

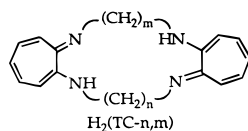
Coupling of Carbon Monoxide to Isocyanides and Enones Induced by Alkyl Zr(IV) and Hf(IV) Tropocoronand Complexes

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Although numerous group 4 organometallic compounds have been prepared with tetraazamacrocyclic ancillary ligands including porphyrins,^{1–5} few of these molecules undergo the C–C bond-forming reactions for which their metallocene analogs are celebrated. Despite similarities between the {Cp₂M} and {(N₄-macrocycle)M} fragment frontier molecular orbitals,⁴ the propensity for alkyl migration to the highly electrophilic imino carbon atoms of many tetraazamacrocycles^{4,5} has severely limited the ability of their metal complexes to promote reductive coupling of ligated groups with small extrinsic substrates. Multiple insertion and coupling reactions, in particular, are quite uncommon owing to this decomposition pathway. Previous work in this laboratory has demonstrated the tetraazamacrocyclic tropocoronand, (TC-*n,m*)^{2–}, to be a robust ligand. Moreover,



simple alterations in the size of the tropocoronand binding cavity afforded control of the coordination geometry and reactivity at the metal center in complexes with a variety of different transition metals.^{6–10} With these properties in mind, we decided to prepare group IV tropocoronand organometallic complexes, [M(TC-*n,m*)R₂], and explore their reactivity with substrates including carbon monoxide, isocyanides, and enones, the first results of which are described here.

At ambient temperature and pressure, [Hf(TC-3,5)(CH₂Ph)₂] (**1**)¹¹ inserts carbon monoxide into the metal–carbon bonds affording [Hf(TC-3,5)(η²-OC(CH₂Ph)₂)] (**2**) in 64% yield.¹² Crystallographic chemical analysis (CCA) revealed **2** to be the first group 4 macrocyclic η²-ketone complex (Figure 1). By contrast, group 4 metallocenes typically insert one CO into a single M–C bond, forming acyl complexes¹³ or, in some instances, enolates.¹⁴ Group 4 metallocene complexes containing η²-ketones and aldehydes can be obtained under forcing conditions,¹⁵ through the use of ancillary ligands such as calix-

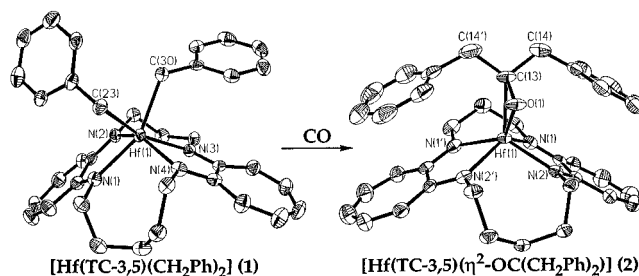


Figure 1. ORTEP diagrams with 50% thermal ellipsoids of [Hf(TC-3,5)(CH₂Ph)₂] (**1**) and its CO insertion product, [Hf(TC-3,5)(η²-OC(CH₂Ph)₂)] (**2**). Selected bond distances (Å) are as follows: for **1**, Hf(1)–C(23), 2.355(4); Hf(1)–C(30), 2.331(5); for **2**, Hf(1)–O(1), 1.993(5); Hf(1)–C(13), 2.217(8); O(1)–C(13), 1.448(9). Primed and unprimed atoms are related by a crystallographic mirror plane.

[4]arenes¹⁶ or by ligand exchange reactions.^{17–20} With group 4 macrocycles, an η²-ketone species similar to **2** was suggested to form transiently upon exposure of a tetraazaannulene complex to carbon monoxide, but this highly reactive fragment rapidly migrated to the ligand, inducing its decomposition.⁴ In the present case, an acyl group formed after initial insertion of CO into the metal–alkyl bond in group 4 macrocyclic complexes may have considerable carbenoid character, which would favor migration of the second alkyl substituent and formation of the η²-ketone moiety. Recent work with [Zr(TC-3,3)Ph₂] and [Zr(TC-3,3)Me₂] has confirmed the generality of this transformation with tropocoronand complexes.²¹

The metrical parameters of the three-membered metalloxirane ring in **2** indicate significant reduction in the bond order of the C–O moiety and a short Hf–O bond of 1.993(5) Å (Figure 1). The Hf–C bond distance of 2.217(8) Å is 0.10–0.15 Å smaller than that in [Cp₂Zr(η²-OCPh₂)₂]₂,²² [Cp₂Zr(η²-OCPh₂)(THF)] (2.301(5) Å),¹⁹ or **1** (2.355(4) Å, 2.331(5) Å), further emphasizing the single-bond character of the C–O unit (1.448(9) Å). Analogous group IV complexes of smaller tropocoronands such as [Zr(TC-3,3)(η²-OC(CH₂Ph)₂)] have similar metalloxirane ring geometric features.²¹

Metallocenes containing η²-ketone ligands such as [Cp₂Zr(η²-OCPh₂)₂] are very reactive, inserting substrates such as α,β-unsaturated esters, phosphorus ylides, and aromatic hydrocarbons.²² Compound **2** is similarly susceptible to nucleophilic attack; over the course of several hours, the Hf–C bond reacts with dichloromethane affording [Hf(TC-3,5)(OCH(CH₂Ph)₂)Cl] (**3**, Figure 2). When isocyanides are present, however, dichloromethane solutions of **2** preferentially react with these ligands to afford the ketenimine complex **4** in good yield (Figure 2).¹² By comparison, a metallocene analogue, [(Cp₂ZrCl)₂(μ-η¹(O),η²-(C,O)CH₂O)],^{17,18,23} containing a bound formaldehyde ligand will insert only one isocyanide into the metal–carbon bond. The resulting four-membered metallacyclic (η¹-iminoacyl)-zirconocene species suggests that **4** may arise through an

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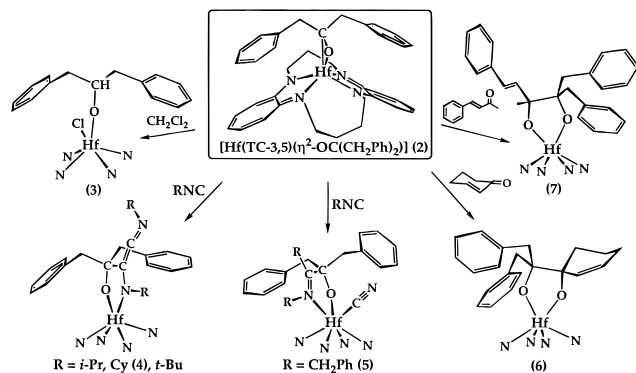


Figure 2. Schematic representation of the reaction of the η^2 -ketone tropocoronand complex **2** with isocyanides, enones, and dichloromethane. All diagrams were generated from crystallographic coordinates and represent accurate structural perspectives of the complexes. ORTEP diagrams and full crystallographic details for **3–8** are supplied as Supporting Information.

analogous intermediate. Although the η^2 -acyl complex $\text{Cp}^*_2\text{-ThCl}(\eta^2\text{-OCCH}_2\text{Ph})$ reacts similarly with isocyanides,²⁴ the reductive coupling of CO + 2RCN to form first the η^2 -ketone and then ketenimines is unprecedented. Even the multiple C–C coupling of isocyanides to generate ketenimine moieties is an unusual transformation with group 4 metallocenes and may require high pressure.²⁵ In contrast, a broad range of Zr and Hf tropocoronand species with varying macrocycle ring size and aryl or alkyl ligands will induce this transformation at room temperature and pressure. Treatment of $[\text{Zr}(\text{TC-3,3})(\eta^2\text{-OCPh}_2)]$ with 2 equiv of 2,6-dimethylphenyl isocyanide, for example, affords a ketenimine product analogous to **4**.²¹

The only alkyl or aryl isocyanide which afforded a different product in the ketenimine synthesis was benzyl isocyanide. Addition of 2 equiv of PhCH_2NC to a dichloromethane solution of **2** yielded **5**, a rare example of group 4 complex containing a terminal cyanide ligand,²⁶ $\nu_{\text{CN}} = 2067 \text{ cm}^{-1}$ (Figure 2). During the formation of **5**, the first equiv of isocyanide most likely inserts into the metalloxirane Hf–C bond, producing a transient η^1 -iminoacyl complex. Reaction of this species with an equiv of benzyl isocyanide might induce the cleavage of the CN–benzyl bond, but the role of the metal center in facilitating this reaction remains a matter to be investigated. Decyanation reactions of benzyl and other isocyanides to afford cyanide ligands have been previously noted.^{27,28}

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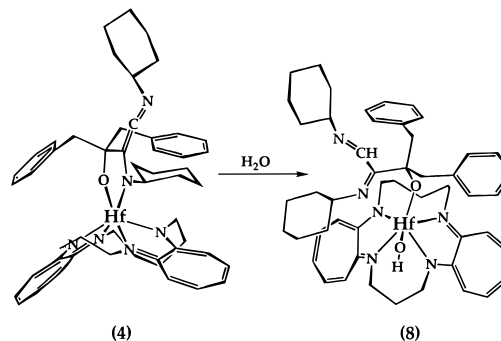


Figure 3. Representation of the hydrolysis of **4** to afford the hydroxide complex **8**. Diagrams of **4** and **8** were generated from crystallographic coordinates. Selected bond lengths (Å) are as follows: for **4**, Hf(1)–O(1), 2.012(3); Hf(1)–N(6), 2.155(4); O(1)–C(23), 1.402(6); for **8**: Hf(1)–O(1), 2.028(6); Hf(1)–OH, 2.075(6); Hf(1)–Nimine, 2.716(7); O(1)–C(23), 1.390(10).

Activated ketones also react with the metalloxirane unit in **2** in a manner analogous to pinacol coupling. One equiv of an enone such as cyclohexenone (**6**)¹² or *trans*-4-phenyl-3-buten-2-one (**7**)¹² (Figure 2) inserts into the Hf–C bond, generating a tropocoronand diolato complex. We have also investigated aspects of the hydrolysis of the newly formed C–C coupled products obtained in this chemistry since, as with the reductive coupling chemistry of CO previously studied in our laboratory, unprecedented organic compounds might be accessed in this manner.²⁹ An initial product in the hydrolysis of **4** is the hydroxide-ligated hafnium tropocoronand complex **8**, obtained following addition of 1 equiv of water to a dichloromethane solution (Figure 3). From the nature of the product, identified by CCA, the first step in the hydrolysis reaction would appear to be coordination of water followed by proton transfer to the bound nitrogen atom and rearrangement to form **8**. In **8** the metal–imine distance is very long, 2.716(7) Å, and the metal–alkoxide and hydroxide bond distances are quite similar, 2.028(6) and 2.075(6) Å, respectively.

In conclusion, organometallic group 4 tropocoronand complexes couple carbon monoxide to a variety of substrates generating complexes incorporating ketenimine, diolate, and cyanide ligands. In contrast to similar tetraazamacrocycles, the TC-*n,m* ligand is relatively robust and not as readily attacked by reactive intermediates in the coupling chemistry. This potential has been further exploited in a series of novel chemical transformations with this system, as will be reported shortly.

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Supporting Information Available: Experimental procedures and characterization data including X-ray structural details for all compounds (75 pages). See any current masthead page for ordering and Internet access instructions.

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