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Catalytic Hydrosilylation of Ketones Using a Co/Zr Heterobimetallic Complex: Evidence for an Unusual Mechanism Involving Ketyl Radicals

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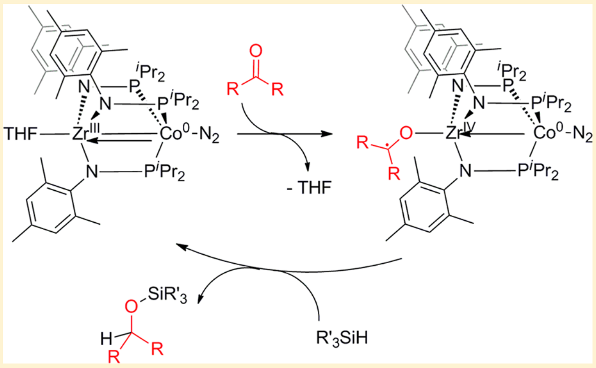
Supporting Information

ABSTRACT: The tris(phosphinoamide)-linked heterobimetallic Co/Zr complex (THF)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ (**1**) has been investigated as a catalyst for the hydrosilylation of ketones with PhSiH$_3$. Catalytic activity superior to monometallic Co or Zr analogues has been observed, demonstrating the importance of cooperative reactivity between Co and Zr. Upon examining stoichiometric reactions, complex **1** was found to be unreactive toward PhSiH$_3$, implying that the mechanism diverges from the typical Chalk−Harrod-type hydrosilylation pathway. In contrast, **1** reacts readily with ketones, and in the case of benzophenone, a radical coupling product [(Ph$_2$CO)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$]$_2$ (**3**) was isolated, implying the intermediacy of a Zr-bound ketyl radical fragment. A radical-based hydrosilylation mechanism is proposed involving hydrogen atom transfer from PhSiH$_3$ to the Zr-bound ketyl-radical.



■ INTRODUCTION

Hydrosilylation is a fundamental organometallic transformation for the reduction of alkenes, carbonyl, and imine functionalities.[1] The most common ketone hydrosilylation catalysts feature noble metals, such as Rh[2] and Ir;[3] however, hydrosilylation is now well-precedented for a variety of first-row transition metals, including titanium,[4−8] zinc,[9,10] copper,[6,11−14] nickel,[15−18] and iron.[19−23] In contrast, there are no reported zirconium-based hydrosilylation catalysts and cobalt-based carbonyl hydrosilylation catalysts have received limited attention.[24−27] Most ketone hydrosilylation mechanisms invoke metal hydride intermediates in the catalytic cycle, but the mechanism of action of cobalt and iron catalysts is not well-understood.[22] Given the propensity of first-row transition metals to undergo one-electron redox processes, one might predict alternative radical hydrosilylation mechanisms to be competitive (if not operative) pathways; however, no firm evidence for such routes has been presented.

A recent theme emerging in catalytic methodology is the use of bimetallic metal complexes to catalyze organic transformations.[28−30] While studies of homobimetallic catalysts are now quite common, comparatively little attention has been placed on early/late heterobimetallic catalysts,[31] particularly given the vast literature on the synthesis of early/late heterobimetallic complexes.[32−35] Several researchers have investigated ketone hydrosilylation reactions catalyzed by early/late heterobimetallic complexes.[31] Nikonov and coworkers screened several heterobimetallic Nb−Rh complexes for the catalytic hydrosilylation of acetophenone and benzaldehyde, but little mechanistic insight was provided and catalytic activities were similar to those observed with monometallic Rh complexes.[36] Similarly, Comte and Le Gendre et al. reported that ketone hydrosilylation with a heterobimetallic Ti−Rh complex proceeds more rapidly than with similar monometallic Rh or Ti complexes.[37] Notably, these heterobimetallic examples of ketone hydrosilylation catalysts utilize metals that are both known to be catalytically competent as monometallic species. A more interesting target, however, is a heterobimetallic system that promotes reactivity that is inaccessible with a monometallic analogue.

Our own work on heterobimetallic complexes focuses on tris(phosphinoamide)-linked early/late heterobimetallic combinations, most notably Zr/Co complexes.[38] We previously reported the synthesis and characterization of a highly reduced Zr/Co complex, (THF)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ (**1**, Mes = 2,4,6-trimethylphenyl), featuring metal−metal multiple bonds and the weakly coordinating labile apical ligands THF and N$_2$.[39] The reduced complex **1** has been shown to react with a series of small molecule substrates, such as I$_2$,[40] CO$_2$,[41] H$_2$,[40] hydrazines,[42] and alkyl halides.[40] The reactions with RX led us to investigate the catalytic activity of heterobimetallic Zr/Co complexes toward Kumada-type cross-coupling reactions between alkyl halides and alkyl Grignard reagents, revealing enhanced catalytic activity relative to monometallic Zr or Co analogues.[43]

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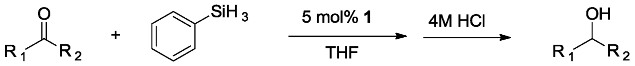
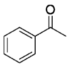
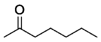
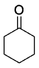
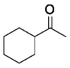
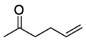
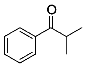
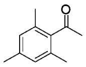
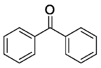
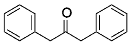
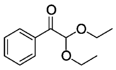
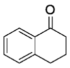
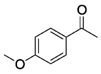
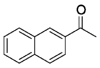
We postulated that reduction of polar substrates, such as ketones, would also be a promising application for Zr/Co heterobimetallic complexes, owing to the polar nature of the Zr−Co bonds in our catalyst precursors and the oxophilic nature of Zr. We began by first examining the hydrosilylation of ketones, and herein we describe the catalytic activity of complex **1** toward the hydrosilylation of ketones and *α*,*β*-unsaturated enones, and provide evidence for an unusual radical hydrosilylation mechanism.

RESULTS AND DISCUSSION

In a simple test reaction, we found that acetophenone was cleanly hydrosilylated by $PhSiH_3$ in the presence of 5 mol % of complex **1** after 6 h at room temperature to afford the corresponding alcohol after acidic workup (Table 1, entry 1). A number of alkyl and aryl ketones were screened to investigate the substrate scope of this catalytic reaction. Dialkyl ketones were hydrosilylated in very high yields at room temperature (entries 2−4), and the ketone functionality of the unsaturated ketone 5-hexene-2-one was hydrosilylated in high yield (98%) with no evidence for reduction of the alkene (entry 5). Complex **1** was also active toward more sterically hindered aryl-substituted ketones (entries 6−8), although in these cases, significantly longer reaction times were required to achieve a high yield at room temperature. Particularly bulky and/or electron-rich ketones (entries 9−13) required long reaction times at elevated temperature (65 °C), and in some cases, 20 mol % LiI was required to obtain moderate-to-high yields. Other additives and solvents were screened in an effort to optimize these reactions, but LiI proved to be the most effective additive (see the Supporting Information). While 5 mol % of complex **1** was utilized for all the reactions shown in Table 1, lower catalyst loadings (2.5 mol %) were also effective, albeit with longer reaction times (Table 2, entries 1−3).

Table 1. Hydrosilylation of Ketones with Phenylsilane Catalyzed by Complex 1[a,b,c,d]



entry	substrate	temp (°C)	Time (h)	yield (%)
1		rt	6	97[b,d]
2		rt	6	98[a]
3		rt	6	98[a]
4		rt	6	98[a]
5		rt	6	98[a]
6		rt	12	94[b]
7		rt	12	93[b]
8		rt	12	98[b]
9		65	12	98[b]
10		65	12	97[b,c]
11		65	12	87[b,c]
12		65	24	80[b,c]
13		65	24	76[b,c]

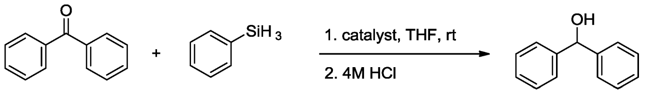
[a] Yield determined using GC/MS. [b] Isolated yield after column chromatography. [c] 20 mol % LiI was added to these reactions to improve the yield. [d] This reaction was run with a ketone/silane ratio of 1.4:1, showing that 1 equiv of silane can serve to reduce more than 1 equiv of ketone.

Examination of the silylated intermediates by GC/MS prior to acidic workup revealed a ∼3:1 ratio of the mono- and disubstituted silylether products from the crude hydrosilylation reaction with a 1:1 silane/ketone ratio ($PhH_2SiOCHMePh$ and $PhHSi(OCHMePh)_2$ in the case of acetophenone; see the Supporting Information). Subsequent hydrolysis of either of these silylethers via addition of 4 M HCl afforded the free alcohol product. Thus, in some cases, a substoichiometric amount of $PhSiH_3$ could be used with no effect on product yield (Table 1, entry 1). Other silanes, such as Ph_3SiH, $^{i}Pr_2ClSiH$, and Et_2SiH_2, were also investigated; however, the yields and reaction times were far inferior to those with $PhSiH_3$ (see the Supporting Information).

To ascertain the role of Co and Zr and the potential cooperative reactivity between these two metals, monometallic analogues of complex **1** were also screened as ketone hydrosilylation catalysts (Table 2). The monometallic Zr metalloligand precursor $(^{i}Pr_2PNMes)_3ZrCl$ did not show any hydrosilylation activity with benzophenone (entry 4), nor did a combination of CoI_2 with 3 equiv of phosphinoamine ligand to generate a monometallic Co complex in situ (entry 5). The isolated Co tris(phosphinoamine) complex $ICo(Ph_2PNH^{i}Pr)_3$ did afford the hydrosilylation product, but in low yield (30%, entry 6). Similar diminished yields were observed, even with longer reaction times, when other Co^{I} tris(phosphine) catalysts, such as $(PPh_3)_3CoI$, were employed as a catalyst (entries 7 and 8). These important control reactions imply that both Co and Zr are playing a role in the catalytic hydrosilylation reaction. Notably, the CO-ligated derivative of **1**, $(THF)Zr(MesNP^{i}Pr_2)_3Co(CO)$, was far less active than **1** (entry 9). At this point, we are unable to discern whether this is a consequence of the less labile CO ligand bound to Co or the decreased reducing nature of this complex.

Several *α*,*β*-unsaturated enones were also investigated under our standard hydrosilylation reaction conditions (Table 3). Complex **1** served as an effective catalyst for conjugate hydrosilylation; however, relatively long reaction times (24 h) and elevated temperatures (65 °C) were required. Chalcone (entry 1) and 1-phenylpent-2-en-1-one (entry 2) both underwent conjugate reduction readily under these conditions to afford moderate-to-high yields of the corresponding ketone upon acid hydrolysis of the silyl enol ether product. No evidence for the 1,2-reduction products (alcohols) was observed by GC-MS. Reduction of benzylideneacetone, however, proceeded more sluggishly and required the addition of 20 mol % LiI, and a mixture of the ketone and unsaturated alcohol product was isolated. In contrast, the hydrosilylation of an *α*,*β*-unsaturated aldehyde (entry 4) afforded the unsaturated alcohol product exclusively in high yield.

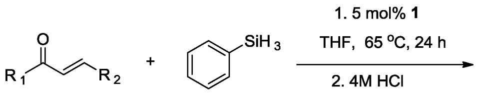
Table 2. Comparison of Catalytic Hydrosilylation Activity of Complex 1 to Monometallic Co and Zr Complexes

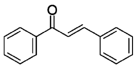
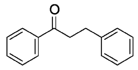
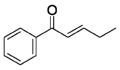
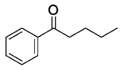
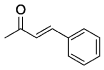
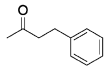
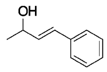
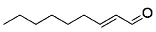
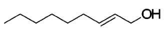


entry	catalyst	catalyst loading (mol %)	time (h)	yield (%)
1	**1**	5	12	98[b]
2	**1**	2.5	12	61[a]
3	**1**	2.5	18	92[a]
4	$(^{i}Pr_2PNMes)_3ZrCl$	5	12	0[a]
5	CoI_2 + $MesNHP^{i}Pr_2$	5/15	12	0[a]
6	$ICo(Ph_2PNH^{i}Pr)_3$	5	12	30[b]
7	$ICo(PPh_3)_3$	5	12	45[b]
8	$ICo(PPh_3)_3$	5	18	63[b]
9	$(THF)Zr(MesNP^{i}Pr_2)_3Co(CO)$	5	12	40[b]

[a] Yield determined using GC/MS. [b] Isolated yield after column chromatography.

Table 3. Reduction of α,β-Unsaturated Enones with Phenylsilane Catalyzed by Complex 1[a,b,c,d,e]



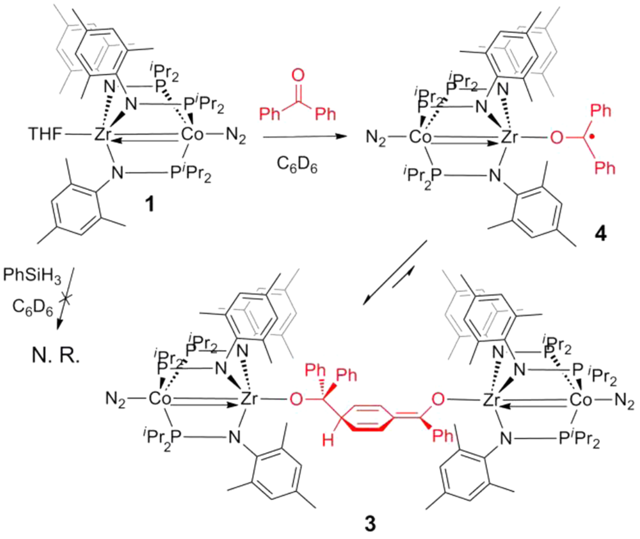
entry	substrate	product	yield [%]
1			90[a]
2			77[a,e]
3			58[a,e]
			22[b]
4			98[c,d]

[a] Isolated yield after column chromatography. [b] Ratio between the two products of entry 3 is 2.6:1 by GC/MS. [c] Yield determined using GC/MS. [d] The reaction was conducted at room temperature for 6 h. [e] 20 mol % LiI was necessary to achieve reasonable yields.

To gain some insight into the mechanism of this hydrosilylation reaction, stoichiometric reactions were conducted. On the basis of the canonical Chalk−Harrod hydrosilylation mechanism,[44] one might have envisioned a mechanism whereby silane is first oxidatively added to the metal center(s), followed by insertion of the ketone substrate into a M−H or M−Si bond.[1] Unexpectedly, however, no reaction occurs when complex **1** is treated with $PhSiH_3$ at room temperature based on ^1H NMR spectroscopy (Scheme 1).

Since complex **1** does not react with $PhSiH_3$, we investigated the reaction between **1** and a typical ketone substrate, benzophenone. Interestingly, this reaction resulted in the formation of a new complex **3** with a complex broad, paramagnetically shifted ^1H NMR spectrum (Scheme 1 and Supporting Information). The solid-state structure of **3** was determined by single-crystal X-ray diffraction (Figure 1), revealing that radical coupling of two ketyl radical fragments has occurred to generate an isobenzopinacol fragment, resulting in an asymmetric tetrametallic complex. The C−C bond lengths corresponding to the coupled benzophenone units in complex **3** are reminiscent of a formulation similar to Gomberg's dimer,[45−48] with lengthened and contracted C−C

Scheme 1



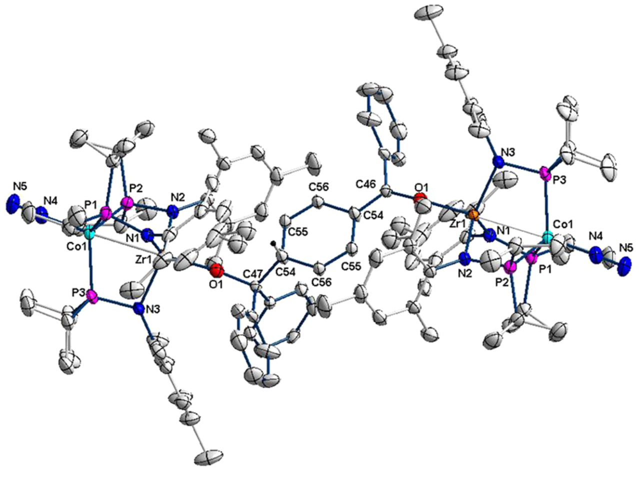


Figure 1. Displacement ellipsoid (50%) representation of complex **3**. Hydrogen atoms except for those bound to C54 have been omitted for clarity. Selected bond lengths (Å): Co−Zr, 2.744(3); Zr−O1, 1.9785(15); O1−C47, 1.477(4); C47−C54, 1.496(5); C54−C55, 1.478(3); C55−C56, 1.343(3); C46−C54, 1.364(4); C46−O1, 1.392(4).

distances in line with the loss of aromaticity in the central six-membered ring (Figure 1).

The benzophenone radical coupling product **3** is similar to the radical coupling products that have been reported using uranium(III)[49,50] and titanium(III)[51−53] complexes. Similar to previous reports, we propose that complex **3** forms via the benzophenone ketyl radical intermediate **4** (Scheme 1) and steric factors likely preclude the formation of the more traditional pinacol coupling products.[54−56] A computational (DFT) investigation of ketyl radical complex **4** was performed using Gaussian 09,[57] and a resulting plot of the Mulliken unpaired spin density is shown in Figure 2. In this triplet species, one unpaired electron resides on the Co center (formally, Co^0), while the second unpaired electron is delocalized throughout the Zr and its bound benzophenone ketyl ligand. While a small percentage of the unpaired spin resides on the Zr center (0.15 electrons), most of the spin density resides on the carbonyl carbon (0.60 electrons) and the *ortho* and *para* (0.18 and 0.20 electrons, respectively) carbons of one of the aromatic rings of the benzophenone. Intermolecular coupling of this ketyl radical through the *para* and benzylic carbons is consistent with this computational prediction. The asymmetric benzophenone dimer **3** does react with $PhSiH_3$ at room temperature over a period of several hours to form the expected silylether product ($PhSiH_2OCHPh_2$), indicating that the radical coupling process is reversible, consistent with the weak C−C bonds in Gomberg's dimer (11−12 kcal/mol)[47] and in $[(silox)_3Ti^{III}(OCPh_2)]_2$ (18 kcal/mol).[51] Consistent with the specificity of the catalytic process to primary silanes, Ph_3SiH does not react with complex **3** under ambient conditions.

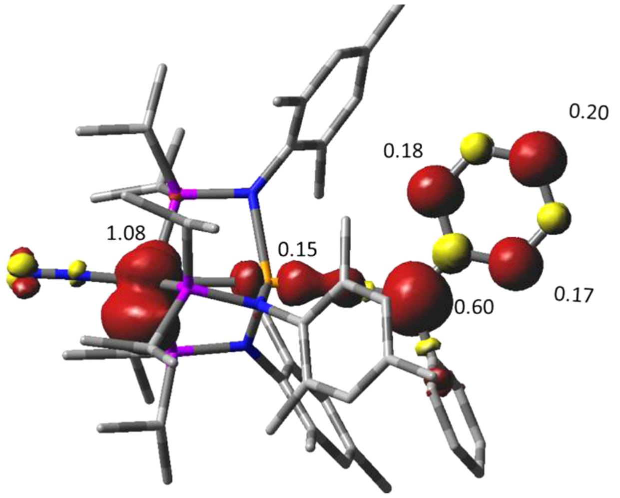
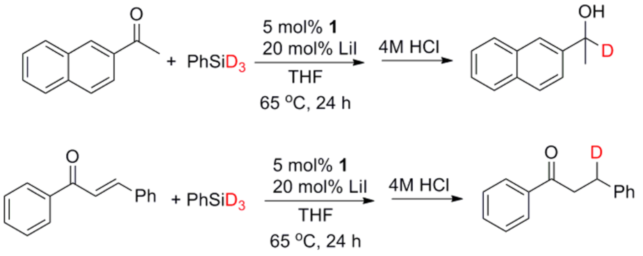


Figure 2. Plot of the Mulliken unpaired spin density surface of the purported ketyl radical complex **4** as calculated using DFT methods (BP86/LANL2TZ(f)/6-311G(d,p)/D95).

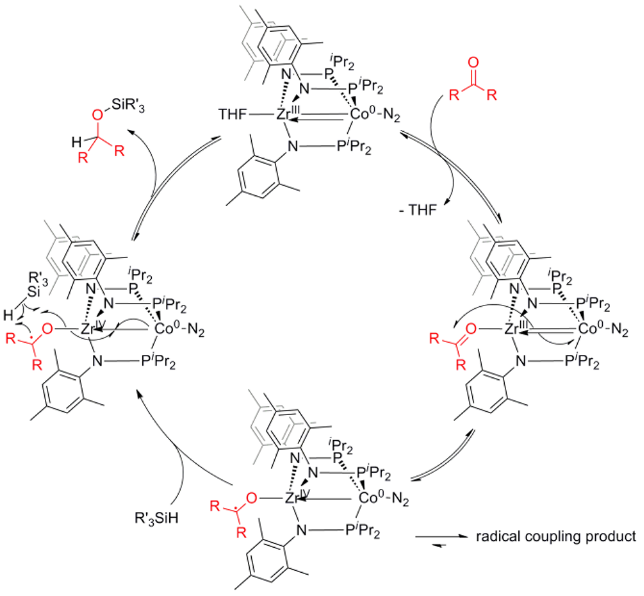
Deuterium labeling studies were carried out to further probe the hydrosilylation mechanism. As would be expected in a prototypical hydrosilylation reaction, treatment of methylnapthylketone with phenylsilane-d_3 under catalytic conditions (5 mol % **1**, 20 mol % LiI, 65 °C, 24 h) resulted exclusively in the product with a deuterium atom in the benzylic position after acidic workup (Scheme 2). Hydrosilylation of the α,β-unsaturated ketone chalcone also undergoes selective deuterium incorporation, this time at the β-position. Comparison of the initial reaction rates for the hydrosilylation reaction of benzophenone with $PhSiH_3$ and $PhSiD_3$ revealed an estimated kinetic isotope effect (KIE) k_H/k_D = 2.1, suggesting that Si−H bond cleavage is rate-determining (see the Supporting Information).

Scheme 2



On the basis of the stoichiometric reactions and the deuterium labeling experiments described above, a catalytic cycle for the hydrosilylation reaction is proposed (Scheme 3).

Scheme 3



Unlike the typical Chalk−Harrod hydrosilylation mechanism, the first step in this Zr/Co-catalyzed process involves ketone coordination, rather than Si−H activation. Upon coordination, an electron is transferred to the ketone, generating a ketyl radical intermediate. Similar one-electron transfer reactions to substrates bound through Zr have been proposed previously with these Zr/Co heterobimetallic systems,[42,58] and this one-electron transfer process is proposed to occur via homolytic cleavage of the Co−Zr bond. The ketyl radical intermediate can dimerize, as in the case of complex **3**, or can be intercepted as a monomer by a $PhSiH_3$. We suggest that the silane reacts by donating a hydrogen atom to the bound ketyl radical,[59] with concomitant formation of a Si−O bond and liberation of the resulting silyl ether to regenerate catalyst **1**. This is consistent with the relatively large KIE of 2.1, which implies that H-atom abstraction is rate-determining. Since this is an inner-sphere process, we propose that the bulky mesityl amide substituents preclude approach of the silane when di- or trisubstituted silanes are used, resulting in no hydrosilylation reactivity when silane reagents bulkier than $PhSiH_3$ are used. The isolated dimerized ketyl radical complex **3** (2.5 mol %) was shown to be a competent catalyst for the hydrosilylation of isopropyl phenyl ketone, affording the corresponding alcohol product in 99% isolated yield upon acid hydrolysis.

These results provide compelling evidence for the intermediacy of the ketyl radical complex **4** in the catalytic hydrosilylation mechanism of benzophenone. We recognize, however, that a different mechanism may be operative for ketones without an aromatic ring to stabilize a ketyl radical intermediate via delocalization. We also note that the requirement of LiI as an additive in certain cases (Table 1, entries 10–13) points toward a more canonical polar-type mechanism in the case of these particularly challenging substrates. However, a control reaction in which 1 equiv of LiI was added to benzophenone dimer **3** lead to formation of an as-yet-unidentified new product, implicating that a simple "Lewis acid" explanation for the role of LiI may not be valid.

■ CONCLUSION

In conclusion, we have examined the catalytic hydrosilylation of ketones by a Zr/Co heterobimetallic complex and have uncovered potential catalytically relevant intermediates that suggest a radical mechanism for this process. The Zr/Co heterobimetallic shows catalytic activity superior to that of Zr or Co monometallic analogues, implying that both Co and Zr play an important role in the catalytic process. It appears, based on stoichiometric reactions, that the catalytic process occurs at the Zr center and Co simply serves to facilitate radical reactivity at Zr by stabilizing the active Zr^{III} center via metal–metal bonding. It is important to point out that this catalyst features inexpensive and naturally abundant metals, and synthetically straightforward ligands. Future studies will focus on developing this and other reactions catalyzed by **1**, and further investigation of the mechanism and the unusual ketyl radical intermediates.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques unless otherwise noted. All glassware was oven or flame-dried immediately prior to use. Tetrahydrofuran and diethyl ether were obtained as HPLC grade without inhibitors; pentane, and benzene were obtained as ACS reagent grade. Tetrahydrofuran, diethyl ether, 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. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. Benzene-d_6 was degassed and dried over 4 Å molecular sieves before use. Complex **1** ((THF)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$),[39] ICo(Ph$_2$P-NH^{i}Pr)$_3$,[60] (THF)Zr(MesNP^{i}Pr$_2$)$_3$Co(CO),[58] and (*E*)-1-phenylpent-2-en-1-one[61] were prepared following literature procedures. All other reagents were purchased from Aldrich, Acros Organics, or Alfa Aesar and dried and degassed thoroughly prior to use. NMR spectra were recorded at ambient temperature unless otherwise stated on a Varian Inova 400 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent and are reported in parts per million. GC-MS data were collected on an Agilent 7890A GC System and 5975C VL MSD with a Triple-Axis Detector, and yields were reported via integration of starting materials and products. 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 microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

[(Ph$_2$CO)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$]$_2$ (3). In a 20 mL scintillation vial, (THF)Zr(MesNP^{i}Pr$_2$)$_3$CoN$_2$ (80 mg, 0.080 mmol) was dissolved in 2 mL of diethyl ether. To this solution was added a solution of benzophenone (16 mg, 0.086 mmol) in 2 mL of diethyl ether. After 5 min of swirling at room temperature, the yellow-orange solution was allowed to stand at −35 °C for 12 h. The brownish-yellow supernatant was decanted from the yellow crystalline solid and discarded. The yellow solid was dried in vacuo, affording 76 mg (85%) of complex **3**. ^{1}H NMR (400 MHz, C_6D_6): δ 9.09, 88.84, 8.59, 8.37, 8.07, 7.99, 7.89, 7.77, 7.68 (m), 7.56 (m), 7.46, 7.36, 7.27, 7.10, 7.00, 6.93, 6.49, 6.34, 5.83, 5.48, 5.41, 5.14, 4.87, 4.04, 3.98, 3.10, 3.00, 2.91, 2.39, 2.31, 2.16, 2.12, 1.98, 1.93, 0.57, 0.13, −0.54, −2.27, −2.75, −3.62, −3.86. UV–vis (C_6H_6, λ(nm) (ε, M^{-1} cm^{-1}): 331 (2.2×10^4). Evans' method (298 K, C_6D_6): 2.41 μB. IR (C_6H_6): 2046 cm^{-1} (Co-N$_2$), 1776 cm^{-1} (C-O). Because of the lability of the N$_2$ ligand, satisfactory elemental analysis was conducted on the N$_2$-free complex. Anal. Calcd for $C_{116}H_{170}N_6O_2P_6Co_2Zr_2$: C, 64.30; H, 7.91; N, 3.88. Found: C, 64.22; H, 7.98; N, 3.82.

Typical Procedure for Hydrosilylation of Ketones. In a nitrogen-filled glovebox, benzophenone (45.0 mg, 0.247 mmol) and phenylsilane (26.8 mg, 0.247 mmol) were weighed into a 20 mL vial. Dry THF (5 mL) and complex **1** (11.5 mg, 0.0115 mmol, 5 mol %) were added. The mixture was stirred at ambient temperature for 12 h. The reaction was removed from the glovebox, and 4 M aqueous HCl solution (1.5 mL) was added to quench the reaction. The organic layer was dried with MgSO$_4$ and filtered, and solvent was subsequently removed in vacuo. The remaining residue was purified by silica gel column chromatography (10:1 hexanes/ethyl acetate). Yield: 44.4 mg (97.6%).

Typical Procedure for Hydrosilylation of α,β-Unsaturated Enones. In a nitrogen-filled glovebox, (*E*)-chalcone (140 mg, 0.69 mmol) and phenylsilane (90 mg, 0.83 mmol) were weighed into a 20 mL vial. Dry THF (7 mL) and complex **1** (32 mg, 0.032 mmol, 5 mol %) were added, and the mixture was stirred at 65 °C for 24 h. The reaction was removed from the glovebox, and 4 M HCl aqueous solution (1.5 mL) was added to quench the reaction. The organic layer was dried with MgSO$_4$ and filtered, and the solvent was subsequently removed in vacuo. The remaining residue was purified by silica gel column chromatography (10:1 hexanes/ethyl cetate). Yield: 131 mg (90.0%).

PhSiD$_3$. This reagent was prepared following a modification of the literature procedure,[62] as follows. Solid LiAlD$_4$ (43 mg, 1 mmol) was added slowly to a solution of trichlorophenylsilane (210 mg, 1 mmol) in THF (7 mL) at −30 °C. The reaction was stirred for 16 h. The resulting solution was filtered through Celite to remove Li salts. The solvent was removed from the filtrate carefully at −30 °C to remove most of the Et$_2$O. The resulting PhSiD$_3$ was used without further purification.

Representative Procedure for NMR Kinetics Used To Estimate KIE. A screw-top NMR tube was charged with trimethoxybenzene (1.1 mg, 0.0065 mmol, internal standard) and PhSiH$_3$ (11.2 μL, 0.0910 mmol). In a 20 mL vial, complex **1** (4.6 mg, 0.0046 mmol) was dissolved in 0.7 mL of THF-d_8. The solution of **1** was added to a separate 20 mL vial containing benzophenone (16.8 mg, 0.0920 mmol). The resulting yellow solution was transferred to the NMR tube and mixed by shaking. The reaction progress was monitored by ^{1}H NMR spectroscopy at 25 °C taking scans every 5 min. The disappearance of the silane was recorded relative to the internal standard, and the data were processed using KaliedaGraph software.

X-ray Crystallography. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections, were carried out using the Bruker Apex2 software.[63] Preliminary cell constants were obtained from three sets of 12 frames. Additional crystallographic details and final CIF data are included as Supporting Information.

Computational Details. All calculations were performed using Gaussian 09, Revision A.02, for the Linux operating system.[57] Density functional theory calculations were carried out using a combination of Becke's 1988 gradient-corrected exchange functional[64] and Perdew's 1986 electron correlation functional[65] (BP86). A mixed-basis set was employed, using the LANL2TZ(f) triple-ζ basis set with effective core potentials for cobalt and zirconium,[66] Gaussian 09's internal 6-311+G(d) for heteroatoms (nitrogen, oxygen, phosphorus), and Gaussian 09's internal LANL2DZ basis set (equivalent to D95 V[67]) for carbon and hydrogen. Using crystallographically determined geometries as a starting point, the geometries were optimized to a minimum, followed by analytical frequency calculations to confirm that no imaginary frequencies were present.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional spectral data, screening of different reaction conditions, computational and crystallographic materials, and crystallographic data for **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Author Contributions

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Notes

The authors declare no competing financial interest.

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