Isocyanide Insertion Reactions with Organometallic Group 4 Tropocoronand Complexes: Formation of η²-Iminoacyl, Enediamido, η²-Imine, and μ-Imido Products

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The reactivity of the tropocoronand complexes [M(TC-3,*n*)R₂] (M = Zr(IV), Hf(IV); *n* = 3, 5; R = CH₂Ph, Ph) with aryl and alkyl isocyanides is described. Alkyl isocyanides induced migration of both benzyl groups to afford the bis(iminoacyl) species [Hf(TC-3,*n*){η²-(R)N=C(CH₂Ph)}₂] (*n* = 5, R = Cy (**1**), *n*-Bu (**2**); *n* = 3, R = Cy (**3**)). Different products were isolated with aryl isocyanides, depending on the rate of substrate addition. Treatment of [M(TC-3,*n*)(CH₂Ph)₂] with excess 2,6-dimethylphenyl isocyanide (ArNC) generated the enediamido compounds [(TC-3,3)MN(Ar)C(CH₂Ph)=C(CH₂Ph)N(Ar)] (M = Zr (**4**), Hf (**5**)) via coupling of two bis(iminoacyl) groups, whereas slow step-wise addition produced [(TC-3,*n*)-MN(Ar)C(CH₂Ph)₂C(=NAr)] (M = Zr, *n* = 3 (**6**); M = Hf, *n* = 3 (**7**), *n* = 5 (**8**)). The η²-imine complex [(TC-3,5)HfN(Ar)C(CH₂Ph)₂] (**9**), an intermediate in the formation of **7**, was isolated and characterized, but the corresponding zirconium species was unstable in solution, decomposing to form the imido-bridged compound {[Zr(TC-3,3)]₂(μ-NAr)₂} (**10**). Altering the nature of the carbon donor ligands also influenced the reactivity. Addition of both aryl and alkyl isocyanides to solutions of [Zr(TC-3,3)Ph₂] (**11**) afforded the η²-imine complexes [(TC-3,3)ZrN(R)C(Ph)₂] R = Cy (**12**), Ar (**13**)), the stability of which may be due in part to interactions between the metal center and a phenyl ring. Electron-withdrawing R substituents enhance this effect. All new compounds were characterized by X-ray crystallography, and plausible mechanisms for the migration reactions are outlined.

Introduction

Much attention has been devoted to the development of methodology for the formation of complicated constructs from simple starting materials such as CO and isocyanides.[1−3] Group 4 metals are especially adept at incorporating small substrates into larger organic molecules.[4−7] Until recently, most of the work in this field has involved the metallocene fragment {Cp₂M}²⁺, but lately the potential of macrocyclic ligand systems to induce coupling reactions has been explored.[8−10] Macrocycles endow group 4 metals with many properties distinct from those of the more traditional cyclopentadienyl ancillary ligands.[11−13] In our work with group 4 organometallic complexes of the tetraazamacrocyclic tropocoronand ligand {TC-*n,m*}²⁻, several unusual reactions with extrinsic substrates were encountered, including the tendency to insert carbon monoxide into both metal−alkyl bonds of [M(TC-n,m)R₂] complexes forming η²-ketone species.[14]

H₂(TC-n,m)
Tropocoronand
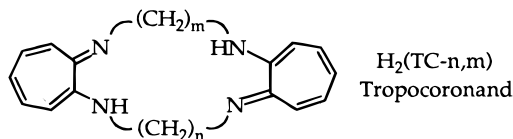
Unless subjected to forcing conditions, [Cp₂MR₂] (M = Zr, Hf) typically insert CO into a single metal−carbon bond.[15,16] The relatively electron-rich tropocoronand ligands alter the electrophilicity at the metal center,

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.
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affecting the reactivity. In comparison to metallocenes, the enhanced carbenoid character of the acyl group formed upon insertion of CO into the first M−C bond of a [M(TC-*n,m*)R$_2$] complex favors migration of the second alkyl substituent to afford an η^2-ketone. These complexes further react with extrinsic substrates, among them enones, ketones, azides, isocyanides, isocyanates, and diazamethanes, incorporating CO into a wide variety of fragments.

In the present article, we describe our studies with the isoelectronic substrate R−N≡C, which further exemplify the ability of organometallic group 4 tropocoronand complexes to undergo migratory insertion reactions. In accord with the reactivity trends previously observed with carbon monoxide, isocyanides promote the migration of alkyl or aryl ligands affording η^2-imine, η^2-iminoacyl, and μ-imido products as well as a new metallacycle incorporating an iminoacyl functionality. Although insertion and coupling reactions involving isocyanides have been well-studied,[17,18] the tropocoronand complexes induce transformations by what appear to be uncommon reaction pathways. The ready availability of substituted alkyl and aryl isocyanides facilitates elaboration of this chemistry, providing methodology for the construction of sophisticated molecules from simple, readily available starting materials.

Experimental Section

Preparation of Compounds. The complexes [M(TC-3,*n*)-(CH$_2$Ph)$_2$] (M = Zr(IV), Hf(IV); *n* = 3, 5) were prepared as previously described.[19] All operations, excluding ligand preparations, were conducted under a pure dinitrogen or argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried according to established protocols and degassed prior to use. Unless otherwise specified, reagents were obtained from commercial suppliers and thoroughly degassed and dried before use. ^{1}H NMR spectra were recorded on a Bruker AM-250 and ^{13}C{^{1}H} NMR spectra on a Varian Unity 300. Due to the limited solubility of the complexes in the solvents used, data were collected at room temperature. Chemical shifts are referenced with respect to the residual solvent peak. FTIR spectra were recorded on a BioRad FTS-135 FTIR spectrometer. All compounds were characterized by crystallographic chemical analysis (CCA), and elemental analyses were obtained on representative species. Several samples sent for elemental analysis contained solvent molecules in the crystal lattice, but the limited thermal stability of the complexes precluded heating them under vacuum.

[Hf(TC-3,5){η^2-(Cy)N=C(CH$_2$Ph)}$_2$] (1). Upon addition of 34.4 μL (0.277 mmol) of cyclohexyl isocyanide, an orange solution of 47.0 mg (0.069 mmol) of [Hf(TC-3,5)(CH$_2$Ph)$_2$] in 1 mL of dichloromethane at −30 °C rapidly turned dark red-orange. The solution was warmed to room temperature and filtered, and several volume equivalents of ether were diffused into the reaction mixture at −30 °C. After 72 h, the resulting orange-yellow crystalline mass was collected, washed with ether, and dried to afford 17 mg (27%) of product. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.30 (m, 8H), 7.12 (m, 2H), 6.83 (m, 4H), 6.30 (d, 2H), 6.00 (m, 4H), 4.83 (m, 1H), 4.52 (m, 1H), 4.13 (m, 2H), 3.93 (m, 3H), 3.73 (m, 1H), 3.47 (m, br, 5H), 2.99 (m, 2H), 2.31 (m, H), 1.76 (m, 5H), 1.50 (m, br, 6H), 1.21 (m, br, 6H). Although the material decomposes over the course of a few hours at room temperature in dichloromethane, a resonance

at δ 255.01, consistent with an η^2-iminoacyl ligand, was detected in the ^{13}C{^{1}H} NMR spectrum. IR (KBr, cm^{-1}): 3024 w, 2924 s, 2848 m, 1589 s, 1562 m, 1508 s, 1500 s, 1469 m, 1448 w, 1432 m, 1425 w, 1414 w, 1388 m, 1359 w, 1322 w, 1263 m, 1226 w, 1203 w, 1081 w, 1020 m, 975 w, 930 w, 888 w, 837 w, 816 w, 747 m, 713 m, 695 m, 542 w, 466 w, 442 vw, 428 vw. Samples sent for elemental analysis consistently analyzed low in carbon, possibly due to gradual decomposition at room temperature.[19]

[Hf(TC-3,5){η^2-(*n*-Bu)N=C(CH$_2$Ph)}$_2$] (2). As described above for **1**, a dichloromethane solution containing 30 mg (0.042 mmol) of [Hf(TC-3,5)(CH$_2$Ph)$_2$] was treated with 17.7 μL (0.170 mmol) of *n*-butyl isocyanide to afford 6 mg (16%) of crystalline product. Owing to the extreme thermal sensitivity and low yield of the material, the complex was characterized only by CCA.

[Hf(TC-3,3){η^2-(Cy)N=C(CH$_2$Ph)}$_2$] (3). Following the procedure outlined above for **1**, small red crystals of **3** were manually separated from the reaction mixture and characterized by CCA. The ^{1}H NMR spectrum of the reaction mixture was complicated by the presence of multiple products, and all attempts to optimize the synthesis of **3** were unsuccessful.

[(TC-3,3)ZrN(Ar)C(CH$_2$Ph)=C(CH$_2$Ph)N(Ar)] (4). At room temperature, a rapidly stirred solution of 40 mg (0.068 mmol) of [Zr(TC-3,3)(CH$_2$Ph)$_2$] in 1.5 mL of dichloromethane was treated with 50 mg (0.381 mmol) of solid 2,6-dimethylphenyl isocyanide in one portion. The color of the mixture immediately turned dark brown, and after 15 min the solution was filtered through Celite. Over the course of several days, ether was diffused into the filtrate at −30 °C, yielding dark red-brown platelike crystals. The material was collected from the reaction mixture, washed with ether and pentane, and dried to afford 27 mg (47%) of product. ^{1}H NMR (CD$_2$Cl$_2$): 7.08 (m, 6H), 6.86 (m, 8H), 6.50 (m, 4H), 6.42 (m, 4H), 6.26 (d, 4H), 3.77 (m, 4H), 3.26 (s, 4H), 3.02 (t, 4H), 2.82 (m, 2H), 2.34 (m, 2H), 1.86 (s, 12H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 163.11, 152.71, 143.96, 134.75, 134.60, 134.43, 129.35, 127.98, 127.12, 125.12, 125.30, 122.04, 120.66, 115.43, 113.83, 51.78, 35.68, 19.18. IR (KBr, cm^{-1}): 3022 w, 2997 w, 2927 m, 2844 w, 1637 w, 1588 s, 1506 s, 1471 m, 1451 w, 1437 m, 1416 m, 1387 w 1378 m, 1363 m, 1344 w, 1273 m, 1230 m, 1212 w, 1196 w, 1186 w, 1140 w, 1101 m, 1088 w, 1033 m, 994 m, 948 w, 887 m, 872 w, 852 w, 834 w, 754 m, 722 s, 696 m, 475 m. CCA revealed single crystals containing one dichloromethane molecule per three molecules of **4**. Analytical data indicated only partial removal of the solvate in vacuo. Anal. Calcd for C$_{52}$H$_{54}$N$_6$-Zr·^{1}/$_6$CH$_2$Cl$_2$ (C$_{52.167}$H$_{54.33}$N$_6$Cl$_{0.33}$Zr): C, 72.15; H, 6.31; N, 9.68. Found: C, 72.32; H, 6.51; N, 9.68.

[(TC-3,3)HfN(Ar)C(CH$_2$Ph)=C(CH$_2$Ph)N(Ar)] (5). Following the procedure outlined for the preparation of **4**, a portion of 50 mg (0.381 mmol) of solid 2,6-dimethylphenyl isocyanide was added to 40 mg (0.059 mmol) of [Hf(TC-3,3)-(CH$_2$Ph)$_2$] in dichloromethane. Slow diffusion of ether into the saturated solution yielded a mixture of small red and dark red-brown crystals. The crude material was redissolved in toluene and filtered, and several volume equivalents of pentane were diffused into the filtrate at −30 °C. Although the product was still contaminated with a small amount of the red crystalline material, the large dark red-brown crystals were collected manually and characterized by CCA.

[(TC-3,3)ZrN(Ar)C(CH$_2$Ph)$_2$C(=NAr)] (6). Over the course of 15 min, 15.7 mg (0.120 mmol) of solid 2,6-dimethylphenyl isocyanide was slowly added in small portions to a rapidly stirred solution of 35 mg (0.059 mmol) of [Zr(TC-3,3)(CH$_2$Ph)$_2$] in 1.5 mL of dichloromethane at −30 °C. After the mixture was warmed to room temperature, the dark red solution was filtered through Celite and several volume equivalents of ether were slowly diffused into the filtrate at −30 °C, producing large, irregularly shaped red crystals. The crystals were collected, washed with ether, and dried to afford 17 mg (34%)

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of product. ^{1}H NMR (CD$_2$Cl$_2$): 7.12 (t, 4H), 6.78 (m, 13H), 6.56 (m, 2H), 6.47 (m, 6H), 6.28 (t, 1H), 3.63 (m, 2H), 3.42 (m, 6H), 3.14 (m, 6H), 2.25 (s, 6H), 2.11 (m, 2H), 2.00 (s, 6H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 163.58, 154.99, 153.39, 141.52, 136.54, 135.89, 131.08, 128.81, 127.83, 127.31, 126.18, 124.78, 123.06, 122.21, 121.11, 114.79, 88.71, 51.37, 45.63, 27.02, 21.89, 19.92. IR (KBr, cm^{-1}): 3055 w, 1999 w, 2918 w, 2878 m, 1592 s, 1574 m, 1509 s, 1471 m, 1449 m, 1431 w, 1418 m, 1395 m, 1367 w, 1340 m, 1275 m, 1230 s, 1206 w, 1190 m, 1138 m, 1105 m, 1091 w, 1032 w, 993 m, 979 w, 942 m, 909 w, 882 m, 859 w, 848 w, 836 w, 824 w, 778 w, 756 w, 733 s, 745 w, 707 w, 694 m, 641 w, 586 w, 529 w, 481 s, 474 m. From the structural analysis as well as ^{1}H NMR spectra, single crystals were observed to contain a dichloromethane molecule. Analytical data indicated the solvate molecule to be removed only partially in vacuo. Anal. Calcd for C$_{52}$H$_{54}$N$_6$Zr·0.5CH$_2$Cl$_2$ (C$_{52.5}$H$_{55}$N$_6$ClZr): C, 70.32; H, 6.18; N, 9.37. Found: C, 70.84; H, 6.17; N, 9.35.

[(TC-3,3)HfN(Ar)C(CH$_2$Ph)$_2$C(=NAr)] (7). By utilizing a procedure similar to the one outlined above for **6**, 14.4 mg (0.110 mmol) of 2,6-dimethylphenyl isocyanide was added to a slurry of 35 mg (0.052 mmol) of [Hf(TC-3,3)(CH$_2$Ph)$_2$] in 1 mL of toluene at −30 °C. When the mixture was warmed to room temperature, the solution became bright red and homogenous, and after an additional 15 min, a brick-red precipitate deposited from the reaction mixture. The solid was collected by filtration, washed with ether and pentane, and dried to afford 18 mg (37%) of crude product. Large bright-red crystals of **7** were obtained after recrystallization from dichloromethane/ether. ^{1}H NMR (CD$_2$Cl$_2$): 7.15 (d of t, 4H), 6.87 (t, 11H), 6.82 (m, 2H), 6.60 (t, 2H), 6.46 (m, 6H), 6.24 (t, 1H), 3.61 (m, 2H), 3.52 (m, 6H), 3.24 (m, 6H), 2.24 (s, 6H), 2.03 (m, br, 2H), 1.98 (s, 6H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 163.77, 155.71, 153.51, 141.65, 137.43, 136.00, 131.05, 128.82, 127.82, 127.29, 125.96, 124.73, 123.06, 122.41, 121.05, 115.43, 87.61, 51.49, 45.94, 26.92, 21.81, 19.89. IR (KBr, cm^{-1}): 3059 w, 3018 w, 2918 m, 2882 w, 2843 w, 1592 s, 1577 m, 1510 s, 1472 m, 1451 w, 1431 m, 1421 m, 1396 m, 1363 w, 1340 m, 1278 m, 1231 s, 1208 w, 1191 w, 1140 w, 1109 m, 1034 w, 998 m, 945 w, 886 m, 759 w, 733 m, 694 w, 477 m.

[(TC-3,5)HfN(Ar)C(CH$_2$Ph)$_2$C(=NAr)] (8). Following the procedure outlined above for the preparation of **6**, the product was isolated in 32% yield. Single crystals were obtained from dichloromethane/ether solutions. ^{1}H NMR (CD$_2$Cl$_2$): 7.18 (m, 4H), 6.83 (m, 12H), 6.60 (m, 4H), 6.54 (m, 3H), 6.34 (m, 1H), 4.21 (m, 2H), 3.60 (m, 2H), 3.41 (m, 8H), 3.01 (m, 2H), 2.12 (s, 6H), 2.08 (m, 2H), 1.85 (s, 6H), 1.29 (m, 2H), 0.93 (m, 2H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 164.89, 164.78, 155.15, 153.39, 141.81, 137.58, 135.91, 135.74, 131.19, 128.68, 127.69, 127.40, 125.80, 124.81, 123.38, 122.51, 120.54, 115.88, 84.51, 52.72, 47.05, 45.93, 28.31, 27.80, 21.57, 19.77, 18.04. IR (KBr, cm^{-1}): 3053 w, 2923 m, 2852 w, 1594 s, 1577 m, 1508 s, 1470 m, 1447 w, 1423 m, 1392 w, 1360 w, 1345 w, 1334 w, 1314 m, 1279 m, 1245 m, 1227 m, 1191 m, 1138 w, 1105 m, 1025 m, 978 w, 938 w, 884 m, 860 w, 846 w, 760 w, 730 m, 716 w, 701 m, 586 w, 471 m.

[(TC-3,3)HfN(Ar)C(CH$_2$Ph)$_2$] (9). A rapidly stirred slurry of 35 mg (0.052 mmol) of [Hf(TC-3,3)(CH$_2$Ph)$_2$] in 1 mL of toluene at −30 °C was treated with 6.6 mg (0.050 mmol) of 2,6-dimethylphenyl isocyanide in several small portions over the course of several minutes. After the addition of isocyanide was complete, the dark red solution was warmed to room temperature and filtered and pentane was slowly diffused into the filtrate over 72 h yielding small, red crystals of **7** in addition to large blocklike crystals of **9**. Single crystals of **9** were manually separated from the mixture and characterized by CCA.

{[Zr(TC-3,3)]$_2$(μ-NAr)$_2$} (10). In a procedure identical to the one described for **9**, a 7.2 mg (0.055 mmol) portion of 2,6-dimethylphenyl isocyanide was added to a slurry of 35 mg

(0.059 mmol) of [Zr(TC-3,3)(CH$_2$Ph)$_2$] in 1.5 mL of toluene at −30 °C. After the mixture was warmed to room temperature, the dark red solution was filtered through Celite and the solution was cooled to −30 °C. Over the course of 24 h, several volume equivalents of ether were diffused into the filtrate, producing a color change to green brown and depositing long, platelike light green-brown crystals. The solid was collected, washed with ether, and dried to afford 13 mg (42%) of product. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.90 (t, 8H), 6.49 (d, 4H), 6.28 (t, 4H), 6.16 (m, 10H), 3.55 (m, 8H), 3.29 (m, 8H), 2.14 (m, 4H), 1.94 (s, 12H), 1.78 (m, 4H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 163.13, 160.60, 134.67, 127.50, 125.11, 118.87, 116.65, 112.78, 50.36, 28.50, 19.89. IR (KBr, cm^{-1}): 2924 m, 2848 m, 1590 s, 1567 m, 1507 s, 1471 w, 1452 w, 1421 m, 1399 w, 1375 m, 1344 w, 1332 w, 1271 m, 1229 s, 1199 s, 1134 w, 1102 m, 1078 w, 1026 w, 992 m, 953 w, 925 w, 887 w, 855 m, 833 w, 817 m, 746 m, 725 s, 694 w, 579 s, 504 m, 463 s. Although ^{1}H NMR spectroscopy, CCA, as well as visual inspection of the crystalline material confirmed the identity of the material, compound **10** consistently analyzed with both low nitrogen and carbon content. Anal. Calcd for C$_{56}$H$_{62}$N$_{10}$Zr$_2$: C, 63.60; H, 5.91; N, 13.24. Found: C, 62.43; H, 5.70; N, 11.41. In an alternative procedure, a mixture of 9.06 μL (0.073 mmol) of 2,6-dimethylaniline and 43 mg (0.073 mmol) of [Zr(TC-3,3)(CH$_2$Ph)$_2$] in 2 mL of dichloromethane was stirred at room temperature for 8 h. The brown solution was filtered, and ether was slowly diffused into the filtrate at −30 °C yielding 22 mg (57%) green-brown crystals of **10**. A unit cell determination as well as a ^{1}H NMR spectrum confirmed the identity of the material.

[M(TC-3,3)Ph$_2$] (M = Zr (11), Hf). A slurry of 276.5 mg (0.487 mmol) of [Hf(TC-3,3)Cl$_2$] in 10 mL of toluene at −30 °C was treated with 0.974 mL of a 1.0 M solution of PhMgBr in THF. The mixture was allowed to warm to room temperature, and after several minutes, 5 mL of tetrahydrofuran and 3 mL of dioxane were added. After an additional 10 min of stirring, the solution was filtered through Celite and the filtrate was evaporated in vacuo. The orange-red residue was redissolved in dichloromethane, filtered through Celite, and evaporated to dryness. The crude product was collected, washed with ether and pentane, and dried to afford 302 mg (62%) of [Hf-(TC-3,3)Ph$_2$]. Recrystallization from a dichloromethane/ether mixture yielded long red needle-like crystals. ^{1}H NMR (CD$_2$-Cl$_2$): δ 7.40 (t, 4H), 7.19 (d, 4H), 6.95 (m, 8H), 6.77 (m, 4H), 3.97 (m, 8H), 2.45 (m, 2H), 1.78 (m, 2H). From the structural analysis, single crystals of [Hf(TC-3,3)Ph$_2$] were found to contain a dichloromethane molecule, and elemental analysis indicated the solvate molecule was only partially removed in vacuo. Anal. Calcd for C$_{32}$H$_{32}$N$_4$Hf·0.5CH$_2$Cl$_2$ (C$_{32.5}$H$_{33}$N$_4$-HfCl): C, 56.28; H, 4.80; N, 8.08. Found: C, 56.66; H, 5.15; N, 8.03. Following an analogous procedure, [Zr(TC-3,3)Ph$_2$] was isolated in 53−62% yield. [Zr(TC-3,3)Ph$_2$] ^{1}H NMR (CD$_2$-Cl$_2$): δ 7.30 (t, 4H), 7.17 (m, 4H), 6.88 (m, 10H), 6.69 (t, 2H), 3.99 (m, 4H), 3.77 (m, 4H), 2.58 (m, 2H), 2.01 (m, 2H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 194.65, 163.25, 135.93, 134.22, 126.74, 124.94, 122.07, 114.31, 51.24.

[(TC-3,3)ZrN(Cy)C(Ph)$_2$] (12). At −30 °C, the addition of 4.6 μL (0.037 mmol) of cyclohexyl isocyanide to a solution of 21 mg (0.037 mmol) of **11** in 1 mL of toluene induced an immediate color change. After the mixture was warmed to room temperature, the dark brown solution was filtered through Celite and several volume equivalents of pentane were diffused into the filtrate over 72 h, yielding red-brown crystals. The filtrate was decanted away from the material, and after pentane and ether washings, 17 mg (68%) of product was isolated. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.09 (m, 8H), 6.90 (m, 4H), 6.51 (m, 6H), 6.36 (t of t, 2H), 3.72 (d of t, 4H), 3.09 (t, 4H), 2.78 (m, br, 3H), 2.15 (m, 2H), 1.48 (m, br, 3H), 1.22 (m, 2H), 1.02 (m, br, 3H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 164.26, 145.01, 135.53, 129.13, 122.58, 120.42, 119.23, 114.15, 50.81, 37.41, 27.20, 26.90, 26.77. IR (KBr, cm^{-1}): 2921 m, 2849 w, 1589 s, 1507 s, 1472 m, 1428 m, 1415 m, 1388 m, 1349 w, 1271 m, 1229 m,

1137 w, 1100 w, 1029 w, 995 w, 939 w, 886 w, 742 w, 723 m, 694 w, 476 m. Single crystals of compound **12** contain one toluene molecule per two Zr complexes, and analytical data were consistent with partial loss of this solvate under vacuo. Anal. Calcd for $C_{39}H_{43}N_5Zr \cdot \frac{1}{4}C_7H_8$ ($C_{40.75}H_{45}N_5Zr$): C, 70.32; H, 6.52; N, 10.06. Found: C, 69.80; H, 6.29; N, 9.56.

[(TC-3,3)M̄N(Ar)C̄(Ph)₂] (M = Zr (13), Hf). Compound **13** and its Hf analog were prepared following identical procedures. In a typical reaction, a 5.5 mg (0.042 mmol) portion of solid 2,6-dimethylphenyl isocyanide was added to a rapidly stirred solution of 23.5 mg (0.042 mmol) of **11** in 1.5 mL of dichloromethane. After 30 min, the dark red-brown solution was filtered and the filtrate was cooled to −30 °C. Over the course of several days, ether was slowly diffused into the reaction mixture, resulting in the formation of several feathery crystalline masses. The solid was collected, washed with pentane, and dried to afford 15 mg (52%) of product. ¹H NMR (CD₂Cl₂) for **13**: 7.08 (m, 8H), 6.92 (t, 4H), 6.69 (d, 2H), 6.54 (m, 6H), 6.44 (t, 1H), 6.37 (t of t, 2H), 3.65 (d of t, 4H), 3.14 (t of d, 4H), 2.44 (m, 2H), 2.06 (m, 2H), 2.01 (s, 6H). ¹³C{¹H} NMR (CD₂Cl₂): δ 163.94, 142.66, 135.83, 129.63, 129.40, 122.39, 120.83, 120.21, 119.44, 114.63, 51.08, 25.96, 25.54. IR (KBr, cm⁻¹): 3047 w, 2918 w, 2872 m, 2826 w, 1589 s, 1507 s, 1471 m, 1429 m, 1416 m, 1387 m, 1346 w, 1271 m, 1230 s, 1172 w, 1137 w, 1101 w, 1030 m, 994 m, 943 w, 886 w, 849 w, 745 m, 725 m, 695 w, 611 w, 477 m. [(TC-3,3)H̄fN-(Ar)C̄(Ph)₂] ¹H NMR (CD₂Cl₂): δ 7.18 (m, 8H), 6.84 (t, 4H), 6.72 (d, 2H), 6.61 (m, 6H), 6.41 (d, 1H), 6.30 (m, 2H), 3.70 (d of t, 4H), 3.25 (t of d, 4H), 2.85 (m, 2H), 2.09 (m, 2H), 2.04 (s, 6H). Anal. Calcd for $C_{41}H_{41}N_5Hf$: C, 62.95; H, 5.28; N, 8.95. Found: C, 62.64; H, 5.37; N, 8.51.

Collection and Reduction of X-ray Data. Crystals were typically obtained by vapor diffusion of ether or pentane into a saturated solution of the complexes at −30 °C as described above. Single crystals were coated with Paratone-N oil, selected under a microscope, attached to a glass fiber, and transferred rapidly to the −85 °C cold stream of a Siemens CCD X-ray diffraction system controlled by a Pentium-based PC running the SMART software package.[20] The program SADABS[21] was used to correct the data for absorption and decay. Data were collected by following standard procedures reported in detail elsewhere.[22]

The structures were solved by direct methods using SIR-92[23] or SHELXS and refined by full-matrix least-squares and Fourier techniques with the SHELXTL-PLUS program package.[24] Space groups were determined from an examination of the systematic absences in the data and confirmed by the successful solution and refinement of the structures. Except in cases where disorder was apparent, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were normally assigned idealized locations and given a thermal parameter equal to 1.2 times that of the carbon atom to which it was attached, unless otherwise noted.

The asymmetric units of compounds **1**, **2**, **6**, and **7** all contain one complete metal complex, but in **3**, the Hf as well as a dichloromethane molecule lie on 2-fold symmetry positions. The structure of compound **4** contains one metal complex in addition to one-half of both a metal species and a dichloromethane solvate molecule. On the 2-fold symmetry element, the metal complex exhibits two orientations for the Ar and phenyl groups. The site occupancy factors for the phenyl group

(20) *SMART: Version 4.0*; Siemens Industrial Automation, Inc.: Madison, WI, 1994.
(21) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.
(22) Feig, A. L.; Bautista, M. T.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 6892−6898.
(23) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovozza, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389−393.
(24) *SHELXTL: Structure Analysis Program*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

Table 1. Crystallographic and Selected Metric Parameters for Products from the Reaction of [Hf(TC-3,*n*)(CH₂Ph)₂] with Cyclohexyl Isocyanide {1 (*n* = 5), 3 (*n* = 3)} and *n*-Butyl Isocyanide {2 (*n* = 5)}

compound	1	2	3·CH₂Cl₂
formula	$C_{50}H_{62}HfN_6$	$C_{46}H_{58}HfN_6$	$C_{49}H_{60}Cl_2HfN_6$
fw	925.55	873.47	982.42
cryst system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	10.3461(4)	10.5664(2)	14.5490(4)
b (Å)	14.0599(5)	13.3583(2)	23.2915(5)
c (Å)	15.6630(6)	15.0730(1)	13.5525(4)
α (deg)	103.386(1)	98.844(1)	
β (deg)	95.368(1)	103.481(1)	101.241(1)
γ (deg)	102.411(1)	94.316(1)	
V (Å³)	2139.96(14)	2030.61(5)	4504.4(2)
Z	2	2	4
T, K	188(2)	188(2)	188(2)
R (%)[a]	3.52	3.62	3.76
wR^2 (%)[b]	7.00	6.38	7.17
Hf−N$_{trop}$ (average)	2.28(1)	2.28(1)	2.28(5)
Hf−N(5/3)	2.206(5)	2.201(5)	2.201(4)
Hf−N(6)	2.217(4)	2.215(4)	
Hf−C$_{iminoacyl}$	2.268(5),2.269(6)	2.252(6),2.263(6)	2.264(5)
(C−N)$_{iminoacyl}$	1.272(7),1.275(7)	1.291(6),1.292(6)	1.275(7)

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

positions were fixed at 0.5, while the factors for the Ar moiety refined to values of 0.53 and 0.47, respectively. Crystals of **5** contain two symmetry inequivalent complexes together with a pentane solvate. Since the carbon atoms exhibited a high degree of thermal motion, the pentane was refined isotropically and hydrogen atoms were omitted from this molecule. In the unit cell of **8**, a highly disordered dichloromethane molecule crystallizes near a mirror plane with an overall site occupancy of 0.5. The disorder was modeled with several partially occupied carbon and chlorine atoms. After the refinement had converged, a large difference Fourier peak (1.4 e⁻/Å³) was located on the mirror-plane midway between two areas of disordered solvent. The asymmetric unit of **9** contains a metal complex as well as a toluene molecule disordered across a 2-fold symmetry position. The toluene atoms were refined isotropically, and hydrogen atoms were not included in the refinement of this molecule. In the structure of **10**, both the dinuclear complex and a toluene solvate molecule are well-ordered on general symmetry positions. The Zr metal center resides on a 2-fold symmetry position in crystals of **11**, which also contain an additional dichloromethane. The solvate molecules were refined anisotropically without inclusion of hydrogen atoms. Compound **12** contained a toluene solvate molecule besides the two symmetry inequivalent metal complexes in the asymmetric unit. One of the two dichloromethane molecules in **13** exhibited two orientations for one chlorine atom. The two positions were refined with site occupancy factors of 0.76 and 0.24, respectively. All of the solvate atoms were refined anisotropically, but hydrogen atoms were not included on the disordered molecule. In the final stages of refinement, a spurious difference Fourier peak (1.55 e⁻/Å³) was located on a 3-fold symmetry position. Even at partial occupancy on this position, a carbon atom refined to unreasonably high thermal parameter and no further attempt was made to assign an atom to this electron density. Crystallographic data and selected metrical parameters are reported in Tables 1−5, and additional experimental details are available as Supporting Information.

Results and Discussion

Bis(η²-iminoacyl) Complexes. Isocyanides typically insert into group 4 metal−carbon bonds producing η²-iminoacyl functionalities.[17] Aryloxide, metallocene, and tetraazamacrocylic[8] complexes all react similarly,

Table 2. Crystallographic and Selected Metric[a] Parameters of Products of [(TC-3,3)-

$\overline{\text{MN(Ar)C(CH}_2\text{Ph)C(CH}_2\text{)N(Ar)]}}$ **(M = Zr (4), Hf (5))**

compound	$4\cdot{}^1/_3\text{CH}_2\text{Cl}_2$	$5\cdot{}^1/_2\text{C}_5\text{H}_{12}$
formula	$\text{C}_{52.33}\text{H}_{54.67}\text{Cl}_{0.67}\text{N}_6\text{Zr}$	$\text{C}_{54.5}\text{H}_{60}\text{HfN}_6$
fw	882.54	977.57
cryst system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$
a (Å)	32.2663(5)	12.2697(2)
b (Å)	17.3947(2)	17.7686(3)
c (Å)	26.0130(3)	44.5468(1)
β (deg)	115.644(1)	94.278(1)
V (Å^3)	13162.0(3)	9664.8(2)
Z	12	8
T, K	188	188
R (%)[b]	6.58	4.80
wR^2 (%)[c]	13.47	8.00
M(1)−N$_{trop}$ (average)	2.216(5)	2.198(3)
M(1)−N(5)	2.185(3)	2.155(3)
M(1)−N(6)	2.178(3)	2.170(3)
N(5)−C(29)	1.413(4)	1.412(5)
N(6)−C(37)	1.416(5)	1.405(5)
C(29)−C(37)	1.347(5)	1.363(6)

[a] Metric data from one of the complexes in the asymmetric unit. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3. Crystallographic and Selected Metric Parameters for [(TC-3,n)-

$\overline{\text{MN(Ar)C(CH}_2\text{Ph)}_2\text{C(=NAr)]}}$ **(n = 3, M = Zr (6), Hf**

(7); n = 5, M = Hf (8)) and [(TC-3,3)HfN(Ar)C-
(CH$_2$Ph)$_2$] (9)

compound	6	7	$8\cdot{}^1/_2\text{CH}_2\text{Cl}_2$	$9\cdot{}^1/_2\text{C}_7\text{H}_8$
formula	$\text{C}_{52}\text{H}_{54}\text{N}_6\text{Zr}$	$\text{C}_{52}\text{H}_{54}\text{HfN}_6$	$\text{C}_{54.5}\text{H}_{59}\text{ClHfN}_6$	$\text{C}_{46.5}\text{H}_{49}\text{HfN}_5$
fw	854.23	941.50	1012.02	856.40
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$Pbcn$	$C2/c$
a (Å)	15.0969(4)	15.0344(5)	32.412(2)	33.3770(5)
b (Å)	10.7570(3)	10.7267(4)	18.5853(12)	13.5048(3)
c (Å)	26.5236(7)	26.4832(9)	16.6215(11)	17.0047(3)
β (deg)	100.909(1)	101.139(1)		93.833(1)
V (Å^3)	4229.5(2)	4190.5(3)	10012.6(11)	7647.7(2)
Z	4	4	8	8
T, K	188(2)	188(2)	188(2)	188(2)
R (%)[a]	3.80	3.52	5.70	2.70
wR^2 (%)[b]	8.54	6.82	10.26	6.03
M−N$_{trop}$ (average)	2.21(3)	2.19(3)	2.20(5)	2.19(2)
M−N(5)	2.154(2)	2.137(4)	2.134(6)	2.020(3)
M−C	2.367(2)	2.336(5)	2.348(8)	2.260(4)
N(5)−C(29/C31)[c]	1.521(2)	1.527(6)	1.511(9)	1.486(5)
N(5)−M−C	58.27(7)	59.1(2)	59.8(2)	40.14(12)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] 6, 7, 9-C(29); 8-C(31).

Table 4. Crystallographic and Selected Metric Parameters for {[Zr(TC-3,3)]$_2$(μ-NAr)$_2$}

compound	$10\cdot\text{C}_7\text{H}_8$
formula	$\text{C}_{63}\text{H}_{70}\text{N}_{10}\text{Zr}_2$
fw	1149.73
cryst system	monoclinic
space group	$C2/c$
a (Å)	37.3596(5)
b (Å)	12.3296(3)
c (Å)	25.4789(6)
β (deg)	113.1210(1)
V (Å^3)	10793.6(4)
Z	8
T, K	188
R (%)[a]	4.11
wR^2 (%)[b]	10.41
Zr(1)−N$_{trop}$ (range, average)	2.180(2)−2.362(2), 2.27(9)
Zr(2)−N$_{trop}$ (range, average)	2.228(2)−2.243(2), 2.236(8)
Zr(1)−N(9),N(10)	2.110(2),2.099(2)
Zr(2)−N(9),N(10)	2.169(2),2.162(2)
Zr(1)−N(9),N(10)-Zr(2)	101.14(9),101.72(9)
N(9)−Zr(1),Zr(2)-N(10)	79.90(9),77.22(8)

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

Table 5. Crystallographic and Selected Metric Parameters for [Zr(TC-3,3)Ph$_2$] (11) and

$\overline{\text{[(TC-3,3)ZrN(R)C(Ph)}_2\text{]}}$ **(R = Cy (12), Ar (13))**

compound	$11\cdot2\text{CH}_2\text{Cl}_2$	$12\cdot{}^1/_2\text{C}_7\text{H}_8$	$13\cdot2\text{CH}_2\text{Cl}_2$
formula	$\text{C}_{34}\text{H}_{36}\text{Cl}_4\text{N}_4\text{Zr}$	$\text{C}_{42.5}\text{H}_{47}\text{N}_5\text{Zr}$	$\text{C}_{41}\text{H}_{47}\text{Cl}_4\text{N}_5\text{Zr}$
fw	733.69	719.07	842.86
cryst system	monoclinic	monoclinic	rhombohedral
space group	$C2/c$	$P2_1/n$	$R\bar{3}$
a (Å)	18.6816(2)	12.9863(1)	37.0719(13)
b (Å)	11.3684(2)	17.9911(4)	
c (Å)	16.1775(2)	30.4661(4)	15.8829(8)
β (deg)	107.856(1)	90.238(1)	
V (Å^3)	3270.27(8)	7118.0(2)	18903.8(13)
Z	4	8	18
T, K	188(2)	188(2)	188(2)
R (%)[a]	3.74	7.46	6.73
wR^2 (%)[b]	9.92	12.19	17.15
Zr(1)−N$_{trop}$ (average)	2.20(2)	2.21(2)	2.22(2)
Zr(1)−N(5)		2.033(5)	2.079(3)
Zr(1)−Ph	2.353(2)		
Zr(1)−C(21)		2.373(6)	2.396(4)
Zr(1)−C(22)		2.721(6)	2.645(4)
Zr(1)−C(23)			2.652(4)
N(5)−C(21)		1.451(8)	1.441(5)
Zr(1)−C(21)−C(22)		87.4(4)	83.6(2)
N(5)−M−C(21)		37.5(2)	36.71(12)

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

although in some instances η^2-imine[25] and η^2-imino[26] complexes can be isolated. Following this trend, the tropocoronand complexes [M(TC-3,n)(CH$_2$Ph)$_2$] (M = Zr(IV)/Hf(IV); n = 3, 5) rapidly react at low temperature with alkyl isocyanides such as cyclohexyl and n-butyl isocyanide, primarily generating the bis(η^2-iminoacyl) compounds [M(TC-3,n){η^2-(R)N=C(CH$_2$Ph)}$_2$]. Several additional, unidentified species are present, as judged by ^{1}H and ^{13}C NMR spectra of the reaction mixtures, particularly with Zr and the smaller macrocycle TC-3,3. For example, the crude mixture from the reaction of [Zr(TC-3,3)(CH$_2$Ph)$_2$] and cyclohexyl isocyanide (CyNC)[27]

(25) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75−80.
(26) Valero, C.; Grehl, M.; Wingbermühle, D.; Kloppenburg, L.; Carpenetti, D.; Erker, G.; Petersen, J. L. *Organometallics* **1994**, *13*, 415−417.

exhibits resonances at 251.66 and 239.81 ppm in its ^{13}C NMR spectrum, consistent with the formation of two distinct compounds containing η^2-iminoacyl moieties. Attempts to optimize the formation of [M(TC-3,3){η^2-(R)N=C(CH$_2$Ph)}$_2$] (M = Zr, Hf; R = alkyl) were unsuccessful. Nevertheless, with the larger TC-3,5 macrocycle, favorable solubility properties permitted isolation of the predominant product, either in moderate yield for [Hf(TC-3,5){η^2-(Cy)N=C(CH$_2$Ph)}$_2$] (1) or in low yield for [Hf(TC-3,5){η^2-(n-Bu)N=C(CH$_2$Ph)}$_2$] (2). Single crystals of [Hf(TC-3,3){η^2-(Cy)N=C(CH$_2$Ph)}$_2$] (3) could also be obtained in some instances.

The structures of all three complexes are presented in Figure 1, and selected crystallographic information is contained in Table 1. The geometry of the iminoacyl groups is unremarkable and essentially indistinguishable from that in a related macrocyclic complex [Zr-(tmtaa){η^2-(t-Bu)N=C(CH$_2$Ph)}$_2$].[8,27] In this tmtaa com-
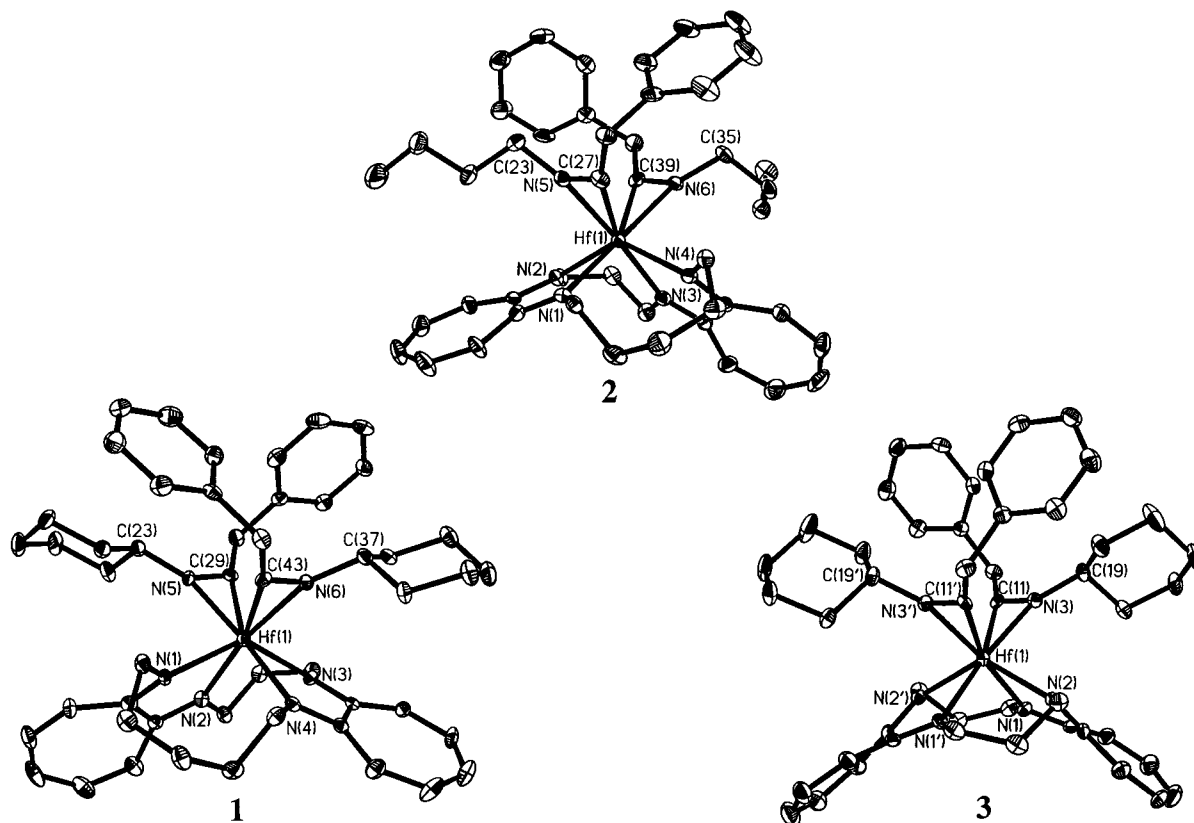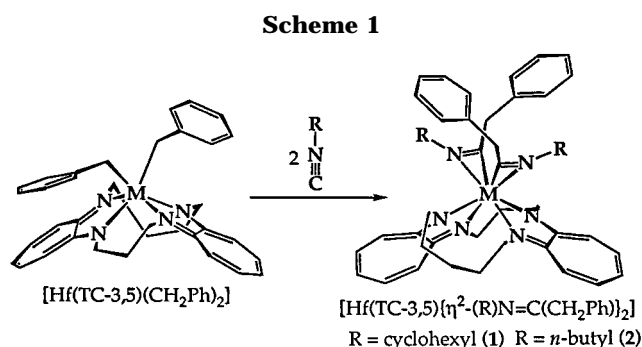
Figure 1. ORTEP diagrams of [Hf(TC-3,5){η^2-(Cy)N=C(CH$_2$Ph)}$_2$] (**1**), [Hf(TC-3,5){η^2-(*n*-Bu)N=C(CH$_2$Ph)}$_2$] (**2**), and [Hf(TC-3,3){η^2-(Cy)N=C(CH$_2$Ph)}$_2$] (**3**) showing 50% ellipsoids and atom-labeling scheme. Primed and unprimed atoms are related by a 2-fold symmetry operation. Selected distances and angles are contained in Table 1.

plex, the metal center is significantly displaced from the mean plane of this ligand and the average M–N distance has increased over that in the dibenzyl starting material by 0.13 Å, presumably due to severe steric congestion at the metal center. The average Hf–N tropocoronand distances in **1**–**3**, on the other hand, are only marginally larger than the average distance of 2.21(2) Å in the starting material, perhaps because the ligand can distort away from the η^2-iminoacyl ligands.

Although able to alleviate unfavorable intramolecular steric interactions, the enhanced flexibility of TC-3,5 makes the complexes less stable in solution. Over the course of several hours at room temperature, the central methylene linker chain carbon atom reacts with the metal center, a common decomposition pathway with larger tropocoronands and group 4 metal centers.[19] Although a characteristic η^2-iminoacyl resonance was detected at δ 255.01,[17] the insolubility of the product at low temperature precluded complete characterization by ^{13}C{^{1}H} NMR spectroscopy. Compound **1** exhibits a stretch at 1562 cm^{-1} in the infrared spectrum, well within the normal range for group 4 η^2-iminoacyls.[17]

Enediamido Complexes. In contrast to the reactivity of the alkyl isocyanides, addition of a large excess of 2,6-dimethylphenyl isocyanide (ArNC)[27] to solutions containing [M(TC-3,3)(CH$_2$Ph)$_2$] (M = Zr(IV)/Hf(IV)) rapidly yielded the new metallacyclic compounds [(TC-3,3)MN(Ar)C(CH$_2$Ph)=C(CH$_2$Ph)N(Ar)] (M = Zr (**4**), Hf (**5**)), (Scheme 1). Mild thermolysis of bis(η^2-iminoacyl) group 4 or 5 metal complexes sometimes induces in-

Scheme 1

tramolecular coupling and formation of enediamido ligands.[28,29] Lowering the energy of the π^*_{CN} orbital with electron-withdrawing substituents facilitates this transformation, and aryl-substituted isocyanides normally couple significantly more rapidly than alkyl isocyanides.[17] In comparison to complexes of other ligand systems, the relatively electron-rich metal center in [M(TC-3,3)(CH$_2$Ph)$_2$] may lower the energy of the π^*_{CN} orbitals even further, rendering the isolation of bis-(η^2-iminoacyl) complexes more difficult. With the judicious choice of ligands, however, stable bis(η^2-iminoacyl) compounds could be prepared with the TC-3,X macrocycle and CH$_2$SiMe$_3$ alkyl groups.[30] This result indi-

(27) Abbreviations used: tmtaa, tetramethyltetraazadibenzo[14]-annulene; CyNC, cyclohexyl isocyanide; ArNC, 2,6-dimethylphenyl isocyanide.

(28) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068–6076.
(29) Berg, F. J.; Petersen, J. L. *Tetrahedron* **1992**, *48*, 4749–4756.
(30) The reaction of [Hf(TC-3,X)(CH$_2$SiMe$_3$)$_2$] (X = xylyl) with 2,6-dimethylphenyl isocyanide affords the bis(iminoacyl) product [Hf(TC-3,X){η^2-(Ar)N=C(CH$_2$SiMe$_3$)}$_2$], as revealed by X-ray crystallography. $P2_1/c$, $Z = 4$, $a = 16.9878(8)$ Å, $b = 11.3387(5)$ Å, $c = 28.7841(13)$ Å, $\beta = 102.070(1)°$.

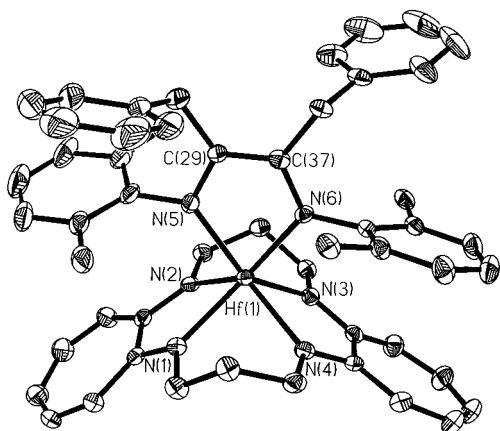**Figure 2.** ORTEP diagram of [(TC-3,3)HfN(Ar)C(CH$_2$-Ph)=C(CH$_2$Ph)N(Ar)] (**5**) showing 30% ellipsoids and the atom labeling scheme. Selected distances and angles are contained in Table 2.

cates that the coupling reaction (Scheme 1) is driven by electronic and not steric factors.

When two iminoacyl groups couple, the resulting ligand can adopt either the enediamido or diazadiene resonance forms depicted below. The structural data

Enediamido   Diazadiene
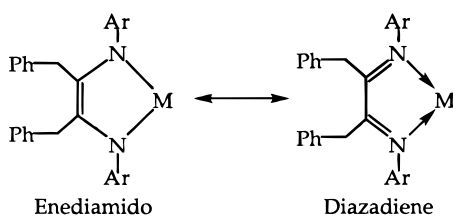
presented in Table 2 indicate that the metallacycles in **4** and **5** have essentially identical metric parameters which are consistent with the features of the enediamido form of the ligand. An ORTEP diagram of **5** is presented in Figure 2. The metal-nitrogen amido distances of 2.185(3) and 2.178(3) Å in compound **4** are typical of Zr−N single bonds and only marginally longer then the metal−nitrogen distances of 2.156(4) and 2.139(4) Å in the bis(amido) complex [Zr(TC-3,3)(NH-Ph-4-*t*-Bu)$_2$].[31] In addition, the C=C distance of 1.347(5) Å and the N−C distances of 1.413(4) and 1.416(5) Å deviate considerably from the respective values in free 1,4-diaza-1,3-butadiene[32] and are well within the normal ranges for double and single bonds, respectively.

Additional evidence for a C=C double bond in the enediamido ligand of **4** is a weak stretch at 1637 cm^{-1} in the infrared spectrum. This value is higher in frequency than those for similar zirconocene enediamido species, which range from 1535 to 1610 cm^{-1}.[33,34] Often, in the solid state structures of group 4 enediamido complexes, a significant fold develops at the angle between the N−Zr−N and N−C=C−N planes. The energy barrier for interconverting the two possible

folded conformations of these planes in solution, however, is generally low ($\Delta G^{\ddagger} < 20$ kcal/mol).[28,33,35] Molecular-orbital calculations and experimental studies on similar zirconocene enediolate species indicate the folding lowers the energy of the HOMO (π) orbital of the C=C bond, significantly enhancing the orbital overlap between the olefin and the electron-deficient metal center.[36] With enediamido complexes, the angle between the two planes can vary from 37.8° in [(OPh-2,6-*t*-Bu)$_2$ZrN(Ar)C(CH$_3$)=C(CH$_3$)N(Ar)][28] to anywhere from 35.7° to 52.1° in zirconocenes.[33,34] In contrast, the five-membered metallacycles in **4** and **5** are essentially planar, the dihedral angles in the two crystallographically independent metal complexes in **4** being 0.1° and 0.5°. Because there is no π-interaction with the metal center, the olefin stretching frequency in **4** increases by comparison to that of similar group 4 enediamido species. The absence of metal−olefin orbital overlap in **4** and **5** further emphasizes the decreased Lewis acidity of the metal center compared to complexes of other ligand systems.

η^2-Imines and Insertion Products. Although **4** can be prepared in moderate yield, the reaction mixtures often contained a second species, the insolubility of which complicated the preparations of pure **5**. At reduced temperature, slow addition of the solid ArNC to [M(TC-3,3)(CH$_2$Ph)$_2$] (M = Zr(IV)/Hf(IV)) enhanced the formation of these compounds. In nonpolar solvents, their insolubility allowed them to be isolated and characterized as the new metallacyclic species [(TC-3,3)-MN(Ar)C(CH$_2$Ph)$_2$C(=NAr)] (M = Zr (**6**), Hf (**7**)). The same synthetic strategy was used to prepare [(TC-3,5)-HfN(Ar)C(CH$_2$Ph)$_2$C(=NAr)] (**8**). These results can be rationalized by assuming that an equivalent of isocyanide first inserts into one metal−alkyl bond of [M(TC-3,*n*)(CH$_2$Ph)$_2$] (*n* = 3, 5), generating a mono(iminoacyl) intermediate. If addition of isocyanide is slow, the remaining benzyl ligand migrates to the iminoacyl group before a second equivalent can react. When the concentration of isocyanide is high, however, a second insertion involving an external isocyanide occurs before the alkyl group can migrate, producing the bis(imino-acyl) precursors to compounds **4** and **5** (Scheme 2). Analogous reactions of mono(iminoacyl) ligands can be induced either thermally[37] or with hydride transfer[38] in zirconocenes or through the addition of an external base to bis(aryloxy)titanium[25] complexes. The decreased electrophilic character of the metal in the tropocoronand complex allows an electron-deficient isocyanide ligand to induce this transformation. Attempts to prepare comparable products with alkyl isocyanides consistently afforded bis(iminoacyl) species. Further support for the mechanism depicted in Scheme 2 is the isolation of the complex [(TC-3,5)HfN(Ar)C(CH$_2$Ph)$_2$] (**9**) from mixtures containing **7**. This material is an intermediate in the formation of **7**, since insertion of a second aryl isocyanide ligand in a 1,1-fashion into **9** can produce

(31) Treatment of [Zr(TC-3,3)(CH$_2$Ph)$_2$] with 2 equiv of 4-*tert*-butylaniline affords [Zr(TC-3,3)(NH-Ph-4-*t*-Bu)$_2$]. The complex cystallizes together with one-half of a dme solvate molecule in the orthorhombic space group *Pbca* with $Z = 8$, $a = 23.4496(8)$ Å, $b = 13.3184(4)$ Å, $c = 25.0602(8)$ Å, $V = 7826.6(4)$ Å^3, R = 6.72%, and wR^2 = 15.21%.

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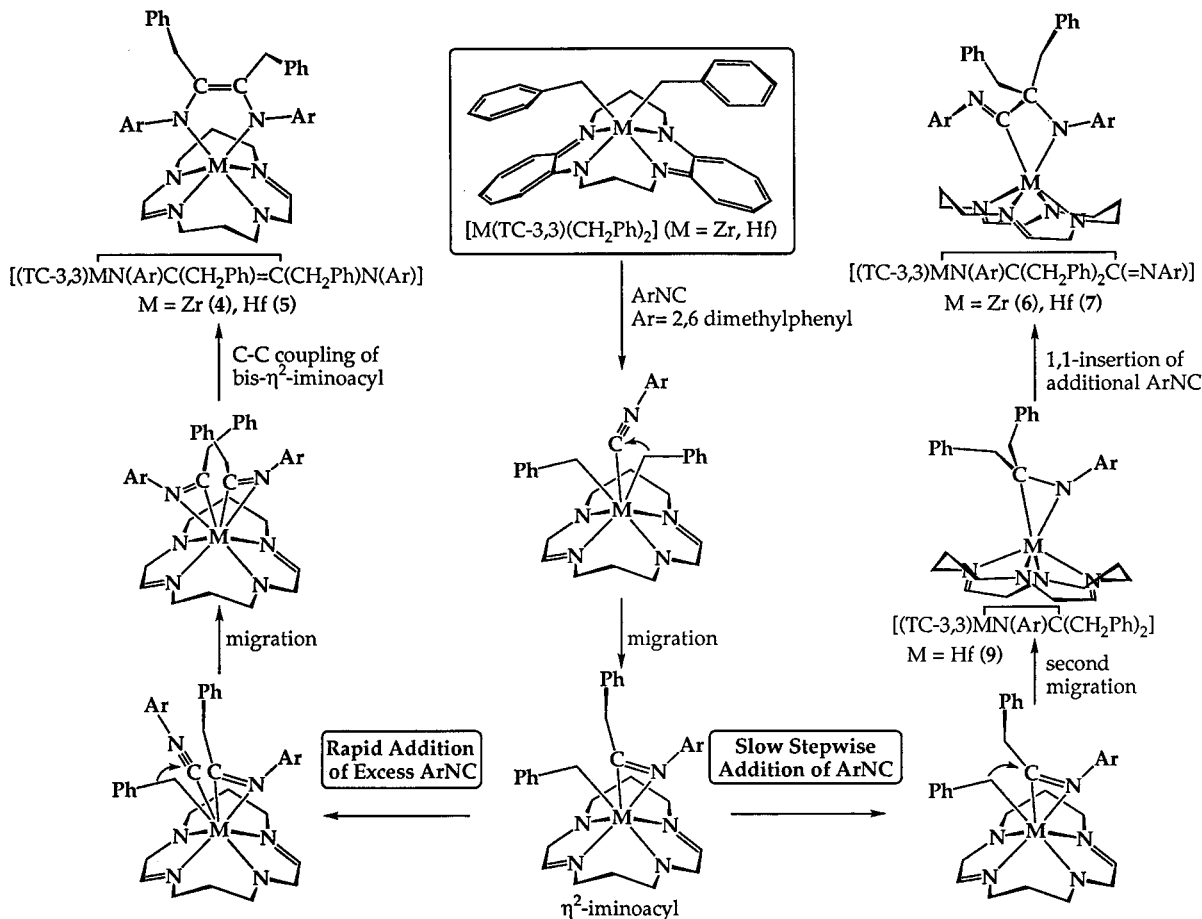
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Scheme 2

7. Zirconocene η^2-imine complexes are similarly susceptible to attack by external substrates, including ketones and nitriles, but in these systems 1,2-insertion reactions are more typical.[39-43]

The structures of **6** and **8** are presented in Figures 3 and 4; selected crystallographic information for **6**, **7**, and **8** is contained in Table 3. The geometric parameters of the metallacycles in all three complexes are essentially indistinguishable, with an iminoacyl group adopting an η^1-bonding mode, an uncommon motif in zirconocene complexes.[44] In compound **6**, the Zr–N distance of 2.154(2) Å and Zr–C distance of 2.367(2) Å are comparable to the Zr–O (2.194(1) Å) and Zr–C distances (2.374(1) Å) in the metalloxirane unit of a related dinuclear zirconocene species $[Cp_2\overline{ZrOCH_2C}(=NR)]_2$, which also contains an iminoacyl moiety.[45] In this dimer, the oxygen atom of the metalloxirane unit bridges two metal centers and stabilizes the electrophilic Zr atom. With the tropocoronand ligand, the relatively
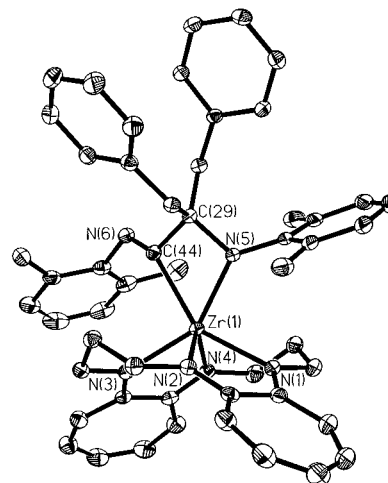
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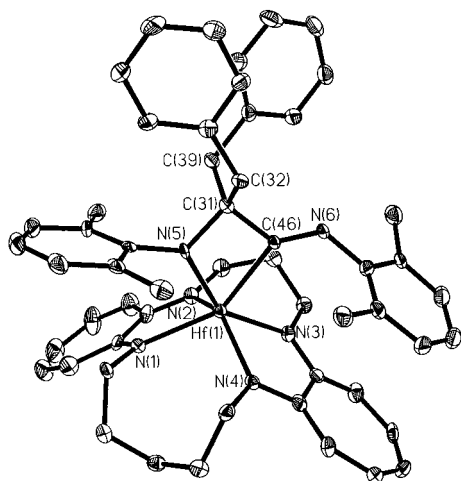

Figure 3. ORTEP diagram of $[(TC-3,3)\overline{ZrN(Ar)C(CH_2}$-$\overline{Ph)_2C}(=NAr)]$ (**6**) showing 30% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 3.

electron-rich metal center remains mononuclear while still preferring to adopt an η^1-binding mode. In the zirconocene complex, the iminoacyl carbon exhibits a resonance at δ 220.2 in the ^{13}C NMR spectrum, marginally upfield from the typical range for η^2-iminoacyl ligands. Despite repeated attempts, no signal was detectable in this region in the ^{13}C NMR spectrum of compounds **6**, **7**, or **8**, possibly owing to the slow decomposition of the complexes in the polar solvent media required to dissolve them. Nevertheless, a

Figure 4. ORTEP diagram of [(TC-3,5)HfN(Ar)C(CH$_2$-Ph)$_2$C(=NAr)] (**8**) showing 50% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 3.
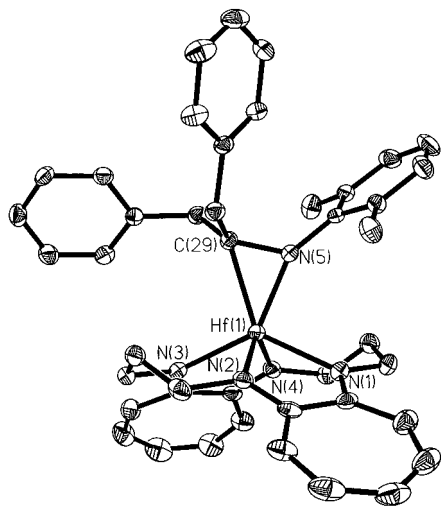

Figure 5. ORTEP diagram of [(TC-3,5)HfN(Ar)C(CH$_2$Ph)$_2$] (**9**) showing 50% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 3.

characteristic C=N stretch is evident in the infrared spectra at 1574 cm^{-1} in **6** and 1577 cm^{-1} in **7** and **8**. These values lie well within the typical range for η^2-iminoacyls but somewhat lower in energy then the iminoacyl group in [Cp$_2$ZrOCH$_2$C(=NR)]$_2$ (1596 cm^{-1}). Finally, comparison of the ^{13}C NMR spectra does reveal one resonance which differs perceptibly among the three complexes, ranging from δ 88.71 in **6** to δ 84.51 in **8**. We tentatively assign the resonance to the quarternary carbon atom of the M–N–C–C metallacycle.

The Hf–N and Hf–C distances of 2.020(3) and 2.260(4) Å, respectively in the structure of the η^2-imine complex **9** (Figure 5; Table 3) are noticeably shorter then the distances in compound **7**, but the mean Hf–tropocoronand nitrogen distance remains the same. Increasing the Hf–N$_{imine}$ distances while maintaining the N–C single bond distance of 1.486(5) Å would further strain an already acute N–Hf–C angle of 40.14(12)°, which perhaps explains this result. The geometric parameters of the metallacycle in **9** are virtually indistinguishable from those of the analogous
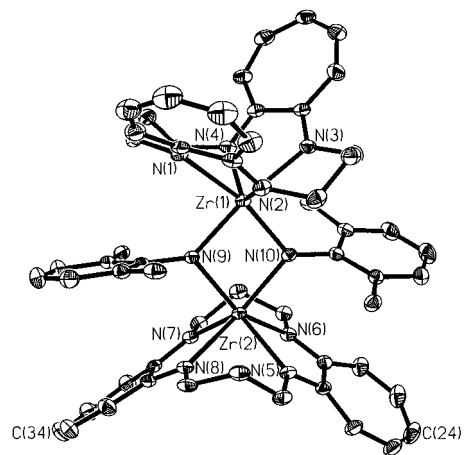
Figure 6. ORTEP diagram of {[Zr(TC-3,3)]$_2$(μ-NAr)$_2$} (**10**) showing 30% ellipsoids and atom-labeling scheme. Selected distances and angles are contained in Table 4.

metallacycle in the η^2-imine zirconocene complex [Cp$_2$-(THF)ZrC(Ph)N(SiMe$_3$)].[40] Once again reflecting the different donating ability of the ligands, the isolation of this zirconocene species requires the stabilizing influence of a THF ligand.
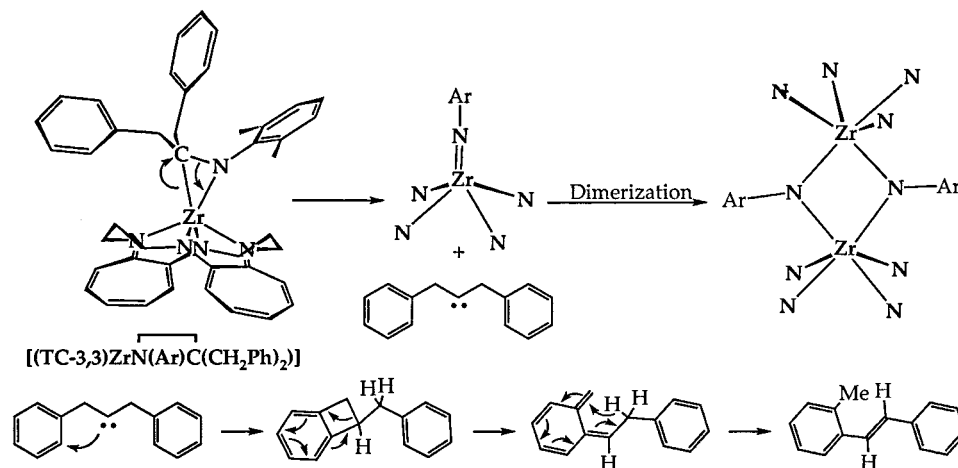
A Di(μ-imido) Complex. Much like the formation of **9**, [Zr(TC-3,3)(CH$_2$Ph)$_2$] reacts rapidly with 1 equiv of ArNC yielding a dark red-brown solution. Over the course of several hours at −30 °C, however, the color of the solution changes and green-brown crystals of the imido-bridged complex {[Zr(TC-3,3)]$_2$(μ-NAr)$_2$} (**10**, Figure 6) are obtained in moderate yield from these mixtures. Selected metrical parameters are contained in Table 4, from which the asymmetry in imido bridges can readily be identified. In particular, the Zr(1)–N$_{imido}$ distances of 2.099(2) and 2.110(2) Å are shorter than the Zr(2)–N$_{imido}$ distances, 2.162(2) and 2.169(2) Å. Accompanying the shorter distances to Zr(1) are two anomalously long Zr(1)-N tropocoronand bonds of 2.328(2) and 2.362(2) Å. In addition, the tropocoronand macrocycles are rotated by 59.0° from the eclipsed conformation, and the two phenylimido ligands are slightly canted away from the perpendicular to the plane defined by C(24)–Zr(2)–C34, the angles being 13.9° and 37.2°. The tropocoronand ligand bound to Zr(1) is significantly rotated with respect to the aryl imido ligands as well as the other macrocycle. Packing interactions in the crystal lattice may perhaps induce strain in the coordination sphere of Zr(1) with the concomitant increase in two Zr−N tropocoronand distances. The Zr(1)−N$_{imido}$ distances in **10** are indistinguishable from those in (Cp$_2$-Zr)$_2$[μ-N(Ph-4-t-Bu)]$_2$,[46] but the obtuse Zr−N−Zr angles in the former cause a significant increase in the metal−metal separation, which is 3.198(1) Å in the zirconocene complex but 3.3055(4) Å in **10**. This metal-metal separation is also significantly greater then the distance of 3.1575(6) Å in [(Me$_4$taa)Zr(μ-N-t-Bu)$_2$Zr(NH-t-Bu)$_2$].[47]

The only product identifiable by GC/MS in the reaction mixture used to prepare **10** was 1-methyl-2-(2-phenylethenyl)benzene, suggesting that the product may form via the mechanism outlined in Scheme 3. After undergoing a retro [1 + 2] cycloaddition, the
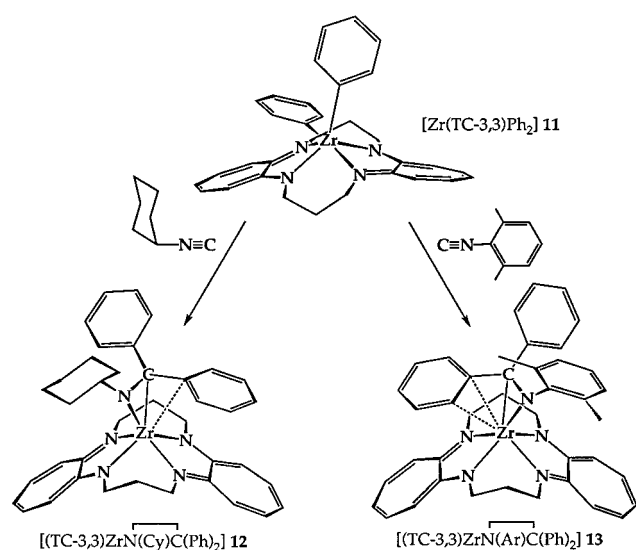
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Scheme 3

[(TC-3,3)ZrN(Ar)C(CH$_2$Ph)$_2$)]

Scheme 4

[Zr(TC-3,3)Ph$_2$] **11**

[(TC-3,3)ZrN(Cy)C(Ph)$_2$] **12**   [(TC-3,3)ZrN(Ar)C(Ph)$_2$] **13**

Figure 7. ORTEP diagram of [Zr(TC-3,3)Ph$_2$] (**11**) showing 50% ellipsoids and atom-labeling scheme. Primed and unprimed atoms are related by a 2-fold symmetry operation. Selected distances and angles are contained in Table 5.

terminal imido intermediate might rapidly dimerize in the absence of trapping agents to form **10**. Ziroconcene imido complexes, such as [CpZr(NAr)], also typically form dinuclear species. Once eliminated, the reactive carbene moiety can either attack the ortho position of a phenyl ring or dimerize to form tetrabenzylethylene. The kinetic inertness of Hf with respect to Zr would retard this chemistry, facilitating the isolation of **9**.

Although inconsistent with the formation of 1-methyl-2-(2-phenylethenyl)benzene, other potentially parallel reactions for the formation of **10** can be envisioned. In the presence of acetone, the isoelectronic complex [Hf-(TC-3,5)(η^2-OC(CH$_2$Ph)$_2$)] appears to undergo a β-hydrogen transfer reaction generating a transient metal–hydride/enolate.[48] An equivalent transformation in the present system would afford a metal–hydride and a vinyl amide identical to an intermediate in the formation of [(OAr)$_2$Ta(=NAr){N(Ar)(CH$_2$CH$_2$Ph)}].[49] Subsequent intramolecular rearrangement of this Ta complex transfers a hydride to a η^2-imine ligand and generates a metallacyclobutene. In the tropocoronand system, attack of the terminal hydride on the vinyl olefin could eliminate dihydrogen and produce a met-
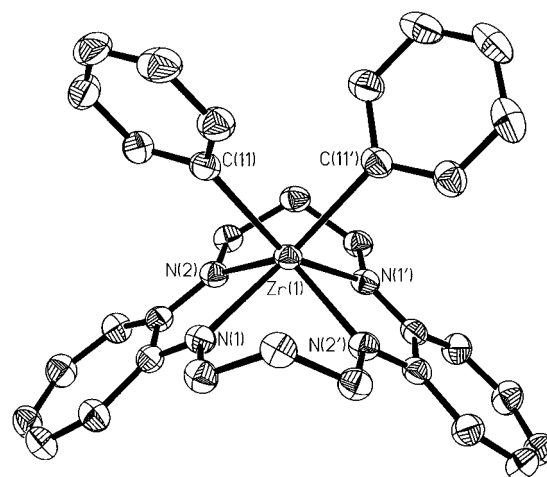
allacyclobutene. As is often the case with zirconocene metallacyclobutenes, such as the Ta example just discussed, this metallacycle could undergo a retro [2 + 2] cycloaddition to afford the terminal imido product and 1 equiv of alkyne. The inability to detect an alkyne in reaction mixtures containing **10** discredits this mechanism.

Phenyl-Substituted η^2-Imines. To further explore the influence of the ancillary ligands on the insertion chemistry, the complexes [M(TC-3,3)Ph$_2$] (M = Zr (**11**), Hf) were prepared. The structure of **11** is depicted in Figure 7. As illustrated in Table 5, replacement of alkyl with aryl ligands has little influence on the M–C and M–N bond lengths. The Zr–R distances decrease minimally from 2.374(3) Å in [Zr(TC-3,3)(CH$_2$Ph)$_2$][19] to 2.353(2) Å in **11**, and the average Zr–N distances are identical, 2.19(1) and 2.20(2) Å, respectively. Altering the R-groups has a profound effect on the reactivity of the complexes, however. Addition of isocyanides to solutions containing **11** or its Hf analog afforded the η^2-imine complexes, [(TC-3,3)MN(R)C(Ph)$_2$], irrespective of the nature of the substituents on the isocyanide. The structures of the products from reactions of **11** with CyNC (**12**) and ArNC (**13**) are displayed in Figure 8 (Scheme 4). Selected metrical parameters are contained

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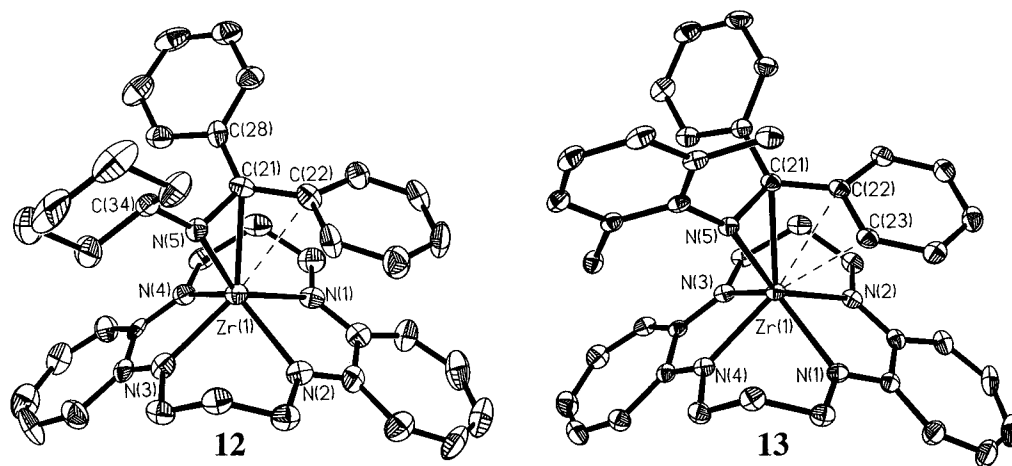
Figure 8. ORTEP diagrams of [(TC-3,3)ZrN(Cy)C(Ph)$_2$] (**12**) and [(TC-3,3)ZrN(Ar)C(PH)$_2$] (**13**) showing 50% ellipsoids and atom labeling scheme. Selected distances and angles are contained in Table 5.

in Table 5, from which the presence of a N(5)−C(21) single bond can be identified. Although the structures of **12** and **13** are similar, the different electronic properties of the CyNC and ArNC substrates are evident in the geometric parameters of the resulting metallacycles. With the more electron-withdrawing aryl isocyanide ligand, the Zr−N(5) and Zr−C(21) bond lengths in **13** (2.079(3, 2.396(4) Å) have increased slightly relative to those in **12** (2.033(5), 2.373(6) Å). The distances in both complexes are significantly longer then the equivalent bond lengths of 2.020(3) and 2.260(4) Å in **9**, reflecting the decrease in the donating ability of the diphenyl-substituted η^2-imine fragment. The distances in **12** and **13** also differ from those in related zirconocene. The Zr−N distances in [(THF)Cp$_2$ZrN(SiMe$_3$)CH(Ph)][40] and [(THF)Cp$_2$ZrN(Ph)CH(Ph)][42] of 2.11(1) and 2.113(4) Å, respectively, are longer than those in **12** and **13**, but the metal−carbon bonds are significantly shorter. Although the geometric parameters and reactivity of these zirconocenes are in agreement with the metallaaziridine bonding formalism depicted below, the metallacycles in **12** and **13** may have some η^1-imine character. This

metallaaziridine η^2-imine η^1-imine
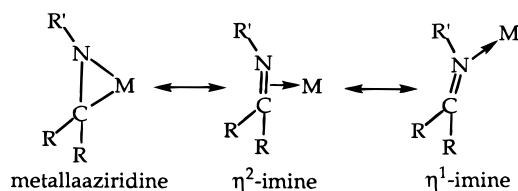
property is suggested by the ^{13}C NMR resonances for C(21), δ 145.01 in **12** and δ 142.66 in **13** which are shifted significantly downfield from the analogous resonance at δ 95 in [(OPh-2,6-*i*-Pr)$_2$(py-4-Et)TiN(t-Bu)C-(CH$_2$Ph)$_2$].[25]

The diminished electron-releasing character of the phenyl substituents on the imine ligand in **12** and **13** renders the metal centers more electron deficient. As a consequence, distortions occur which allow the metal center to acquire additional electron density from the phenyl rings. The Zr(1)−C(21)−C(22) angles (Figure 8)

are acute, being 87.4(4)° in **12** and 83.6(2)° in **13**, and although dissimilar, the Zr−C(21) distances are within the typical range for Zr−ipso-carbon interactions, 2.721(6) and 2.645(4) Å, respectively.[50] For comparison, the angles at the benzyl carbon atoms in **9** are normal, 120.6(3)° and 118.9(3)°. In **13**, a further twist in the Zr(1)−C(21)−C(22)−C(23) torsion angle provides some overlap between the metal center and the π electrons of the aromatic ring, as indicated by the Zr(1)−C(22) and Zr(1)−C(23) distances of 2.645(4) and 2.652(4) Å, respectively. These features are not manifested in the ^{13}C NMR spectra of the two complexes, however, which are symmetric and suggest the fluxional behavior in solution.

In contrast to most metallaaziridines[39−43] including **9**, the metallacycles in **12** and **13** are unreactive toward extrinsic substrates, even in the presence of excess isocyanide. Attempts thermally to induce insertion of a second equivalent of isocyanide to afford products comparable to **6**−**8** resulted in complex mixtures. This stability of the ligand in the presence of extrinsic substrates reinforces the description of the imine bonding in **12** and **13**, as previously deduced from their geometric and spectroscopic properties. In particular, the ligand has significant η^1 character which is stabilized by π interaction with the phenyl substituents.

Conclusions

A diverse set of products are obtained from migratory insertion reactions of isocyanides and group 4 tropocoronand alkyl and aryl complexes, reflecting the electronic properties of the substrate as well as the carbon-donor ligands. By comparison to zirconocene analogs, the tropocoronand ligand is more electron-releasing and the reactivity of the complexes is affected by the decreased electrophilicity of the metal center. Addition of alkyl isocyanides to [M(TC-3,3)(CH$_2$Ph)$_2$] affords bis-(η^2-iminoacyl) complexes. Aryl isocyanides react similarly but, in certain instances, induce coupling of the bis(η^2-iminoacyl) ligands to afford enediamido ligands. Migration of alkyl groups to the iminoacyl functionality is facile in these systems, and slow addition of aryl

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isocyanide produces η^2-imino groups. Formation of the latter is enhanced by replacement of the benzyl ligands with aryl ligands in the precursor complex, the relative electron-withdrawing character of which deactivates the first insertion product toward further insertion chemistry. With benzyl groups, the η^2-imine moiety can decompose to form μ-imido complexes and also insert a second equivalent of isocyanide in a 1,1-fashion. In migratory insertion reactions of these tropocoronand complexes, subtle alterations in the electronic character of the system allow for the construction of complex organic fragments from readily available starting materials.

Supporting Information Available: Tables of crystal data and structure refinement results, atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles for **1**, **2**, **3**·CH_2Cl_2, **4**·$^1/_3CH_2Cl_2$, **5**·$^1/_2C_5H_{12}$, **6**, **7**, **8**·$^1/_2CH_2Cl_2$, **9**·$^1/_2C_7H_8$, **10**·C_7H_8, **11**·$2CH_2Cl_2$, **12**·$^1/_2C_7H_8$, and **13**·$2CH_2Cl_2$ (145 pages). Ordering information is given on any current masthead page.

OM9706830