Synthesis of Chiral Heterobimetallic Tris(Phosphinoamide) Zr/Co Complexes

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ABSTRACT. Herein we report the synthesis and characterization of new heterobimetallic Zr/Co complexes incorporating chiral phosphinoamide ligands. The chiral phosphinoamine ligand (*R*-PhCH₃CH)NHP^{*i*}Pr₂ (**1**) is used to synthesize a tris(phosphinoamide) Zr metalloligand ClZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃ (**2**), which can be further treated with CoI₂ to afford the chiral Zr/Co heterobimetallic complex ClZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃CoI (**3**). Complex **3** can be reduced by two electrons to produce Zr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃CoN₂ (**4**). In an alternative strategy, a mixed-ligand derivative featuring two achiral phosphinoamide ligands and one chiral ligand was targeted. Thermolysis of Zr(NMe₂)₄ with ^{*i*}Pr₂PNHXyl in toluene produces (Me₂N)₂Zr(^{*i*}Pr₂PNXyl)₂ (**5**), which can be transformed in I₂Zr(^{*i*}Pr₂PNXyl)₂ (**6**) via *in situ* treatment with Me₃SiI. A third chiral phosphinoamide ligand can then be installed to generate IZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)(XylNP^{*i*}Pr₂)₂ (**7**). Treatment of complex **7** with CoI₂ affords IZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)(XylNP^{*i*}Pr₂)₂CoI (**8**). Complexes **3**, **7**, and **8** were structurally characterized and a preliminary screening of the catalytic hydrosilylation of acetophenone with reduced complex **4** revealed a very poor yield and essentially no enantioselectivity.

KEYWORDS: heterobimetallic complex, ketone hydrosilylation, asymmetric catalysis, metal-metal bond

Introduction

Transition metal catalysis has progressed significantly in the 21st century and by carefully choosing a metal and designing a specific coordination sphere, chemists are now able to tune their catalysts to perform a large array of reactions with complete chemo-, regio- and stereoselectivity. Binuclear complexes have been recognized to have reactivity that is unlike either of the corresponding monometallic analogs, and early/late heterobimetallic complexes have specifically become targets in the recent literature [1-4]. Early/late heterobimetallic compounds incorporate a Lewis acidic transition metal center from the left side of the periodic table with a more electron rich metal from the right side of the d-block. By incorporation of a second metal center, the electronic behavior and reactivity of the resulting compounds can be modified. Early/late heterobimetallic complexes can participate in reactions in which both metal centers play a crucial role. This so-called “cooperative reactivity” can arise either from distinct interactions of each metal with the substrate or through enhanced redox properties facilitated by the metal-metal interaction.

In recent years, our group has used LX-type phosphinoamide ligands to construct flexible scaffolds that support a range of heterobimetallic complexes [5, 6]. Among these studies, we uncovered a tris(phosphinoamide) Zr/Co complex $\text{ClZr}(\text{MesNP}^i\text{Pr}_2)_3\text{CoI}$ (Mes = 2,4,6-trimethylphenyl) that can be reduced by two-electrons to generate a highly reactive metal-metal multiply-bonded complex $(\text{THF})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{CoN}_2$ that features a short Zr-Co distance and weakly bound ligands in the apical positions of both Co and Zr (Scheme 1) [7, 8].

(THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ reacts with a variety of substrates through one- (e.g. ROH, N₂H₄) [9, 10], two- (e.g. I₂, RX, CO₂) [11, 12], and four-electron redox processes (RN₃) [13]. The versatile multielectron redox chemistry of (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ is particularly remarkable given that the oxidation states of the two metals were found to be Zr^{IV} and Co^{-I} using XANES (X-ray Absorption Near Edge Structure) spectroscopy [14], so Co is serving as the sole source of electrons in all of the aforementioned multielectron redox processes.

Scheme Error! No text of specified style in document.. Two-electron reduction of ClZr(MesNP^{*i*}Pr₂)₃CoI to generate (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂.

While exploring the reactivity and catalytic applications of (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂, we found this complex is an effective catalyst for the hydrosilylation of ketones [15]. For example, treatment of acetophenone with 5 mol% (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ and PhSiH₃ gave the corresponding alcohol in 97% isolated yield after acidic workup. The reaction is quite general for both alkyl and aryl ketones, and hydrosilylation of α - β -unsaturated ketones proceeds selectively without reduction of the C=C bond. Initially, we considered that the mechanism for hydrosilylation could be similar to the classic mechanism for hydrosilylation reported by Chalk and Harrod [16], but limited reactivity was observed between (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ and PhSiH₃ implying that an alternative mechanism was likely at play. A stoichiometric reaction

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4 between benzophenone and $(\text{THF})\text{Zr}^{\text{IV}}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}^{-\text{I}}(\text{N}_2)$ afforded an isobenzopinacol-
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6 bridged Zr/Co complex that arises via dimerization of two molecules of the Zr-bound ketyl
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8 radical complex $(\text{Ph}_2\text{C}^{\bullet}\text{O})\text{Zr}^{\text{IV}}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}^0(\text{N}_2)$, as shown in Scheme 2 [15, 17]. Further,
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10 stable Zr-bound ketyl radical complexes could be isolated from similar reactions using
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12 fluorenone or *para*-substituted diaryl ketones [17]. This stoichiometric reaction, along with
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14 kinetic and deuterium labelling studies, strongly suggested a radical mechanism involving one-
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16 electron transfer from Co to a Zr-bound ketone substrate, followed by hydrogen atom abstraction
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18 from silane to generate the silyl ether product (Scheme 3). The intermediacy of a Co-bound ketyl
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20 radical substrate was ruled out by experiments in which the labile N_2 ligand bound to cobalt was
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22 replaced with an irreversibly bound CO ligand. It was found that without an open coordination
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24 site at cobalt, (1) hydrosilylation proceeds, albeit with lower yield [15], and (2) Zr-bound ketyl
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26 radicals can be isolated [17].
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34 **Scheme 2.** Reaction of the $\text{Zr}^{\text{IV}}/\text{Co}^{-\text{I}}$ complex $(\text{THF})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{CoN}_2$ with benzophenone to
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36 generate a $\text{Zr}^{\text{IV}}/\text{Co}^0$ isobenzopinacol-bridged complex via a Zr-bound ketyl radical intermediate.
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Scheme 3. Proposed mechanism for benzophenone hydrosilylation catalyzed by (THF)Zr(MesNPⁱPr₂)₃CoN₂ [15].

To further probe this mechanism and to explore the potential utility of heterobimetallic Zr/Co catalysts in organic transformations, we now turn our attention to methods to incorporate chiral substituents into the heterobimetallic Zr/Co framework in an effort to promote asymmetric hydrosilylation. Transition metal-catalyzed hydrosilylation of ketones is an industrially relevant method to generate optically active secondary alcohols [18]. While chiral alcohols can be obtained by a reduction with a library of ketoreductases [19] or via chiral resolution [20], the most elegant approach is transition metal catalysis on a prochiral substrate [21]. Building upon the success of Wilkinson's catalyst, RhCl(PPh₃)₃ [22, 23], rhodium-catalyzed hydrosilylation of ketones using chiral ligands has become a popular and efficient route to chiral alcohols [24-26]. Numerous other examples of asymmetric ketone hydrosilylation catalysts using noble metals such as Ir [21], Ru [27], and Pd [28] have been reported, but for practical purposes it would be preferable to use cheaper and more naturally earth abundant transition metals. Indeed, there are reports of asymmetric hydrosilylation using Ti metallocenes [29-31], Cu [32-34], and Fe [35-37]

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4 based catalytic systems. While there are examples of hydrosilylation using heterobimetallic
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6 complexes [38-40], to our knowledge there are no examples of *asymmetric* hydrosilylation
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8 catalyzed by a heterobimetallic complex.
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11 In this work, we discuss our attempts to design asymmetric variants of our Zr/Co
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13 heterobimetallic complexes. Given our evidence for substrate binding at the Zr center, our efforts
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15 have focused on incorporation of chiral amide substituents in close proximity to the substrate
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17 binding site. Since the ketone hydrosilylation reaction is proposed to proceed via a ketyl radical
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19 intermediate, we posited that enantioinduction could occur during the H-atom abstraction step if
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21 an appropriately restricted chiral binding pocket were present. Enantioselective reactions
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23 controlled via radical processes are known in the literature and a comprehensive review of the
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25 topic has been produced by Sibi [41]. The most common enantioselective radical reactions use a
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27 chiral Lewis acid to which a radical intermediate is complexed, and examples of asymmetric
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29 reactions involving ketyl radicals have been reported using excess SmI₂ as the radical source
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31 with an external chiral ligand [42-44]. Thus, design of a chiral heterobimetallic Zr/Co complex
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33 may provide a distinct economic advantage over other methods for enantiocontrolled reactions of
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35 ketyl radical intermediates.
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44 45 **Results and Discussion**

46 47 48 **Synthesis of a Tris(phosphinoamide)-linked Zr/Co Heterobimetallic Complex with Three** 49 50 **Chiral Phosphinoamide ligands** 51 52

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54 Efforts toward the synthesis of a chiral heterobimetallic complex to be screened as a
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56 catalyst for asymmetric hydrosilylation began with commercially available (*R*)- α -
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58 methylbenzylamine as a source of chirality. Treatment of (*R*)- α -methylbenzylamine with
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4 ClP^{*i*}Pr₂ in the presence of external base cleanly produced the desired phosphinoamine (*R*-
5 PhCH₃CH)NHP^{*i*}Pr₂ (**1**) in 93% yield. The physical properties as well as the ¹H and ³¹P NMR
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7 spectra of **1** exactly matched those reported in the literature for the opposite enantiomer [45].
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9 Deprotonation of **1** with *n*-BuLi rapidly formed the lithiated phosphinoamide salt *in situ*, and
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11 treatment with ZrCl₄ at low temperature afforded the Zr tris(phosphinoamide) complex ClZr((*R*-
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13 PhCH₃CH)NP^{*i*}Pr₂)₃ (**2**) as a white powder in 36% yield. A single peak at 6.00 ppm in the ³¹P
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15 NMR spectrum of **2** implies that all three phosphinoamide ligands are in identical environments.
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17 However, the inequivalence of the two *iso*-propyl environments on the ligand is quite evident
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19 from the ¹H NMR spectrum as a result of the stereocenter in the ligand. For example, two peaks
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21 at 2.24 ppm and 1.74 ppm in the ¹H NMR spectrum are assigned to the two inequivalent *iso*-
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23 propyl methine protons on the phosphorus atom of the ligand. The ¹H NMR resonances
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25 associated with the *iso*-propyl groups are relatively broad at room temperature, suggesting
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27 fluxional behavior resulting from Zr-P bond lability as has been observed for previous Zr
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29 tris(phosphinoamide) complexes [7, 46].
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Scheme 4. Synthesis of a heterobimetallic Zr/Co complex **3** incorporating three chiral ligands.

In a procedure analogous to that reported for other Zr/Co bimetallic complexes [7, 47], complex **2** was stirred with CoI_2 in CH_2Cl_2 for 48 hours to afford $\text{ClZr}((R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_3\text{CoI}$ (**3**) as a bright green solid in 85% yield (Scheme 4). The ^1H NMR spectrum of complex **3**, as prepared, is quite complicated, with a large number of paramagnetically broadened peaks with chemical shifts ranging from -4 to 120 ppm (Figures S4 and S5). We suggest that this is the result of a mixture of isomers, including the C_3 -symmetric species $\text{ClZr}(\mu\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_3\text{CoI}$ with three bridging phosphinoamide ligands, and at least one type of $(\eta^2\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)\text{Zr}(\mu\text{-X})(\mu\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_2\text{CoX}$, where halide scrambling is also possible. Although this mixture can be carried on without further purification to afford a single reduction product (*vide infra*), a single C_3 -symmetric product $\text{ClZr}(\mu\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_3\text{CoI}$ (**3**) as a bright green solid in 85% yield (Scheme 4). The ^1H NMR spectrum of complex **3**, as prepared, is quite complicated, with a large number of paramagnetically broadened peaks with chemical shifts ranging from -4 to 120 ppm (Figures S4 and S5). We suggest that this is the result of a mixture of isomers, including the C_3 -symmetric species $\text{ClZr}(\mu\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_3\text{CoI}$ with three bridging phosphinoamide ligands, and at least one type of $(\eta^2\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)\text{Zr}(\mu\text{-X})(\mu\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_2\text{CoX}$, where halide scrambling is also possible. Although this mixture can be carried on without further purification to afford a single reduction product (*vide infra*), a single C_3 -symmetric product $\text{ClZr}(\mu\text{-(}R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_3\text{CoI}$ (**3**) as a bright green solid in 85% yield (Scheme 4).

PhCH₃CH)NP^{*i*}Pr₂)₃CoI can be isolated via crystallization. Crystalline **3** has only 11 distinct ¹H NMR resonances, consistent with the three phosphinoamide ligands arranged symmetrically around Zr and Co (Figure S6). The measured solution state magnetic moment of **3** was 3.22 μB, consistent with the two unpaired electrons expected for a Zr^{IV}/Co^I complex.

The formulation of complex **3** as a heterobimetallic Zr/Co complex bridged by three phosphinoamide ligands was confirmed via X-ray crystallography (Figure 1). Complex **3** crystallizes in the chiral space group *P*2₁2₁2₁ and the absolute stereochemistry was established as *R* at each stereocenter by using Flack parameter refinement. The Zr-Co distance in **3** is 2.6499(3) Å and is comparable to similar ClZr(R[']NPR₂)₃CoI compounds synthesized by our group and found to possess significant Co→Zr dative interactions (2.63–2.73 Å) [7].

Figure 1. Displacement ellipsoid (50%) representation of complex **3**. For clarity, hydrogen atoms and toluene solvate molecules have been omitted. Relevant interatomic distances (Å) and angles (°): Co-Zr, 2.6499(3); Zr-N1, 2.1268(15); Zr-N2, 2.1313(15); Zr-N3, 2.1095(15); Co-P1, 2.3544(5); Co-P2, 2.3424(5); Co-P3, 2.3639(6), Zr-Cl, 2.4387(6); Co-I, 2.5744(3); Cl-Zr-Co,

179.78(1); I-Co-Zr, 176.45(1); P1-Co-P2, 105.87(2); P1-Co-P3, 106.178(19); P2-Co-P3, 112.470(19); N1-Zr-N2, 119.63(6); N1-Zr-N3, 117.07(6); N2-Zr-N3, 121.83(6).

Scheme 5. Two-electron reduction of **3** to form complex **4**.

Bulk chemical reduction of **3** (crystalline or as-prepared) by two electrons with Na/Hg under a dinitrogen atmosphere gave brown-red $\text{Zr}((R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)_3\text{CoN}_2$ (**4**) in 64% yield after benzene extraction to ensure removal of NaX salts (Scheme 5). Complex **4** is diamagnetic, and its ¹H NMR spectrum does not show any resonances corresponding to a THF solvent molecule bound to Zr, suggesting a trigonal pyramidal Zr center with an open coordination site. The infrared spectrum of compound **4** features a strong vibration at 2063 cm^{-1} , assigned as a Co-N₂ stretch. As a measure of backbonding, the N₂ stretching frequency is an excellent reporter of the relative electron density at Co in **4** compared to its congeners. The $\nu(\text{N}_2)$ of **4** is significantly higher than that of any of our group's previously published $(\text{L})\text{Zr}(\text{R}'\text{NPR}_2)_3\text{CoN}_2$ compounds (Table 1). For example, the stretches of $(\text{THF})\text{Zr}(\text{XylNP}^i\text{Pr}_2)_3\text{CoN}_2$ and $(\text{THF})\text{Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{CoN}_2$ are 2045 and 2026 cm^{-1} , respectively (Xyl = 3,5-dimethylphenyl) [8, 47]. A more direct comparison, however, can be made with the $[\text{}^i\text{PrNP}^i\text{Pr}_2]^-$ -ligated derivative, $\text{Zr}(\text{}^i\text{PrNP}^i\text{Pr}_2)_3\text{CoN}_2$, owing to its more comparable *N*-alkyl substituents and “naked” Zr center. Indeed, the $\nu(\text{N}_2)$ of $\text{Zr}(\text{}^i\text{PrNP}^i\text{Pr}_2)_3\text{CoN}_2$ is also high in energy at 2056 cm^{-1} . It can be concluded

that the Co center in **4** is the least electron rich of the series of heterobimetallic Zr/Co complexes, although the reason for this is not immediately clear and may be related to either the relative donating ability of the phosphinoamide ligand or a stronger dative Co→Zr interaction competing with N₂ for electron density.

Table 1. Comparison of $\nu(\text{N}_2)$ in a series of Zr/Co heterobimetallic complexes.

Complex	$\nu(\text{N}_2)^a$	Reference
Zr((<i>R</i> -PhCH ₃ CH)NP ^{<i>i</i>} Pr ₂) ₃ CoN ₂ (4)	2063 cm ⁻¹	this work
(THF)Zr(XylNP ^{<i>i</i>} Pr ₂) ₃ CoN ₂	2045 cm ⁻¹	[47]
(THF)Zr(MesNP ^{<i>i</i>} Pr ₂) ₃ CoN ₂	2026 cm ⁻¹	[8]
Zr(^{<i>i</i>} PrNP ^{<i>i</i>} Pr ₂) ₃ CoN ₂	2056 cm ⁻¹	[8]

^a Data collected in C₆H₆ using a KBr solution cell.

To probe the activity of reduced complex **4** as a catalyst for the hydrosilylation of ketones, 10 mol% of complex **4** was treated with acetophenone and PhSiH₃ in THF for 24 hr at room temperature. After an acidic workup only 9% of the starting material had been converted to the corresponding alcohol as determined using GC/MS, and chiral HPLC analysis showed an essentially racemic mixture of the *R* and *S* products. The diminished reactivity of **4** compared to (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ was initially surprising, but a rationale is readily provided when one considers the electronic differences between the two complexes. The 37 cm⁻¹ higher $\nu(\text{N}_2)$ of **4** suggests a much more electron poor Co center. Since the proposed mechanism for the hydrosilylation reaction invokes a one-electron transfer from Co to the ketone substrate [15, 17], the less reducing Co center in **4** leads to a far less active a catalyst.

Synthesis of a Tris(phosphinoamide)-linked Zr/Co Heterobimetallic Complex with Two Achiral and One Chiral Phosphinoamide ligand

In light of the diminished reactivity of **4** towards acetophenone hydrosilylation, we sought an alternative asymmetric catalyst design strategy that would preserve the reactivity of the C_3 -symmetric (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ complex. We envisioned an asymmetric complex comprised of just one chiral phosphinoamide ligand, as shown in Figure 2 where the star represents a chiral substituent. Incorporation of an achiral aryl group on two of the ligands would allow us to produce a complex more electronically similar to (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ to promote the desired catalytic activity, while the third chiral phosphinoamide ligand would provide the necessary enantioinduction to perform hydrosilylation asymmetrically.

Figure 2. Generic catalyst design, where the star represents a chiral substituent.

In pursuit of this goal, Zr(NMe₂)₄ was heated in a toluene solution with two equivalents of ^{*i*}Pr₂PNHMe_s in an effort to generate a (Me₂N)₂Zr(MesNP^{*i*}Pr₂)₂ precursor. However, only one ligand was incorporated and after extended heating at reflux, decomposition began to occur before any spectroscopic evidence for disubstitution was observed. Under the assumption that steric factors were at play, we chose to use a phosphinoamine with smaller *N*-aryl substituents and found that heating Zr(NMe₂)₄ with ^{*i*}Pr₂PNHXyl in toluene effects the transformation to (Me₂N)₂Zr(^{*i*}Pr₂PNXyl)₂ (**5**) in around 80% conversion based on ³¹P NMR spectroscopy (Scheme

6). Free ligand as well as the mono-substituted Zr species were also observed as minor byproducts. Without further purification, Zr complex **5** was converted cleanly to $\text{I}_2\text{Zr}(\text{}^i\text{Pr}_2\text{PNXyl})_2$ (**6**) via substitution with Me_3SiI in 76% isolated yield over two steps (Scheme 6). Complex **6** can be viewed as a useful Zr precursor for the synthesis of bimetallic complexes with a mixed ligand set. For the purposes of this study, we focused on the incorporation of a chiral ligand, but note that complex **6** could be a useful tool to probe the effect of substitution of only one ligand on the electronic structure and reactivity of Zr/Co heterobimetallic systems in general.

Scheme 6. Synthesis of Zr starting material **6** with two achiral ligands

Scheme 7. Synthesis of chiral tris(phosphinoamide) Zr complex **6**

To append a chiral ligand to Zr, chiral phosphinoamine **1** was deprotonated with $n\text{-BuLi}$

and then added dropwise to Zr precursor **6** at low temperature, producing $\text{IZr}((R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)(\text{XylNP}^i\text{Pr}_2)_2$ (**7**) in 89% yield (Scheme 7). The ^{31}P NMR spectrum of **7** has three distinct resonances at -0.61, -0.69, and -2.79 ppm (Figure S15). The ^1H NMR spectrum of complex **7** is consistent with a molecule with C_s symmetry (Figure S16). All six isopropyl methine peaks are chemically and magnetically distinct, and integration of the spectrum clearly establishes a 2:1 ratio of *N*-xylyl to *N*-CHCH₃Ph groups. The structure of complex **7** was confirmed crystallographically and is shown in Figure 3.

Figure 3. Displacement ellipsoid (50%) representations of **7** with hydrogens omitted for clarity (A) and hydrogens and *iso*-propyl carbon atoms removed for clarity (B).

With Zr complex **7** in hand, the chiral heterobimetallic Zr/Co complex (η^2 -(*R*-

$\text{PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)\text{Zr}(\mu\text{-I})(\mu\text{-XylNP}^i\text{Pr}_2)_2\text{CoI}$ (**8**) was formed in 97% yield in a reaction of Zr metalloligand **7** with CoI_2 (Scheme 8). Complex **8** has a solution state magnetic moment of 3.35 μB , in line with two unpaired electrons and an $S = 1$ ground state. The ^1H NMR spectrum of **8** features 18 distinct broad signals between -9 and +39 ppm (Figure S18). The structure of **8** was determined using single crystal X-ray diffraction and the solid state structure (Figure 4) reveals that complex **8** adopts a structure in which two $[\text{XylNP}^i\text{Pr}_2]^-$ ligands and one iodide ligand bridge the Zr and Co centers while the chiral $[(R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2]^-$ ligand binds η^2 to the Zr center. While tris(phosphinoamide) Zr/Co complexes comprised of three $[\text{MesNP}^i\text{Pr}_2]^-$ or $[\text{}^i\text{PrNP}^i\text{Pr}_2]^-$ ligands adopt geometries with three phosphinoamide ligands bridging the two metal centers [7], the tris- $[\text{XylNP}^i\text{Pr}_2]^-$ derivative and complex **8** apparently favor a halide-bridged configuration [47]. The metal–metal distance of 2.762(1) Å compares well with other halide bridged Zr/Co tris(phosphinoamide complexes of the same general form and indicates a weak dative $\text{Co} \rightarrow \text{Zr}$ interaction [11, 47]. In addition to establishing connectivity, the solid state structure of **8** also confirms that the chiral ligand has maintained its stereocenter throughout the synthesis.

Scheme 8. Synthesis of Zr/Co heterobimetallic complex 8

Figure 4. Displacement ellipsoid (50%) representation of **8**. For clarity, all hydrogen atoms have been omitted and only one position of disordered *iso*-propyl groups is shown.

In an effort to isolate a two-electron reduced dinitrogen complex to be screened in catalytic reactions, complex **8** was reduced with excess Na/Hg. However, efforts to isolate the desired L-Zr((*R*-PhCH₃CH)NP^{*i*}Pr₂)(XylNP^{*i*}Pr₂)₂CoN₂ complex (L = THF or open) were unsuccessful and substantial quantities of free phosphinoamine ligands were observed in ¹H and ³¹P NMR spectra of the reaction mixture.

Conclusions

We have successfully synthesized several chiral heterobimetallic Zr/Co complexes. Using three chiral ligands, we have synthesized a reduced C₃-symmetric bimetallic complex with chiral amide substituents on each of three phosphinoamide linkers. While this complex was relatively straightforward to prepare, it was shown to have limited catalytic activity for the

hydrosilylation of ketones. Using the infrared stretching frequency of the Co-bound N₂ ligand as a direct measure of the electron density at Co, Zr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃CoN₂ (**4**) is found to be significantly less electron-rich than the previously reported more active (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂ catalyst, and we posit that this is the origin of the diminished reactivity of **4**. Based on this finding, it is important that the incorporation of chiral functionalities into the Zr/Co tris(phosphinoamide) system is executed in such a way that perturbation of the electron-rich Co center is minimal. To maintain as much electronic similarity as possible to (THF)Zr(MesNP^{*i*}Pr₂)₃CoN₂, a synthetic route to tris(phosphinoamide) Zr/Co complexes possessing two [XylNP^{*i*}Pr₂]⁻ ligands and one chiral phosphinoamide ligand was also developed. However, a reduced dinitrogen-bound precatalyst was too unstable to isolate and screen as a catalyst in this case. Unfortunately, complex **4** produced essentially racemic hydrosilylation products. This result alone does not disprove our previously proposed mechanism for this reaction, as it is quite likely that the reaction pocket around the Zr center could be too large to induce asymmetry and hindering the approach of a primary silane or an H-atom might require more sterically hindered chiral functionalities.

Nevertheless, the synthetic protocol for mixed-ligand complex **8** involves the synthesis of a bis(phosphinoamide) Zr precursor, I₂Zr(^{*i*}Pr₂PNXyl)₂ (**6**), which is a useful intermediate for generating a family of tris(phosphinoamide) metalloligands with a 2:1 ratio of phosphinoamide ligands with different phosphorus and nitrogen substituents allowing future opportunities for further catalyst design.

Experimental Section

General Considerations

All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or using standard Schlenk techniques and were stirred magnetically unless otherwise noted. All glassware was oven or flame-dried immediately prior to use. Benzene, dichloromethane, diethyl ether, pentane, tetrahydrofuran, and toluene were degassed and dried by sparging with ultra-high-purity argon gas, followed by passage through a series of drying columns using a Seca Solvent System by Glass Contour. All solvents were stored over 3 Å molecular sieves and frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. For column chromatography purposes, hexanes and ethyl acetate were obtained as ACS reagent grade and used without further purification. Benzene-*d*₆, CDCl₃, and CD₂Cl₂ were degassed via freeze-pump-thaw cycles and dried over 3 Å molecular sieves before use. NMR spectra were recorded at ambient temperature unless otherwise stated on a Varian Inova 400 MHz or an Agilent Technologies 400-MR instrument. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent and are reported in parts per million (ppm). ³¹P NMR chemical shifts were referenced to an external standard of 85% H₃PO₄. GC-MS data were collected on an Agilent 7890A GC System and 5975C VL MSD with a Triple-Axis Detector. Infrared spectra were recorded on a Varian 640-IR spectrometer controlled by Resolutions Pro software. UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using Cary WinUV software. Elemental micro-analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ. ⁱPr₂PNHXyl was prepared via a literature procedure.[47] Anhydrous CoI₂ was purchased from a commercial vendor and heated to 100°C under vacuum for at least 12 hours prior to use. All other reagents and solvents were obtained from commercial sources and used without further purification.

X-Ray Crystallography

All operations were performed on a Bruker–Nonius Kappa Apex2 diffractometer, using graphite–monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software [48]. Preliminary cell constants were obtained from three sets of 12 frames. Crystallographic data and refinement parameters are included in Table 2 and on pages S12–S17 of the Supporting Information file.

Table 2. Crystallographic data collection and refinement parameters for **3**, **7** and **8**.

	3 •C ₇ H ₈	7	8
chemical formula	C ₄₉ H ₇₇ ClCoIn ₃ P ₃ Zr	C ₄₂ H ₆₉ In ₃ P ₃ Zr	C ₄₂ H ₆₉ CoI ₂ N ₃ P ₃ Zr
fw	1113.60	927.07	1112.91
<i>T</i> (K)	120 K	120 K	120 K
λ (Å)	0.71073	0.71073	0.71073
<i>a</i> (Å)	13.3111(11)	14.1519(7)	13.4661(5)
<i>b</i> (Å)	17.1820(14)	14.1520(7)	13.7067(4)
<i>c</i> (Å)	22.5584(18)	22.8352(11)	13.4759(5)
α (°)	90	90	90
β (°)	90	90	99.002(2)
γ (°)	90	90	90
<i>V</i> (Å ³)	5159.4(7)	4573.4(4)	2456.69(9)
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁
<i>Z</i> , <i>Z</i> '	4, 1	4, 1	2, 1
Flack Parameter	0.012(7)	0.019(6)	0.022(15)
<i>D</i> _{calcd} (g/cm ³)	1.434	1.346	1.504
μ (mm ^{−1})	1.302	1.051	1.934
<i>R</i> ₁ (<i>I</i> > 2 σ) ^a	0.0231	0.0206	0.0390

wR_2 (all data) ^a	0.0560	0.0499	0.0768
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$$^a R_I = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$$

Synthesis of (*R*-PhCH₃CH)NHP^{*i*}Pr₂ (**1**)

Phosphinoamine **1** was prepared using modifications of a literature procedure.[45] To a solution of (*R*)- α -methylbenzylamine (7.79 g, 64.3 mmol), triethylamine (6.51 g, 64.3 mmol), and DMAP (0.165 g, 1.35 mmol) in 50 mL of pentane was added ClP^{*i*}Pr₂ (11.0 g, 70.5 mmol) dropwise. The resulting suspension was allowed to stir overnight, then the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated *in vacuo* to give a yellow oil. The oil was dissolved in 5 mL of pentane, filtered through a plug of silica gel and concentrated *in vacuo* to give phosphinoamine **1** as a viscous colorless oil (13.4 g, 93%). The spectroscopic data were identical to those previously reported in the literature for the opposite, *S*, enantiomer.

Synthesis of ClZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃ (**2**)

To a –35 °C solution of phosphinoamine **1** (1.47 g, 6.53 mmol) in 10 mL of Et₂O was added *n*-BuLi (1.6 M in hexanes, 4.5 mL, 7.2 mmol) dropwise. The resulting yellow solution was warmed to room temperature and allowed to stir overnight to ensure complete deprotonation. In a cold well cooled with liquid nitrogen, a suspension of ZrCl₄ (0.509 g, 2.18 mmol) in 10 mL of Et₂O was cooled. The phosphinoamide solution was added dropwise to the suspension of ZrCl₄, and the reaction mixture was allowed to warm to room temperature and stir overnight. The resulting orange solution was dried under vacuum, and the remaining residue was dissolved in 15 mL of CH₂Cl₂ and filtered through Celite to remove LiCl. The filtrate was dried *in vacuo*, pentane (10 mL) was added to the remaining solids, and Zr complex **2** was collected via filtration as a tan solid. Crystallization from a concentrated solution of **2** in Et₂O at –35 °C gave analytically pure **2.3** as a white crystalline solid (0.723 g, 41%). ¹H NMR (400 MHz, CDCl₃): δ

7.84 (d, $J = 7.4$ Hz, 6H, *o*-Ph), 7.25 (t, $J = 7.4$ Hz, 6H, *m*-Ph), 7.15 (t, $J = 7.4$ Hz, 3H, *p*-Ph), 4.55 (br m, 3H, PhCHCH₃R), 2.24 (br m, 3H, CH(CH₃)₂), 1.88 (d, $J = 6.8$ Hz, 9H, PhCHCH₃R), 1.75 (br m, 3H, CH(CH₃)₂), 1.54 (br m, 9H, CH(CH₃)₂), 1.39 (br m, 9H, CH(CH₃)₂), 0.94 (br m, 9H, CH(CH₃)₂), 0.34 (br m, 9H, CH(CH₃)₂); ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 150.4, 127.9 (2C), 126.2, 62.2, 33.8 (br s), 28.0, 23.8 (br s), 22.5 (br s), 20.4, 19.6 (br s), 18.6 (m); ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 6.00. Anal. Calcd for C₄₂H₆₉ClN₃P₃Zr: C, 60.37; H, 8.32; N, 5.03. Found: C, 60.17; H, 8.20; N, 4.89.

Synthesis of ClZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃CoI (**3**)

To a solution of Zr complex **2** (0.506 g, 0.605 mmol) in 10 mL of CH₂Cl₂ was added CoI₂ (0.193 g, 0.616 mmol). The suspension was stirred at room temperature for 48 hours. The dark green reaction mixture was then filtered through Celite and concentrated to give a green foamy residue. To this was added of pentane (10 mL) and the solids were stirred overnight. The pentane washings were decanted and the remaining bright green solids dried *in vacuo* to give Zr/Co bimetallic **3** (0.523 g, 85%). Single crystals suitable for X-ray crystallography were grown from either a concentrated toluene solution of **3** or via layering pentane onto a concentrated CH₂Cl₂ solution of **3** at -35 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ 118.7, 20.0, 13.1, 8.7, 7.5, 7.2, 4.0, 2.3, -0.4 (d, $J = 18$ Hz), -0.7 (d, $J = 15$ Hz), -3.8. Evans' Method (298 K, CD₂Cl₂): 3.22 μB; UV-vis (THF; λ, nm (ε, M⁻¹ cm⁻¹)): 270 (8.5 × 10³), 380 (4.4 × 10³), 645 (5.2 × 10²); Anal. Calcd for C₄₂H₆₉N₃P₃ClIZrCo: C, 49.39; H, 6.81; N, 4.11. Found: C, 49.38; H, 6.90; N, 4.12.

Synthesis of Zr((*R*-PhCH₃CH)NP^{*i*}Pr₂)₃CoN₂ (**4**)

A 0.5% by weight Na amalgam was prepared by the addition of Na (0.030 g, 1.32 mmol) to Hg (6.1 g) in 3 mL of THF. To this was added a green solution of **3** (0.523 g, 0.512 mmol) in 5 mL

of THF. The reaction solution gradually turned from a dark green color to a dark red color over the span of 5 minutes. After 2 hours, the reaction mixture was decanted off the amalgam and dried in vacuo. The remaining residue was extracted in 10 mL of benzene and the resulting suspension was filtered to remove sodium halide salts. The filtrate was lyophilized to give brown-red solids of **4** (0.316 g, 70%). ^1H NMR (400 MHz, C_6D_6): δ 7.36 (d, $J = 7.5$ Hz, 6H, *m*-Ph), 7.14 (t, $J = 7.5$ Hz, 6H, *o*-Ph), 6.98 (t, $J = 7.1$ Hz, 3H, *p*-Ph), 4.81 (m, 3H, PhCHCH₃R), 2.98 (m, 3H, CH(CH₃)₂), 2.61 (m, 3H, CH(CH₃)₂), 1.48 (m, 27H overlapping, CH(CH₃)₂), 1.31 (m, 9H, CH(CH₃)₂), 1.18 (d, $J = 6.4$ Hz, 9H, PhCHCH₃R); ^{13}C { ^1H } NMR (100.6 MHz, C_6D_6): δ 151.7, 128.9, 126.8, 125.9, 58.1 (m), 33.7 (m), 31.9 (m), 30.4 (m), 22.0 (m), 20.5 (m), 19.9, 19.5; ^{31}P { ^1H } NMR (162 MHz, C_6D_6): δ 38.3 (br). IR (C_6H_6): 2063 cm^{-1} (Co–N₂); UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)): 345 (1.1×10^4). Anal. Calcd for $\text{C}_{42}\text{H}_{69}\text{N}_5\text{P}_3\text{ZrCo}$: C, 56.86; H, 7.84; N, 7.89. Found: C, 56.52; H, 8.02; N, 7.54.

Synthesis of $(\text{Me}_2\text{N})_2\text{Zr}(\text{}^i\text{Pr}_2\text{PNHXyl})_2$ (**5**) and $\text{I}_2\text{Zr}(\text{}^i\text{Pr}_2\text{PNXyl})_2$ (**6**)

A screwtop pressure tube was charged with a solution of $\text{Zr}(\text{NMe}_2)_4$ (2.24 g, 8.37 mmol) and $\text{}^i\text{Pr}_2\text{PNHXyl}$ (3.98 g, 16.8 mmol) in 30 mL of toluene. The tube was sealed, removed from the glovebox and heated at 90 °C for 24 h. The ^{31}P NMR spectrum of the resulting mixture revealed ~80% conversion to $(\text{NMe}_2)_2\text{Zr}(\text{}^i\text{Pr}_2\text{PNXyl})_2$ (**5**) with a peak at δ 15.6 ppm. The reaction mixture, which also contained $\text{}^i\text{Pr}_2\text{PNHXyl}$, was dried *in vacuo* to obtain crude **5** as a thick yellow oil that was used without further purification. ^1H NMR (400 MHz, C_6D_6): δ 6.93 (s, 4H, *o*-Xyl), 6.55 (2, 2H, *o*-Xyl), 3.36 (s, 12H, N(CH₃)₂), 2.52 (m, 4H, CH(CH₃)₂), 2.28 (s, 12H, CH₃-Xyl), 1.05-1.18 (overlapping m, 24H, CH(CH₃)₂); ^{31}P { ^1H } NMR (162 MHz, C_6D_6): δ 15.6 (br).

Crude **5** was dissolved in of pentane (30 mL) and Me₃SiI (3.35 g, 16.8 mmol) was added dropwise with strong stirring. A bright yellow precipitate was immediately observed. The reaction mixture was stirred overnight and stored in the freezer for several hours to ensure complete precipitation. The pentane was decanted, and the remaining solids were washed with 10 mL of pentane and dried to give **6** as a bright yellow solid (5.20 g, 76% over 2 steps). ¹H NMR (400 MHz, C₆D₆): δ 6.64 (s, 4H, *o*-Xyl), 6.43 (s, 2H, *p*-Xyl), 2.49 (m, 4H, CH(CH₃)₂), 2.07 (s, 12H, CH₃-Xyl), 1.23 (m, 12H, CH(CH₃)₂), 1.14 (m, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ 150.9, 138.24 125.9, 120.9, 28.8, 21.6, 20.8 (br), 20.0 (m); ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 7.08. Anal. Calcd for C₂₈H₄₆I₂N₂P₂Zr: C, 41.13; H, 5.67; N, 3.43. Found: C, 40.98; H, 5.74; N, 3.42.

IZr((*R*-PhCH₃CH)NP^{*i*}Pr₂)(XylNP^{*i*}Pr₂)₂ (7**)**

To a -35 °C solution of phosphinoamine **1** (0.354 g, 1.12 mmol) in 5 mL of Et₂O was added *n*-BuLi (1.6 M in hexanes, 0.89 mL, 1.4 mmol) dropwise. The resulting yellow solution was warmed to room temperature and allowed to stir for 1 h. In a cold well cooled with liquid nitrogen, a suspension of **6** (1.05 g, 1.28 mmol) in 10 mL of Et₂O was cooled. The solution of phosphinoamide ligand was added dropwise to the suspension of **6**, then allowed to warm to room temperature and stir overnight. The yellow suspension was then dried in vacuo, and the remaining solids were dissolved in pentane and filtered through Celite. The yellow filtrate was concentrated to give **7** as an off-white foamy solid (1.06 g, 89%). Single crystals suitable for X-ray crystallography were grown from a concentrated solution of **7** in pentane at -35 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, *J* = 7.3 Hz, 2H, *m*-Ph), 7.26 (t, *J* = 7.3 Hz, 2H, *o*-Ph), 7.17 (t, *J* = 7.3 Hz, 1H, *p*-Ph), 6.79 (s, 2H, *o*-Xyl), 6.71 (s, 2H, *o*-Xyl), 6.57 (s, 1H, *p*-Xyl), 6.55 (s, 1H, *p*-Xyl), 5.15 (dq, *J* = 13.5, 6.9 Hz, 1H, PhCHCH₃R), 2.75 (m, 1H, CH(CH₃)₂), 2.68–2.50 (m, 2H

overlapping, $\text{CH}(\text{CH}_3)_2$), 2.43 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.29 (s, 6H, $\text{CH}_3\text{-Xyl}$), 2.25 (s, 6H, $\text{CH}_3\text{-Xyl}$), 2.21–2.01 (m, 2H overlapping, $\text{CH}(\text{CH}_3)_2$), 1.65 (d, $J = 6.9$ Hz, 3H, PhCHCH_3R), 1.46–1.10 (m, 24H overlapping, $\text{CH}(\text{CH}_3)_2$), 1.05–0.81 (m, 9H overlapping, $\text{CH}(\text{CH}_3)_2$), 0.58 (m, 3H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 152.0 (d, $J = 8.2$ Hz), 151.4 (d, $J = 8.5$ Hz), 146.2, 137.0, 137.0, 127.7, 127.4, 126.2, 123.3, 122.7, 121.9 (d, $J = 3.6$ Hz), 121.0 (d, $J = 4.3$ Hz), 61.4 (d, $J = 7.2$ Hz), 33.9, 28.6 (d, $J = 12.0$ Hz), 27.9, 26.0 (dd, $J = 19.1, 3.6$ Hz), 25.6 (d, $J = 2.4$ Hz), 23.7, 22.2, 21.5 (d, $J = 15.3$ Hz), 21.3, 21.2 (2C), 21.2 (2C), 21.0, 20.9 (dd, $J = 10.4, 3.2$ Hz), 20.6 (dd, $J = 10.6, 1.6$ Hz), 19.8 (d, $J = 8.8$ Hz), 19.7 (d, $J = 8.8$ Hz), 19.5 (d, $J = 8.3$ Hz), 19.4 (br s), 18.0 (d, $J = 6.8$ Hz), 17.9, 13.9; ^{31}P NMR $\{^1\text{H}\}$ (162 MHz, CDCl_3): δ –0.61 (d, $J = 11.3$ Hz), –0.69, –2.79 (d, $J = 11.3$ Hz). Anal. Calcd for $\text{C}_{42}\text{H}_{69}\text{IN}_3\text{P}_3\text{Zr}$: C, 54.41; H, 7.50; N, 4.53. Found: C, 54.34; H, 7.55; N, 4.71.

$(\eta^2\text{-}(R\text{-PhCH}_3\text{CH})\text{NP}^i\text{Pr}_2)\text{Zr}(\mu\text{-I})(\mu\text{-XylNP}^i\text{Pr}_2)_2\text{CoI}$ (8**)**

To a solution of **7** (0.336 g, 0.363 mmol) in 10 mL of CH_2Cl_2 was added CoI_2 (0.124 g, 0.397 mmol). The suspension was stirred at room temperature for 24 hr. The dark green reaction mixture was then filtered through Celite and concentrated to give a green foamy solid. The residue became a sticky solid upon the addition of pentane (10 mL $\times$ 2). The yellow pentane washes were decanted and the remaining bimetallic complex **8** was dried to give a green foamy solid (0.391 mg, 97%). Single crystals suitable for X-ray crystallography were grown via layering a concentrated solution of **8** in Et_2O with pentane at -35 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ 39.0 (v br), 30.1 (v br), 10.4, 8.3 (d, $J = 8.6$ Hz), 7.4, 7.3, 7.1, 3.2 (d, $J = 14.6$ Hz), 2.2, 2.0, 1.8, 1.3, 1.2, 1.1, 0.1, –0.3, –0.8, –8.9; Evans' Method (298 K, CD_2Cl_2): 3.35 μB ; UV–vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 293 (6.8×10^3), 363 (3.3×10^3), 389 (2.7×10^3), 686 (1.0×10^3),

728 (9.4×10^2); Anal. Calcd for $C_{42}H_{69}N_3P_3I_2ZrCo$: C, 45.33; H, 6.25; N, 3.78. Found: C, 45.12; H, 6.12; N, 3.51.

General procedure for hydrosilylation of acetophenone

To a stirred solution of Zr/Co reduced complex **4** (0.030 mmol) in THF (2 mL) was added a solution of acetophenone (0.036 g, 0.30 mmol) and $PhSiH_3$ (0.032 g, 0.30 mmol) in THF (3 mL). The reaction mixture was stirred for 24 hr, removed from the glovebox and quenched by the addition of 4 M HCl (3 mL). The reaction mixture was extracted with Et_2O (3×3 mL), dried over $MgSO_4$ and concentrated to dryness. The crude reaction mixture was purified by preparative TLC (9:1 Hexanes/ $EtOAc$) and analyzed by chiral HPLC. **HPLC Analysis of the product:** Chiralcel OD; solvent system: 97/3 Hex/IPA; 1.0 mL/min; ret. times: 11.8 min (*R*), 14.4 min (*S*).

Appendix A. Supplementary data

Spectroscopic data for compounds **1-8**. CCDC 1426196-1426198 contain the supplementary crystallographic data for **3**, **7**, and **8**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: [\(+44\) 1223-336-033](tel:+441223336033); or e-mail: deposit@ccdc.cam.ac.uk. Crystallographic data collection and refinement details for the structures of **3**, **7**, and **8** can be found in the supplementary information file.

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Chiral phosphinoamide ligands are used to construct chiral heterobimetallic Zr/Co complexes with either three linking chiral ligands or a 2:1 ratio of achiral to chiral ligands.