Carbonyl and Ester C-O Bond Hydrosilylation Using κ^4-Diimine Nickel Catalysts

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ABSTRACT

The synthesis of alkylphosphine-substituted α-diimine (DI) ligands and their subsequent addition to $Ni(COD)_2$ allowed for the preparation of **(^{iPr2PPr}DI)Ni** and **(^{tBu2PPr}DI)Ni**. The solid state structures of both compounds were found to feature a distorted tetrahedral geometry that is largely consistent with the reported structure of the diphenylphosphine-substituted variant, **(^{Ph2PPr}DI)Ni**. To explore and optimize the synthetic utility of this catalyst class, all three compounds were screened for benzaldehyde hydrosilylation activity at 1.0 mol% loading over 3 h at 25 °C. Notably, **(^{Ph2PPr}DI)Ni** was found to be the most efficient catalyst while phenyl silane was the most effective reductant. A broad scope of aldehydes and ketones were then hydrosilylated, and the silyl ether products were hydrolyzed to afford alcohols in good yield. When attempts were made to explore ester reduction, inefficient dihydrosilylation was noted for ethyl acetate and no reaction was observed for several additional substrates. However, when an equimolar solution of allyl acetate and phenyl silane was added to 1.0 mol% **(^{Ph2PPr}DI)Ni**, complete ester C-O bond hydrosilylation was observed within 30 min at 25 °C to generate propylene and $PhSi(OAc)_3$. The scope of this reaction was expanded to include six additional allyl esters, and under neat conditions, turnover frequencies of up to 990 h^{-1} were achieved. This activity is believed to be the highest reported for transition metal-catalyzed ester C-O bond hydrosilylation. Proposed mechanisms for **(^{Ph2PPr}DI)Ni**-mediated carbonyl and allyl ester C-O bond hydrosilylation are also discussed.

INTRODUCTION

Homogeneous hydrosilylation catalysts have a rich history of development and are widely used by the chemical industry for the preparation of value-added products and materials.[1] In the 1950s, researchers at Dow Corning discovered that $H_2PtCl_6 \cdot 6H_2O$ mediates the hydrosilylation of olefins[2] and Pt catalysts are still used to prepare silicone-based coatings, sealants, and consumer products due to their exceptional activity.[3] Approximately 15 years later, Ojima and co-workers found that $(Ph_3P)_3RhCl$ (Wilkinson's Catalyst)[4] exhibits impressive activity for a related transformation, the hydrosilylation of carbonyl-containing compounds.[5] Although carbonyl hydrosilylation has only recently been used to prepare silicones,[6] chiral Rh catalysts have been extensively utilized to generate alcohols from ketones in an asymmetric fashion.[7]

Although Pt- and Rh-based hydrosilylation catalysts remain popular, the cost[8] and toxicity[9] associated with these metals are inherently disadvantageous. For this reason, recent efforts to develop carbonyl hydrosilylation catalysts have focused on the utilization of Earth-abundant metals including Mn,[10] Fe,[11] Co,[12] Cu,[13] and Zn.[14] Homogenous compounds of Ni are known to mediate alkene hydrosilylation;[15] however, their propensity to catalyze carbonyl hydrosilylation has remained relatively understudied. In 2009, Guan and co-workers reported that [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiH (Figure 1, **A**) catalyzes aldehyde hydrosilylation with turnover frequencies (TOFs) of 250 h^{-1}.[16] Later that year, Mindiola and co-workers achieved aldehyde and ketone hydrosilylation TOFs of 287 h^{-1} and 14 h^{-1}, respectively, upon heating solutions of substrate, $HSiEt_3$, [(PN^{i}Pr$_3$)Ni(μ^2-Br)]$_2$ (Figure 1, **B**), and KO^{t}Bu to 100 °C.[17] The leading example of Ni-catalyzed aldehyde hydrosilylation in terms of ambient temperature activity was published by Postigo and Royo in 2012, whereby TOFs of up to 2304 h^{-1} were achieved using $PhSiH_3$ and (Cp*-NHC^{Me})Ni(O^{t}Bu) (Figure 1, **C**).[18] At 60 °C, a half-sandwich Ni complex (Figure 1, **D**) developed by Albrecht and co-workers was found to hydrosilylate aldehydes with initial TOFs of up to 23,000 h^{-1}.[19] Compounds of this type have also been employed to reduce aldehydes and ketones in the presence of Ph_2SiH_2.[20] A (PBP)Ni borane complex developed by the Peters Group has been used to reduce benzaldehydes in the presence of $PhSiH_3$ and extensive mechanistic studies suggest that the ligand is chemically non-innocent.[21] Most recently, Schmidt and co-workers reported a cationic (κ^2-PN)Ni(allyl) precatalyst for carbonyl hydrosilylation.[22]

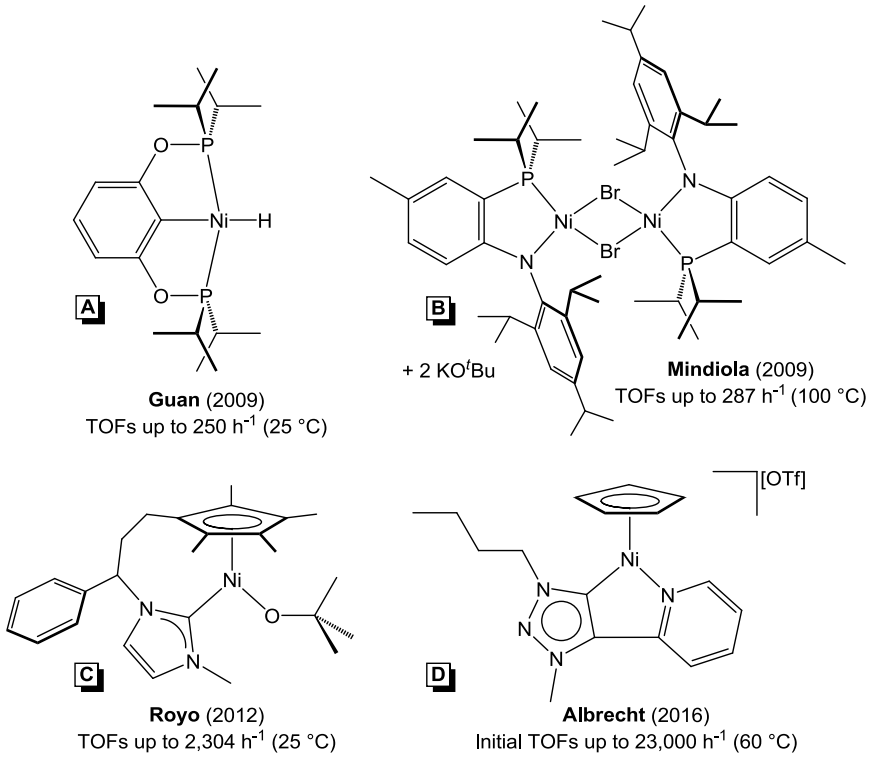
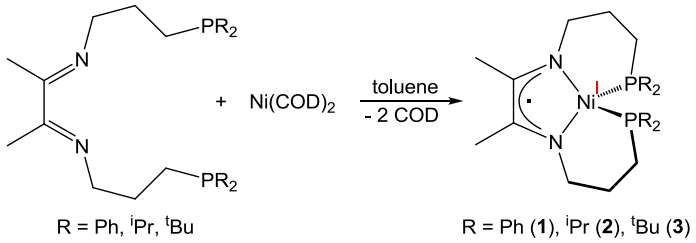


Figure 1. A selection of leading Ni catalysts for carbonyl hydrosilylation.

In 2013, our group synthesized the tetradentate α-diimine (DI) Ni compound, **(^{Ph2PPr}DI)Ni** (**1**, Scheme 1), which features a propylene bridge between the imine and phosphine donor groups.[23] At 5.0 mol% loading, **1** was found to catalyze the hydrosilylation of cyclohexanone and diisopropyl ketone to yield a mixture of silyl ethers over the course of 24 h at 25 °C.[23] Herein, we report the synthesis and characterization of two alkylphosphine variants and compare their carbonyl hydrosilylation activity to **1**. Following optimization, a broad scope of aldehyde and ketone hydrosilylation was achieved with modest TOFs of 41 h^{-1} and 4 h^{-1}, respectively. Attempts to hydrosilylate esters allowed for the dihydrosilylation of ethyl acetate at 60 °C to yield a mixture of $(EtO)PhSiH_2$ and $(EtO)_2PhSiH$. While many other esters were unaffected, unsubstituted allyl esters were selectively cleaved to produce propylene and tricarboxyphenylsilanes via ester C-O bond hydrosilylation with unprecedented activity.

RESULTS AND DISCUSSION:

Synthesis and Characterization. We have previously shown that the addition of ^{Ph2PPr}DI to $Ni(COD)_2$ results in displacement of both COD ligands and the formation of **1**.[23] Knowing that **1** is capable of catalyzing carbonyl hydrosilylation at a relatively high catalyst loading (5 mol%), we desired to screen alkylphosphine-substituted catalysts and a variety of silanes while optimizing the conditions of this transformation. First, **^{iPr2PPr}DI** and **^{tBu2PPr}DI** were prepared via Schiff-base condensation of 2,3-butanedione with the respective (3-aminopropyl)phosphine (for details see experimental section). Chelate addition to a solution of $Ni(COD)_2$ in toluene allowed for the formation of the respective tetradentate Ni complex, (**^{iPr2PPr}DI)Ni** (**2**) and (**^{tBu2PPr}DI)Ni** (**3**), after 18 h at 25 °C (Scheme 1). Analysis by ^{31}P NMR spectroscopy revealed that **2** and **3** each contain a single phosphorus environment, with resonances at 52.33 and 73.59 ppm, respectively (Figures S8 and S11 of the Supporting Information).



Scheme 1. Synthesis of compounds **1**-**3**.

Crystals of **2** and **3** were grown from saturated diethyl ether solutions at -35 °C and analyzed by single crystal X-ray diffraction. The solid state geometry of **2** can be described as distorted tetrahedral (Figure 2), and it is nearly identical to that reported for **1** as judged by the P1-Ni1-P2 angles of 113.58(2) (for **1**) and 113.80(3)° (for **2**). In contrast, the sterically-demanding *tert*-butyl groups of **3** repel one another, leading to a wider P1-Ni1-P2 angle of 131.35°. As observed for **1**, inspection of the ligand bond lengths determined for **2** and **3** reveal shortened C2-C3/C2A contacts of 1.420(3) and 1.423(4) Å, along with elongated C-N distances of 1.350(3) and 1.339(3) Å, respectively (Table 1). These metrical parameters are consistent with single electron DI chelate reduction,[24] indicating that the electronic structures of **2** and **3** are likely best described as having a Ni(I) center that is antiferromagnetically coupled to a DI radical anion (Scheme 1).[23] Comparable electronic structure assignments have been reported for low-valent Fe[25] and Co[26] compounds featuring **^{Ph2PPr}DI**.

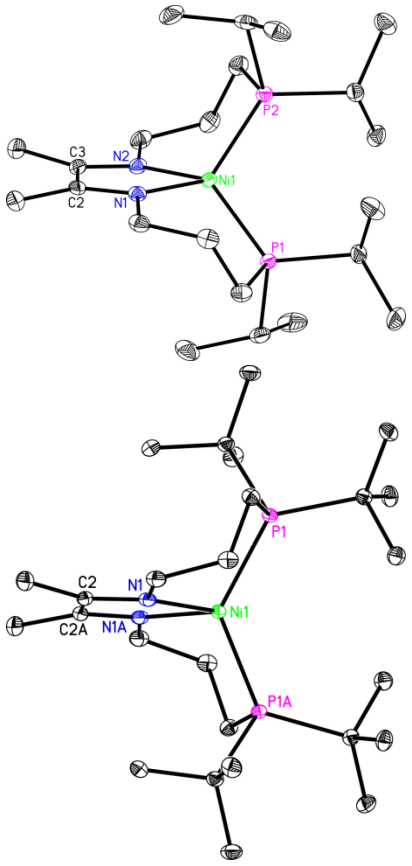


Figure 2. Molecular structures of **2** (top) and **3** (bottom) drawn with 30% probability ellipsoids. Hydrogen atoms removed for clarity. Atom labels ending with "A" are symmetry generated.

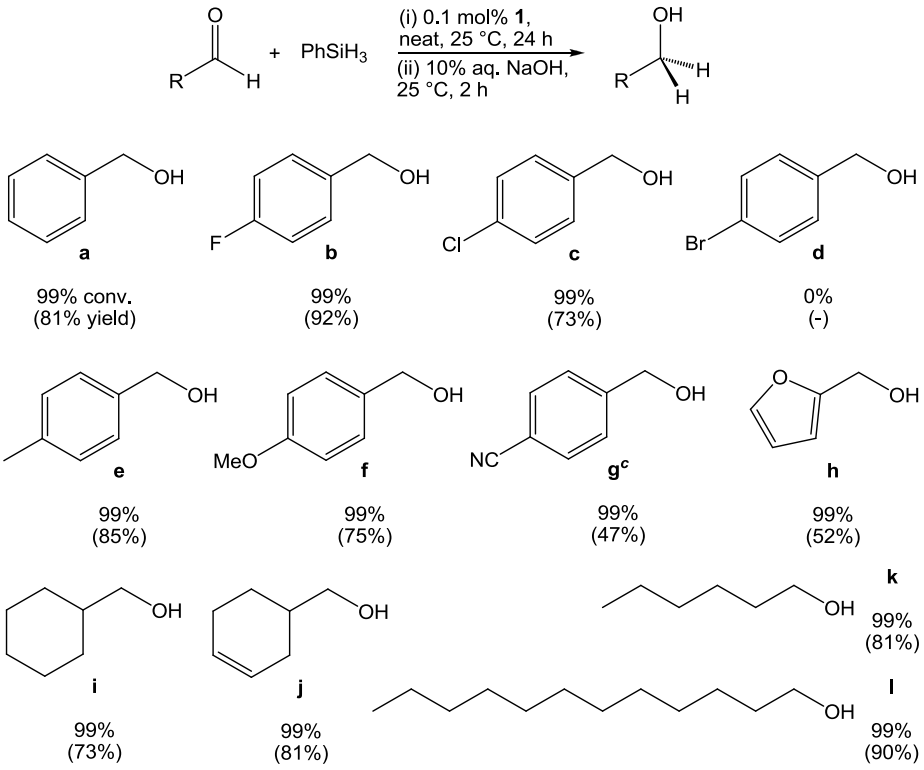
Table 1. Bond Lengths (Å) and Angles (˚) determined for **1**,[23] **2**, and **3**.

	1[23]	**2**	**3**
Ni1-N1	1.9369(17)	1.933(2)	1.9582(17)
Ni1-N2/N1A	1.9250(18)	1.931(2)	1.9582(17)
Ni1-P1	2.1343(6)	2.1455(7)	2.2262(5)
Ni1-P2/P1A	2.1345(6)	2.1544(7)	2.2262(5)
N1-C2	1.340(3)	1.350(3)	1.339(3)
N2/N1A-C3/C2A	1.341(3)	1.350(3)	1.339(3)
C2-C3/C2A	1.414(3)	1.420(4)	1.423(4)
N1-Ni1-N2/N1A	81.88(7)	82.46(9)	80.53(10)
N1-Ni1-P1	99.09(5)	97.54(7)	94.34(5)
N2/N1A-Ni1-P2/P1A	94.14(5)	96.12(6)	94.34(5)
P1-Ni1-P2/P1A	113.58(2)	113.80(3)	131.35(3)

Carbonyl Hydrosilylation. With **1**-**3** in hand, the ambient temperature benzaldehyde hydrosilylation activity of each compound was evaluated in the presence of $PhSiH_3$. Using 1.0 mol% **1** in benzene-d_6 solution, complete conversion to a mixture of silyl ethers was observed within 3 h at 25 °C by ^{1}H NMR spectroscopy. Under the same conditions, catalysts **2** and **3** were found to achieve considerably lower conversion percentages of 8% and 67%, respectively (*vide infra*). Using **1**, attempts to broaden the silane scope beyond $PhSiH_3$ revealed only 14% benzaldehyde hydrosilylation when Ph_2SiH_2 was used as the reductant, while no conversion was observed in the presence of Et_2SiH_2, iPr_2SiH_2, $^tBu_2SiH_2$, Et_3SiH, Me_2PhSiH, or Ph_3SiH.

Although the limited silane scope and ineffectiveness of **2** and **3** should be considered disappointing, we proceeded to perform a substrate scope and functional group tolerance study using **1**. Adding 0.1 mol% **1** to a neat solution of benzaldehyde and $PhSiH_3$ resulted in a mixture of silyl ethers after 24 h at 25 °C. Treatment of the products with 10% aqueous NaOH allowed for the isolation of pure benzyl alcohol in 81% yield. Under these optimized conditions, 11 additional aldehydes were screened (Table 2), with **1** showing tolerance for fluoro (**b**), chloro (**c**), and ether (**f**,**h**) functional groups. Compound **1** also exhibits chemoselectivity for the hydrosilylation of carbonyls over nitriles (**g**) and olefins (**j**), even though it is known to mediate alkyne hydrosilylation.[23] Interestingly, upon adding **1** to an equimolar mixture of 4-bromobenzaldehyde and $PhSiH_3$, the solution immediately turned blue in color (from characteristic red) and no conversion of the substrate was observed (**d**). This observation is likely due to C-Br bond oxidative addition; however, attempts to characterize the paramagnetic solid resulting from 4-bromobenzaldehyde addition to **1** have proven unsuccessful. For the other entries in Table 2, aldehyde hydrosilylation TOFs of 41 h^{-1} were achieved.

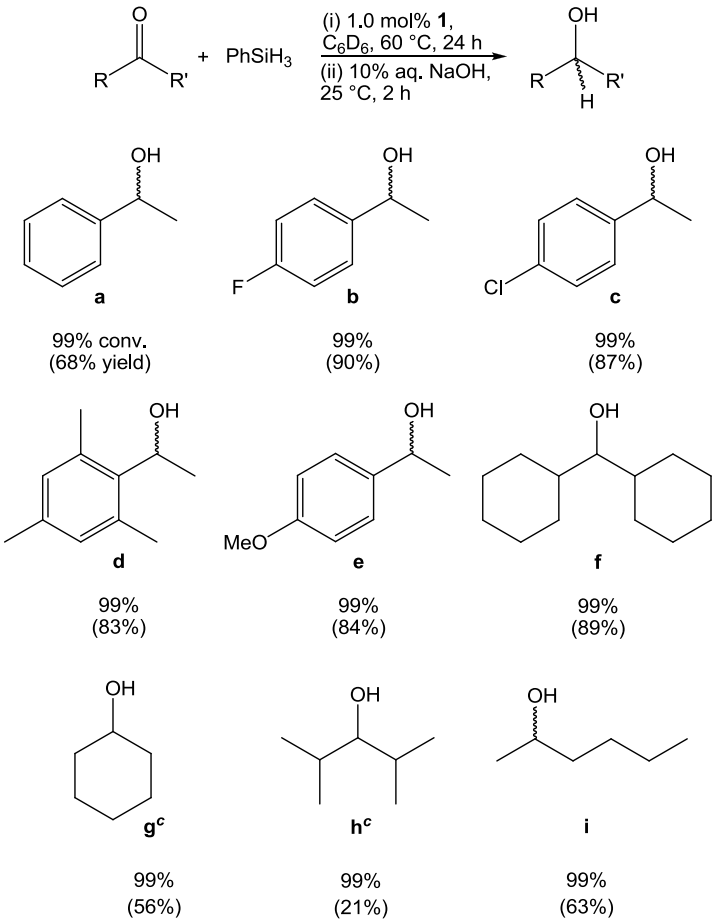
Table 2. Hydrosilylation of aldehydes using 0.1 mol% **1** and $PhSiH_3$ at 25 °C.[a,b]



[a]Percent conversion determined by ^{1}H NMR spectroscopy (TOF = 41 h^{-1} for all substrates except **d**).
[b]Isolated yields of the corresponding alcohol in parentheses (spectroscopic analysis provided in the SI).
[c]Approximately 0.5 mL of benzene was added to aid solubility.

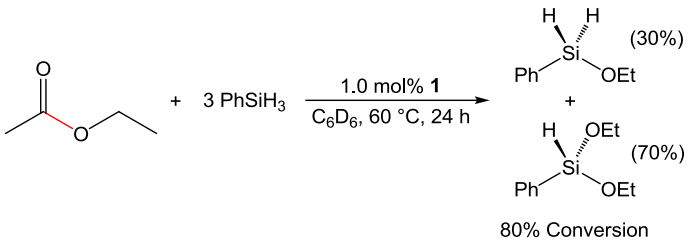
When acetophenone was combined with $PhSiH_3$ and 1.0 mol% **1**, reduced activity was observed and heating to 60 °C was required to achieve >99% conversion to silyl ethers. As with aldehydes, treatment of the acetophenone-derived products with 10% aqueous NaOH allowed for isolation of 1-phenylethanol in 68% yield (Table 3, **a**). Acetophenone substitution did not influence conversion (**b**-**e**) and **1** was found capable of reducing sterically hindered ketones including 2',4',6'-trimethylacetophenone (**d**), dicyclohexylketone (**f**), and diisopropylketone (**h**) under these conditions. For each substrate in Table 3, modest TOFs of 4 h^{-1} were observed at 60 °C. In general, it can be stated that the carbonyl hydrosilylation activity of **1** is lower than what has been observed using other well-defined Ni catalysts.[16,18,19]

Table 3. Hydrosilylation of ketones using 1.0 mol% **1** and $PhSiH_3$ at 60 °C.[a,b]



[a]Percent conversion determined by ^{1}H NMR spectroscopy (TOF = 4 h^{-1} for all substrates). [b]Isolated yields of the corresponding alcohol in parentheses. [c]This substrate was previously converted to a mixture of silyl ethers using 5.0 mol% **1** and $PhSiH_3$ (see reference 23).

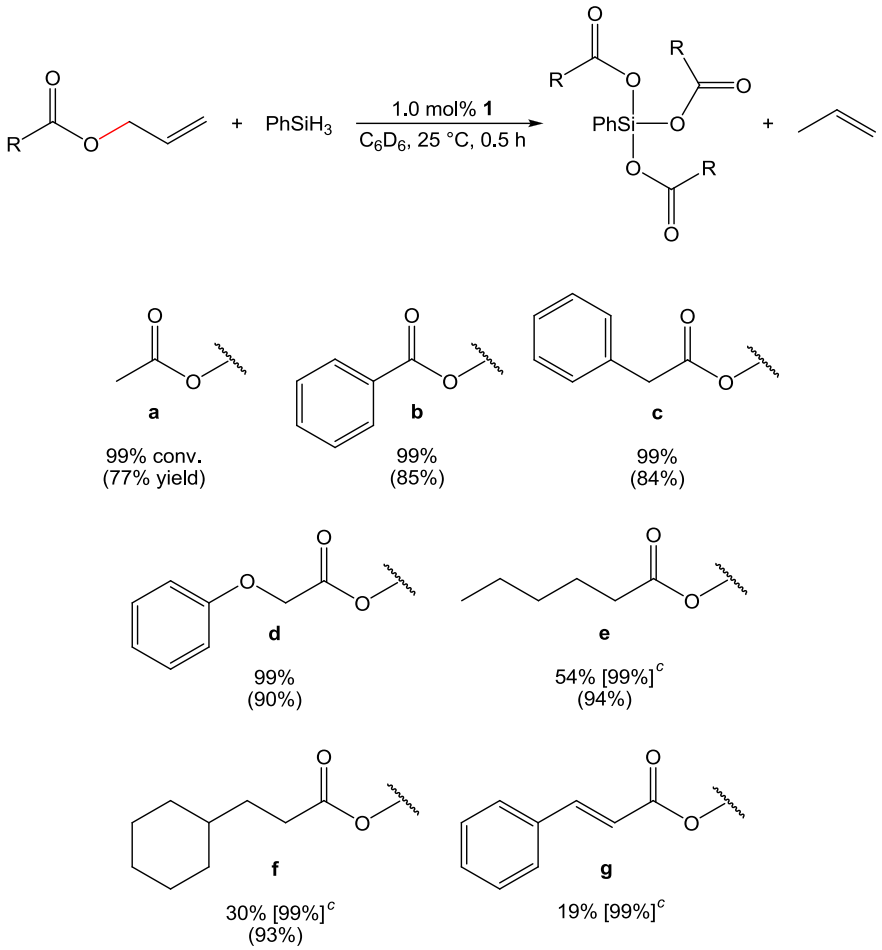
Carboxylate Hydrosilylation. To further expand the scope of **1**-mediated hydrosilylation, the reduction of esters was also investigated. Ethyl acetate was combined with $PhSiH_3$ and 1.0 mol% **1** and heated at 60 °C for 24 h. Analysis via ^{1}H NMR spectroscopy revealed 46% ethyl acetate reduction, with 99% consumption of $PhSiH_3$, to yield a mixture of $(EtO)PhSiH_2$ and $(EtO)_2PhSiH$ in a 1:4 ratio. Since the reductant was prematurely consumed under these conditions, this experiment was repeated over 24 h using 3 equivalents of $PhSiH_3$ and 80% ethyl acetate dihydrosilylation was noted (Scheme 2). Disappointingly, many other esters (methyl benzoate, ethyl benzoate, ethyl 4-fluorobenzoate, ethyl 4-methoxybenzoate, ethyl cinnamate, and phenyl acetate) were not reduced at temperatures as high as 90 °C.



Scheme 2. Ethyl acetate dihydrosilylation using 1.0 mol% **1** at 60 °C.

However, when allyl acetate was combined with $PhSiH_3$ and 1.0 mol% **1** in a J. Young tube, a color change from red to pale yellow occurred almost immediately, in conjunction with vigorous bubbling. Analysis by ^1H NMR spectroscopy revealed the evolution of propylene (indicating cleavage of the ester C-O bond) and complete consumption of allyl acetate was observed after 30 min at 25 °C. Upon precipitating the catalyst with I_2, filtering through a glass frit, and removing excess $PhSiH_3$, a single silyl ester product, $PhSi(OAc)_3$, was isolated in 77% yield (Table 4, **a**). Attempts to achieve this transformation using $Ni(COD)_2$ in place of **1** revealed no conversion, while **2** and **3** afforded 8% and 0% conversion, respectively. These observations highlight the importance of the ^{Ph2PPr}**DI** ligand, and more specifically, the role of phosphine substitution as it relates to catalytic C-O cleavage. Using **1**, six additional unsubstituted allyl esters were screened for ester C-O bond hydrosilylation, with allyl benzoate (**b**), allyl 2-phenylacetate (**c**), and allyl 2-phenoxyacetate (**d**) all reaching completion within 30 min (TOF = 3.3 min^{-1}). Allyl hexanoate (**e**), allyl cyclohexylpropionoate (**f**), and allyl cinnamate (**g**) were partially reduced after 30 min and required 3 h to reach completion (TOF = 33 h^{-1}). The entries in Table 4 are believed to be the first known examples of tricarboxysilane synthesis via ester C-O bond hydrosilylation.[27]

Table 4. Hydrosilylation of allyl esters using 1.0 mol% **1** and $PhSiH_3$ at 25 °C.[a,b]



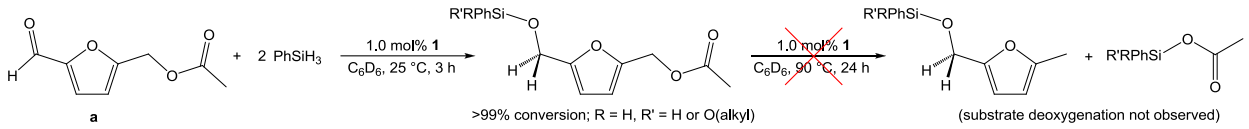
[a]Percent conversion determined by ^{1}H NMR spectroscopy. [b]Yield in parenthesis of isolated tricarboxyphenylsilane. [c]Determined after 3 h.

Efforts were also made to maximize the efficiency of allyl acetate C-O bond hydrosilylation. Adding a 3:1 mixture of allyl acetate and $PhSiH_3$ to 1.0 mol% **1** in benzene-d_6 solution allowed for complete Si-H bond utilization to generate $PhSi(OAc)_3$ within 1 h at 25 °C. To maximize the TOF of this transformation, a neat solution of allyl acetate and $PhSiH_3$ was added to 0.1 mol% **1**. Rapid gas evolution was observed along with a color change from red to pale yellow. After 1 h, the reaction turned red in color (indicating that the precatalyst had been regenerated following substrate consumption) and analysis by ^{1}H NMR spectroscopy revealed >99% conversion to a mixture of silyl esters (TOF = 990 h^{-1}). No conversion was observed in the absence of **1**.

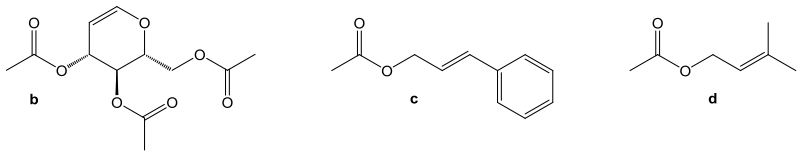
The selectivity and activity observed for this transformation are noteworthy. As observed in Scheme 2, it is very common for esters to undergo dihydrosilylation to yield a mixture of silyl ethers.[10f,n,m,11f,14a,28] Moreover, it has been shown that ester reduction in the presence of silane

reductant can result in silyl acetal formation via carbonyl hydrosilylation[29] or ether formation following deoxygenation.[30] Selective ester C-O bond hydrosilylation to form carboxysilane has been observed using 4 mol% $Co_2(CO)_8$; however, this transformation required heating to 200 °C over the course of 6 h (maximum TOF = 4 h^{-1}).[31] Examples of catalytic allyl ester C-O bond hydrosilylation are very rare and are limited to Pt-catalyzed allyl acetate hydrosilylation.[32] In each of these examples, a mixture of alkene hydrosilylation and C-O cleavage products was observed due to poor catalyst selectivity.[33] The maximum ester C-O bond hydrosilylation TOF of 990 h^{-1} achieved using **1** is believed to be the highest reported for any known catalyst.

To bridge the primary findings of this study, an attempt was made to reduce and cleave the ester C-O bond of 5-(acetoxymethyl)furfural (Scheme 3, **a**). Notably, this substrate is a derivative of 5-(hydroxymethyl)furfural, which has been identified as a promising biomass-derived platform chemical.[34] In the presence of 1.0 mol% **1** and two equivalents of $PhSiH_3$, complete hydrosilylation of the aldehyde functionality was achieved after 3 h at ambient temperature (Figure S69). However, cleavage of the allyl ester C-O bond to form the silyl ether of 5-methylfurfuryl alcohol was not observed, even upon heating to 90 °C for 24 h. To further demonstrate that the transformation described in Table 4 is limited to α-allyls, D-glucal triacetate, cinnamyl acetate, and prenyl acetate (Scheme 3, **b-d**) were screened for **1**-mediated ester C-O bond hydrosilylation. In each case, no conversion was noted after heating to 90 °C for 24 h.

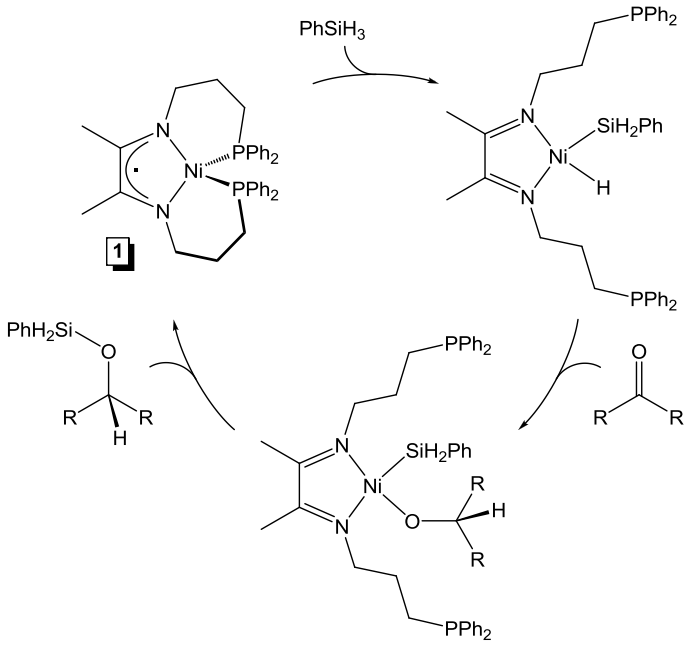


Substituted allyl esters not cleaved by **1** in the presence of $PhSiH_3$ after 24 h at 90 °C:



Scheme 3. Attempts to hydrosilylate the ester C-O bond of substituted allyl acetates using **1**.

Mechanistic Clues and Relevance to Prior Work. Throughout our study of **1**-mediated carbonyl and carboxylate hydrosilylation, efforts have been made to collect mechanistic information. When aldehydes or ketones are independently added to **1**, no reaction is observed over the range of temperatures employed for catalysis. However, upon adding 100 equivalents of $PhSiH_3$ to **1**, slow silane coupling to form PhH_2SiSiH_2Ph[35] and $(PhH_2Si)_2SiH(Ph)$[36] occurs at ambient temperature (~35% conversion after 24 h, see Figures S70 and S71). Although these silane coupled products are also generated during catalysis, no change to the catalyst is observable by ^{31}P NMR spectroscopy. This experiment indicates that Si-H oxidative addition is accessible, even though Ni(II) intermediates are not persistent. Once formed, carbonyl hydrosilylation is likely to proceed following substrate insertion into the newly formed Ni-H bond and Si-O reductive elimination (Scheme 4).

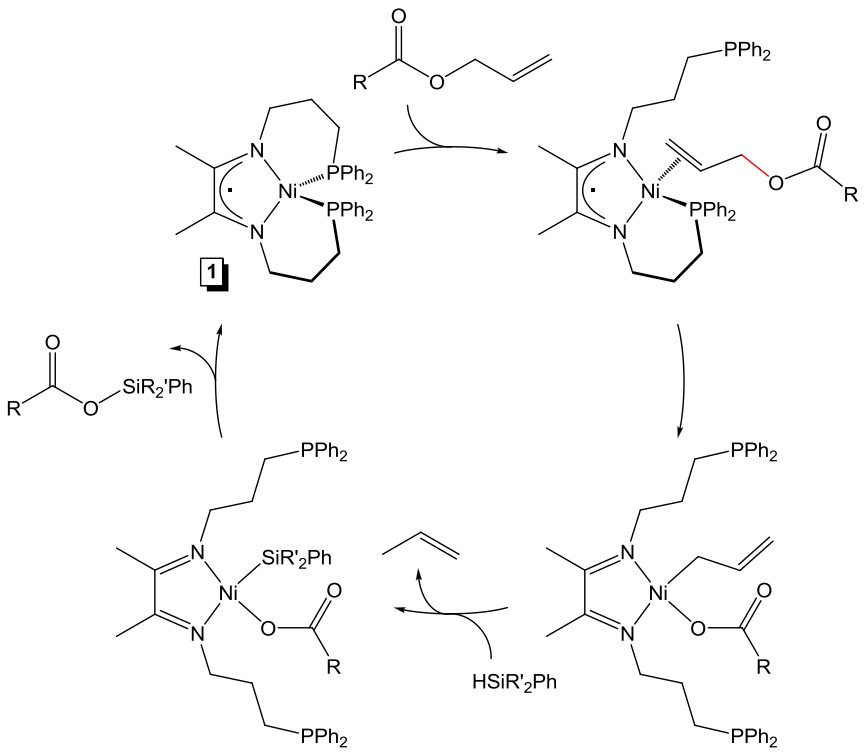


Scheme 4. Proposed modified Ojima mechanism for (DI)Ni-mediated carbonyl hydrosilylation.

Experiments have also been conducted to determine why **1** outperforms precatalysts **2** and **3** for carbonyl and ester C-O bond hydrosilylation. Repeating **1**-mediated benzaldehyde hydrosilylation (Table 2, **a**) in the presence of 20 equivalents of PMe_3 (relative to catalyst) resulted in only 3% percent conversion after 3 h (Figure S72) and ^{31}P NMR spectroscopy revealed the formation of new Ni compounds including $Ni(PMe_3)_4$ (-21.81 ppm, Figure S73). To gain additional insight, 2 equivalents of PMe_3 were added directly to **1**. After 1 h at 25 °C, ^{31}P

NMR spectroscopy revealed near complete PMe_3 consumption and partial conversion of **1** to two Ni compounds: $Ni(PMe_3)_4$ and a second possessing resonances at 25.88 (q) and -24.69 (d) ppm [proposed to be (κ^1-*P*-^{Ph2PPr}DI)$Ni(PMe_3)_3$] (Figure S74). Given that the diphenylphosphine substituents of ^{Ph2PPr}DI are readily displaced from Ni by a stronger σ-donating phosphine such as PMe_3 (even though the chelate effect is in place), it can be proposed that the trialkylphosphine substituents of **2** and **3** are less likely to be substituted by silane or substrate during catalysis.

The trialkylphosphine substituents of **2** and **3** render these compounds particularly poor catalysts for ester C-O bond hydrosilylation. When 20 equivalents of PMe_3 relative to **1** were added prior to allyl acetate hydrosilylation (Table 4, **a**), only 12% conversion was noted after 30 min at 25 °C. Moreover, only free ligand, $Ni(PMe_3)_4$, and free PMe_3 were observed by ^{31}P NMR spectroscopy. Upon adding each substrate in Table 4 to a benzene-d_6 solution of **1** and $PhSiH_3$, the solution immediately changes from red to yellow in color. When a stoichiometric quantity of allyl benzoate was added to **1** in the absence of $PhSiH_3$, a similar color change was noted over the course of 24 h at 25 °C and analysis indicated that the resulting product is NMR silent (no new ^{31}P resonances were observed). Although our attempts to isolate and characterize an allyl ester addition product of this type have proven unsuccessful, seminal work by Yamamoto and co-workers to monitor the oxidative addition of esters at low-valent Ni offers valuable insight.[37] In 1976, they identified two distinct pathways for ester cleavage; acyl C-O bond cleavage (as observed in Scheme 2) and the ester C-O bond cleavage pathway utilized in Table 4.[38] Furthermore, in the absence of reductant, it was found that allyl acetate cleavage occurred exclusively via ester C-O bond activation (as we have found in Table 4). Therefore, it is believed that **1**-mediated allyl ester cleavage is likely to occur following olefin coordination and allylic C-O bond oxidative addition,[39] as shown in Scheme 5. The trialkylphosphine substituents in **2** and **3** appear to inhibit olefin coordination and subsequent catalysis.



Scheme 5. Proposed mechanism for (DI)Ni-mediated allyl ester C-O bond hydrosilylation.

Finally, it should be noted that the Ni-catalyzed reductive cleavage of allyl esters was recently demonstrated by Jiang and co-workers, who used $NiCl_2$ and $NaBH_4$ to prepare partially deoxygenated glycals within 5 min at room temperature (TOF = 100 min^{-1} based on Ni).[40,41] When considered alongside our results, it can be said that Ni catalysts are particularly effective at cleaving α-allyl ester C-O bonds under reducing conditions.

CONCLUSIONS

The synthesis and characterization of two trialkylphosphine-substituted (κ^4-DI)Ni compounds has been described. The solid state structures of **(^{iPr2PPr}DI)Ni** and **(^{tBu2PPr}DI)Ni** suggest that both compounds feature a singly-reduced DI chelate that is antiferromegnetically coupled to Ni(I), as reported for **(^{Ph2PPr}DI)Ni**. Although these three compounds were found to be structurally similar, **(^{Ph2PPr}DI)Ni** exhibited considerably higher activity for the hydrosilylation of benzaldehyde and allyl acetate ester C-O bond hydrosilylation. Seven α-allyl esters were cleaved to yield tricarboxyphenylsilanes and optimization of this transformation has allowed for leading TOFs of up to 990 h^{-1}. Mechanistic experiments suggest that the trialkylphosphine substituents of

(^{iPr2PPr}DI)Ni and **(^{tBu2PPr}DI)Ni** inhibit carbonyl and ester C-O bond hydrosilylation by preventing Si-H oxidative addition and olefin coordination, respectively.

EXPERIMENTAL SECTION

General Considerations: All reactions were performed inside an MBraun glovebox under an atmosphere of purified nitrogen. Toluene, tetrahydrofuran, diethyl ether, and pentane were purchased from Sigma-Aldrich, purified using a Pure Process Technology solvent system, and stored in the glovebox over activated 4Å molecular sieves and sodium before use. Benzene-d_6 was purchased from Cambridge Isotope Laboratories or Oakwood Chemicals and dried over 4Å molecular sieves and potassium. Celite was obtained from Acros Organics. Bis(1,5-cyclooctadiene) nickel was purchased from Strem. Benzaldehyde, *p*-tolualdehyde, *p*-methoxybenzaldehyde, furfural, cyclohexanecarboxaldehyde, *p*-chloroacetophenone, diisopropyl ketone, cyclohexanone, 2-hexanone, and allyl cyclohexyl propionoate were sourced from Sigma Aldrich. *p*-Chlorobenzaldehyde, hexanal, decanal, cyclohex-3-enylcarbaldehyde, acetophenone, 2,4,6-trimethylacetophenone, *p*-methoxyacetophenone, dicyclohexylketone, allyl phenyl acetate, allyl phenoxyacetate, allyl hexanoate, ethyl cinnamate, phenyl acetate, methyl benzoate, ethyl benzoate, ethyl 4-methoxybenzoate, 5-(acetoxymethyl)furfural, and 2,3-butanedione were purchased from TCI America. *p*-Bromobenzaldehyde, *p*-cyanobenzaldehyde, *p*-fluoroacetophenone, allyl acetate, allyl cinnamate, ethyl 4-fluorobenzoate, cinnamyl acetate, D-glucal triacetate, and phenyl silane were purchased from Oakwood Chemicals. *p*-Fluorobenzaldehyde was obtained from Acros. Allyl benzoate and prenyl acetate were purchased from Combi Blocks. Ethyl acetate was purchased from Mallinckrodt Chemicals. All liquid substrates were dried over 4Å molecular sieves prior to use. All solid substrates were recrystallized from diethyl ether prior to use. 3-(Di-*i*-propylphosphino)-propylamine,[42] 3-(di-*t*-butylphosphino)-propylamine,[42] 3-(diphenylphosphino)propylamine,[43] **^{Ph2PPr}DI**,[23] and **(^{Ph2PPr}DI)Ni**[23] were synthesized according to literature procedure.

Solution nuclear magnetic resonance (NMR) spectra were recorded at room temperature on either a Varian 400 MHz, Bruker 400 MHz, or Varian 500 MHz NMR spectrometer. All ^{1}H NMR and ^{13}C NMR chemical shifts (ppm) are reported relative to $Si(Me)_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{31}P NMR chemical shifts (ppm) are reported relative to phosphoric acid.

X-ray Crystallography: Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in the glovebox and transferred to glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX Diffractometer equipped with Mo Kα radiation (Arizona State University). A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least-squares procedures on [F^2] (SHELXL). The crystallographic data collected for compounds **2** and **3** has been deposited with The Cambridge Crystallographic Data Centre (CCDC) and assigned the numbers 1586336 and 1586337, respectively. Crystallographic parameters can be found in Table S1.

Preparation of ^{tBu2PPr}DI. In a glove box, a 100 mL thick-walled glass bomb was charged with 2,3-butanedione (98.9 mg, 1.15 mmol), *p*-toluenesulfonic acid (4 mg, 0.029 mmol), and 5 mL of toluene. After stirring for 5 min, 3-(di-*t*-butylphosphino)propylamine (465.0 mg, 2.31 mmol) in 5 mL toluene and 4 Å molecular sieves were added. The vessel was sealed and stirred at 90 °C for 4 days. The reaction was subsequently cooled to room temperature, filtered through a bed of Celite, and the solvent removed *in vacuo*. The resulting yellow oil was dissolved in a minimal mixture of diethyl ether and pentane and cooled to -35 °C. White crystals identified as **^{tBu2PPr}DI** were isolated in 26.2% yield (136.6 mg, 0.302 mmol). Analysis for $C_{26}H_{54}N_2P_2$: Calc. C, 68.38% H, 11.92%, N, 6.13% Found C, 68.36% H, 11.99% N, 6.01%. ^{1}H NMR (benzene-d_6): 3.39 (t, J = 6.4 Hz, 4H), 2.09 (s, 6H), 2.02 (dd, J = 14.8, 7.0 Hz, 4H), 1.55 (m, 4H), 1.13 (d, J = 10.9 Hz, 36H). ^{13}C NMR (benzene-d_6): 168.23, 53.68 (d, J = 14.2 Hz), 32.40 (d, J = 25.8 Hz), 31.74 (d, J = 22.7 Hz), 30.25 (d, J = 13.8 Hz), 19.75 (d, J = 21.8 Hz). ^{31}P NMR (benzene-d_6): 26.58 (s).

Preparation of (^{iPr2PPr}DI)Ni (2). In a glove box, a 100 mL thick-walled glass bomb was charged with 2,3-butanedione (90.0 mg, 1.05 mmol), *p*-toluenesulfonic acid (4 mg, 0.029 mmol), and 5 mL of toluene. After stirring for 5 min, 3-(di-*i*-propylphosphino)propyl amine (388.0 mg, 2.21 mmol) in 5 mL toluene and 4 Å molecular sieves were added. The vessel was sealed and stirred at 70 °C for 5 d. The reaction was subsequently cooled to room temperature, filtered through a bed of Celite, and the solvent was removed *in vacuo*. The resulting yellow oil was dissolved in a minimal amount of toluene and added to $Ni(COD)_2$ (178.0 mg, 0.65 mmol) dissolved in 10 mL toluene in a 20 mL scintillation vial. The resulting red solution was stirred overnight, filtered

through a bed of Celite, and the solvent was removed *in vacuo*. The red solid was dissolved in a minimal amount of diethyl ether and cooled to -35 °C. A red crystalline solid identified as **2** was isolated in 84% yield relative to $Ni(COD)_2$ (249.0 mg, 0.54 mmol). Analysis for $C_{22}H_{46}N_2P_2Ni$: Calc. C, 57.54% H, 10.10%, N, 6.10% Found C, 57.66% H, 10.45% N, 5.99%. ^{1}H NMR (benzene-d_6): 2.90 (m, 1H), 2.79 (m, 1H), 2.59 (m, 1H), 2.01 (m, 1H), 1.85 (m, 2H), 1.45 (t, J = 6.2 Hz, 3H), 1.39 (dd, J = 14.6, 6.7 Hz, 3H), 1.14 (dd, J = 13.5, 7.2 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H), 0.50 (dd, J = 15.1, 6.7 Hz, 3H), 0.41 (m, 1H). ^{13}C NMR (benzene-d_6): 140.97, 57.01, 30.10 (d, J = 5.2 Hz), 30.03 (d, J = 5.7 Hz), 29.66 (d, J = 3.2 Hz), 29.56 (d, J = 3.8 Hz), 22.97 (d, J = 5.7 Hz), 22.88 (d, J = 5.4 Hz), 19.87 (t, J = 3.7 Hz), 19.63 (t, J = 4.9 Hz), 18.52 (t, J = 5.3 Hz), 17.02 (t, J = 2.7 Hz), 15.98 (t, J = 3.7 Hz), 15.35 (d, J = 5.6 Hz), 15.26 (d, J = 5.1 Hz). ^{31}P NMR (benzene-d_6): 52.33 (s).

Preparation of (^{tBu2PPr}DI)Ni (3). In a glove box, a 20 mL scintiallation vial was charged with 18.9 mg of $Ni(COD)_2$ (0.0689 mmol) and 10 mL of toluene. Recrystallized **^{tBu2PPr}DI** (31.2 mg, 0.0689 mmol) in 5 mL toluene was slowly added. The solution immediately turned red and was stirred for 24 h, followed by filtration through Celite and removal of solvent *in vacuo*. The material was dissolved in a minimal quantity of diethyl ether and cooled to -35 °C. A red crystalline solid identified as **3** was isolated in 74% yield (26.3 mg, 0.0512 mmol). Analysis for $C_{26}H_{54}N_2P_2Ni$: Calc. C, 60.60% H, 10.56%, N, 5.43% Found C, 59.64% H, 10.32% N, 5.25%. ^{1}H NMR (benzene-d_6): 2.78 (m, 2H), 2.62 (m, 2H), 2.22 (m, 2H), 1.96 (m, 2H), 1.30 (d, J = 9.9 Hz, 18H), 1.21 (d, J = 9.9 Hz, 18H), 0.68 (t, J = 4.8 Hz, 6H), 0.43 (t, J = 12.0 Hz, 2H). ^{13}C NMR (benzene-d_6): 140.64 (t, J = 4.1 Hz), 55.20 (s), 30.82 (bs), 30.72 (bs), 26.12 (t, J = 7.3 Hz), 17.70 (t, J = 1.8 Hz), 16.28 (t, J = 5.8 Hz). ^{31}P NMR (benzene-d_6): 73.59 (s).

General Procedure for Hydrosilylation of Aldehydes with 0.1 mol% 1: Under inert atmosphere, a 20 mL scintillation vial was charged with approximately 0.0030 g of **1** (0.00504 mmol). Aldehyde (approx. 5.04 mmol) and $PhSiH_3$ (approx. 5.04 mmol) were combined and added to the catalyst. The resulting solution was stirred at room temperature for 24 h. Using ^{1}H NMR spectroscopy, >99% conversion was observed after 2 h (except for Table 2, entry **d**). The solution was then hydrolyzed with 2 mL of 10% aqueous NaOH and the organic product was extracted with diethyl ether (3x2 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed *in vacuo* to isolate the alcohol.

General Procedure for Hydrosilylation of Ketones with 1.0 mol% 1: In a glove box, ketone (approx. 0.7 mmol) and $PhSiH_3$ (approx. 0.7 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (approx. 4.0 mg, 0.007 mmol). The resulting red solution was dissolved in benzene-d_6, transferred into a J. Young NMR tube, and heated at 60 °C for 24 h. Conversion of >99% was observed by ^1H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the alcohol product was isolated.

General Procedure for the Hydrosilylation of Allyl Esters with 1.0 mol% 1: Under an inert atmosphere, allyl ester (0.554 mmol) and $PhSiH_3$ (0.554 mmol) were combined in a 20 mL scintillation vial and then transferred into a vial containing **1** (approx. 3.3 mg, 0.00554 mmol) in 0.5 mL benzene-d_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. Greater than 99% conversion was observed via ^1H NMR spectroscopy, after which 1 equivalent of I_2 in benzene (relative to Ni, approx. 20 µL of a 0.248 M solution) was added. The solution was allowed to sit for 1 h, filtered, and the volatile components were removed under reduced pressure to isolate the respective tricarboxyphenylsilane.

CONFLICTS OF INTEREST

The authors declare the following competing financial interest(s): R. J. T. retains rights to **1** through US20160176908 and WO2014201082. This catalyst has been commercialized by Sigma-Aldrich Corporation (a subsidiary of Merck KGaA).

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NOTES

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Electronic Supplementary Information

Electronic Supplementary Information (ESI) available: metrical parameters for **2** and **3**, catalytic procedures, and NMR spectroscopic identification of compounds and organic products. See DOI: 10.1039/x0xx00000x

Accession Codes

CCDC 1586336 and **1586337** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223336033.

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