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Direct Reaction of Aroyl Cyanides with Azazirconacyclopentadienes: Synthesis and Structural Characterization of Stabilized Azazirconacyclopentenes

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Summary: The direct reaction of aroyl cyanide with azazirconacyclopentadiene takes place at room temperature in THF. The X-ray crystal structure analysis of the product **2e** *shows a novel azazirconacycle with a bidentate O−C−N unit. Hydrolysis of the newly formed zirconacycle affords the N-substituted benzamide derivative in good yield.*

Zirconacycles are attractive intermediates in an impressive array of synthetic methodology and have received much attention in recent years.[1] In comparison with other metallacycles, zirconacycles have several advantages. (i) They are easily prepared by reductive coupling of unsaturated compounds such as alkynes, alkenes, nitriles, or ketones on a zirconocene equivalent. (ii) They are relatively stable under normal conditions. (iii) They have been proven to be efficient precursors for a wide range of selective transformation reactions. They are generally not reactive toward carbon electrophiles, possibly due to the steric hindrance caused by the bulky cyclopentadienyl ligands.[2] Most of the chemistry of five-membered zirconacycles has therefore focused on indirect reaction pathways, i.e., through transmetalation of Zr−R bonds with metal salts such as Cu, Zn, Li, Bi, and Ni to increase the reactivity.[3] There have only been limited reports of the direct reaction of zirconacycles with carbon electrophiles. Examples include reactions with CO,[4a,b] aldehydes,[4c−e] and isocyanides,[4f] carbenoid insertion,[4g] 1,1-cycloaddition to propynoates,[4h] Michael addition to activated alkenes,[4i] and insertion of lithiated aryl alkynes.[4j] Recently, we reported the direct insertion of aroyl cyanides into zirconacyclopentenes and -pentanes, which afforded a controllable synthesis of homoallyl ketones and multiply substituted cyclopentadienes.[5] We now report the selective reaction of aroyl cyanides with azazirconacyclopentadienes and the unique X-ray crystal structure of the zirconium-containing complex. It is noteworthy that there has been much less investigation of the reactivity of nitrogen-containing metallacycles,[6] and there has been no report for the direct reaction of carbon electrophiles with azazirconacyclopentadienes, to the best of our knowledge.

Alkynes undergo selective intermolecular coupling with nitriles using a zirconocene−ethylene complex.[7] Hydrolysis of the thus formed azazirconacyclopentadiene **1** with aqueous HCl solution affords α,β-unsaturated ketones in good to excellent yields. Initially, aldehydes or acyl chlorides were chosen for the reaction with zirconacycle **1**. However, only complicated reaction mixtures were observed. Acyl cyanides are known to be more reactive acylating reagents than acid chlorides, since the adjacent cyano group enhances the reactivity of the carbonyl group. As we expected, acyl cyanides reacted smoothly with zirconacycle **1** to afford the zirconium complex **2** in reasonable yields (eq 1). The reaction of ArCOCN with **1** was significantly faster; thus, with use of a 1:1 molar ratio of Zr to ArCOCN, the azametallacyclopentene **2** was formed within 30 min under ambient conditions. When a large excess of acyl cyanide was used, only one ArCOCN molecule was incorporated into the product, while the Zr−C(sp^2) bond of the azazirconacyclopentadiene remained intact. Interestingly, the CN group was found to be located at the quaternary carbon neighboring the nitrogen

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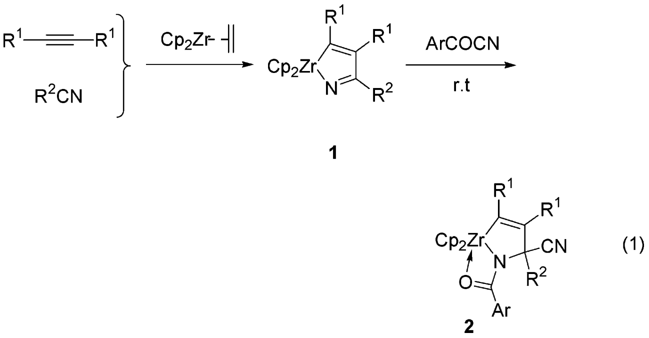

atom in complex **2**. Remarkably, complex **2** proved to be stable to air and water in its solid state, allowing a convenient separation through column chromatography on silica gel. It is noteworthy that air-stable, C−Zr σ-bond-containing complexes are rare.[6f,8] Chemoselectivity in this case was different from those of some three- or four-membered heterozirconacycles. Bergman et al. investigated the selective insertion of CO, RCHO, or RCH═NR′ into the Zr−C bonds of azazirconacyclobutenes.[6a−d] Norton et al. observed a similar selectivity for the insertion of isocyanates or carbodiimides into the Zr−C bond rather than the Zr−N bond of the zirconocene imine complex.[9] Hillhouse et al. found that the reaction of aldehydes with oxametallacyclobutene led exclusively to insertion into the Zr−C(sp^2) bond.[10] Despite the large number of zirconacycles containing Zr−N bonds, only a few known complexes, including the diphenylhydrazido(2−) complex $Cp_2Zr(N_2Ph_2)$ and an azaoxazirconacycle, have undergone Zr−N bond insertion reactions.[11]

Representative reactions of various azazirconacyclopentadienes with acyl cyanides are given in Table 1. Zirconacycles **1** bearing alkyl or mixed alkyl−aryl substituents all undergo selective reactions with acyl cyanides. Thus, the reaction of zirconacycle **1a** prepared by coupling of 4-octyne and benzonitrile with benzoyl cyanide gave **2a** in 62% yield. Functionalized acyl cyanides bearing a chlorine or a methyl group afforded the products **2f**,**i** in 48 and 40% yields, respectively. It is noteworthy that when *p*-bromobenzonitrile was used to prepare the zirconacycle, the removal of residual magnesium salts by adding 1,4-dioxane and filtration was required in order to get a good yield of **2d**.

The ^1H NMR spectrum of **2b** showed two sets of singlets at 6.07 and 6.11 ppm, and its ^{13}C NMR spectrum revealed two singlets at 109.8 and 110.2 ppm, which were assigned to cyclopentadienyl ligands. Additionally, the ^{13}C NMR spectrum of **2b** showed peaks at 68.1, 123.5, 177.0 ,and 192.2 ppm assignable to the quaternary carbon, CN, NCOPh, and ═CZr units, respectively. These results suggested that an sp^2-hybridized carbon was bonded to zirconium. Therefore, the data are most consistent with the reaction of benzoyl cyanide with the Zr−N bond. The X-ray crystal structure studies on the zirconium complex **2e** provided clear evidence for the five-membered azametallacyclic framework, as illustrated in Figure 1.

The Zr−C(14) distance of 2.326(4) Å is comparable to that found for Zr^{IV}−C(sp^2)-containing metallacycles.[12] The sets of atoms Zr, N(1), C(12), C(13), C(14) and Zr, O(1), C(11), N(1) are coplanar, and the torsion angle of C(14)−Zr−O(1)−C(11) is −3.3(3)°. The N(1)−C(11) distance (1.305(5) Å) is slightly longer than the accepted value for a N(sp^2)═C(sp^2) double bond (1.28 Å),[13] and the O(1)−C(11) distance (1.284 (4) Å) is slightly but significantly shorter than the value observed for O−C(sp^2) single bonds (e.g. 1.357(6) Å for the zirconocene β-ketone enolate $Cp_2ZrMe[OC(Et_2C(COOMe)═CEt_2)]$[14] and 1.363(7) Å for the zirconocene ester enolate *rac*-(EBI)Zr[OC(O^iPr)═CMe_2]$_2$.[15] These distances fall into the ranges for normal amide structures,[16] suggesting some electronic delocalization over the

Table 1. Direct Reaction of Acyl Cyanides with Azazirconacycles

R^1—≡—R^1	R^2CN	ArCOCN	Product	Yield[a]
Pr—≡—Pr	PhCN	PhCOCN	**2a**	62
Et—≡—Et	PrCN	PhCOCN	**2b**	59
Bu—≡—Bu	PrCN	PhCOCN	**2c**	55
Ph—≡—Ph	*p*-BrC_6H_4CN	PhCOCN	**2d**	52
Pr—≡—Pr	PrCN	PhCOCN	**2e**	50
Pr—≡—Pr	PrCN	*p*-ClC_6H_4COCN	**2f**	48
Ph—≡—Ph	*p*-$MeOC_6H_4CN$	PhCOCN	**2g**	46
Ph—≡—Ph	PrCN	PhCOCN	**2h**	42
Pr—≡—Pr	PrCN	*p*-MeC_6H_4COCN	**2i**	40
Pr—≡—Pr	MeCN	PhCOCN	**2j**	16[b]

[a] Isolated yields. Unless noted, all the reactions were performed at room temperature for 1 h. [b] 50 °C, 1 h.

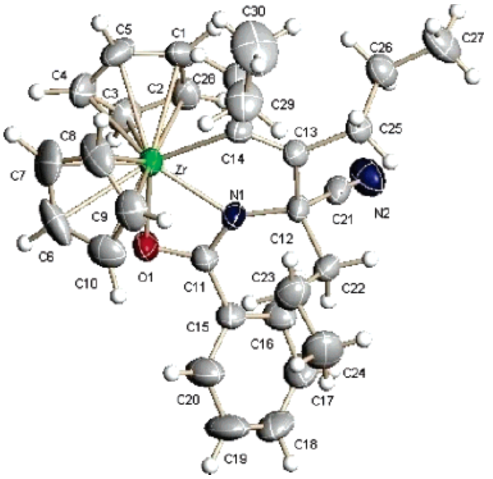

Figure 1. ORTEP drawing of complex **2e**. Selected bond lengths (Å) and angles (deg): Zr−N(1) = 2.186(3), Zr−O(1) = 2.296(3), Zr−C(14) = 2.326(4), O(1)−C(11) = 1.284(4), N(1)−C(11) = 1.305(5), N(1)−C(12) = 1.453(4), C(12)−C(13) = 1.538(5), C(13)−C(14) = 1.335(5); N(1)−Zr−O(1) = 57.06(11), N(1)−Zr−C(14) = 68.63(13), O(1)−Zr−C(14) = 125.39(12), O(1)−C(11)−N(1) = 111.7(3), C(11)−O(1)−Zr = 93.2(2), C(12)−N(1)−Zr = 128.4(2).

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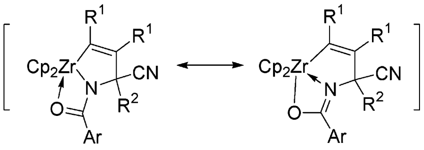
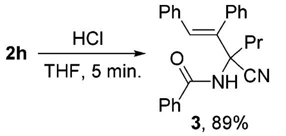
O−C−N unit caused by the resonance of the nitrogen lone pair with the carbonyl π-system. The distance for Zr−N(1) (2.186(3) Å) is indicative of a single bond,[17] while the Zr−O(1) distance (2.296(3) Å) suggests a dative interaction between carbonyl oxygen and the metal; both values are also within the limits typical for an amido ligand which bonds the metal in a C,N-bidentate fashion, such as in $Cp_2Zr(R)[O-C(R)NAr]$.[18] The values of the N(1)−C(12) and C(12)−C(13) distances correspond well to single bonds. The air and water stability thus can be explained by the bidentate coordination mode of the O−C−N moiety, which gives an electronically saturated (18-electron) zirconium center. According to the above results, especially the sp^2-hybridized character of the N atom in **2e**, the molecular structure of **2** is represented by the resonance structures of a Lewis formula (**A**) and a seven-membered oxazirconacycle (**B**) with an intramolecularly coordinated Zr−N bond.



A **B**

The details of the conversion of **1** to the final azazirconacyclopentenes are not yet clear. Possible mechanisms that may account for this reaction involve selective insertion of acyl cyanide into the Zr−N bond[11] of zirconacycle **1** followed by β-elimination of a cyano group; subsequent nucleophilic addition/cyclization affords the product **2**. Hydrolysis of **2h** gave the *N*-(1-cyano-2,3-diphenyl-1-propylallyl)benzamide **3** in 89% yield (eq 2). β-Elimination of the leaving group (halide or alkoxy group) from zirconacycles has been reported, which resulted in the formation of carbozirconation products such as allylzirconation, alkynylzirconation, and vinylzirconation.[19] We also reported that the CN group could be eliminated from the zirconium intermediates.[5] The preferred insertion of Zr−N bond into the Zr−C bond may be due to facile CN group elimination and subsequent formation of a stabilized zirconium complex. Alternatively, a mechanism which involves addition of ArCOCN across the imine function to afford **2** cannot be ruled out.



(2)

3, 89%

In conclusion, we have discovered the direct reaction of acyl cyanide with azazirconacyclopentadienes, which afforded a novel azazirconacycle with a bidentate O−C−N unit, as characterized by X-ray crystal analysis. This chemistry was different from those of some three- or four-membered azazirconacycles, in which the reaction with carbon electrophiles exclusively occurred at the zirconium−carbon bond. Clarification of the reaction mechanism and further applications of this chemistry are in progress.

Experimental Section

All reactions were carried out using standard Schlenk techniques under nitrogen. THF was distilled from sodium/benzophenone. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. NMR spectra were recorded at room temperature in $CDCl_3$ (containing 1% TMS) on a Varian XL-300 MHz spectrometer. High-resolution mass spectra were obtained by using HP5989A and IonSpec 4.7 T FTMS mass spectrometers. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. Single-crystal X-ray diffraction data were collected on Bruker SMART APEX diffractiometers with molybdenum anodes.

Typical Procedure for the Preparation of Azazirconacyclopentene Product 2a. To a solution of Cp_2ZrCl_2 (0.37 g, 1.25 mmol) in THF (5 mL) was added EtMgBr (1.0 M THF solution, 2.5 mmol) at −50 °C. After this mixture was stirred for 1 h at the same temperature, 4-octyne (0.11 g, 1.0 mmol) was added and the reaction mixture was warmed to 0 °C and stirred for 1 h. Benzonitrile (0.10 mL, 1.0 mmol) was added, and the mixture was heated to 50 °C for 3 h. Then, benzoyl cyanide (0.14 g, 1.0 mmol) was added to the reaction solution containing azazirconacyclopentadiene **1a**. After this mixture was stirred at room temperature for 1 h, the solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel (1/6 ethyl acetate/petroleum ether). A white solid of **2a** (0.35 g, 62%) was obtained. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.73 (t, $J = 7.2$ Hz, 3H, CH_3), 0.85−0.95 (m, 1H, CH_2), 1.00 (t, $J = 7.5$ Hz, 3H, CH_3), 1.37−1.53 (m, 2H, CH_2), 1.58−1.69 (m, 2H, CH_2), 1.80−2.00 (m, 2H, CH_2), 2.18−2.28 (m, 1H, CH_2), 6.15 (s, 5H, Cp), 6.19 (s, 5H, Cp), 6.98 (d, $J = 7.5$ Hz, 2H, Ph), 7.15 (t, $J = 7.5$ Hz, 2H, Ph), 7.24−7.32 (m, 4H, Ph), 7.37−7.40 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.96, 15.63 (CH_3), 22.29, 23.32, 31.80, 39.30 (CH_2), 73.24 (C*CN*), 109.90, 110.14 (Cp), 120.20 (CN), 126.07, 127.20, 127.79, 127.90, 128.37, 130.91, 132.98, 141.43, 145.01 (Ph), 178.08 (COPh), 189.19 (═CZr). IR (KBr, cm^{-1}): 2222 (w), 1604 (m), 1521 (s), 1483 (s), 802 (s). Mp: 156−157 °C. HRMS (*m*/*z*): calcd for $C_{33}H_{34}N_2OZr$ 564.1718, found 565.1791 $[M + H]^+$. Anal. Calcd for $C_{33}H_{34}N_2OZr$: C, 70.04; H, 6.06; N, 4.95. Found: C, 69.98; H, 5.93; N, 4.74.

Data for **2b** are as follows. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.67 (t, $J = 7.2$ Hz, 3H, CH_3), 1.00−1.13 (m, 2H, CH_2), 1.18 (t, $J = 7.2$ Hz, 6H, CH_3), 1.57−1.80 (m, 2H, CH_2), 1.98−2.10 (m, 2H, CH_2), 2.17−2.31 (m, 2H, CH_2), 6.07 (s, 5H, Cp), 6.11 (s, 5H, Cp), 7.43−7.49 (m, 3H, Ph), 7.61−7.64 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.61, 14.08, 14.87 (CH_3), 15.57, 21.45, 28.69, 37.09 (CH_2), 68.07 (C*CN*), 109.81, 110.16 (Cp), 123.45 (CN), 126.44, 128.52, 130.80, 134.64, 141.68 (Ph), 177.06 (COPh), 192.17 (═CZr). IR (KBr, cm^{-1}): 2218 (w), 1604 (m), 1529 (s), 1486 (s), 799 (s). Mp: 146−148 °C. HRMS (*m*/*z*): calcd for $C_{28}H_{32}N_2OZr$ 502.1562, found 503.1634 $[M + H]^+$. Anal. Calcd for $C_{28}H_{32}N_2OZr$: C, 66.75; H, 6.40; N, 5.56. Found: C, 66.41; H, 6.39; N, 5.36.

Data for **2c** are as follows. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.67 (t, $J = 7.2$ Hz, 3H, CH_3), 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), 1.00 (t, $J = 7.2$ Hz, 3H, CH_3), 1.06−1.20 (m, 2H, CH_2), 1.30−1.51 (m, 6H, CH_2), 1.54−1.80 (m, 4H, CH_2), 1.85−2.02 (m, 2H, CH_2), 2.11−2.24 (m, 2H, CH_2), 6.04 (s, 5H, Cp), 6.10 (s, 5H, Cp), 7.44−7.46 (m, 3H, Ph), 7.60−7.63 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.58, 13.84, 14.13 (CH_3), 15.47, 23.73, 24.24, 28.86, 31.28, 32.32, 36.58, 37.09 (CH_2), 68.01 (C*CN*), 109.81, 110.15 (Cp), 123.33 (CN), 126.40, 128.44, 130.71, 134.60, 140.66 (Ph), 177.00 (COPh), 190.89 (═CZr). IR (KBr, cm^{-1}): 2220 (w), 1559 (m), 1539 (s), 1489 (s), 1416 (s), 801 (s). Mp: 147−149 °C. HRMS (*m*/*z*): calcd for $C_{32}H_{40}N_2OZr$ 558.2188, found 558.2182. Anal. Calcd for $C_{32}H_{40}N_2OZr$: C, 68.65; H, 7.20; N, 5.00. Found: C, 68.38; H, 7.07; N, 4.71.

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Data for **2d** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 6.13 (s, 5H), 6.29 (s, 5H), 6.51–6.55 (m, 2H), 6.80–6.86 (m, 4H), 6.90–6.93 (m, 2H), 7.01–7.07 (m, 3H), 7.14–7.25 (m, 5H), 7.32–7.36 (m, 3H). ^{13}C NMR (CDCl$_3$): δ 72.98 (C*CN*), 111.01, 111.76 (Cp), 119.12, 121.99, 123.05, 125.96, 126.76, 127.29, 127.64, 127.83, 128.12, 130.99, 131.48, 131.63, 132.33, 138.24, 139.55, 145.89, 149.93 (Ar), 178.09 (COPh), 192.69 (=CZr). The signal for CN was not identified. IR (KBr, cm^{-1}): 2228 (w), 1593 (m), 1516 (s), 1481 (s), 797 (s), 70 (s). Mp: 247–249 °C. HRMS (*m*/*z*): calcd for $C_{39}H_{29}N_2OBrZr$ 710.0510, found 710.0505. Anal. Calcd for $C_{39}H_{29}N_2OBrZr$: C, 65.72; H, 4.10; N, 3.93. Found: C, 65.31; H, 4.16; N, 3.58.

Data for **2e** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.67 (t, $J = 7.2$ Hz, 3H, CH$_3$), 0.97 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.02 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.07–1.19 (m, 2H, CH$_2$), 1.47–1.75 (m, 6H, CH$_2$), 1.78–2.00 (m, 2H, CH$_2$), 2.04–2.22 (m, 2H, CH$_2$), 6.02 (s, 5H, Cp), 6.09 (s, 5H, Cp), 7.43–7.47 (m, 3H, Ph), 7.59–7.62 (m, 2H, Ph). ^{13}C NMR (CDCl$_3$): δ 13.61 (CH$_3$), 15.21 (CH$_3$), 15.46 (CH$_2$), 15.69 (CH$_3$), 22.60, 23.44, 31.53, 37.10, 39.45 (CH$_2$), 68.01 (C*CN*), 109.83, 110.16 (Cp), 123.34 (CN), 126.39, 128.46, 130.73, 134.59, 140.84 (Ph), 177.04 (COPh), 191.09 (=CZr). IR (KBr, cm^{-1}): 2219 (w), 1606 (w), 1531 (s), 1426 (s), 803 (s). Mp: 140–142 °C. Anal. Calcd for $C_{30}H_{36}N_2OZr$: C, 67.75; H, 6.82; N, 5.27. Found: C, 67.71; H, 6.84; N, 5.06.

Data for **2f** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.70 (t, $J = 7.2$ Hz, 3H, CH$_3$), 0.96 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.02 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.06–1.26 (m, 2H, CH$_2$), 1.47–1.80 (m, 6H, CH$_2$), 1.82–1.99 (m, 2H, CH$_2$), 2.04–2.20 (m, 2H, CH$_2$), 6.03 (s, 5H, Cp), 6.08 (s, 5H, Cp), 7.43 (d, $J = 8.4$ Hz, 2H, Ar), 7.58 (d, $J = 8.4$ Hz, 2H, Ar). ^{13}C NMR (CDCl$_3$): δ 13.67 (CH$_3$), 15.21 (CH$_3$), 15.49 (CH$_2$), 15.70 (CH$_3$), 22.60, 23.44, 31.56, 37.20, 39.44 (CH$_2$), 67.93 (C*CN*), 109.88, 110.20 (Cp), 123.32 (CN), 128.11, 128.83, 132.86, 136.99, 140.72 (Ar), 175.55 (COPh), 191.28 (=CZr). IR (KBr, cm^{-1}): 2219 (w), 1600 (m), 1553 (m), 1485 (s), 802 (s). Mp: 170–171 °C. HRMS (*m*/*z*): calcd for $C_{30}H_{35}ClN_2OZr$ 564.1485, found 565.1558 [M + H]$^+$. Anal. Calcd for $C_{30}H_{35}ClN_2OZr$: C, 63.63; H, 6.23; N, 4.95. Found: C, 63.47; H, 6.34; N, 4.69.

Data for **2g** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 3.75 (s, 3H, OMe), 6.13 (s, 5H, Cp), 6.30 (s, 5H, Cp), 6.52–6.54 (m, 2H), 6.73–6.93 (m, 8H), 7.04 (t, $J = 7.5$ Hz, 2H), 7.16–7.24 (m, 6H), 7.30–7.32 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 55.22 (OMe), 72.97 (C*CN*), 110.88, 111.73 (Cp), 119.50 (CN), 122.87, 125.70, 126.09, 126.55, 127.22, 127.80, 127.98, 131.08, 131.40, 132.49, 132.61, 138.65, 146.49, 150.23, 159.09 (Ar), 177.91 (COPh), 191.42 (=CZr). IR (KBr, cm^{-1}): 2228 (w), 1737 (m), 1507 (s), 1475 (s), 801 (s), 705 (s). Mp: 250–251 °C. HRMS (*m*/*z*): calcd for $C_{40}H_{32}N_2O_2Zr$ 662.1511, found 662.1505. Anal. Calcd for $C_{40}H_{32}N_2O_2Zr$: C, 72.36; H, 4.86; N, 4.22. Found: C, 72.30; H, 4.97; N, 4.06.

Data for **2h** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.63 (t, $J = 7.2$ Hz, 3H, CH$_3$), 0.87–1.25 (m, 2H, CH$_2$), 1.46–1.63 (m, 2H, CH$_2$), 6.06 (s, 5H, Cp), 6.20 (s, 5H, Cp), 6.92–7.01 (m, 4H, Ph), 7.02–7.12 (m, 6H, Ph), 7.44–7.50 (m, 3H, Ph), 7.69–7.72 (m, 2H, Ph). ^{13}C NMR (CDCl$_3$) δ 13.44 (CH$_3$), 15.65, 36.27 (CH$_2$), 68.27 (C*CN*), 111.09, 111.65 (Cp), 122.51 (CN), 122.85, 126.04, 126.12, 126.49, 127.16, 127.27, 128.61, 130.33, 131.07, 134.45, 139.11, 142.75, 150.57 (Ar), 177.67 (COPh), 195.08 (=CZr). IR (KBr, cm^{-1}): 2219 (w), 1538 (s), 1415 (s), 1017 (m), 801 (s) cm^{-1}. Mp: 225–227 °C. HRMS (*m*/*z*): calcd for $C_{36}H_{32}N_2OZr$ 598.1561, found 599.1634 [M + H]$^+$. Anal. Calcd for $C_{36}H_{32}N_2OZr$: C, 72.08; H, 5.38; N, 4.67. Found: C, 71.86; H, 5.27; N, 4.35.

Data for **2i** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.68 (t, $J = 7.2$ Hz, 3H, CH$_3$), 0.97 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.02 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.06–1.18 (m, 2H, CH$_2$), 1.51–1.61 (m, 2H, CH$_2$), 1.63–1.79 (m, 4H, CH$_2$), 1.83–2.00 (m, 2H, CH$_2$), 2.03–2.21 (m, 2H, CH$_2$), 2.39 (s, 3H, Me), 6.03 (s, 5H, Cp), 6.08 (s, 5H, Cp), 7.24 (d, $J = 8.4$ Hz, 2H, Ar), 7.53 (d, $J = 8.4$ Hz, 2H, Ar). ^{13}C NMR (CDCl$_3$): δ 13.69 (CH$_3$), 15.25 (CH$_3$), 15.50 (CH$_2$), 15.73 (CH$_3$), 21.55 (Me), 22.65, 23.47, 31.59, 37.09, 39.51 (CH$_2$), 68.06 (C*CN*), 109.81, 110.15 (Cp), 123.42 (CN), 126.63, 129.09, 131.74, 140.92, 141.16 (Ar), 177.20 (COAr), 191.00 (=CZr). IR (KBr, cm^{-1}): 2219 (w), 1613 (s), 1559 (s), 1497 (s), 801 (s). Mp: 187–189 °C. HRMS (*m*/*z*): calcd for $C_{31}H_{38}N_2OZr$ 544.2031, found 544.2026. Anal. Calcd for $C_{31}H_{38}N_2OZr$: C, 68.21; H, 7.02; N, 5.13. Found: C, 67.94; H, 6.85; N, 4.81.

Data for **2j** are as follows. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.96 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.02 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.31 (s, 3H, Me), 1.47–1.62 (m, 2H, CH$_2$), 1.69–1.76 (m, 2H, CH$_2$), 2.00–2.07 (m, 4H, CH$_2$), 6.02 (s, 5H, Cp), 6.10 (s, 5H, Cp), 7.45–7.48 (m, 3H, Ph), 7.70–7.73 (m, 2H, Ph). ^{13}C NMR (CDCl$_3$): δ 15.18, 15.74 (CH$_3$), 22.89, 23.20 (CH$_2$), 24.69 (Me), 31.49, 39.14 (CH$_2$), 65.04 (C*CN*), 109.84, 110.10 (Cp), 123.27 (CN), 127.29, 128.60, 131.13, 134.19, 143.43 (Ph), 176.65 (COPh), 187.94 (=CZr). IR (KBr, cm^{-1}): 2221 (w), 1732 (s), 1527 (s), 1451 (s), 801 (s). HRMS (*m*/*z*): calcd for $C_{28}H_{32}N_2OZr$ 502.1562, found 502.1556. Anal. Calcd for $C_{28}H_{32}N_2OZr$: C, 66.75; H, 6.40; N, 5.56. Found: C, 66.83; H, 6.39; N, 5.34.

***N*-(1-Cyano-2,3-diphenyl-1-propylallyl)benzamide (3).** Hydrogen chloride was prepared by dropping concentrated sulfuric acid into concentrated hydrochloric acid and dried by passing through a wash bottle containing concentrated sulfuric acid. The product **3** was obtained by treatment of **2h** (0.11 g, 0.2 mmol) with dry HCl gas in THF (3 mL) at room temperature for 5 min. The solvent was evaporated in vacuo, and the crude product was purified by chromatography on silica gel (1/20 ethyl acetate/petroleum ether). A white solid of **3** (67 mg, 89%) was obtained. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 1.05 (t, $J = 7.2$ Hz, 3H, CH$_3$), 1.76–1.80 (m, 2H, CH$_2$), 1.99–2.08 (m, 2H, CH$_2$), 6.08 (s, 1H, NH), 6.86–6.89 (m, 2H), 7.04–7.11 (m, 3H), 7.12–7.15 (m, 2H), 7.27 (s, 1H, =CH), 7.32–7.39 (m, 3H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.60–7.63 (m, 3H). ^{13}C NMR (CDCl$_3$): δ 13.42 (CH$_3$), 17.73, 39.84 (CH$_2$), 60.38 (C*CN*), 118.29 (CN), 127.02, 127.38, 127.79, 128.22, 128.47, 128.78, 129.38, 129.97, 131.35, 131.89, 133.21, 135.02, 135.15, 135.92 (Ar), 166.68 (COPh). IR (KBr, cm^{-1}): 3294 (m), 1651 (s), 1521 (s), 1487 (s), 693 (s). Mp: 155–156 °C. HRMS (*m*/*z*): calcd for $C_{26}H_{24}N_2O$ 380.1889, found 381.1961 [M + H]$^+$. Anal. Calcd for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36; N, 7.36. Found: C, 82.05; H, 6.42; N, 7.23.

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Supporting Information Available: CIF files giving crystallographic data for complex **2e** and figures giving ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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