\pm 2)$ kcal mol^{-1}. The reaction of a derivative of complex **1**, in which one of the two N_β-bonded phenyl rings was perdeuterated with half an equivalent of 3-hexyne gave an NH/ND distribution in the reaction product of 1:1, thereby indicating that $k_H/k_D = 1$ and thus the absence of a kinetic isotope effect. This result implied that neither the C–H-bond cleavage nor the H-atom rearrangement with the formation of the N–H bond, were involved in the rate-determining step.

Based on the experimental evidence, computational modeling of the mechanism of the reaction of zirconium complex **1** with 2-butyne by DFT (B3PW91) revealed a potential reaction pathway. This modeling has now been extended to a comparative study for two alkynes, 2-butyne and diphenylacetylene, to assess the influence that the nature of the acetylene substrate has upon the reaction profile. More importantly, we were interested to find out whether the formation of compounds **7a** and **9** in part followed a similar pathway and whether there was a common key reaction intermediate that represented the point of bifurcation in the reaction sequence.

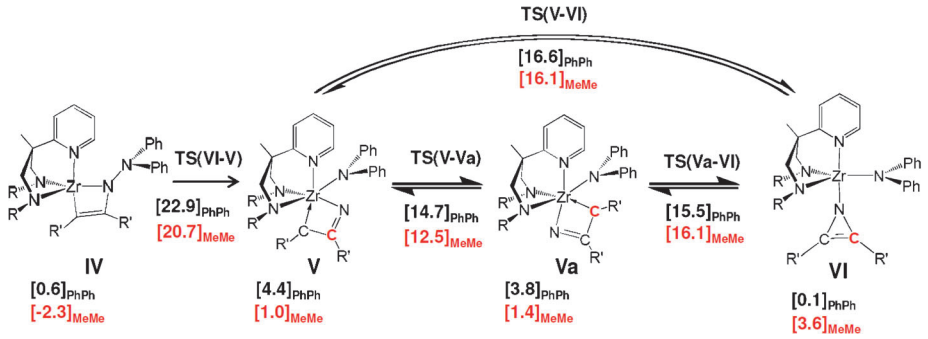
First, the [2+2]-cycloaddition of 2-butyne and diphenylacetylene to the Zr=N bond was modeled (Scheme 5: conversion of **I**→**IV**). This reaction step had previously been studied in detail for titanium–hydrazides by Clot, Mountford, and co-workers.[2d] As for titanium, we found that cycloaddition occurred without prohibitive energetic barriers, thereby giving rise to the metallacyclic intermediates $\mathbf{IV_{MeMe}}$ and $\mathbf{IV_{PhPh}}$.

In a subsequent rate-determining step, the N–N bond was broken and "azaallyl" species **V** was formed; the activation barrier ($\Delta G^{\neq} = 21$ kcal mol^{-1}) for 2-butyne was close to the experimental value ($24(\pm 2)$ kcal mol^{-1}) that was observed for the sterically more-demanding 3-hexyne. From metallacyclic intermediates $\mathbf{V_{MeMe}}$ and $\mathbf{V_{PhPh}}$ no low-activation-barrier pathways to the reaction products were found from a systematic search of the active conformational and configurational space. However, their rearrangement into their constitutional isomers, azirinido complexes $\mathbf{VI_{MeMe}}$ and $\mathbf{VI_{PhPh}}$ (Scheme 6), allowed the subsequent transformations to proceed without prohibitive activation barriers.[17]

The conversion of intermediates $\mathbf{VI_{MeMe}}$ and $\mathbf{VI_{PhPh}}$ was found to be the key branching point in determining the course of the reaction. In this context, the high ring-strain and strongly electrophilic nature of the metalated azirine unit was decisive. Attack upon the neighboring diphenylamido ligand may occur at two points, the *ortho* position of the N-arene ring and the amido nitrogen atom, of which the latter displayed marked nucleophilicity. Intermediates $\mathbf{VI_{MeMe}}$ and $\mathbf{VI_{PhPh}}$ were converted into their corresponding seven-membered metallacyclic complexes, $\mathbf{VIII_{MeMe}}$ and $\mathbf{VIII_{PhPh}}$ (Scheme 7), through nucleophilic attack of a carbon atom in the *ortho* position of a phenyl ring of the NPh_2 fragment at one of the (electrophilic) carbon atoms of the metalated azirine ring to form intermediates $\mathbf{VII_{MeMe}}$ and $\mathbf{VII_{PhPh}}$ ($\Delta G = -20.7$ and -13.5 kcal mol^{-1}, respectively) via the relatively low activation barrier, **TS(VI-VII)** ($\Delta G^{\neq} = 19.8$ and 18.3 kcal mol^{-1}, respectively).



Scheme 5. Reaction profile (DFT, B3PW91) of the cycloaddition of diphenylacetylene and 2-butyne to the hydrazinediido unit in compound **1** (**I**→$\mathbf{IV_{MeMe}}$/$\mathbf{IV_{PhPh}}$) and subsequent (rate-determining) N–N-bond scission to give the diphenylamido (azaallyl) intermediates $\mathbf{V_{MeMe}}$ and $\mathbf{V_{PhPh}}$ (R = TBS). Energies are given in parentheses, free energies in square brackets.



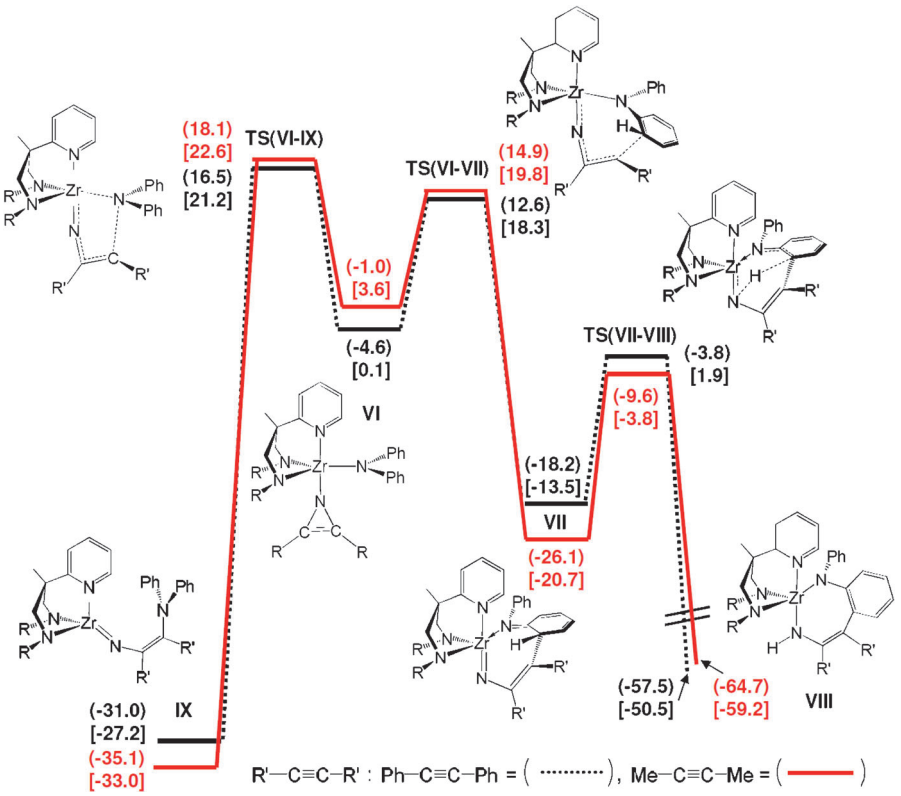
Scheme 6. Reaction profile (DFT, B3PW91) of the transformation of the [2+2] cycloaddition products $\mathbf{IV_{MeMe}}$ and $\mathbf{IV_{PhPh}}$ into the isomeric azaallyl intermediates $\mathbf{V_{MeMe}}$/$\mathbf{V_{PhPh}}$ and $\mathbf{Va_{MeMe}}$/$\mathbf{Va_{PhPh}}$ and into the key azirinido species $\mathbf{VI_{MeMe}}$/$\mathbf{VI_{PhPh}}$ (R = TBS). Energies are given in parentheses, free energies in square brackets.

Alternatively, the vinylimido products (**IX**; Me: $\Delta G = -33.0$ kcal mol^{-1}, Ph: $\Delta G = -27.2$ kcal mol^{-1}) were directly obtained from $\mathbf{VI_{MeMe}}$ and $\mathbf{VI_{PhPh}}$ through the transition state **TS(VI-IX)** via nucleophilic attack of the amido nitrogen on the electrophilic carbon on the metal-bonded azirine. This transition state appeared to be slightly higher in free enthalpy than **TS(VI-VII)**; however, given the accuracy of the computational method,[19] these differences may not be significant. Thus, both pathways appeared to be feasible and the selection of one over the other was expected to be governed by subtle structural variations in the substrates, which was consistent with the experimentally observed behavior, as discussed above. Notably, transition states **TS(VI-IX)** and **TS(VI-VII)** should be viewed as very early owing to the high electrophilicity of the attacking carbon of the azirine ring.

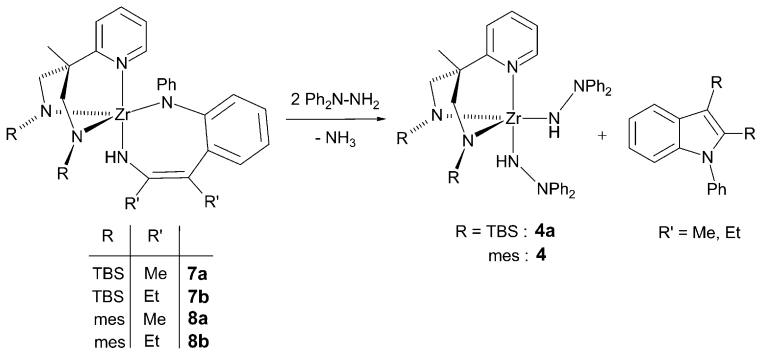
En route to a catalytic formation of substituted indoles: As mentioned above, Bergman and co-workers showed that their diazazirconacycles could be hydrolyzed with 5% HCl to yield *N*-phenylindoles.[9] Because hydrazides and amides have similar pK_a values,[20] and hydrazine has been shown to replace amido ligands (a method also employed in this work), we tried to protonate the zirconacycles by reacting them in toluene with a slight excess of diphenyl hydrazine.

The reaction of compounds **7a** and **7b** and **8a** and **8b** with two molar equivalents of diphenylhydrazine gave their corresponding bis-hydrazido(1−) complexes **4a** and **4**, along with one equivalent of 1-phenyl-2,3-dimethylindole and 1-phenyl-2,3-diethylindole (Scheme 8). On following the conversion of compound **8a** by ^{1}H NMR spectroscopy, only the disappearance of the signals that were attributed to the starting materials and the growth of those assigned to complex **4** and 1-phenyl-2,3-dimethylindole were observed, along with some non-specific degradation. No intermediate species were detected and the kinetics at low conversion was first order in both compound **8a** and the hydrazine. This result implied that the rate-determining step was the initial attack of the hydrazine onto the metallacycle and that the subsequent transformations that led to compound **4** and the indole were rapid. This situation was related to the non-observation of the primary products of the aminolysis of the metallacyclic intermediate of the catalytic mechanism postulated for the Group-4-metal-catalyzed hydroamination of alkynes.[21,22]

Because bis-hydrazido complexes such as compounds **4a** and **4** may be precursors in the formation of hydrazinediido compounds,[13] the reaction sequence leading to the indoles was thought to be part of a catalytic cycle for the direct gen-



Scheme 7. Competitive reaction profiles (DFT, B3PW91) of the transformation the 2,3-azirinido species $\mathbf{VI}_{\mathbf{MeMe}}$ and $\mathbf{VI}_{\mathbf{PhPh}}$ into metallacycles $\mathbf{VIII}_{\mathbf{MeMe}}$ and $\mathbf{VIII}_{\mathbf{PhPh}}$ as well as into the vinylimido species $\mathbf{IX}_{\mathbf{MeMe}}$ and $\mathbf{IX}_{\mathbf{PhPh}}$ (R = TBS). Energies are given in parentheses, free energies in square brackets.



R	R'	
TBS	Me	**7a**
TBS	Et	**7b**
mes	Me	**8a**
mes	Et	**8b**

Scheme 8. Hydrazinolysis of the metallacyclic compounds **7a** and **7b** and **8a** and **8b** with diphenylhydrazine to give bis-hydrazido complexes **4a**/**4** and the corresponding indoles.

eration of substituted indoles from alkynes and hydrazines via metallacyclic intermediates, such as compounds **7a** and **7b** and **8a** and **8b**; that is, without involving hydrazones and subsequent Fischer-type transformations.[5] The reaction of alkynes and 1,1-disubstituted hydrazines in the presence of compounds **2a** or **2b**, even at elevated temperatures, did not lead to the formation of hydrazones, even in trace quantities. Therefore, the zirconium–bis(dimethylamides) were not catalyst precursors for the potential hydrohydrazination of alkynes, but rather gave the isolated indoles through a different mechanistic pathway, as discussed above.

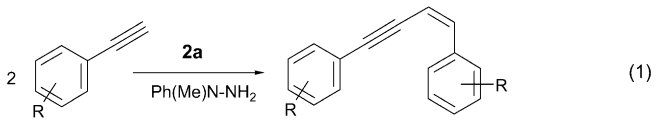
The reaction of 1.2 equivalents of several diarylhydrazines and various substituted alkynes (1 equiv) at ambient temperature (or at 80 °C) in the presence of 10 mol % [Zr-{$(NXyl)_2N_{py}$}$(NMe_2)_2$] (**2a**) gave their corresponding indole derivatives. For unsymmetrical internal alkynes, the indole with the bulkier substituent at the 3-position was the major product (Table 3, Ind2 and Ind5), whereas terminal alkynes exclusively gave the indole substituted at the 3-position (Table 3, Ind4, Ind6, Ind8, and Ind9). We also noted that in the reactions with unsymmetrical diarylhydrazines, the more-electron-rich aryl ring was preferentially incorporated into the indole unit (Table 4, Ind10 and Ind12). This result was consistent with the stoichiometric reactivity shown in Scheme 3 and with attack of the postulated azirinido fragment on the N-aryl ring in intermediate **VI** (Scheme 7) as the reaction of an electrophile with the "nucleophilic" aromatic ring.

The molecular structure of Ind12, which showed the expected substitution pattern that resulted from electrophilic attack at the more-electron-rich *para*-methoxy-substituted phenyl ring, was established by X-ray diffraction (Figure 5).

Based on the combined experimental and computational evidence presented above, we propose the mechanistic cycle shown in Scheme 9 for the catalytic formation of the N-substituted indoles from 1,2-diarylhydrazines and alkynes. The key intermediate, hydrazinediido complex **A**, is formed by dissociation of the axial pyridine ligand in a pre-equilibrium, as we observed experimentally.

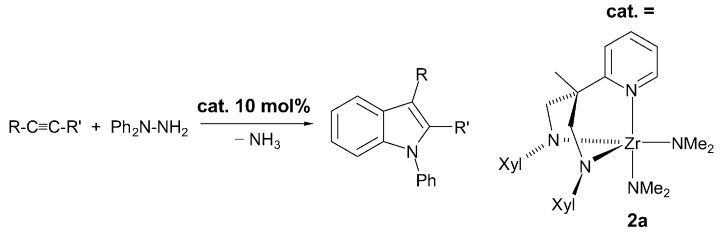
To our surprise, the replacement of 1,1-diarylhydrazines by 1-methyl-1-phenylhydrazine changed the reactivity towards alkynes dramatically: whilst reactions with disubstituted alkynes gave *N*-methyl indoles in poor yields, the attempted conversion with terminal alkynes did not yield any indole product at all. Instead, head-to-head *cis*-1,3-enynes were formed selectively and in good yields, provided that

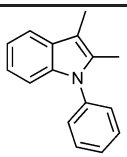
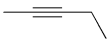
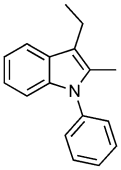
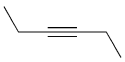
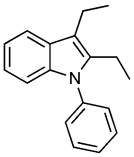
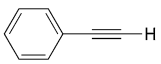
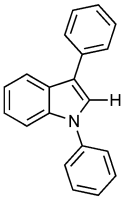
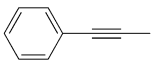
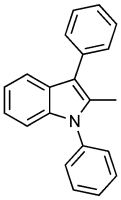
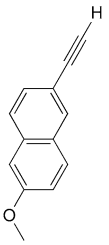
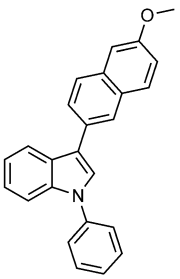
the terminal alkyne carried an aromatic substituent [Eq. (1)] (see the Supporting Information).



(1)

Table 3. Catalytic indole syntheses of diphenylhydrazine with various alkynes.



Entry	Alkyne	Indole	Ratio of regioisomers[a]	*t* [h]	*T* [°C]	Yield [%]
Ind1			–	24	RT	84
Ind2			2:1	24	RT	59
Ind3			–	24	RT	36
Ind4			>9:1[b]	24	RT	74
Ind5			2:1[b]	24	RT	56
Ind6			>9:1[b]	24	RT	56

At this stage, we are not able to suggest a mechanism for coupling reactions at zirconium, but it is presumably very similar to the reaction pathways proposed by Takaki and coworkers[23] for yttrium- and lanthanide catalysts.[24] In that work, amines were employed as co-catalysts, and, in our case, the hydrazine also seems to play the role of a catalytic proton-transfer reagent, albeit with greater activity and selectivity.

Conclusion

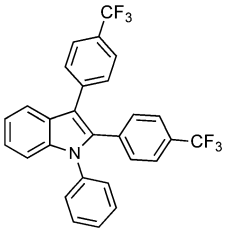
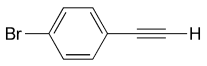
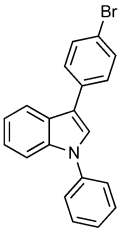
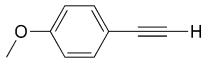
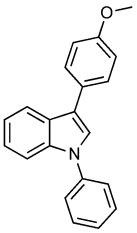
The outcome of stoichiometric and catalytic transformations that involve a cascade of reaction steps crucially depends on the activation barriers associated with each of their elementary transformations. It is assumed that several alternative reaction pathways are often kinetically accessible from a given intermediate. Such points of bifurcation in the resulting reaction network are governed by small increments in the free enthalpies of activation and thus subtle structural variations of the substrate. In favorable cases, such as the catalytic multistep synthesis of indoles presented herein, a deeper understanding of the mechanism may offer insight into the factors that determine the selectivity of a given transformation.

Experimental Section

All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon by using standard Schlenk techniques or by working in a glove box. Solvents were dried over sodium (toluene, methyl cyclohexane), potassium (hexanes) or sodium/potassium alloy (pentane, Et_2O), distilled, and degassed prior to use. Deuterated solvents were dried over potassium (C_6D_6, [D_8]toluene, [D_8]THF), vacuum distilled, and stored in ampoules with Teflon valves under an argon atmosphere. Samples for NMR spectroscopy were prepared under an argon atmosphere in 5 mm Wilmad tubes equipped with J. Young Teflon valves. ^{1}H, ^{13}C, ^{29}Si, ^{19}F and ^{15}N NMR spectra were recorded on Bruker Avance 200, 400, and 600 NMR spectrometers and were referenced internally, by using the residual protiosolvent (^{1}H) or solvent (^{13}C) resonances, or externally, to $CFCl_3$ or $^{15}NH_3$. Elemental analysis was recorded by the analytical service at the Heidelberg Chemistry Department. The hydrazinediido complex [Zr{$(NTBS)_2N_{py}$}$(NNPh_2)$(py)] (**1**) and the bis-amido complex [Zr{$(NMes)_2N_{py}$}$(NMe_2)_2$] (**2b**) were prepared according to literature procedures.[10,12] Substituted diphenyl hydrazines, [D_{10}]$^{15}N_{\alpha}$-1,1-diphenylhydrazine and [D_5]1,1-diphenylhydrazine were prepared according to literature procedures for the parent compound.[16] All other reagents were obtained from commercial sources and used as received unless otherwise stated.

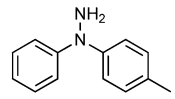
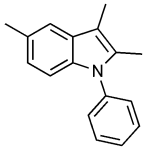
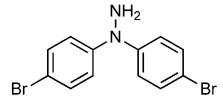
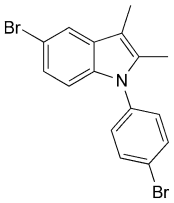
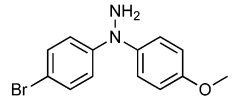
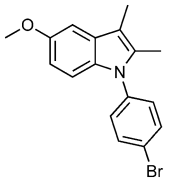
Preparation of [Zr{$(NMes)_2N_{py}$}$(NHNPh_2)(NMe_2)$] (3): [Zr{$(NMes)_2N_{py}$}$(NMe_2)_2$] (0.50 g, 0.86 mmol) and 1,1-diphenylhyadrazine (0.16 g, 0.86 mmol) were dissolved in toluene (30 mL). After stirring the reaction mixture at RT

Table 3. (Continued)

Entry	Alkyne	Indole	Ratio of regioisomers[a]	t [h]	T [°C]	Yield [%]
Ind7			–	24	RT	11
Ind8			>9:1[b]	24	80	70
Ind9			5:1[b]	24	80	44

[a] Determined by ^{1}H NMR spectroscopy. [b] Major isomer shown.

Table 4. Catalytic indole synthesis of various diarylhydrazines with 2-butyne.

Entry	Hydrazine	Indole	Ratio of regioisomers[a]	t [h]	T [°C]	Yield [%]
Ind10			3:2[b]	24	80	43
Ind11			–	24	80	52
Ind12			>9:1[b]	24	RT	15

[a] Determined by ^{1}H NMR spectroscopy. [b] Major isomer shown.

for 1 day, the solution was filtrated and the volatile compounds were removed under reduced pressure to yield [Zr{(NMes)$_2$N$_{py}$}(NHNPh$_2$)(NMe$_2$)] as a yellow solid. Yield 0.38 g (0.53 mmol, 62%); ^{1}H NMR (600 MHz, C_6D_6, 296 K): δ = 1.01 (s, 3H; CH_3), 1.71 (s, 6H; $C_6H_2Me_3$), 2.29 (s, 6H; $C_6H_2Me_3$), 2.57 (s, 6H; N(CH_3)$_2$), 2.61 (s, 6H; $C_6H_2Me_3$), 2.79 (d, ^2J(H,H) = 12.20 Hz, 2H; CHH), 3.90 (d, ^2J(H,H) = 12.20 Hz, 2H; CHH), 6.08 (s, 1H; NH), 6.53 (ddd, ^3J(H(5)$_{py}$,H(4)$_{py}$) = 6.5 Hz, ^3J(H(5)$_{py}$,H(6)$_{py}$) = 6.5 Hz, ^4J(H(5)$_{py}$,H(3)$_{py}$) = 1.0 Hz, 1H; H(5)$_{py}$), 6.70 (t, ^3J(H$_p$,H$_o$) = 6.5 Hz, 2H; H_p), 6.82 (d, ^3J(H(3)$_{py}$,H(4)$_{py}$) = 8.1 Hz, 1H; H(3)$_{py}$), 6.90 (s, 2H; $C_6H_2Me_3$), 6.97 (t, ^3J(H$_m$,H$_o$) = 6.5 Hz, ^3J(H$_m$,H$_p$) = 6.5 Hz, 4H; H_m), 7.02 (dt, ^3J(H(4)$_{py}$,H(3)$_{py}$) = 7.9 Hz, ^3J(H(4)$_{py}$,H(5)$_{py}$) = 7.9 Hz, ^4J(H(4)$_{py}$,H(6)$_{py}$) = 1.8 Hz, 1H; H(4)$_{py}$), 7.04 (s, 2H; $C_6H_2Me_3$), 8.20 ppm (dd, ^3J(H(6)$_{py}$,H(5)$_{py}$) = 5.3 Hz, ^4J(H(6)$_{py}$,H(4)$_{py}$) = 1.2 Hz, 1H; H(6)$_{py}$); ^{13}C {^{1}H} NMR (C_6D_6, 150 MHz, 296 K): δ = 18.0 (q, C_6H_2(CH_3)$_3$), 18.4 (q, C_6H_2(CH_3)$_3$), 20.9 (q, C_6H_2(CH_3)$_3$), 24.5 (q, CH_3), 39.7 (q, N(CH_3)$_2$), 46.3 (s, CCH$_3$), 66.6 (t, CH_2), 117.9 (d, C_o), 118.7 (d, C_p), 120.2 (d, C(3)$_{py}$), 122.0 (d, C(5)$_{py}$), 128.5 (d, C_m), 129.4 (d, m-$C_6H_2Me_3$), 130.0 (d, C(4)$_{py}$), 133.1, 134.3 (d, o,p-$C_6H_2Me_3$), 147.4 (d, C(6)$_{py}$), 147.9 (s, N$C_6H_2Me_3$), 149.8 (s, NC_6H_5), 162.8 ppm (s, C(2)$_{py}$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): δ = 165.6 (NMe$_2$), 177.5 ($NC_6H_2Me_3$), 189.0 (N_αH), 289.0 ppm (L-N_{py}); IR (Nujol, NaCl): $\tilde{\nu}$ = 3263 (w), 3057 (w), 2924 (s), 2854 (s), 2761 (w), 1577 (m), 1465 (s), 1376 (m), 1301(m), 1224 (m), 1094 (w), 1024 (w), 935 (m), 851 (w), 800 (w), 743 (m), 691 cm^{-1} (w); elemental analysis calcd (%) for $C_{41}H_{50}N_6Zr$: C 68.58, H 7.02, N 11.70; found: C 68.60, H 7.04, N 11.86.

Preparation of [Zr{(NTBS)$_2$N$_{py}$}(HNNPh$_2$)$_2$] (4a): The formation of compound **4a** in the reaction of the metallacycles with diphenylhydrazine was confirmed by comparison of the spectra to an authentic sample, which was prepared as follows: To a stirring solution of [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (200 mg, 0.27 mmol) in toluene (20 mL) was added a solution of diphenylhydrazine (49.6 mg, 0.27 mmol) in toluene (5 mL). The mixture was stirred overnight at RT, filtered, and the volatile compounds were removed under reduced pressure. [Zr{(NTBS)$_2$N$_{py}$}(HNNPh$_2$)$_2$] was obtained in quantitative yield as a yellow solid. ^{1}H NMR (600 MHz, C_6D_6, 296 K): δ = −0.04, 0.13 (s, 6H; Si(CH_3)$_2$), 0.63 (s, 18H; SiC(CH_3)$_3$), 1.04 (s, 3H; CH_3), 3.37 (d, ^2J(H,H) = 12.5 Hz, 2H; CHH), 3.91 (d, ^2J(H,H) = 12.5 Hz, 2H; CHH), 5.94 (brs, 1H; NH), 6.08 (brs, 1H; NH), 6.50 (ddd, ^3J(H(5)$_{py}$,H(4)$_{py}$) = 7.7 Hz, ^3J(H(5)$_{py}$,H(6)$_{py}$) = 5.6 Hz, ^4J(H(5)$_{py}$,H(3)$_{py}$) = 0.9 Hz, 1H; H(5)$_{py}$), 6.82–6.87 (m, 3H; H(3)$_{py}$, p-H_{PhA}), 6.90 (t, J(p-H$_{ph}$,m-H$_{ph}$), 2H; p-H_{PhB}), 7.00 (dt, ^3J(H(4)$_{py}$,H(3)/H(5)$_{py}$) = 7.8 Hz, ^4J(H(4)$_{py}$,H(6)$_{py}$) = 1.5 Hz, 1H; H(4)$_{py}$), 7.17–7.23 (m, 8H; m-H_{PhA}, m-H_{PhB}), 7.31 (d, ^3J(o-H$_{ph}$,m-H$_{ph}$) = 8.6 Hz, 4H; o-H_{PhB}), 7.50 (d, ^3J(o-H$_{ph}$,m-H$_{ph}$) = 8.5 Hz, 4H; o-H_{PhA}), 9.15 ppm (dd, ^3J(H(6)$_{py}$,H(5)$_{py}$) = 5.5 Hz, ^4J(H(6)$_{py}$,H(4)$_{py}$) = 0.9 Hz, H(6)$_{py}$), ^{13}C {^{1}H} NMR (150 MHz, C_6D_6, 296 K): δ = −4.2, −4.0 (Si(CH_3)$_2$), 20.4 (SiC(CH$_3$)$_3$), 24.7 (CCH$_3$), 27.7 (SiC(CH_3)$_3$), 47.8 (CCH$_3$), 63.6 (CH_2), 120.5 (o-C_{PhA}), 121.1 (p-C_{PhA}, C(3)$_{py}$), 121.3 (C(5)$_{py}$), 121.6 (o-C_{PhB}), 122.3 (p-C_{PhB}), 128.9 (m-C_{PhA}), 129.0 (m-C_{PhB}), 138.3 (C(4)$_{py}$), 147.2 (C(6)$_{py}$), 151.1 (i-C_{PhA}), 152.3 (i-C_{PhB}), 161.6 ppm (C(2)$_{py}$); ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 296 K): δ = 3.11 ppm (Si(CH$_3$)$_2$$t$Bu); ^{15}N NMR (60 MHz, C_6D_6, 296 K): δ = 112.6 (NPh$_{2B}$), 115.3 (NPh$_{2A}$), 174.9 (NSi(CH$_3$)$_2$$t$Bu), 192.7 ($N$H), 194.6 ($N$H), 291.6 (L$N_{py}$); IR (Nujol, NaCl): $\tilde{\nu}$ = 3242 (w), 3189 (w), 1931 (w), 1587 (s), 1466 (s), 1377 (m), 1310 (w), 1254 (m), 1168 (w), 1087 (sh), 1050 (s), 864 (s), 829 (s), 769 (m), 748 (s), 693 (m), 666 cm^{-1} (w); elemental analysis calcd (%) for $C_{45}H_{63}N_7Si_2Zr$·0.5 C_7H_8: C 65.05, H 7.54, N 10.97; found: C 65.10, H 7,73, N 10.52.

NMR-scale preparation of [Zr{(NMes)$_2$N$_{py}$}(HNNPh$_2$)$_2$] (4): The formation of compound **4** in the reaction of the metallacycles with diphenylhy-

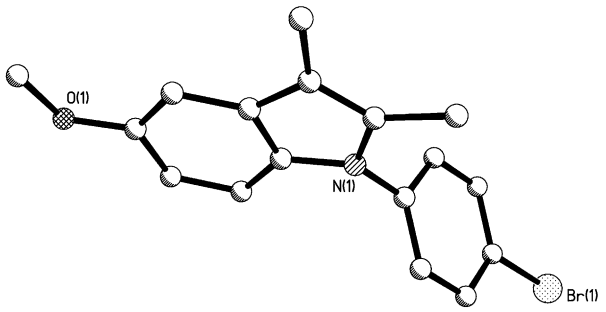
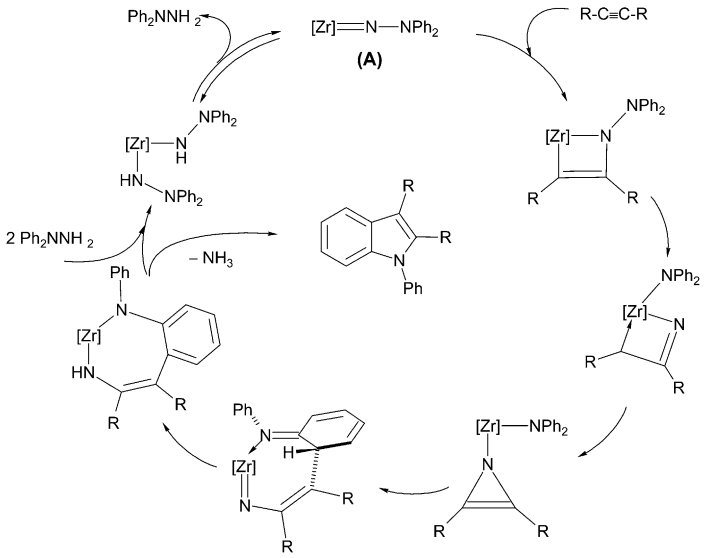


Figure 5. Molecular structure of indole Ind12.



Scheme 9. Proposal of a mechanistic cycle for the catalytic formation of indoles from 1,2-diarylhydrazines and alkynes.

drazine was confirmed by comparison with an authentic sample, which was prepared as follows: To a solution of $[Zr\{(NMes)_2N_{py}\}(NMe_2)_2]$ (10.00 mg, 0.02 mmol) in C_6D_6 were added two equivalents of diphenylhydrazine (6.40 mg, 0.04 mmol). The reaction mixture was heated to 80 °C for 3 d. Analysis by NMR spectroscopy indicated the formation of the title compound and a small quantity of $[Zr\{(NMes)_2N_{py}\}(NHNPh_2)(NMe_2)]$. By treating the sample with an excess of diphenylhydrazine, complete conversion into the bis-hydrazido complex was observed. ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta = 0.98$ (s, 3H; $C_{Mes}H_3$), 1.53 (s, 6H; *o*-CH_3), 2.31 (s, 6H; *p*-CH_3), 2.61 (brs, 6H; *o*-CH_3), 2.78 (d, ^3J(H,H) = 12.1 Hz, 2H; CH_2), 3.56 (d, ^3J(H,H) = 12.1 Hz, 2H; CH_2), 5.87 (brs, 1H; N*H*), 6.37 (brs, 1H; N*H*), 6.56 (t, $^3J(H(5)_{py},H(4)_{py}) = 6.5$ Hz, $^3J(H(5)_{py},H(6)_{py}) = 6.2$ Hz, 1H; $H(5)_{py}$), 6.72 (t, $^3J(p\text{-}H_{Ph},m\text{-}H_{Ph}) = 7.4$ Hz, 4H; $H_{p\text{-}Ph}$), 6.78 (d, $^3J(H(3)_{py},H(4)_{py}) = 8.1$ Hz, 1H; $H(3)_{py}$), 6.83 (s, 2H; 2×HL_{Mes}), 6.85–7.02 (m, 16H; $H(4)_{py}$, $H_{o\text{-}Ph}$, $H_{m\text{-}Ph}$), 7.02–7.06 (m, 3H; 2× HL_{Mes}, $H_{o\text{-}Ph}$ or $H_{m\text{-}Ph}$), 9.22 ppm (d, $^3J(H(6)_{py},H(5)_{py}) = 5.8$ Hz, 1H; $H(6)_{py}$); ^{13}C NMR (150 MHz, C_6D_6, 296 K): $\delta = 18.3$ (*o*-CH_3), 18.6 (*o*-CH_3), 21.1 (*p*-CH_3), 24.5 (CCH_3), 46.6 (CCH_3), 65.8 (CH_2), 119.3 ($C_{o\text{-}Ph}$), 120.3 ($C(3)_{py}$), 122.4 ($C(5)_{py}$), 128.4, 128.6 ($C_{o\text{-}Ph}$, $C_{m\text{-}Ph}$), 129.8, 129.9 ($C_{Mes}H$), 133.5, 134.5, 135.3 (CCH_3), 139.4 ($C(4)_{py}$), 147.1 (NC_{Mes}), 147.9 ($C(6)_{py}$), 162.3 ppm ($C(2)_{py}$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta = 186.9$ (*N*-CH_2-L), 284.3 ppm (N_{py}) (*N*H not observed).

Preparation of $[Zr\{(NXyl)_2N_{py}\}(NNMePh)(dmap)_2]$ (5): $[Zr\{(NXyl)_2N_{py}\}(NMe_2)_2]$ (68.00 mg, 0.12 mmol, see the Supporting Information), DMAP (45.30 mg, 0.37 mmol), and methylphenylhydrazine (15.12 mg, 0.12 mmol) were dissolved in toluene (3 mL). After standing at RT under reduced pressure for 1 d, a red solid precipitated as thin needles. The solvent was removed by filtration and the crude product was washed with pentane (3 mL) to yield $[Zr\{(NXyl)_2N_{py}\}(NNMePh)(dmap)_2]$ as red needles. Yield: 43.00 mg (52.0 μmol, 42 %). Single-crystal X-ray analysis was obtained from these needles at RT. ^{1}H NMR (600 MHz, [D_8]THF, 296 K): $\delta = 1.83$ (s, 12H; CH_3 (xylyl)), 2.91–2.96 (m, 12H; CH_3 (dmap)), 3.17 (s, 3H; $NNCH_3$), 3.31 (d, ^2J(H,H) = 11.9 Hz, 1H; CH*H*), 3.41 (d, ^2J(H,H) = 11.9 Hz, 1H; CH*H*), 3.51 (d, ^2J(H,H) = 13.2 Hz, 1H; CH*H*), 3.35–3.66 (m, 1H; CH*H* overlay with residual solvent signal), 5.77 (s, 2H; $H_{p\text{-}Xyl}$), 6.13 (t, $^3J(H_p,H_m) = 7.1$ Hz, 1H; *p*-Ar*H*), 6.44–6.50 (m, 4H; *CH*$CNMe_2$, coordinated dmap overlay with uncoordinated dmap), 6.63 (s, 4H; $H_{o\text{-}Xyl}$), 6.75 (t, $^3J(H_m,H_o/H_p) = 7.4$ Hz, 2H; H_m), 6.86–6.91 (m, 3H; $H(5)_{py}$, *o*-Ar*H*), 7.53 (d, $^3J(H(6)_{py},H(5)_{py}) = 5.2$ Hz, 1H; $H(6)_{py}$), 7.80 (t, $^3J(H(4)_{py},H(5)_{py}) = 7.4$ Hz, 1H; H_{4py}), 7.82–7.87 (m, 1H; $H(3)_{py}$), 8.20 ppm (d, $^3J(H_o,H_m) = 6.3$ Hz, 4H; N*CH;* dmap) CCH_3 was not assigned; ^{13}C{^{1}H} NMR (150 MHz, [D_8]THF, 296 K): $\delta = C$$CH_3$ and CCH_3 could not be assigned, 21.0 (CH_3 (xylyl)), 38.0 (($N(CH_3)_2$), dmap), 41.6 ($NNCH_3$), 62.6, 63.4 (CH_2), 106.2 (*CH*$CNMe_2$, dmap), 108.7, 120.6 ($C(5)_{py}$, $C_{o\text{-}Ar}$), 111.4 ($C_{p\text{-}Ph}$), 112.7 (*o*-$C_6H_3Me_2$), 113.6 ($C_{o\text{-}Ph}$), 114.9 (*p*-$C_6H_3Me_2$), 127.0 ($C_{m\text{-}Ph}$), 134.8 (*m*-$C_6H_3Me_2$), 138.2 ($C(4)_{py}$), 138.6 ($C(3)_{py}$), 147.1 ($C(6)_{py}$), 147.2 (NPh), 147.9 ($C(2)_{py}$); 149.8 ($NC_6H_3Me_2$), 150.0 ($CNMe_2$, dmap), 152.0 ppm (N*C*H, dmap); IR (Nujol, NaCl): $\tilde{\nu}$ = 2924 (s), 2854 (s), 2601 (w), 1599 (m), 1463 (s), 1377 (m), 1260 (m), 1190 (w), 1090 (m), 1015 (m), 801 (m), 721 cm^{-1} (w); elemental analysis calcd (%) for $C_{48}H_{61}N_9Zr$: C 66.79, H 6.95, N 15.24; found: C 67.06, H 7.08, N 15.34.

Preparation of $[Zr\{(NXyl)_2N_{py}\}(NNPh_2)(dmap)_2]$ (6): $[Zr\{(NXyl)_2N_{py}\}(NMe_2)_2]$ (50.00 mg, 0.09 mmol, see the Supporting Information), DMAP (33.25 mg, 27.23 μmol), and 1,1-diphenylhyadrazine (16.75 g, 90.93 μmol) were dissolved in toluene (10 mL). After standing at RT for 1 d, a red solid precipitated as thin needles. The solvent was removed by filtration and the crude product was washed with pentane (10 mL) to yield $[Zr\{(NXyl)_2N_{py}\}(NNPh_2)(dmap)_2]$ as red needles. Yield 56.80 mg (64.01 μmol, 67 %). Single-crystal X-ray analysis was obtained from these needles at RT. ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta = 1.45$ (s, 3H; CH_3), 2.11 (s, 12H; CH_3 (dmap)), 2.31 (s, 12H; CH_3 (Xylyl), 3.61 (d, ^2J(H,H) = 12.3 Hz, 2H; CH*H*), 3.91 (d, ^2J(H,H) = 12.3 Hz, 2H; CH*H*), 5.71 (d, ^2J(H,H) = 6.8 Hz, 1H; $H(3)_{py}$), 5.89, 6.17 (s, 2H; $H_{p\text{-}Xyl}$) (brs, 4H; dmap), 6.41 (brs, 4H; $H_{o\text{-}Xyl}$), 6.72 (tt, 7.01 $^3J(H_p,H_m) = 7.3$ Hz, $^2J(H_p,H_o) = 1.0$ Hz, 2H; *p*-Ar*H*), 6.75–6.78 (m, 1H; $H(4)_{py}$), 6.98 (t, $^3J(H_m,H_o) = 7.3$ Hz, $^3J(H_m,H_p) = 7.3$ Hz, 4H; *m*-Ar*H*), 7.12 (m, 1H; $H(5)_{py}$), 7.20 (dd, $^3J(H_o,H_m) = 8.6$ Hz, $^4J(H_o,H_p) = 1.1$ Hz, 4H; *o*-Ar*H*), 7.98 (d, $^3J(H(6)_{py},H(5)_{py}) = 7.7$ Hz, 1H; $H(6)_{py}$), 8.31 ppm (brs, 4H; dmap); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, 296 K): $\delta = 22.2$ (CH_3 (Xylyl)), 26.6 (CH_3), 38.9 (CH_3 (dmap)), 45.9 (CCH_3), 62.5 (CH_2), 10.5.9, 106.3 (dmap, $C(3)_{py}$), 114.0 (*p*-$C_6H_3Me_2$), 116.9 (*o*-$C_6H_3Me_2$), 119.4 ($C(5)_{py}$), 120.4, 120.5 ($C(6)_{py}$, $C(4)_{py}$), 121.2, 121.3 ($C_{m\text{-}Ph}$, $C_{o\text{-}Ph}$), 127.9 ($C_{o\text{-}Ph}$), 136.5 (*m*-$C_6H_3Me_2$), 138.2 (dmap), 152.5, 155.1 (NPh2, $NC_6H_3Me_2$), 165.4 ppm ($C(2)_{py}$); IR (Nujol, NaCl): $\tilde{\nu}$ = 3061 (w), 2924 (s), 2854 (s), 1613 (s), 1577 (m), 1533 (m), 1464 (s), 1377 (m), 1317 (m), 1296 (m), 1260 (m), 1226 (m), 1099 (w), 1004 (m), 941 (w), 812 (s), 697 cm^{-1} (w); elemental analysis calcd (%) for $C_{51}H_{59}N_9Zr$: C 68.88, H 6.69, N 14.18; found: C 68.98, H 6.80, N 13.96.

Preparation of $[Zr\{(NTBS)_2N_{py}\}\{\kappa^2\text{-}NPh)NC_6H_4C(Me)\text{=}C(Me)NH\}]$ (7a): To a stirring solution of $[Zr\{(NTBS)_2N_{py}\}(NNPh_2)(py)]$ (400 mg, 0.54 mmol) in toluene (20 mL) was added a solution of 2-butyne (48 μL, 0.54 mmol) in toluene (2 mL). The reaction mixture was stirred for 8 h at RT, filtered, and the volatile compounds were removed under reduced pressure. The resulting orange solid was extracted with pentane (3× 10 mL) and the combined extracts were dried in vacuo to yield 120 mg (32 %) of $[Zr\{(NTBS)_2N_{py}\}\{(Ph)NC_6H_4(Me)\text{=}C(Me)NH\}]$ as an orange solid. ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta = -0.37$, -0.26, 0.11, 0.40 (s, 3H; $Si(CH_3)_2$), 0.80, 1.06 (s, 9H; $SiC(CH_3)_3$), 1.09 (s, 3H; CH_3), 1.91 (s, 3H; $HNC(CH_3)$), 2.26 (s, 3H; $ArC(CH_3)$) 3.33, 3.52, 3.85, 3.95 (d, ^2J(H,H) = 12.4 Hz, 1H; CH_2), 5.46 (brs, 1H; N*H*) 6.46 (ddd, $^3J(H(5)_{py},H(4)_{py}) = 7.7$ Hz, $^3J(H(5)_{py},H(6)_{py}) = 5.4$ Hz, $^4J(H(5)_{py},H(3)_{py}) = 1.1$ Hz, 1H; $H(5)_{py}$), 6.63 (d, $^3J(o\text{-}H_{Ph},m\text{-}H_{Ph}) = 8.0$ Hz, 2× H *o*-H_{NPh}), 6.54 (t, $^3J(p\text{-}H_{NPh},m\text{-}H_{NPh}) = 7.3$ Hz, 1H; *p*-H_{NPh}), 6.82 (d, $^3J(H(3)_{py},H(4)_{py}) = 8.0$ Hz, 1H; $H(3)_{py}$), 6.95 (dt, $^3J(H(4)_{py},H(3)/H(5)_{py}) = 8.0$ Hz, $^4J(H(4)_{py},H(6)_{py}) = 1.7$ Hz, 1H; $H(4)_{py}$), 7.13 (t, $^3J(m\text{-}H_{NPh},o/p\text{-}H_{NPh}) = 8.0$ Hz, 2H; *m*-H_{NPh}), 7.17 (dt, $^3J(H_{Ar},H_{Ar}) = 7.8$ Hz, $^4J(H_{Ar},H_{Ar}) = 1.6$ Hz

1H; H_{Ar}), 7.25 (dt, $^3J(H_{Ar},H_{Ar})=7.8$ Hz, $^4J(H_{Ar},H_{Ar})=1.6$ Hz 1H; H_{Ar}), 7.29 (dd, $^3J(H_{Ar},H_{Ar})=7.8$ Hz, $^4J(H_{Ar},H_{Ar})=1.6$ Hz 1H; H_{Ar}), 7.61 (dd, $^3J(H_{Ar},H_{Ar})=7.8$ Hz, $^4J(H_{Ar},H_{Ar})=1.6$ Hz, 1H; H_{Ar}), 9.07 ppm (dd, $^3J(H(6)_{py},H(5)_{py})=5.5$ Hz, $^4J(H(6)_{py},H(4)_{py})=1.6$ Hz, 1H; $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=-1.7$, -4.2, -4.1, -2.7 (Si-(CH_3)$_2$), 20.6 (SiC(CH$_3$)$_3$), 21.5 (HNC(CH_3)), 25.1 (CCH_3), 24.6 (ArC-(CH_3)) 27.6, 27.7 (SiC(CH_3)$_3$), 49.6 (CCH_3), 62.8, 63.3 (CH_2), 105.0 (HNC(CH$_3$)), 116.8 (o-C_{NPh}), 117.0 (p-C_{NPh}), 120.5 ($C(3)_{py}$), 122.1 ($C(5)_{py}$), 126.3 (C_{Ar}), 127.0 (C_{Ar}), 129.2 (m-C_{NPh}), 130.9 (C_{Ar}), 131.3 (C_{Ar}), 139.8 ($C(4)_{py}$), 141.5 (C_{Ar}), 142.5 (C_{Ar}), 147.6 (C=C(Me)Ar), 149.2 ($C(6)_{py}$), 153.7 (i-C_{NPh}), 162.6 ppm ($C(2)_{py}$); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 296 K): $\delta=3.29$, 3.88 ppm (Si(CH$_3$)$_2t$Bu); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=174.2$, 180.0 (N-Si(CH$_3$)$_2t$Bu), 190.1 (NH), 199.8 (NPh$_2$), 281.2 ppm (LN_{py}); IR (Nujol, NaCl): $\tilde{\nu}=3051$ (w), 2725 (w), 2672 (w), 1602 (m), 1463 (s), 1377 (s), 1342 (w), 1291 (m), 1260 (m), 1199 (w), 1089 (w), 1034 (m), 908 (m), 891 (m), 852 (s), 828 (m), 799 (w), 780 (w), 721 (m), 666 cm^{-1} (w); elemental analysis calcd (%) for $C_{37}H_{57}N_5Si_2Zr$: C 61.78, H 7.99, N 9.74; found: C 62.02, H 7.96, N 9.59.

Preparation of [Zr{(NTBS)$_2$N$_{py}$}{κ^2-N(Ph)NC$_6$H$_4$C(Et)=C(Et)NH}] (7b): To a stirring solution of [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (200 mg, 0.27 mmol) in toluene (20 mL) was added a solution of 3-hexyne (22.6 mg, 0.27 mmol) in toluene (1 mL). The reaction mixture was stirred for 8 h at RT, filtered, and the volatile compounds were removed under reduced pressure. [Zr{(NTBS)$_2$N$_{py}$}{(Ph)NC$_6$H$_4$(Et)C=C(Et)NH}] was obtained in quantitative yield as an orange solid. Single crystals suitable for X-ray diffraction were grown from a saturated solution in toluene at RT. ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta=-0.43$, -0.32, 0.16, 0.4 (s, 3H; Si-(CH_3)$_2$), 0.83 (s, 9H; SiC(CH_3)$_3$), 1.08 (m, 12H; SiC(CH_3)$_3$, CH_3), 1.11 (t, ^3J(H,H)=7.6 Hz, 3H; CH$_2$CH_3-A), 1.20 (t, ^3J(H,H)=7.6 Hz, 3H; CH$_2$CH_3-B), 2.02 (dt, ^2J(H,H)=14.4 Hz, ^3J(H,H)=7.6 Hz, 2H; CHHCH$_3$-B), 2.67 (dt, ^2J(H,H)=14.4 Hz, ^3J(H,H)=7.6 Hz, 2H; CHHCH$_3$-A), 2.76–2.85 (m, 4H; CHHCH$_3$-A, CHHCH$_3$-B), 3.29, 3.58, 3.84, 3.99 (d, ^2J(H,H)=12.5 Hz, 1H; CH_2), 5.76 (brs, 1H; NH) 6.46 (ddd, $^3J(H(5)_{py},H(4)_{py})=7.6$ Hz, $^3J(H(5)_{py},H(6)_{py})=5.4$ Hz, $^4J(H(5)_{py},H(3)_{py})=1.1$ Hz, 1H; $H(5)_{py}$), 6.64–6.73 (m, 3H; o-H_{NPh}, p-H_{NPh}), 6.82 (d, ^3J(H(3),H(4))=8.1 Hz, 1H; $H(3)_{py}$), 6.95 (dt, $^3J(H(4)_{py},H(3)/(5)_{py})=7.9$ Hz, $^4J(H(4)_{py},H(6)_{py})=1.8$ Hz, 1H; $H(4)_{py}$), 7.12 (m, 2H; m-H_{NPh}), 7.17 (m, 2H; H_{Ar}), 7.35 (dd, $^3J(H_{Ar},H_{Ar})=7.5$ Hz, $^4J(H_{Ar},H_{Ar})=2.0$ Hz, 1H; H_{Ar}), 7.61 (dd, $^3J(H_{Ar},H_{Ar})=7.5$ Hz, $^4J(H_{Ar},H_{Ar})=2.0$ Hz 1H; H_{Ar}), 9.02 ppm (dd, $^3J(H(6)_{py},H(5)_{py})=5.4$ Hz, $^4J(H(6)_{py},H(4)_{py})=1.6$ Hz, $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=-5.0$, -4.3, -4.2, -3.4 (Si(CH_3)$_2$), 12.6 (CH$_2$CH_3-B), 16.6 (CH$_2$CH_3-A), 20.5, 20.7 (SiC-(CH$_3$)$_3$), 25.0 (CCH_3), 28.2 (SiC(CH_3)$_3$), 28.3 (CH_2CH$_3$-B), 29.0 (CH_2CH$_3$-A), 49.5 (CCH_3), 62.7, 63.5 (CH_2), 112.7 (HNC(Et)), 116.8 (o-C_{NPh}), 117.5 (p-C_{NPh}), 120.5 ($C(3)_{py}$), 122.0 ($C(5)_{py}$), 125.8 (C_{Ar}), 127.1 (C_{Ar}), 129.0 (m-C_{NPh}), 131.2 (C_{Ar}), 132.3 (C_{Ar}), 139.6 ($C(4)_{py}$), 143.4 (C_{Ar}), 146.1 (C_{Ar}), 147.2 (C=C(Et)Ar), 148.9 ($C(6)_{py}$), 154.4 (i-C_{NPh}), 162.6 ppm ($C(2)_{py}$); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 296 K): $\delta=3.27$, 3.76 ppm (Si-(CH$_3$)$_2t$Bu); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=172.7$ (NSi(CH$_3$)$_2t$Bu), 181.2 (NH; NSi(CH$_3$)$_2t$Bu), 199.0 (NPh$_2$), 281.2 ppm (LN_{py}); IR (Nujol, NaCl): $\tilde{\nu}=3192$ (w), 2900 (s), 2727 (w), 2032 (w), 1600 (m), 1464 (s), 1377 (s), 1340 (w), 1260 (m), 1194 (w),1110 (m), 1087 (m), 1030 (s), 909 (m), 890 (m), 860 (s), 828 (m), 801 (w), 774 (m), 748 (w), 727 (m), 694 (w), 667 cm^{-1} (w); elemental analysis calcd (%) for $C_{39}H_{61}N_5Si_2Zr\cdot0.5\,C_7H_8$: C 64.34, H 8.26, N 8.83; found: C 64.59, H 8.34, N 8.45.

Preparation of [Zr{(NTBS)$_2$N$_{py}$}{κ^2-N(Ph)NC$_6$H$_4$C(Ph)=C(Ph)NH}] (7c): To a stirring solution of [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (200 mg, 0.27 mmol) in toluene (20 mL) was added a solution of diphenylacetylene (48 mg, 0.27 mmol) in toluene (5 mL). The reaction mixture was stirred for 4 h at RT, filtered, and the volatile compounds were removed under reduced pressure. The resulting orange solid was washed with pentane (3×10 mL) before drying in vacuo to yield 140 mg (60%) of [Zr-{(NTBS)$_2$N$_{py}$}{(Ph)N-C$_6$H$_4$-(Ph)C=C(Ph)NH}] as a yellow solid. Single crystals suitable for X-ray diffraction were grown from a saturated toluene solution at RT. ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta=-0.24$, -0.14, -0.02, 0.19 (s, 3H; Si(CH_3)$_2$), 0.81, 0.94 (s, 9H; SiC(CH_3)$_3$), 1.07 (s, 3H; CH_3), 3.37, 3.46, 3.88, 3.97 (d, ^2J(H,H)=12.6 Hz, 1H; CH_2), 6.22 (brs, 1H; NH), 6.28 (t, $^3J(H(5)_{py},H(4)_{py})=5.5$ Hz, 1H; $H(5)_{py}$), 6.75 (t, $^3J(p$-H_{NPh},m-H_{NPh})=6.9 Hz, 1H; p-H_{NPh}), 6.79–6.87 (m, 3H; $H(3)_{py}$, o-H_{NPh}), 6.88–6.97 (m, 5H; m-H_{CCPhA}, m-H_{CCPhB}, $H(4)_{py}$), 6,99–7.09 (m, 3H; p-H_{CCPhA}, p-H_{CCPhB}, H_{Ar}), 7.15 (sub-C_6D_6, 1H; H_{Ar}), 7.18–7.26 (m, 4H; m-H_{NPh}, o-H_{CCPhB}), 7.34–7.43 (m, 3H; o-H_{NPh}, H_{Ar}), 7.47 (d, $^3J(H_{Ar},H_{Ar})=7.8$ Hz, 1H; H_{Ar}), 9.07 ppm (d, $^3J(H(6)_{py},H(5)_{py})=4.0$ Hz, 1H; $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=-4.7$, -4.3, -4.1, -1.8 (Si-(CH_3)$_2$), 20.4, 20.7 (SiC(CH$_3$)$_3$), 25.2 (CCH_3), 28.0, 28.4 (SiC(CH_3)$_3$), 49.6 (CCH_3), 62.9, 63.2 (CH_2), 115.0 (C=C), 117.5 (o-C_{NPh}), 120.6 ($C(3)_{py}$), 122.2 ($C(5)_{py}$), 124.9, 126.0, 126.3, 127.5, 127.7, 127.9 (C_{Ar}, C_{Ar}, m-C_{PhA}, m-C_{PhB}, p-C_{PhA}, p-C_{PhB}), 129.2, 129.3 (m-C_{NPh}, o-C_{PhB}), 131.7 (C_{Ar}), 133.7 (o-C_{PhA}), 135.5 (C_{Ar}), 139.8 ($C(4)_{py}$), 143.0, 146.1 (2-C_{Ar}), 146.7 (i-C_{PhA}), 146.9 (C=C), 149.0 ($C(6)_{py}$), 150.5 (i-C_{PhB}), 144.5 (i-C_{NPh}), 162.6 ppm ($C(2)_{py}$); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 296 K): $\delta=3.29$, 3.88 ppm (Si-(CH$_3$)$_2t$Bu); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=177.6$, 185.9 (NSi-(CH$_3$)$_2t$Bu), 190.3 (NH), 201.2 (NPh$_2$), 279.3 ppm (LN_{py}); IR (Nujol, NaCl): $\tilde{\nu}=3290$ (m), 2733 (w), 2681 (w), 1592 (s), 1466 (s), 1378 (s), 1260 (w), 1136 (w), 1110 (m), 1087 (m), 1033 (s), 936 (m), 908 (s), 890 (s), 854 (m), 775 (w), 723 (m), 698 (w), 667 (w), 629 cm^{-1} (w); elemental analysis calcd (%) for $C_{47}H_{61}N_5Si_2Zr$: C 66.93, H 7.29, N 8.30; found: C 67.20, H 7.41, N 8.19.

Preparation of [Zr{(NTBS)$_2$N$_{py}$}{κ^2-N(Ph)NC$_6$H$_4$C(4-Br-Ph)=C(4-Br-Ph)NH}] (7d): To a stirring solution of [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (200 mg, 0.27 mmol) in toluene (20 mL) was added a suspension of bis(4-bromo)phenylacetylene (90 mg, 0.27 mmol) in toluene (5 mL). The reaction mixture was stirred for 4 h at RT, filtered, and the volatile compounds were removed under reduced pressure. The crude product was recrystallized from n-hexane at −20 °C. [Zr{(NTBS)$_2$N$_{py}$}{(Ph)NC$_6$H$_4$(4-Br-Ph)C=C(4-Br-Ph)NH}] was obtained as a yellow solid. Yield: 180 mg (60%); ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta=-0.28$, -0.19, -0.06, -0.09 (s, 3H; Si(CH_3)$_2$), 0.77 (s, 9H; SiC(CH_3)$_3$), 0.90 (s, 9H; SiC(CH_3)$_3$), 1.04 (s, 3H CH_3), 3.34, 3.42, 3.84, 3.93 (d, ^2J(H,H)=12.5 Hz, 1H; CH_2), 5.94 (brs, 1H; NH), 6.46 (ddd, $^3J(H(5)_{py},H(4)_{py})=7.5$ Hz, $^3J(H(5)_{py},H(6)_{py})=5.5$ Hz, $^4J(H(5)_{py},H(3)_{py})=0.9$ Hz, 1H; $H(5)_{py}$), 6.72–6.76 (m, 3H; o-H_{NPh}, p-H_{NPh}), 6.78 (d, ^3J(H(3),H(4))=8.33 Hz, 1H; $H(3)_{py}$), 6.86 (d, $^3J(H_{Ar},H_{Ar})=8.3$ Hz, 2H; H_{Ar}), 6.91 (dt, $^3J(H(4)_{py},H(3)/H(5)_{py})=7.9$ Hz, $^4J(H(4)_{py},H(6)_{py})=1.7$ Hz, 1H; $H(4)_{py}$), 7.00, 7.43 (d, $^3J(H_{Ar},H_{Ar})=8.3$ Hz, 2H; H_{Ar}), 7.06–7.08 (m, 1H; H_{Ar}), 7.11 (d, $^3J(H_{Ar},H_{Ar})=8.3$ Hz, 2H; H_{Ar}), 7.19 (t, ^3J(m-H_{Ph},o/p-H_{Ph})=8.1 Hz, 2H; m-H_{NPh}), 7.15–7.17 (m, 1H; H_{Ar}), 7.30 (dd, $^3J(H_{Ar},H_{Ar})=8.0$ Hz, $^4J(H_{Ar},H_{Ar})=1.6$ Hz, 1H; H_{Ar}), 7.34 (dd, $^3J(H_{Ar},H_{Ar})=8.0$ Hz, $^4J(H_{Ar},H_{Ar})=1.2$ Hz 1H; H_{Ar}), 9.01 ppm (dd, $^3J(H(6)_{py},H(5)_{py})=5.5$ Hz, $^4J(H(6)_{py},H(4)_{py})=1.3$ Hz, $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=-4.8$, -4.2, -4.1, -1.9 (Si(CH_3)$_2$), 20.3, 20.7 (SiC(CH$_3$)$_3$), 25.1 (CCH_3), 27.9, 28.4 (SiC(CH_3)$_3$), 49.5 (CCH_3), 62.8, 63.1 (CH_2), 113.5 (HNC(Ar-p-Br)), 117.0 (o-C_{NPh}), 117.3 (p-C_{NPh}), 119.1 ($C(3)_{py}$), 120.1 ($C(5)_{py}$), 120.6 (C_{Ar}), 122.3 (C_{Ar}), 126.5 (m-C_{NPh}), 127.9 (C_{Ar}), 129.4 (C_{Ar}), 130.8 (C_{Ar}), 130.9 (C_{Ar}), 131.3 (C_{Ar}), 135.3 (C_{Ar}), 140.2 ($C(4)_{py}$), 143.1 (C=C(Ar-p-Br)Ar), 143,1 (CBr), 145.2 (CBr), 145.3 (CBr), 148.9 ($C(6)_{py}$), 149.6 (CBr), 154.3 (i-C_{NPh}), 162.4 ppm ($C(2)_{py}$); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 296 K): $\delta=3.88$, 4.48 ppm (Si(CH$_3$)$_2t$Bu); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=179.7$, (N-Si(CH$_3$)$_2t$Bu), 187.9 (NH; NSi(CH$_3$)$_2t$Bu), 201.1 (NPh$_2$), 278.9 ppm (LN_{py}); IR (Nujol, NaCl): $\tilde{\nu}=3289$ (w), 2854 (s), 2054 (w), 1596 (s), 1464 (s), 1377 (s), 1296 (w), 1250 (m), 1121 (w), 1078 (w), 1030 (m), 854 (m), 829 (m), 774 (m), 748 (m), 723 (w), 666 cm^{-1} (w); elemental analysis calcd (%) for $C_{47}H_{59}N_5Br_2Si_2Zr$: C 56.38, H 5.94, N 6.99; found: C 56.35, H 5.96, N 7.00.

Preparation of [Zr{(NTBS)$_2$N$_{py}$}{κ^2-*N*(Ph)NC$_6$H$_4$C(Me)=C(Ph)NH}] (7e) and regioisomer [Zr{(NTBS)$_2$N$_{py}$}{κ^2-*N*(Ph)NC$_6$H$_4$C(Ph)=C(Me)NH}] (7e′): To a stirring solution of [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (200 mg, 0.27 mmol) in toluene (20 mL) was added a solution of 1-phenyl-1-propyne (31.2 mg, 0.27 mmol) in toluene (1 mL). The reaction mixture was stirred for 8 h at RT, filtered, the volatile compounds were removed under reduced pressure, and the residue was recrystallized from cold (−78 °C) pentane. The mixture of [Zr{(NTBS)$_2$N$_{py}$}{κ^2-*N*(Ph)NC$_6$H$_4$C(Me)=C(Ph)NH}] (7e) and [Zr{(NTBS)$_2$N$_{py}$}{κ^2-*N*(Ph)NC$_6$H$_4$C(Ph)=C(Me)NH}] (7e′) was obtained as an orange solid. Yield: 168 mg (80%) **7e**: ^{1}H NMR (600 MHz, C_6D_6, 296 K): $\delta=-0.34$, -0.19, 0.12, 0.41 (s, 3H; Si(CH_3)$_2$), 0.81, 1.02 (s, 9H; SiC(CH_3)$_3$), 1.08 (s, 3H; CH_3), 1.91 (s, 3H;HNC(CH_3)), 3.34, 3.54, 3.87, 3.98 (d, ^{2}J(H,H)=12.4 Hz, 1H; CH_2), 5.65 (brs, 1H; NH) 6.28–6.32 (m, 1H; $H(5)_{py}$), 6.68–

7.60 (m , 16H; H_{Ar}), 9.05 ppm (d, $^3J(H(6)_{py},H(5)_{py})=5.4$ Hz, $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=-4.9$, -1.5 ($Si(CH_3)_2$), 20.6 ($SiC(CH_3)_3$), 25.3 ($C{=}CCH_3$), 28.0, 28.1 ($SiC(CH_3)_3$), 49.3 (CCH_3), 62.7, 63.2 (CH_2), 114.2 ($C{=}C(CH_3)$), 116.4–145.3 (C_{Ar}), 146.7 ($C{=}C$(Me)Ar), 146.8–154.1 (C_{Ar}), 162.1 ppm ($C(2)_{py}$); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 296 K): $\delta=3.49$, 4.08 ppm ($Si(CH_3)_2tBu$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=176.1$, 183.4 (N-$Si(CH_3)_2tBu$), 186.7 (NH), 200.8 (NPh_2), 280.6 ppm (L-N_{py}); **7e′**: ^1H NMR (600 MHz, C_6D_6, 296 K): $\delta=-0.20$, -0.18, 0.00, 0.11 (s, 3H; $Si(CH_3)_2$), 0.84, 0.94 (s, 9H; $SiC(CH_3)_3$), 1.06 (s, 3H; CH_3), 2.29 (s, 3H; $C{=}C(CH_3)$), 3.37, 3.39, 3.84, 3.88 (d, $^2J(H,H)=12.4$ Hz, 1H; CH_2), 5.96 (br s, 1H; NH), 6.28–6.32 (m, 1H; $H(5)_{py}$), 6.68–7.60 (m , 16H; H_{Ar}), 9.12 (dd, $^3J(H(6)_{py},H(5)_{py})=5.2$ Hz, $^4J(H(6)_{py},H(4)_{py})=1.6$ Hz, $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=-4.9$, -1.5 ($Si(CH_3)_2$), 21.9 ($C{=}CCH_3$), 27.9, 23.3 ($SiC(CH_3)_3$, 49.7 (CCH_3), 62.3, 63.0 (CH_2), 106.3 ($C{=}C(CH_3)$), 116.4–142.8 (C_{Ar}), 144.2 ($C{=}C(CH_3)$), 146.8–154.1 (C_{Ar}), 162.4 ppm ($C(2)_{py}$); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 296 K): $\delta=3.54$, 4.51 ppm ($Si(CH_3)_2tBu$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=175.8$, 181.4 ($NSi(CH_3)_2tBu$), 194.2 (NH), 199.9 (NPh_2), 279.8 ppm (LN_{py}); IR (Nujol, NaCl) (**9a+9b**): $\tilde{\nu}=3293$ (w), 3174 (w), 3056 (sh), 2733 (w), 2680 (w), 2042 (s), 1594 (s), 1488 (sh), 1465 (s), 1377 (s), 1290 (m), 1260 (m), 1248 (m), 1191 (w), 1162 (w), 1135 (w), 1034 (m), 959 (w), 905 (s), 887 (m), 854 (s), 828 (sh), 777 (w), 750 (m), 699 (m), 667 cm^{-1} (w); elemental analysis calcd (%) for $C_{42}H_{59}N_5Si_2Zr{\cdot}0.5\,C_7H_8$: C 66.05, H 7.67, N 8.46; found: C 66.05, H 7.82, N 8.43.

Preparation of [Zr{$(NMes)_2N_{py}$}{κ²-N(Ph)NC_6H_4C(Me)=C(Me)NH}] (8a): [Zr{$(NMes)_2N_{py}$}$(NMe_2)_2$] (250 mg, 0.43 mmol), 1,1-diphenylhydrazine (80 mg, 0.43 mmol), and 2-butyne (34 μL, 0.43 mmol) were dissolved in toluene (15 mL). After stirring the reaction mixture at 80 °C for 2 days, the volatile compounds were removed under reduced pressure and the crude product was washed with pentane (10 mL) to obtain [Zr{$(NMes)_2N_{py}$}{κ²-N(Ph)NC_6H_4C(Me)=C(Me)NH}] as a yellow solid. Yield 145 mg (47%). Single crystals suitable for X-ray diffraction were grown from a saturated solution in pentane at RT. ^1H NMR (600 MHz, C_6D_6, 296 K): $\delta=0.99$ (s, 3H; CH_3), 1.24 (s, 3H; o-CH_3), 1.42 (s, 3H; (HNC-(CH_3)), 1.92 (s, 3H; Ar-C(CH_3)), 2.06 (s, 3H; o-CH_3), 2.19–2.21 (m, 6H; p-CH_3), 2.39 (s, 3H; o-CH_3), 2.66 (s, 3H; o-CH_3), 2.88 (d, $^2J(H,H)=12.9$ Hz, 1H; CHH), 2.94 (d, $^2J(H,H)=12.3$ Hz, 1H; CHH), 3.49 (d, ^2J-(H,H) = 12.3 Hz, 1H; CHH), 3.88 (d, $^2J(H,H)=12.9$ Hz, 1H; CHH), 5.68 (s, 1H; NH), 6.44 (ddd, $^3J(H(5)_{py},H(6)_{py})=6.8$ Hz, $^3J(H(5)_{py},H(4)_{py})=5.4$ Hz $^4J(H(5)_{py},H(3)_{py})=1.2$ Hz, 1H; $H(5)_{py}$), 6.53 (dt, $^3J(H,H)=7.6$ Hz, $^4J(H,H)=1.2$ Hz, 1H; H_{Ar}), 6.65 (s, 1H; L_{Mes}), 6.67–6.80 (m, 5H; HL_{Mes}, H_{Ar}), 6.87 (d, $^3J(H(3)_{py},H(4)_{py})=7.9$ Hz, 1H; $H(3)_{py}$), 6.92 (s, 1H; L_{Mes}), 6.96–7.00 (m, 1H; L_{Mes}), 7.03 (dt, $^3J(H(4)_{py},H(3)_{py})=7.9$ Hz, $^4J(H(4)_{py},H(6)_{py})=1.4$ Hz, 1H; $H(4)_{py}$), 7.11–7.16 (m, 3H; H_{Ar}), 7.18 (d, $^3J(H,H)=7.8$ Hz, 1H; H_{Ar}), 9.07 ppm (d, $^3J(H,H)=5.3$ Hz, 1H; $H(6)_{py}$); ^{13}C NMR (150 MHz, C_6D_6, 296 K): $\delta=17.3$ (o-CH_3), 18.1 (o-CH_3), 18.3 (o-CH_3), 19.6 (p-CH_3), 20.4 (o-CH_3), 20.8 (HNC(CH_3)), 21.0 (p-CH_3), 23.2 (Ar-C(CH_3)), 24.8 (CCH_3), 46.4 (CCH_3), 66.4, 66.5 (CH_2), 103.1 (HNC(CH_3)), 116.3 (CH_{Ar}), 117.6 (CH_{Ar}), 121.3 ($C3_{py}$), 122.6 ($C5_{py}$), 126.4 (CH_{Ar}), 126.6 (CH_{Ar}), 128.3 (CH_{Ar}), 128.8 ($C_{Mes}H$), 129.5 (CH_{Ar}), 129.7 ($C_{Mes}H$), 129.8 ($C_{Mes}H$), 130.2 (CH_{Ar}), 131.0 (CH_{Ar}), 131.1 ($C_{Mes}H$), 131.8 (o-CCH_3), 131.9 (o-CCH_3), 132.8 (p-CCH_3), 133.7 (p-CCH_3), 134.3 (o-CCH_3), 134.4 (o-CCH_3), 137.7 (C_{Ar}), 139.6 ($C(4)_{py}$), 142.8 (C=C(Me)Ar), 147.7 (NC_{Mes}), 148.2 ($C(6)_{py}$), 149.5 (NC_{Mes}), 150.2 (C_{Ar}), 154.1 (C_{Ar}), 162.0 ppm ($C(2)_{py}$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $d=189.4$, 191.6 ($NC_{Mes}H_2$), 189.6 (NH), 204.5 (NC_6H_5), 284.0 ppm (N_{py}); IR (Nujol, NaCl,): $\tilde{\nu}=2929$ (s), 2854 (s), 1596 (w), 1463 (s), 1377 (s), 1303 (w), 1260 (w), 1223 (w), 1150 (w), 1093 (w), 1018 (m), 800 (m), 722 cm^{-1} (s); elemental analysis calcd (%) for $C_{43}H_{49}N_5Zr$: C 71.03, H 6.79, N 9.63; found: C 70.58, H 6.91, N 9.48.

Preparation of [Zr{$(NMes)_2N_{py}$}{κ²-N(Ph)NC_6H_4C(Et)=C(Et)NH}] (8b): [Zr({$(NMes)_2N_{py}$}$(NMe_2)_2$] (400 mg, 0.69 mmol), 1,1-diphenylhydrazine (127 mg, 0.69 mmol), and 3-hexyne (79 μL, 0.69 mmol) were dissolved in toluene (20 mL). After stirring the reaction mixture at 80 °C for 2 days, the volatile compounds were removed under reduced pressure. The crude product was washed with pentane (10 mL) to obtain [Zr-{$(NMes)_2N_{py}$}{κ²-N(Ph)NC_6H_4C(Et)=C(Et)NH}] as a yellow solid. Yield 271 mg (53%); ^1H NMR (600 MHz, C_6D_6, 296 K): $\delta=0.63$ (t, $^3J(H,H)=7.5$ Hz, 3H; CH_2CH_3-A), 0.93 (t, $^3J(H,H)=7.5$ Hz, 3H; CH_2CH_3-B), 1.00 (s, 3H; CH_3), 1.23 (s, 3H; o-CH_3), 1.57–1.66 (m, 1H; CHHCH$_3$-A), 2.08 (s, 3H; o-CH_3), 2.17–2.26 (m, 7H; 2 p-CH_3, CHHCH$_3$-A), 2.35–2.43 (m, 5H; o-CH_3, CHHCH$_3$-B, CHHCH$_3$-B), 2.69 (s, 3H; o-CH_3), 2.88, 2.96, 3.48, 3.90 (d, $^2J(H,H)=12.6$ Hz, 1H; CH_2), 5.64 (s, 1H; NH), 6.39 (ddd, $^3J(H(5)_{py},H(4)_{py})=6.7$ Hz, $^3J(H(5)_{py},H(6)_{py})=5.8$ Hz, $^4J(H(5)_{py},H(3)_{py})=1.5$ Hz, 1H; $H(5)_{py}$), 6.55 (t, $^3J(H_{Ar},H_{Ar})=7.1$ Hz, 1H; H_{Ar}), 6.65–6.80 (m, 6H; HL_{Mes}, H_{Ar}), 6.87 (d, $^3J(H(3)_{py},H(4)_{py})=8.4$ Hz, 1H; $H(3)_{py}$), 6.93 (s, 1H; HL_{Mes}), 6.98–7.04 (m, 3H; $H(4)_{py}$, $1\times HL_{Mes}$, $1\times H_{Ar}$), 7.13–7.18 (m, 2H; H_{Ar}), 7.31 (d, $^3J(H_{Ar},H_{Ar})=8.0$ Hz, 1H; H_{Ar}), 9.04 ppm (dt, $^3J(H(6)_{py},H(5)_{py})=5.2$ Hz, $^4J(H(6)_{py},H(4)_{py})=0.8$ Hz, 1H; $H(6)_{py}$); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 296 K): $\delta=13.2$ (CH_2CH_3-A), 16.4 (CH_2CH_3-B), 17.3 (o-CH_3), 17.9 (o-CH_3), 18.1 (o-CH_3), 19.4 (o-CH_3), 20.7 (p-CH_3), 20.8 (p-CH_3), 24.6 (CCH_3), 27.5, 27.9 (CH_2CH_3-A, CH_2CH_3-B), 46.3 (CCH_3), 66.2, 66.3 (CH_2), 109.2 (HNC(Et)), 117.2 (CH_{Ar}), 117.3 (CH_{Ar}), 121.1 ($C(3)_{py}$), 122.4 ($C(5)_{py}$), 126.4 (CH_{Ar}), 126.5 (CH_{Ar}), 128.7 (CH_{Ar}), 129.3 (CH_{Ar}), 129.4 ($C_{Mes}H$), 129.5 ($C_{Mes}H$), 129.7 ($C_{Mes}H$), 130.0 ($C(4)_{py}$), 130.6 (CH_{Ar}), 131.6 ($C_{Mes}H$), 132.0 (o-CCH_3), 132.7 (o-CCH_3), 133.5 (p-CCH_3), 134.1 (o-CCH_3), 134.3 (o-CCH_3), 139.4 (CH_{Ar}), 147.5 (CH_{Ar}), 147.8 ($C(6)_{py}$), 149.1 (NC_{Mes}), 149.2 (NC_{Mes}), 150.1 (C_{Ar}), 153.6 (C_{Ar}), 161.9 ppm ($C(2)_{py}$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=184.7$ (NH), 188.7, 190.5 ($NC_{Mes}H_2$), 202.9 (NC_6H_5), 283.2 ppm (N_{py}); IR (Nujol, NaCl): $\tilde{\nu}=3176$ (w), 2961 (s), 2727 (w), 2664 (w), 2610 (w), 1596 (m), 1466 (s), 1377 (s), 1295 (m), 1225 (m), 1152 (w), 1094 (w), 892 (m), 848 (m), 722 (s), 690 cm^{-1} (w); elemental analysis calcd (%) for $C_{45}H_{53}N_5Zr$: C 71.57, H 7.07, N 9.27; found: C 71.34, H 7.23, N 9.16.

Preparation of [Zr{$(NMes)_2N_{py}$}{N(p-F-Ph)NC_6H_4C(Me)=C(Me)NH}] (8c): [Zr{$(NMes)_2N_{py}$}$(NMe_2)_2$] (200 mg, 0.37 mmol), 1-(4-fluorophenyl)-1-phenylhydrazine (69.0 mg, 0.37 mmol), and 2-butyne (27.14 μL, 0.37 mmol) were dissolved in toluene (10 mL). After stirring the reaction mixture at 80 °C for 2 days, the volatile compounds were removed under reduced pressure to afford [Zr{$(NMes)_2N_{py}$}{N(p-F-Ph)NC_6H_4C(Me)=C(Me)NH}] in quantitative yield. Analytically pure samples were obtained by washing the yellow solid with pentane (10 mL). ^1H NMR (600 MHz, C_6D_6, 296 K): $\delta=0.98$ (s, 3H; $C_{Mes}H_3$), 1.29 (s, 3H; o-CH_3), 1.43 (s, 3H; HNC(CH_3)), 1.86 (s, 3H; Ar-C(CH_3)), 1.95 (s, 3H; o-CH_3), 2.18–2.23 (m, 6H; p-CH_3), 2.38 (s, 3H; o-CH_3), 2.65 (s, 3H; o-CH_3), 2.85–2.92 (m, 2H; CH_2), 3.50 (d, $^3J(H,H)=12.8$ Hz, 1H; CH_2), 3.87 (d, ^3J-(H,H) = 13.1 Hz, 1H; CH_2), 5.67 (s, 1H; NH), 6.48 (tt, $^3J(H(5)_{py},H(4)_{py})=6.6$ Hz, $^3J(H(5)_{py},H(6)_{py})=6.1$ Hz, $^4J(H(5)_{py},H(3)_{py})=1.1$ Hz, 1H; $H(5)_{py}$), 6.51–6.59 (m, 3H; $2\times H_{FAr}$, H_{Ar}), 6.64–6.72 (m, 4H; $2\times HL_{Mes}$, $2\times H_{Ar}$), 6.81–6.91 (m, 4H; $1\times HL_{Mes}$, $2\times H_{FAr}$, $H(3)_{py}$), 6.96 (s, 1H; HL_{Mes}), 7.01 (s, 1H; HL_{Mes}), 7.05 (tt, $^3J(H(4)_{py},H(5)/H(3)_{py})=8.0$ Hz, $^4J(H(4)_{py},H(6)_{py})=1.1$ Hz, 1H; $H(4)_{py}$), 9.04 ppm (d, $^3J(H(6)_{py},H(5)_{py})=5.1$ Hz, 1H; $H(6)_{py}$); ^{13}C NMR (150 MHz, C_6D_6, 296 K): $\delta=17.5$ (o-CH_3), 18.1 (o-CH_3), 18.2 (o-CH_3), 19.6 (o-CH_3), 20.2 (HNC(CH_3), 20.8 (p-CH_3), 21.0 (p-CH_3), 23.2 (Ar-C(CH_3)), 24.8 (CCH_3), 46.4 (CCH_3), 66.4 (CH_2), 66.5 (CH_2), 103.1 (HNC(CH_3)), 115.1 (CH_{FAr}), 116.7, 116.8 (CH_{Ar}),121.4 ($C(3)_{py}$), 122.7 ($C(5)_{py}$), 126.5 (CH_{FAr}), 128.4, 129.6, 129.7, 130.3, 130.8, 131.2 ($C_{Mes}H$; CH_{Ar}), 131.8, 139.9, 132.8 133.9, 134.2, 134.3 (CCH_3), 137.8 (C_{Ar}), 139.7 ($C(4)_{py}$), (142.8 Ar-$C(CH_3)$), 147.3 (C_{Ar}) 148.0 ($C(6)_{py}$), 149.2 (NC_{Mes}), 150.1 (NC_{Mes}), 155.7 (C_{FAr}), 157.3 (C_{FAr}), 162.0 ppm ($C(2)_{py}$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): $\delta=189.1$ (NCH_2L), 189.3 (NH), 192.7 (NCH_2L), 201.3 (NC_6H_4F), 284.0 ppm (N_{py}); ^{19}F NMR (376 MHz, C_6D_6, 296 K): $\delta=-128.2$ ppm (ptt, $^3J(F,H)=8.8$ Hz, $^4J(F,H)=4.6$ Hz); IR (Nujol, NaCl,): $\tilde{\nu}=2923$ (s), 2853 (s), 1593 (w), 1463 (s), 1377 (s), 1298 (w), 1223 (w), 1150 (w), 1093 (w), 1018 (m), 851 (w), 798 (w), 722 cm^{-1} (w); elemental analysis calcd (%) for $C_{43}H_{48}FN_5Zr$: C 69.31, H 6.49, N 9.40; found: C 68.95, H 6.73, N 9.38.

Preparation of [Zr{$(NMes)_2N_{py}$}{ κ²-N(Ph)$NC_6H_3CH_3$C(Me)=C(Me)NH}] (8d): [Zr{$(NMes)_2N_{py}$}$(NMe_2)_2$] (250 mg, 0.43 mmol), 1-phenyl-1-(p-tolyl)hydrazine (85.7 mg, 0.43 mmol), and 2-butyne (34 μL, 0.43 mmol) were dissolved in toluene (15 mL). After stirring the reaction mixture at 80 °C for 4 days, the volatile compounds were removed under reduced pressure and the crude product was washed with pentane (10 mL) to obtain 270 mg of [Zr{$(NMes)_2N_{py}$}{ κ²-N(Ph)$NC_6H_3CH_3$C(Me)=C(Me)NH}] as a yellow solid (85%). ^1H NMR (600 MHz, C_6D_6, 296 K): $\delta=1.08$ (s, 3H; $^LCH_3$), 1.25 (s, 3H; o-CH_3), 1.46 (s, 3H; (HNC(CH_3)), 1.94 (s, 3H; Ar-C-(CH_3)), 2.09 (s, 3H; o-CH_3), 2.14 (s, 3H; $C_6H_3CH_3$), 2.20–2.23 (m, 6H; p-

CH_3), 2.41 (s, 3H; *o*-CH_3), 2.68 (s, 3H; *o*-CH_3), 2.90 (d, ^2J(H,H) = 12.3 Hz, 1H; C*H*H), 2.96 (d, ^2J(H,H) = 12.6 Hz, 1H; C*H*H), 3.51 (d, ^2J(H,H) = 12.1 Hz, 1H; CH*H*), 3.91 (d, ^2J(H,H) = 12.6 Hz, 1H; CH*H*), 5.68 (s, 1H; N*H*), 6.46 (ddd, ^3J(H(5)$_{py}$,H(6)$_{py}$) = 6.0 Hz, ^3J(H(5)$_{py}$,H(4)$_{py}$) = 6.6 Hz ^4J(H(5)$_{py}$,H(3)$_{py}$) = 1.4 Hz, 1H; *H*(5)$_{py}$), 6.54 (td, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.2 Hz, 1H; H_{Ar}), 6.64–6.74 (m, 4H; 2 × *H*L$_{Mes}$+2 × H_{Ar}), 6.87–6.90 (m, 1H; *H*(3)$_{py}$), 6.94–7.06 (m, 5H; 3 × H_{Ar}, 2 × HL$_{Mes}$, *H*(4)$_{py}$), 7.17 (t, 1H; H_{Ar} , overlay with C_6D_6), 7.21 (d, ^3J(H,H) = 7.9 Hz, 1H; H_{Ar}), 9.12 ppm (d, ^3J(H,H) = 5.1 Hz, 1H; *H*(6)$_{py}$); ^{13}C NMR (150 MHz, C_6D_6, 296 K): δ = 17.3 (*o*-CH_3), 17.9 (*o*-CH_3), 18.0 (*o*-CH_3), 19.4 (*o*-CH_3), 20.2 (Ar-C(*CH*3), 20.6 ($C_6H_3CH_3$), 20.6, 20.8 (*p*-CH_3), 22.8 (HNC(*C*H$_3$)), 24.6 (*C*CH$_3$), 46.3 (*C*CH$_3$), 66.3, 66.4 (CH_2), 102.8 (HN*C*(CH$_3$)), 116.1 (*C*H$_{Ar}$), 121.1 (*C*(3)$_{py}$), 122.4 (*C*(5)$_{py}$), 125.9 (*C*H$_{Ar}$), 126.2 (*C*H$_{Ar}$), 126.3 (*C*H$_{Ar}$), 128.6 (*C*H$_{Ar}$), 129.3 (*C*H$_{Ar}$), 129.5 (*C*H$_{Ar}$), 129.6 (*C*H$_{Ar}$), 129.9 (*C*H$_{Ar}$), 130.8 (*C*H$_{Ar}$), 131.0 (*C*H$_{Ar}$), 131.5 (*C*H$_{Ar}$), 132.7, 133.4, 134.1, 134.2, 134.3, 137.7 (C_q), 139.4 (*C*(4)$_{py}$), 142.5 (*C*=C(Me)Ar), 148.1 (*C*(6)$_{py}$), 150.1, 151.7 (C_q), 162.0 ppm (*C*(2)$_{py}$); ^{15}N NMR (60 MHz, C_6D_6, 296 K): δ = 187.8 (*N*H), 189.0, 190.7 (*N*C$_{Mes}$H$_2$), 187.8 (*N*H), 204.5 (*N*C$_6$H$_5$), 284.1 ppm (*N*$_{py}$); IR (Nujol, NaCl): $\tilde{\nu}$ = 2923 (s), 2853 (s), 2756 (w), 1577 (m), 1464 (s), 1370 (m), 1300 (w), 1223 (w), 1154 (w), 1093 (w), 1025 (w), 934 (m), 851 (m), 802 (w), 782 (w), 743 (m), 691 cm^{-1} (w); elemental analysis calcd (%) for $C_{43}H_{49}N_5Zr$: C 71.31, H 6.94, N 9.45; found: C 70.28, H 7.04, N 8.79.

Preparation of [Zr{(NTBS)$_2$N$_{py}$}(=NC(Me)=C(Me)NPh$_2$)(py)] (9): To a stirring solution of [Zr{(NTBS)$_2$N$_{py}$}(NNPh$_2$)(py)] (400 mg, 0.54 mmol) in toluene (20 mL) was added a solution of 2-butyne (48 μL, 0.54 mmol) in toluene (2 mL). The reaction mixture was stirred for 4 h at RT, filtered, and the volatile compounds were removed under reduced pressure. The resulting orange solid was washed with pentane (3 × 10 mL) before drying in vacuo to yield 200 mg (44 %) of [Zr{(NTBS)$_2$N$_{py}$}(=NC(Me)=C(Me)NPh$_2$)(py)] as an orange solid. Single crystals suitable for X-ray diffraction were grown from a saturated solution in toluene at RT. ^{1}H NMR (600 MHz, C_6D_6, 296 K): δ = −0.21, 0.18 (s, 6H; Si(CH_3)$_2$), 0.74 (s, 18H; SiC(CH_3)$_3$), 1.04 (s, 3H; CH_3), 2.12 (s, 3H; C=C(CH_3)NPh$_2$), 2.31 (s, 3H;=N(CH_3)C=C) 3.42 (d, ^2J(H,H) = 12.8 Hz, 2H; CH*H*), 3.82 (d, ^2J(H,H) = 12.8 Hz, 2H; C*H*H), 6.57–6.61 (m 3H; *H*(5)$_{py}$, *m*-*H*$_{py}$), 6.80 (d, ^3J_H(H(3)$_{py}$,H(4)$_{py}$) = 8.1 Hz, 1H; *H*(3)$_{py}$), 6.83–6.87 (m, 3H; *p*-*H*$_{py}$, *p*-*H*$_{Ph}$), 7.05 (dt, ^3J(H(4)$_{py}$,H(3)/H(5)$_{py}$) = 8.1 Hz, ^4J(H(4)$_{py}$,H(6)$_{py}$) = 1.8 Hz, 1H; *H*(4)$_{py}$), 7.23 (m, 4H; *m*-*H*$_{Ph}$), 7.65 (m, 4H; *o*-*H*$_{Ph}$), 9.01 (m, 2H *o*-*H*$_{py}$), 9.78 ppm (dd, ^3J(H(6)$_{py}$,H(5)$_{py}$) = 5.3 Hz, ^4J(H(6)$_{py}$,H(4)$_{py}$) = 1.8 Hz, *H*(6)$_{py}$); ^{13}C {^{1}H} NMR (150 MHz, C_6D_6, 296 K): δ = −4.2, −3.0 (Si-(*C*H$_3$)$_2$), 17.0 (=N(*C*H$_3$)C=C), 20.4 (Si*C*(CH$_3$)$_3$), 25.4 (*C*CH$_3$, C=C-(*C*H$_3$)NPh$_2$), 27.7 (SiC(*C*H$_3$)$_3$), 46.9 (*C*CH$_3$), 64.5 (CH_2), 106.6 (*C*=C), 119.7 (*p*-*C*$_{Ph}$), 120.4 (*C*(3)$_{py}$), 120.5 (*o*-*C*$_{Ph}$), 121.0 (*C*(5)$_{py}$), 124.0 (*m*-*C*$_{py}$), 129.0 (*m*-*C*$_{Ph}$), 138.3 (*C*(4)$_{py}$), 138.4 (*p*-*C*$_{py}$), 148.4 (*i*-*C*$_{Ph}$), 149.5 (C=*C*), 151.7 (*C*(6)$_{py}$, *o*-*C*$_{py}$), 160.5 ppm (*C*(2)$_{py}$); ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 296 K): δ = 0.20 ppm (*Si*(CH$_3$)$_2$*t*Bu); ^{15}N NMR (60 MHz, C_6D_6, 296 K): δ = 106,7 (*N*Ph$_2$), 150.0 (*N*Si(CH$_3$)$_2$*t*Bu), 278.1 (*N*py), 289.5 (L*N*$_{py}$), 340.9 ppm (Zr=N); IR (Nujol, NaCl): $\tilde{\nu}$ = 1585 (w), 1463 (s), 1309 (m), 1260 (w), 1242 (w), 1210 (w), 1088 (m), 1069 (m), 888 (s), 867 (s), 827 (m), 198 (w), 773 (w), 744 (m), 722 (s), 702 (m), 667 cm^{-1} (w); elemental analysis calcd (%) for $C_{42}H_{62}N_6Si_2Zr$: C 63.18, H 7.83, N 10.53; found: C 62.60, H 7.88, N 10.81.

Computational studies: The DFT-B3PW91 computational tool was used to model all the systems with a 6–31 g(d) basis set for C, N, and H atoms.[25] An SDD+f function effective core potential basis set[26] was used for Zr atoms. All calculations were carried out by using the GAUSSIAN03 program package.[27] Stationary points were verified by frequency analysis.

Crystal structure determination: Crystal data and details of the structure determinations are listed in Table 5 and Table 6. Preliminary accounts of the structures of compounds **7b** and **8a** have been published elsewhere.[11] Full shells of intensity data were collected at low temperatures (T = 100 K) with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected

Table 5. Single-crystal X-ray diffraction data of compounds **3**, **5**, **6**, **7b**, and **7c**.

	3	**5**	**6**	**7b**	**7c**
formula	$C_{41}H_{50}N_6Zr$	$C_{70}H_{81}N_9Zr$	$C_{65}H_{74.50}N_9Zr$	$C_{46}H_{69}N_5Si_2Zr$	$C_{53}H_{67}N_5Si_2Zr$
M_r	718.09	1139.66	1073.06	839.46	921.52
crystal system	triclinic	triclinic	monoclinic	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P\bar{1}$	$I4_1/a$
a [Å]	10.386(5)	10.265(5)	11.245(6)	10.803(5)	22.31(1)
b [Å]	12.711(7)	12.848(6)	15.603(9)	12.103(5)	
c [Å]	15.679(7)	25.954(12)	17.233(11)	18.445(8)	38.11(2)
α [°]	112.776(9)	76.109(7)		99.28(1)	
β [°]	104.416(8)	83.15(2)	108.98(2)	96.82(1)	
γ [°]	96.382(7)	67.129(6)		103.95(1)	
V [Å^3]	1798(2)	3060(2)	2859(3)	2278(2)	18960(15)
Z	2	2	2	2	16
F(000)	756	1208	1135	896	7808
ρ_{calcd} [Mg m^{-3}]	1.326	1.237	1.246	1.224	1.291
μ(Mo$_{K\alpha}$) [mm^{-1}]	0.344	0.229	0.241	0.330	0.324
max., min. transmission factors	1.0000, 0.8937	0.7464, 0.6781	1.0000, 0.8444	1.0000, 0.9170	1.0000, 0.8461
θ [°]	1.8–30.5	2.1–32.4	1.9–30.0	1.1–32.3	1.8–27.9
index ranges (indep. set) h,k,l	−14..14, −18..16, 0..22	−15..15, −18..19, 0..38	−15..14, −21..21, 0..24	−16..15, −17..17, 0..27	−20..20, 0..29, 0..50
total reflns	44189	77649	67599	57830	184687
unique reflns [R_{int}]	10956 [0.0819]	20256 [0.0506]	16644 [0.0802]	15069 [0.0331]	11307 [0.0662]
[$I \geq 2\sigma(I)$]	8287	16050	13085	12937	7994
parameters refined	446	731	750	557	543
GOF on F^2	1.070	1.029	1.047	1.035	1.190
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0572, 0.1207	0.0434, 0.0914	0.0534, 0.1089	0.0368, 0.0871	0.0666, 0.1883
R indices (all data) $R(F)$, $wR(F^2)$	0.0861, 0.1324	0.0644, 0.1008	0.0812, 0.1221	0.0468, 0.0940	0.1034, 0.2194
absolute structure parameter			0.04(3)		
largest residual peaks [e Å^{-3}]	1.616, −0.716	0.858, −0.511	0.774, −0.605	1.231, −0.902	1.394, −1.066

Table 6. Single-crystal X-ray diffraction data of compounds **8a**, **8b**, **8c**, and Ind12.

	8a	**8b**	**8c**	Ind12
formula	$C_{43}H_{49}N_5Zr$	$C_{45}H_{53}N_5Zr$	$C_{43}H_{48}FN_5Zr$	$C_{17}H_{16}BrNO$
M_r	727.09	755.14	745.08	330.22
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	24.721(10)	12.194(6)	24.905(4)	13.882(7)
b [Å]	12.275(6)	12.461(7)	12.238(2)	14.936(8)
c [Å]	26.305(10)	14.278(7)	26.308(4)	14.703(7)
α [°]		69.90(1)		
β [°]	110.790(9)	76.51(1)	111.508(3)	104.50(1)
γ [°]		81.55(1)		
V [Å^3]	7463(6)	1976(2)	7460(2)	2951(3)
Z	8	2	8	8
$F(000)$	3056	796	3120	1344
ρ_{calcd} [Mg m^{-3}]	1.294	1.269	1.327	1.486
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.332	0.316	0.337	2.780
max., min. transmission factors	0.7461, 0.6807	0.7464, 0.6367	0.7452, 0.6747	0.8209, 0.6764
θ [°]	1.0–29.1	1.9–30.5	1.0–25.0	1.8–26.4
index ranges (indep. set) h,k,l	−33..31, 0..16, 0..36	−16..17, −16..17, 0..20	−29..27, 0..14, 0..31	−17..17, −18..18, −18..18
total reflns	167231	47377	135180	55222
unique reflns [R_{int}]	20058 [0.0917]	12016 [0.0633]	13138 [0.1299]	6036 [0.0418]
[$I \geq 2\sigma(I)$]	14379	9597	8877	5272
parameters refined	909	472	927	367
GOF on F^2	1.002	1.042	1.021	1.023
R indices [$F > 4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0426, 0.0796	0.0436, 0.0995	0.0576, 0.1069	0.0232, 0.0566
R indices (all data) $R(F)$, $wR(F^2)$	0.0767, 0.0916	0.0636, 0.1095	0.1013, 0.1189	0.0303, 0.0603
absolute structure parameter	0.553, −0.506	1.207, −0.966	0.963, −0.610	0.416, −0.342

for air and detector absorption, Lorentz and polarization effects;[28] absorption by the crystal was treated numerically[29] or with a semiempirical multiscan method.[29–31]

The structures were solved by the charge-flip procedure[32] (compounds **3**, **7b**, **8a**–**8c**, and Ind12), by the heavy-atom method combined with structure expansion by direct methods applied to difference structure factors[33] (complex **7c**) or by direct methods with dual-space recycling[34] (compounds **5** and **6**) and refined by full-matrix-least-squares methods based on F^2 against all unique reflections.[35] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally placed at calculated positions and refined with a riding model. When justified by the quality of the data, the position of the hydrogen atom on N(4) was taken from difference Fourier syntheses and refined.

Suitable geometry and adp restraints were applied to the disordered solvent molecules in the structures of compounds **6** and **7b** as well as to the disordered groups in compound **7b**. Owing to severe unresolvable disorder and fractional occupancy, electron density attributed to the solvent of crystallization (benzene) was removed from the structure (and the corresponding F_{obs}) of compound **7c** by using the BYPASS procedure,[33] as implemented in PLATON (SQUEEZE).[33] Crystals of compound **8c** were twinned; after de-twinning (approx. twin fraction 0.83:0.17), refinement was carried out against all observations involving domain 1.

CCDC-811035 (**7b**), CCDC-811036 (**8a**), and CCDC-851907 (**3**), CCDC-851908 (**5**), CCDC-851909 (**6**), CCDC-851910 (**7c**), CCDC-851911 (**8b**), CCDC-851912 (**8c**), and CCDC-851913 (Ind12) 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.

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