

Synthesis and Reactivity of Cationic Group 4 Tropocoronand Complexes

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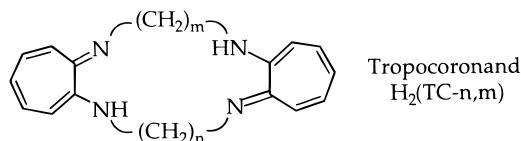
The tropocoronand complexes $[M(\text{TC-3,3})(\text{CH}_2\text{Ph})_2]$ ($M = \text{Zr}, \text{Hf}$) react with either oxidants or protic reagents to afford the five-coordinate cations $[M(\text{TC-3,3})(\text{CH}_2\text{Ph})]^+$, in which the benzyl ligand interacts weakly in an η^2 manner with the group 4 metal center. Isocyanides react with the resulting cations to afford ketenimine complexes, whereas benzophenone inserts into the $M\text{--C}$ bond to yield $[M(\text{TC-3,3})\{\eta^1\text{-OCPh}_2(\text{CH}_2\text{Ph})\}]^+$. These properties reflect the greater electron-releasing character of the tropocoronand ligands compared to cationic zirconium complexes of other tetraaza macrocyclic ligands and to zirconocenes.

Introduction

Significant attention has focused on delineating the characteristics of cationic group 4 metal centers because of their high reactivity and utility in catalysis.^{1–3} When an alkyl substituent is removed from a $L_n\text{MR}_2$ species, the enhanced Lewis acidity of the d^0 metal center polarizes the metal–ligand bonds and produces cations that are considerably more reactive than their neutral precursors. Group 4 metallocene cations $\{\text{Cp}_2\text{MR}\}^+$ have proved to be especially useful in this regard, being able to polymerize olefins in a controlled manner and induce a variety of insertion and coupling reactions.^{4,5}

Recently, macrocyclic auxiliary ligands have been employed to prepare group 4 metal organometallic complexes, and although the systems are less efficient as olefin polymerization catalysts, the resulting complexes exhibit many distinctive and promising attributes.^{6–12} Previous work in this laboratory demonstrated the tetraazamacrocyclic tropocoronand ligand $\{\text{TC-3,3}\}^{2-}$ to be a particularly good electron donor in $\text{Zr}(\text{IV})$ and $\text{Hf}(\text{IV})$ complexes, especially by comparison

to other macrocycles, aryloxides, and the bis(cyclopentadienyl) fragment. All of these ligands systems for-



mally donate the same number (12) of electrons to the metal.¹³ By decreasing the electrophilicity of the d^0 metal, the tropocoronand ligand attenuates the $M\text{--R}$ interaction, affording novel reactions such as the insertion of isocyanate into the $\text{C}\text{--}\text{O}$ bond of $[\text{Hf}(\text{TC-3,5})(\eta^2\text{-OC}(\text{CH}_2\text{Ph})_2)]$.¹⁴ In the present work, we have extended our studies to cationic tropocoronand group 4 organometallic complexes, where the reduction in the number of strong σ -donor ligands was expected to enhance even further the differences in Lewis acidity between tropocoronands and their metallocene analogues. As reported here, the use of tropocoronand ligands influences not only the insertion chemistry but also the structural properties of the resulting complexes.

Results and Discussion

Following the methodology previously developed for the synthesis of cationic group 4 complexes,^{4,7,15,16} we prepared $[M(\text{TC-3,3})(\text{CH}_2\text{Ph})](\text{BPh}_4)$ ($M = \text{Zr}$ (**1a**), Hf (**1b**)) cations from $[M(\text{TC-3,3})(\text{CH}_2\text{Ph})_2]$ ¹³ in modest yields (21–56%) either by oxidation with $[\text{Cp}_2\text{Fe}](\text{BPh}_4)$ or protonation with 1 equiv of $(\text{HNMe}_3)(\text{BPh}_4)$. Crystallographic chemical analysis (CCA) (Figure 1; Table 1) revealed **1a** and **1b** to have five-coordinate, distorted square-pyramidal geometries. These complexes repre-

(1) Collmann, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442–2469 and references therein.

(3) *Applied Homogeneous Catalysis with Organometallic Complexes*; Cornils, B.; Hermann, W. A., Eds.; VCH: Weinheim, Germany, 1996.

(4) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387 and references therein.

(5) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255–270.

(6) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493–8494.

(7) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Peterson, J. L. *Organometallics* **1995**, *14*, 371.

(8) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1997**, *16*, 2556–2561.

(9) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801–5811.

(10) Brand, H.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 95–96.

(11) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469–4473.

(12) Black, D. G.; Jordan, R. F.; Rogers, R. D. *Inorg. Chem.* **1997**, *36*, 103–108.

(13) Scott, M. J.; Lippard, S. J. *Inorg. Chim. Acta* **1997**, *263*, 287–299.

(14) Scott, M. J.; Lippard, S. J. *Organometallics* **1998**, *17*, 466–474.

(15) Nikonov, G. I.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1107–1112.

(16) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282–3302.

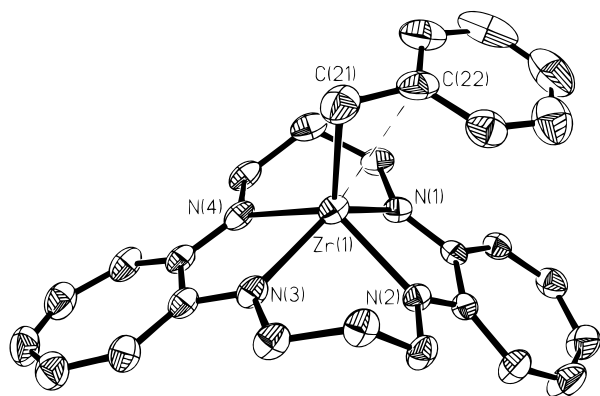


Figure 1. ORTEP diagram of the cation in $[\text{Zr}(\text{TC-3,3})\text{-(CH}_2\text{Ph)}](\text{BPh}_4)$ (**1a**) showing 50% ellipsoids and the atom-labeling scheme. Selected distances and angles for both **1a** and **1b** are available in Table 1.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{M}(\text{TC-3,3})(\text{CH}_2\text{Ph})](\text{BPh}_4)$, M = Zr (1a**), Hf (**1b**)^a**

Zr(1)–N(1)	2.149(3)	Hf(1)–N(1)	2.126(4)
Zr(1)–N(2)	2.140(3)	Hf(1)–N(2)	2.118(4)
Zr(1)–N(3)	2.149(3)	Hf(1)–N(3)	2.136(4)
Zr(1)–N(4)	2.146(3)	Hf(1)–N(4)	2.117(4)
Zr(1)–C(21)	2.279(4)	Hf(1)–C(21)	2.266(5)
Zr(1)–C(22)	2.687(4)	Hf(1)–C(22)	2.745(5)
N(1)–Zr(1)–N(2)	72.42(10)	N(1)–Hf(1)–N(2)	73.27(14)
N(1)–Zr(1)–N(3)	132.38(10)	N(1)–Hf(1)–N(3)	133.87(14)
N(1)–Zr(1)–N(4)	86.74(10)	N(1)–Hf(1)–N(4)	87.19(14)
N(2)–Zr(1)–N(3)	85.16(10)	N(2)–Hf(1)–N(3)	85.85(14)
N(2)–Zr(1)–N(4)	124.02(10)	N(2)–Hf(1)–N(4)	126.50(14)
N(3)–Zr(1)–N(4)	71.67(11)	N(3)–Hf(1)–N(4)	72.77(14)
N(1)–Zr(1)–C(21)	121.07(13)	N(1)–Hf(1)–C(21)	118.2(2)
N(2)–Zr(1)–C(21)	117.84(13)	N(2)–Hf(1)–C(21)	115.7(2)
N(3)–Zr(1)–C(21)	106.53(13)	N(3)–Hf(1)–C(21)	107.9(2)
N(4)–Zr(1)–C(21)	117.45(13)	N(4)–Hf(1)–C(21)	117.5(2)
Zr(1)–C(21)–C(22)	88.6(2)	Hf(1)–C(21)–C(22)	91.6(3)

^a Numbers in parentheses are estimated standard deviations in the last digit(s) listed. See Figure 1 for atom-labeling scheme.

sent some of the few examples^{6,7,16} of group 4 cations which can be isolated without a stabilizing interaction with either the counterion or extrinsic bases such as aniline, THF, or acetonitrile.⁴ The acute M–CH₂–Ph angles of 88.6(2)° (**1a**) and 91.6(3)° (**1b**) and the short M–C(22) distances of 2.687(4) (**1a**) and 2.745(5) Å (**1b**) reflect η^2 -binding of the benzyl group. This interaction stabilizes the complexes in the absence of a sixth ligand, but the M–R bond is weak compared with other formally pentacoordinate, cationic complexes. The analogous distance and angle in one of the few examples of a structurally characterized pentacoordinate cationic Zr(IV) complex, $[\text{Zr}(\text{MeBr}_2\text{Ox})_2(\eta^2\text{-CH}_2\text{Ph})]^+$, where MeBr₂Ox = 2-Me-5,7-Br₂-8-quinolinolato, are 2.448(5) Å and 80.0(3)°, respectively.¹⁶

The lack of a strong interaction between the ipso carbon and the metal is also evident in the ¹H NMR spectra of **1a** and **1b**, which do not display the significant upfield shift of the ortho proton resonance characteristic of η^2 -coordination of benzyl ligands.^{4,8} Although the interaction with the ipso carbon atom is not strong, the acute angle at C(21) and the downfield shift of the C(21) resonance in the ¹³C NMR spectrum, from δ 72.18 in $[\text{M}(\text{TC-3,3})(\text{CH}_2\text{Ph})_2]$ to 76.31 in **1b**, are consistent with increased in Lewis acidity at the metal

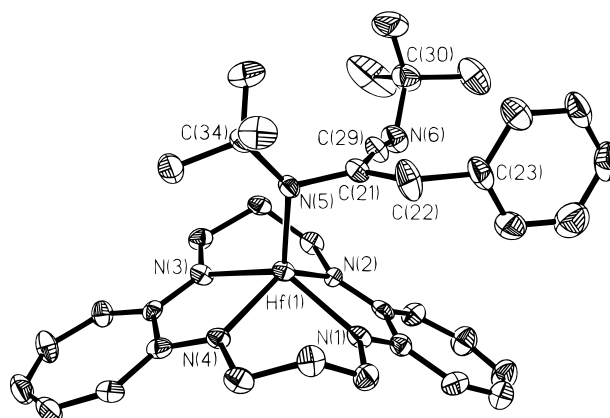


Figure 2. ORTEP diagram of the cation in $[\text{Hf}(\text{TC-3,3})\text{N}(t\text{-Bu})(\text{C}\{=\text{C}=\text{N}-t\text{-Bu}\}\{\text{CH}_2\text{Ph}\})](\text{BPh}_4)$ (**2b**) showing 50% ellipsoids and the atom-labeling scheme. Selected distances and angles for both **2a** and **2b** are contained in Table 2.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{M}(\text{TC-3,3})\text{N}(t\text{-Bu})(\text{C}\{=\text{C}=\text{N}-t\text{-Bu}\}\{\text{CH}_2\text{Ph}\})](\text{BPh}_4)$, M = Zr (2a**), Hf (**2b**)^a**

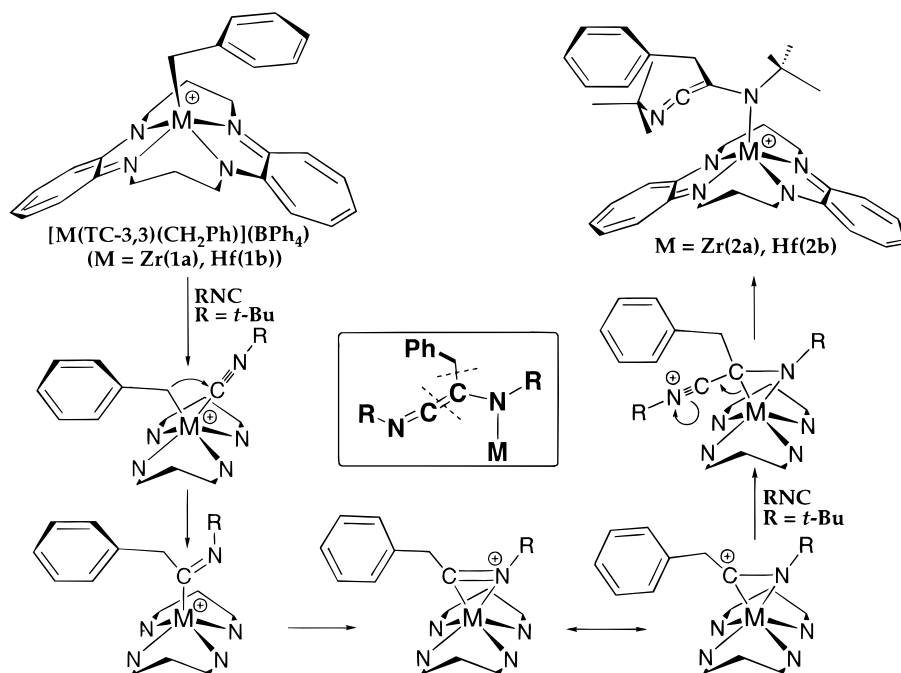
Zr(1)–N(1)	2.150(4)	Hf(1)–N(1)	2.137(5)
Zr(1)–N(2)	2.161(4)	Hf(1)–N(2)	2.145(5)
Zr(1)–N(3)	2.145(5)	Hf(1)–N(3)	2.121(5)
Zr(1)–N(4)	2.139(4)	Hf(1)–N(4)	2.123(5)
Zr(1)–N(5)	2.036(4)	Hf(1)–N(5)	2.024(5)
Zr(1)–C(21)	2.724(5)	Hf(1)–C(21)	2.734(6)
C(21)–C(29)	1.314(8)	C(21)–C(29)	1.328(9)
N(6)–C(29)	1.230(8)	N(6)–C(29)	1.229(8)
N(1)–Zr(1)–N(2)	71.9(2)	N(1)–Hf(1)–N(2)	73.1(2)
N(1)–Zr(1)–N(3)	128.9(2)	N(1)–Hf(1)–N(3)	132.9(2)
N(1)–Zr(1)–N(4)	86.9(2)	N(1)–Hf(1)–N(4)	87.8(2)
N(1)–Zr(1)–N(5)	118.1(2)	N(1)–Hf(1)–N(5)	115.4(2)
N(2)–Zr(1)–N(3)	88.1(2)	N(2)–Hf(1)–N(3)	87.0(2)
N(2)–Zr(1)–N(4)	131.2(2)	N(2)–Hf(1)–N(4)	130.7(2)
N(2)–Zr(1)–N(5)	117.0(2)	N(2)–Hf(1)–N(5)	118.4(2)
N(3)–Zr(1)–N(4)	71.8(2)	N(3)–Hf(1)–N(4)	73.5(2)
N(3)–Zr(1)–N(5)	112.9(2)	N(3)–Hf(1)–N(5)	111.6(2)
N(4)–Zr(1)–N(5)	111.7(2)	N(4)–Hf(1)–N(5)	110.9(2)
C(21)–C(29)–N(6)	170.2(6)	C(21)–C(29)–N(6)	171.8(8)

^a Numbers in parentheses are estimated standard deviations in the last digit(s) listed. See Figure 2 for atom-labeling scheme.

center following removal of one of the alkyl substituents. As was the case for the neutral $[\text{M}(\text{TC-}n,m)\text{Y}_2]$ and related metallocene complexes,¹³ the spectral and structural (longer M–Y bonds) results demonstrate that **1a** and **1b** are significantly less electrophilic compared to cationic zirconocene analogues, and the difference is especially apparent in the absence of a stabilizing ligand such as THF.

Reaction of **1a and **1b** with Isocyanides.** Nucleophiles usually bind to cationic group 4 metals before inserting into a metal–carbon bond. Compounds **1a** and **1b** react similarly, even though they have reduced electrophilicity.⁴ Addition of several equivalents of *tert*-butyl isocyanide to dichloromethane solutions of **1a** and **1b** induced a rapid color change from orange to orange-red and formation of the ketenimine complexes $[\text{M}(\text{TC-3,3})\text{N}(t\text{-Bu})(\text{C}\{=\text{C}=\text{N}-t\text{-Bu}\}\{\text{CH}_2\text{Ph}\})](\text{BPh}_4)$, M = Zr (**2a**), Hf (**2b**) (Figure 2; Table 2). As in the precursor complexes, the metal centers adopt a square-pyramidal stereochemistry with the four nitrogen atoms of the macrocycle bonding in the equatorial plane. Although the M–N distances are essentially indistinguishable,

Scheme 1



the distance to the apical ligand decreases dramatically from 2.279(4) Å in **1a** to 2.036(4) Å in **2a**, reflecting the enhanced orbital overlap with the amide functionality. The M–C(21) distances of 2.724(5) Å in **2a** and 2.734(6) Å in **2b** suggest that the metal center may still maintain some degree of orbital communication with the carbon atom of the apical ligand. The linear C=C=N angle of 170.2(6)° in **2a** and short C=C and C=N distances of 1.314(8) and 1.230(8) Å, respectively, are consistent with those observed in other group 4 ketenimine species, as is the intense stretch at 1988 cm^{−1} in the infrared spectrum of **2b**.^{17,18}

The products isolated can be rationalized by double insertion of *tert*-butyl isocyanide into the metal–carbon bond of **1a** and **1b**, as outlined in Scheme 1. Several observations support this proposal. After binding to the metal center, isocyanides typically insert into the M–R bonds in organometallic group 4 complexes containing ligands such as cyclopentadienyl, aryloxy, and tetraazamacrocycles including tropocoronands.^{14,19} The nitrogen atom of the isocyanide then rapidly coordinates, forming an η²-iminoacyl complex. Normally, in these systems, additional extrinsic substrates either bind directly to the metal center²⁰ or insert, in a 1,1- or 1,2-fashion, into the M–C bond of the η²-iminoacyl moiety.^{21,22} With **1a** and **1b**, however, the electrophilic nature of the bound carbon atom promotes nucleophilic attack by an additional equivalent of isocyanide, forming the ketenimine complexes **2a** and **2b**. The carbon atoms

of η²-iminoacyl groups in a few zirconocene systems having constrained metallacycles are also susceptible to such direct nucleophilic attack by external isocyanides, but unlike the reactions of **2a** and **2b**, pressures of up to 12 kbar are required to induce this reversible conversion.¹⁸ The decreased electrophilicity of the metal in the tropocoronands may disfavor binding of a second equivalent of isocyanide and could facilitate direct nucleophilic attack on the intermediate, although there is no direct evidence for this pathway. The result is irreversible conversion to the ketenimine moiety at room temperature and pressure.

Reaction of 1a and 1b with Benzophenone. Cationic group 4 complexes readily bind carbonyl groups owing to their high Lewis acidity. Except in rare instances,²³ the carbonyl-containing substrate inserts into the metal–carbon bond producing an alkoxide ligand. Ordinarily, the metal center then rapidly binds a second equivalent of substrate in order to stabilize the metal-alkoxy species.⁷ Both **1a** and **1b** also insert benzophenone into the metal–carbon bond forming the alkoxides [M(TC-3,3){η¹-OCPh₂(CH₂Ph)}], M = Zr (**3a**), Hf (**3b**) (Figure 3). In contrast to most group 4 complexes, however, the metal center does not bind a second equivalent of ketone, even in the presence of a large excess of substrate. As indicated above, the donating character of the tropocoronand ligand system tempers the Lewis acidity of the metal center and stabilizes the resulting pentacoordinate species. Although the electron-withdrawing phenyl substituents may exert some influence, the Zr–O distance of 1.927(4) Å in **3a** is only marginally longer than the analogous distance of 1.899(3) Å in [Cp₂Zr(O-*t*-Bu)(THF)], despite the presence of an additional THF ligand.²⁴ When compared to other tropocoronand complexes, for example, the bis(iminoacyl)

(17) Scott, M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411–3412.

(18) Valero, C.; Grehl, M.; Wingbermhle, D.; Kloppenburg, L.; Carpenetti, D.; Erker, G.; Petersen, J. L. *Organometallics* **1994**, *13*, 415–417.

(19) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

(20) Bochman, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556–2563.

(21) Bocarsly, J. R.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2380–2383.

(22) Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857–5868.

(23) Sun, Y.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1997**, *16*, 2509–2513.

(24) Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092–2094.

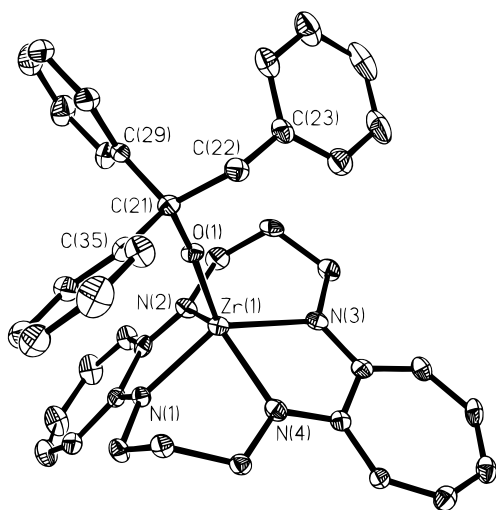


Figure 3. ORTEP diagram of the cation in $[\text{Zr}(\text{TC-3,3})\{\eta^1\text{-OCPh}_2(\text{CH}_2\text{Ph})\}](\text{BPh}_4)$ (**3a**) showing 50% ellipsoids and atom-labeling scheme. Selected bond distances (Å) and angles (deg): Zr(1)–O(1), 1.927(4); Zr(1)–N(1), 2.139(4); Zr(1)–N(2), 2.153(4); Zr(1)–N(3), 2.147(5); Zr(1)–N(4), 2.134(5); O(1)–C(21), 1.418(6); Zr(1)–O(1)–C(21), 170.6(3).

cyl) species $[\text{Hf}(\text{TC-3,3})\{\eta^2\text{-CyN}=\text{C}(\text{CH}_2\text{Ph})\}_2]$,²² the coordination sphere of the metal center in **3a** appears to be relatively unencumbered. Electronic factors, rather than the stereochemical requirements of the bulky phenoxide ligand, therefore, appear to be responsible for the long Zr–O bond.

In summary, we have isolated and characterized stable cationic organometallic zirconium(IV) and hafnium(IV) complexes of the tropocoronand ligand system which react to afford ketenimine and alkoxide products. A comparison of the structural data for both **1a** and **3a** with those of zirconocene-based systems suggests that the donor properties of the tropocoronand ligand are similar to that of the bis(cyclopentadienyl)zirconium fragment when coordinated by an auxiliary ligand such as THF. Furthermore, by comparison to other ligands, the decreased Lewis acidity of the tropocoronand complex attenuates the electrophilicity of the ancillary carbon-based ligands and influences their reactivity with substrates such as isonitriles. Similar results with the complexes $[\text{M}(\text{TC-}n,m)\text{R}_2]$ have recently been reported¹⁴ which, together with the present work, highlight some of the unique coupling reactions which can be promoted by organometallic group 4 tropocoronand complexes.

Experimental Section

Preparation of Compounds. The complexes $[\text{M}(\text{TC-3,3})\text{-(CH}_2\text{Ph)}_2]$ ($\text{M} = \text{Zr(IV), Hf(IV)}$) were synthesized as described.¹³ All operations, excluding ligand preparations, were conducted under a pure dinitrogen or argon atmosphere by 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. ^1H NMR spectra were recorded on a Bruker AM-250 and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra on a Varian Unity 300 spectrometer. 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 CCA, and elemental analyses were obtained on representative species.

Preparation of $[\text{M}(\text{TC-3,3})(\text{CH}_2\text{Ph})](\text{BPh}_4)$, $\text{M} = \text{Zr}$ (1a**), **Hf** (**1b**).** In a typical reaction, a rapidly stirred dark red solution of 279 mg (0.411 mmol) of $[\text{Hf}(\text{TC-3,3})(\text{CH}_2\text{Ph})_2]$ in 2 mL of dichloromethane was treated with a 156 mg (0.411 mmol) portion of $(\text{HNMe}_3)(\text{BPh}_4)$ at -30°C . The mixture was allowed to warm to room temperature, and after several minutes, the solution became bright orange and homogeneous. With a further 15 min of stirring, a precipitate formed in the mixture. Following the addition of 0.5 mL of ether, the mixture was cooled to -30°C . The resulting bright orange solid was collected, washed with ether and pentane, and dried to yield 190 mg (51%) of **1b**. The crude material was recrystallized from dichloromethane/ether or chlorobenzene/ether to afford large orange rhombohedral crystals. An analogous procedure was used to obtain **1a**, typical yields being 43–56%. Alternatively, substitution of the amine in the synthetic scheme with $[\text{Cp}_2\text{Fe}](\text{BPh}_4)$ also generated **1a** and **1b**, although the yields were lower (21–36%). **1a**: ^1H NMR (CD_2Cl_2) δ 7.49 (t, $J = 10.7$ Hz, 4H), 7.32 (m, 11H), 7.00 (m, 12H), 6.84 (m, 8H), 3.75 (m, 4H), 3.44 (d of t, $J = 2.0, 7.2$ Hz, 4H), 2.70 (s, 2H, CH_2), 2.44 (m, 2H), 1.96 (m, 2H); IR (KBr, cm^{-1}) 3051m, 3029w, 2996w, 2981m, 2901w, 1589s, 1512vs, 1478m, 1454w, 1433m, 1423w, 1416m, 1378s, 1363m, 1354w, 1341m, 1281m, 1228s, 1180w, 1137w, 1107w, 1080w, 1035w, 996m, 941w, 886m, 848w, 790w, 730vs, 705vs, 614w, 603m, 490m, 437w. **1b**: ^1H NMR (CD_2Cl_2) δ 7.54 (t, $J = 10.6$ Hz, 4H), 7.30 (m, 8H), 7.17 (t, $J = 7.6$ Hz, 2H), 7.06 (t, $J = 9.4$ Hz, 2H), 6.99 (m, 8H), 6.86 (m, 11H), 3.78 (m, 4H), 3.51 (m, 4H), 2.46 (s, 2H, CH_2), 2.43 (m, 2H), 2.30 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 163.44, 138.94, 136.56, 130.40, 128.49, 128.40, 126.24 (m), 124.91, 122.34, 119.02, 76.31 (Hf–C), 50.44, 24.01; IR (KBr, cm^{-1}) 3051m, 2991w, 2981m, 2901w, 1591s, 1580w, 1513vs, 1476m, 1454w, 1434w, 1424m, 1376s, 1362m, 1342m, 1283m, 1229s, 1139w, 1112w, 1083w, 1038w, 1031w, 1001m, 942w, 886w, 821w, 786w, 731vs, 705s, 614w, 604w, 486m. Anal. Calcd for $\text{C}_{51}\text{H}_{49}\text{BN}_4\text{Hf}$: C, 67.50; H, 5.44; N, 6.18. Found: C, 67.30; H, 5.33; N, 5.92.

Preparation of $[\text{M}(\text{TC-3,3})\text{N}(t\text{-Bu})(\text{C}\equiv\text{N}-t\text{-Bu})\{\text{CH}_2\text{Ph}\}](\text{BPh}_4)$, $\text{M} = \text{Zr}$ (2a**), **Hf** (**2b**).** In a typical procedure, a slurry of 31.2 mg (0.034 mmol) of **1b** in dichloromethane was treated with 14.4 μL (0.138 mmol) of *tert*-butyl isocyanide at -30°C . The mixture was allowed to warm to room temperature and filtered through Celite, and the filtrate was cooled to -30°C . Over the course of several days, ether was slowly diffused into the solution, resulting in the formation of large red-orange crystals. The solid was collected, washed with ether, and dried to afford 19 mg (52%) of **1b**. Following the procedure outlined above, compound **2a** was obtained in moderate yield (32–47%). Although **2b** is stable in solution, complex **2a** decomposes in a matter of hours in dichloromethane at room temperature. For X-ray crystallographic studies, crystals of **2a** were grown in a mixture of dichloromethane/pentane at -30°C . Single crystals of **2b** were obtained from chlorobenzene/ether solutions. **2a**: ^1H NMR (CD_2Cl_2) δ 7.49 (m, 4H), 7.31 (m, 11H), 7.00 (m, 12H), 6.82 (m, 8H), 4.05 (m, br, 4H), 3.40 (m, vbr, 6H), 2.50 (m, vbr, 4H), 1.24 (s, 9H), 0.89 (s, 9H). **2b**: ^1H NMR (CD_2Cl_2) δ 7.51 (t, $J = 10.8$ Hz, 4H), 7.32 (m, 11H), 7.00 (m, 12H), 6.83 (m, 8H), 4.00 (m, br, 4H), 3.44 (m, vbr, 4H), 2.66 (m, vbr, 4H), 2.00 (m, vbr, 2H), 1.23 (s, 9H), 0.88 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 183.93, 165.63, 165.00, 164.36, 163.32, 138.30, 137.42, 136.52, 130.00, 128.93, 127.49, 126.66, 126.23 (m), 122.32, 118.16, 72.00, 60.53, 59.78, 50.10, 42.335, 32.70, 29.96, 25.73; IR (KBr, cm^{-1}) 3054m, 2998w, 2980m, 1988m, 1592s, 1513vs, 1473m, 1432m, 1420m, 1379m, 1363s, 1347m, 1281m, 1231s, 1184w, 1140w, 1112w, 1085w, 1031w, 1003m, 970w, 942w, 886w, 848w, 731s, 704vs, 612m, 487w, 472w. Anal. Calcd for $\text{C}_{61}\text{H}_{67}\text{BN}_4\text{Hf}\cdot 0.5\text{CH}_2\text{Cl}_2$

(C_{61.5}H₆₈BClN₆Hf): C, 66.19; H, 6.14; N, 7.53. Found: C, 66.37; H, 6.06; N, 7.13.

Preparation of [M(TC-3,3){ η^1 -OCPh₂(CH₂Ph)}](BPh₄), M = Zr (3a), Hf (3b). A slurry of 28 mg (0.031 mmol) of **1b** in 1.5 mL of dichloromethane was treated with a 6.2 mg (0.034 mmol) portion of solid benzophenone at -30 °C. The solution rapidly changed color from orange to bright yellow-orange and became homogeneous upon warming to room temperature. The reaction mixture was filtered, and several volume equivalents of ether were diffused into the filtrate at -30 °C over the course of several days. The solid material was collected, washed with ether, and dried to afford 15 mg (45%) of feathery yellow-orange crystals. An identical procedure was used to prepare **3a**, but after the addition of ether, solutions of the complex tended to form oily residues, hindering characterization of the material. Single yellow crystals of **3a** were selected manually and characterized by CCA. **3b**: ¹H NMR (CD₂Cl₂) δ 7.54 (t, J = 10.4 Hz, 4H), 7.32 (m, 18H), 6.99 (m, 11H), 6.83 (m, 10H), 6.60 (d, J = 7.4 Hz, 2H), 3.80 (s, 2H, CH₂), 3.61 (m, 4H), 3.38 (m, 4H), 2.16 (m, 2H), 1.84 (m, 2H); ¹³C{¹H} NMR (CD₂Cl₂) δ 163.73, 148.19, 138.79, 137.35, 136.56, 130.85, 129.05, 128.42, 127.95, 127.70, 127.26, 126.26 (m), 122.33, 118.82, 89.74, 50.00, 48.74, 24.46; IR (KBr, cm⁻¹) 3053m, 3028w, 2981m, 2940w, 1592s, 1579w, 1514vs, 1477m, 1434m, 1422s, 1385w, 1370vs, 1345m, 1288m, 1233s, 1185w, 1142w, 1094w, 1081w, 1060m, 1039w, 1031w, 1004m, 941w, 885m, 848w, 791w, 732s, 703vs, 654w, 610m, 568w, 490m. Anal. Calcd for C₆₄H₅₉BN₄HfO: C, 70.56; H, 5.46; N, 5.14. Found: C, 69.72; H, 5.35; N, 5.10.

Crystallographic Studies. Crystals were 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.²⁵ The program SADABS was used to correct the data for absorption and decay.²⁶ Data were collected by following standard procedures reported in detail elsewhere.²⁷

The structures were solved by direct methods or Patterson analysis and refined by full-matrix least-squares and Fourier techniques with the SHELXTL-PLUS program package.²⁸ 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.

Crystallographic Data for [M(TC-3,3)(CH₂Ph)](BPh₄), M = Zr (1a), Hf (1b). Complex **1a**: C₅₁H₄₉BN₄Zr, fw = 819.97, monoclinic, space group $P2_1/n$, a = 15.1054(4) Å, b = 17.0209(3) Å, c = 17.6343(5) Å, β = 114.683(1)°, V = 4119.7(2) Å³, Z = 4, 15 812 reflections collected, 5849 unique reflections (R_{merge} , 4.57%), 4307 reflections $> 2\sigma$, R = 4.21%, wR^2 = 7.92%, GOF = 1.006. Complex **1b**: C₅₁H₄₉BHfN₄, fw = 907.24, monoclinic, space group $P2_1/n$, a = 15.1125(4) Å, b = 17.0404(3) Å, c = 17.6455(5) Å, β = 114.664(1)°, V = 4129.6(2) Å³, Z = 4, 16 002 reflections collected, 5898 unique reflections (R_{merge} , 4.58%), 4855 reflections $> 2\sigma$, R = 3.35%, wR^2 = 6.07%, GOF = 1.065.

Crystallographic Data for [M(TC-3,3)N(*t*-Bu)(C{=C=N-*t*-Bu}){CH₂Ph)}](BPh₄), M = Zr (2a), Hf (2b). Complex **2a**·C₅H₁₂: C₆₆H₇₉BN₆Zr, fw = 1058.38, monoclinic, space group $P2_1/n$, a = 13.1636(3) Å, b = 27.7436(2) Å, c = 17.2289(2) Å, β = 106.698(1)°, V = 6026.8(2) Å³, Z = 4, 23 052 reflections collected, 8518 unique reflections (R_{merge} , 6.70%), 6123 reflections $> 2\sigma$, R = 7.00%, wR^2 = 17.51%, GOF = 1.126. Six carbon atom positions were isotropically refined for the pentane solvate molecule, and hydrogen atoms were not included in the refinement of this molecule. The four central carbon atoms were refined at full occupancy, while the two outer positions were refined with site occupancy factors of 0.5. Complex **2b**·1.5C₆H₅Cl: C₇₀H_{74.5}BN_{6.5}HfN₆, fw = 1242.33, monoclinic, space group $P2_1/n$, a = 13.3377(2) Å, b = 27.7601(1) Å, c = 17.2046(3) Å, β = 106.612(1)°, V = 6104.23(14) Å³, Z = 4, 35 157 reflections collected, 13 817 unique reflections (R_{merge} , 10.32%), 7563 reflections $> 2\sigma$, R = 7.34%, wR^2 = 9.49%, GOF = 1.134. In the structure of **2b**, a chlorobenzene solvate molecule is disordered across an inversion center. The site occupancy of the chlorine atom was fixed at 0.5, and the molecule was refined isotropically without hydrogen atoms.

Crystallographic Data for [Zr(TC-3,3){ η^1 -OCPh₂(CH₂Ph)}](BPh₄) (3a). C₆₄H₅₉BN₄OZr, fw = 1002.18, triclinic, space group $P1$, a = 12.9462(3) Å, b = 14.1065(5) Å, c = 15.9917(5) Å, α = 109.207(1)°, β = 96.004(1)°, γ = 106.110(1)°, V = 2587.11(14) Å³, Z = 2, 10 078 reflections collected, 6910 unique reflections (R_{merge} , 5.56%), 4592 reflections $> 2\sigma$, R = 6.88%, wR^2 = 11.62%, GOF = 1.088.

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Supporting Information Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles for all compounds (59 pages). Ordering information is given on any current masthead page.

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(25) SMART: Version 4.0; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

(26) Program written by Prof. George Sheldrick at the University of Göttingen which corrects data collected on Siemens CCD and multiwire detectors for absorption and decay.

(27) Feig, A. L.; Bautista, M. T.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 6892–6898.

(28) SHELXTL: Structure Analysis Program; Siemens Industrial Automation, Inc.: Madison, WI, 1995.