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Green and Efficient Synthesis of Bidentate Schiff Base Ru Catalysts for Olefin Metathesis

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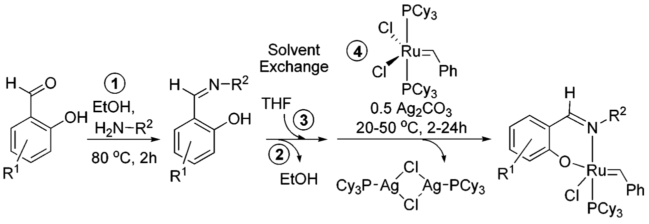
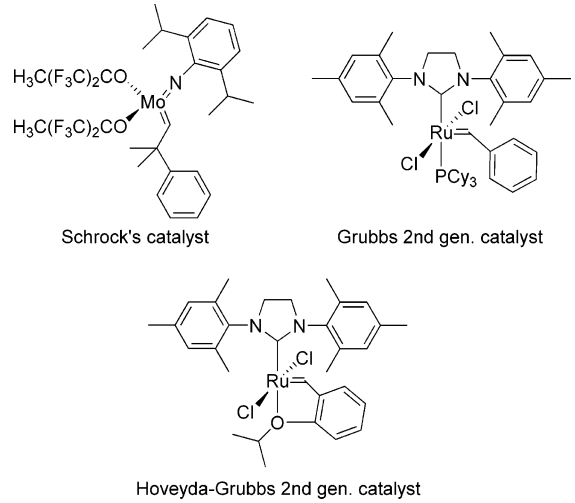


A simple, green synthetic protocol to bidentate Schiff base substituted ruthenium carbene complexes is described. These complexes are potent catalysts for olefin metathesis, but the original synthetic route employs the Schiff base ligands in the form of highly toxic thallium(I) salts. The new protocol involves a two-step, quasi-one-pot approach and silver(I) carbonate as base. The target ruthenium carbene complexes are obtained in yields that are similar to, or better than, those of the original protocol.

During recent years, olefin metathesis[1-3] has seen extraordinary development and has turned out to be a very versatile and efficient tool in organic synthesis. A huge variety of carbo- and heterocycles can be synthesized by means of ring-closing metathesis, starting with acyclic dienes as substrates. Such strategies have proven to be very useful for the synthesis of highly complex natural products.[4]

This astonishing advance has been made possible by the progress in the synthesis of transition-metal alkylidene catalysts for the olefin metathesis reaction. Several such catalysts are currently commercially available, for example, the molybdenum complexes of Schrock[5] and the ruthenium complexes of Grubbs[6] and Hoveyda;[7] see structures in Chart 1. The Schrock catalysts have demonstrated higher catalytic activities, while the Grubbs catalysts have proven to tolerate the presence of a broad range of functional groups and excellent air-stability.

CHART 1. Schrock's Catalyst, Grubbs Second-Generation Catalyst, and Hoveyda−Grubbs Second-Generation Catalyst



Schrock's catalyst
Grubbs 2nd gen. catalyst
Hoveyda-Grubbs 2nd gen. catalyst

The Hoveyda catalysts possess many of the properties of the Grubbs second-generation catalysts and are more stable and thus easily recyclable.[7] The selectivity for the alkene double bond makes the Grubbs catalyst a highly valuable tool in organic synthesis as inexpensive and easily available olefins can be utilized as synthons for the preparation of otherwise not easily accessible molecules. Ruthenium-based catalysts have therefore become the first-choice catalysts for organic synthesis. During recent years, a huge effort has been dedicated to further develop and improve the characteristics of the Grubbs-type ruthenium catalysts. In this context, in 1998, Grubbs and co-workers[8a] disclosed a new class of ruthenium-based catalyst for olefin metathesis involving bidentate Schiff base ligands. Even thought those catalysts were shown to be less active at room temperature compared to the first-generation Grubbs catalyst, they displayed other important advantages; namely, the new catalysts were highly thermally stable under standard catalytic reaction conditions, they show high catalytic activity in RCM reactions when performed at elevated temperatures (advantageous for RCM reactions), the catalysts tolerate polar protic solvents, for example, methanol, and they reveal excellent air and moisture stability, which make them more suitable for large-scale use. The synthetic protocol for the bidentate Schiff base Ru catalysts

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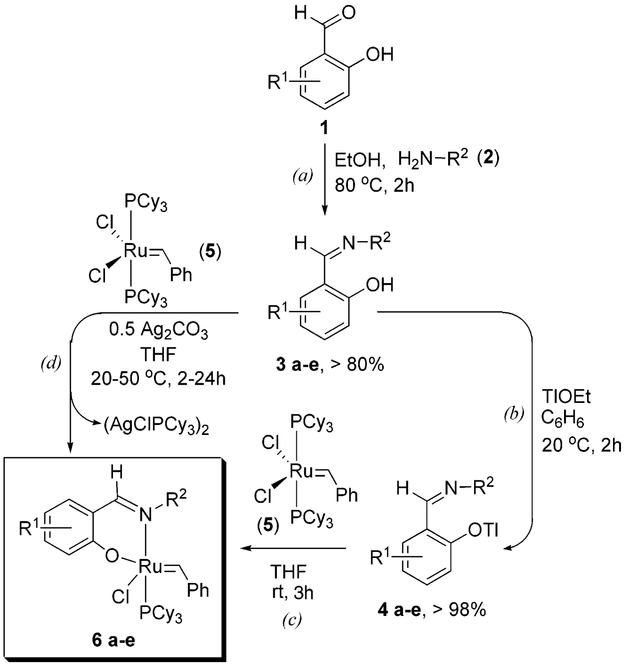
SCHEME 1



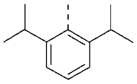
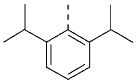
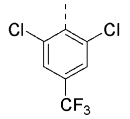
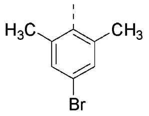
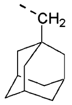
Grubb's procedure: pathway *(a)+(b)+(c)*
New procedure: pathway *(a)+(d)*

disclosed by Grubbs and co-workers is efficient and provides medium to high yields (54−85%), where the outcome of the various syntheses appears to depend on the bulkiness of the bidentate ligand. However, from a safety and environmental point of view, the synthetic protocol is saddled with a serious drawback, namely the use of a thallium(I) as counterion for various 2-alkyliminomethylphenol anions. Thallium and its derivatives are extremely toxic; consequently, the use of this procedure is normally not advisable. As also stated by Grubbs and collaborators, "several salts have been tested, but thallium(I) salts were proved to be the most efficient", and they therefore decided to use this procedure to synthesize a variety of Schiff base ligands and their corresponding catalysts. The original synthetic pathway is represented by reactions (*a*) + (*b*) + (*c*) in Scheme 1, with yields given in the ultimate right-hand column of Table 1.

A project in progress in our laboratory involves the design, synthesis, and investigation of novel ruthenium alkylidene complexes intended for use as catalysts for olefin metathesis.[3] In this context, a combined theoretical approach that embraces quantum chemistry (DFT), multivariate regression, and data analysis was developed with the goal of designing and predicting new monodentate dative ligands for new olefin metathesis Ru-based catalysts.[9] This work led us further to the synthesis and investigation of bidentate Schiff base ligands. As a result of this work, we disclose herein a short, efficient, and environmentally benign alternative synthetic process for the preparation of bidentate Schiff base Ru catalysts for olefin metathesis.

Our strategy involved the preparation of the imine **3** as previously described by Grubbs and collaborators.[8] The complexation with ruthenium was conducted by reacting one Schiff base equivalent with 1 equiv of Grubbs first-generation catalyst in presence of a 0.5 equiv of Ag_2CO_3 used as base;[10] see pathway (*d*) of Scheme 1.

TABLE 1. Experimental Results: Attempts To Synthesize a Series of Bidentate Schiff Base Ru Catalysts for Olefin Metathesis

	Substituents in **3**, **4**, and **6**		New proc. Yield [%]	Grubb's proc. Yield [%]
	R^1	R^2		
a	H		<4	75
b	4-NO_2		87	82
c	4-NO_2		89	85
d	4-NO_2		96	80
e	4-NO_2		78	54

The recomplexation of Ru (0.012 mmol of Grubbs first-generation catalyst **5**) was conducted in dry THF (1 mL) at a temperature of 40 °C. Samples of the reaction mixture were withdrawn during the course of the reaction and successively investigated by ^1H NMR. Reaction monitoring revealed that the signals related to the Grubbs first-generation catalyst disappeared gradually throughout a reaction period of 3−4 h. Furthermore, signals from the free ligand **3** were observed only in very small quantities (<4%).

The complexation utilizing the ligands **3b**−**e** all provided excellent outcomes, namely a yield in the range 78−96%, which is as good as or better than the previously disclosed protocol[8] (see right-hand column of Table 1 for benchmarking purposes). The complexation reaction, utilizing the ligand **3a** that lacks the electron-withdrawing *p*-nitro group, however, provided only a tiny yield, <2%.[11] Attempts to improve the outcome of this reaction by prolonged reaction time and elevated temperature did not afford any significant improvements (a yield of only ~4% was measured[12]). In our opinion, the major reason for the unsuccessful complexation of ligand **3a** is due to the relatively weak base (silver carbonate) that is used for the deprotonation of the phenolic group. pK_a of **3a** is 8.83 ± 0.35[13] and, for example, the pK_a of **3b** is 5.81 ± 0.30,[13] which is a large difference in the pK_a value, namely $\Delta pK_a \approx 3$.

The preliminary protocol was up-scaled by a factor of 30 (0.36 mmol) although with a solvent volume of 20 mL. The

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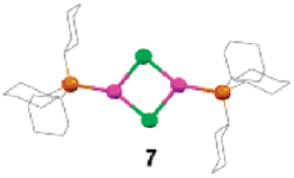
(11) The yield was estimated by means of ^1H NMR. The NMR analysis showed also that 40−45% of the Grubbs catalyst was decomposed. The unreacted ligand **3a** was not decomposed and was only observed as the neutral phenol and not in the deprotonated form.

(12) The yield was estimated by means of ^1H NMR. The NMR analysis showed also that a complete decomposition of the Grubbs catalyst had taken place. The unreacted ligand **3a** was not decomposed and was only observed as the neutral phenol and not in the deprotonated form.

(13) The value is estimated by using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris. The value is retrieved from CA using SciFinder Scholar.

CHART 2. Molecular Structure of Isolated Byproduct (μ_2-Chloro)(tricyclohexylphosphine)silver 7 As Obtained from X-ray Crystal Diffractometer Analysis



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reactions were conducted as on the small scale, but with a prolonged reaction time (6−8 h). The isolation and workup of the Ru catalyst was performed by filtering the reaction mixture, providing a white product isolated on the filter, which was washed with cold THF. The catalyst (found in the filtrate, the THF solution) was isolated by removing the solvent under reduced pressure. The isolated catalyst was further purified by dissolving the solid in a minimum volume (150−200 mL) of *n*-pentane and then precipitating by cooling to −84 °C.

The off-white solid isolated on the filter (from the filtration of the reaction mixture) was collected, dissolved in methylene chloride, and then again filtered. The methylene chloride solution was left at room temperature for the slow evaporation of the solvent. A suitable crystal was selected from the solid obtained and analyzed on an X-ray diffractometer, which revealed the product to be (μ_2-chloro)(tricyclohexylphosphine)silver **7**, Chart 2, previously described by Bowmaker and collaborators.[14] The first step of the reaction involves phosphine ligand dissociation. Imines are known to be good ligands for ruthenium. Thus, it is reasonable to expect that the imine group first coordinate to ruthenium. Subsequently, deprotonation takes place on the phenolic group. The phenolic anion coordinates then to ruthenium to substitute the chloride anion, but is difficult to predict if this proceed via an associative, dissociative, or interchange mechanism. The liberated chloride ions reacts with silver ions to produce the un-soluble silver chloride that reacts further with the previously liberated tricyclohexylphosphine ligand to produce the (μ_2-chloro)(tricyclohexylphosphine)silver **7**.

In conclusion, we have designed and developed a simple, efficient green synthetic process to some bidentate Schiff base Ru catalysts for olefin metathesis. The process appears to operate successfully with electron-deficient aromatic imines and is performed in a two-step, quasi-one-pot protocol providing the target Ru complex in excellent yield and selectivity, although with stoichiometric quantities of (μ_2-chloro)(tricyclohexylphosphine)silver (**7**). The side product can easily be isolated from which silver can be recovered making the process both economical and environmentally benign.

Experimental Section

Synthesis of Schiff Base Bidentate Ligands 3a−e. The synthesis of the bidentate imine ligands (**3a−e**) was carried out using the same protocol as previously disclosed by Grubbs and co-workers or a slightly modified version thereof.[8] The salicylaldehyde (**1**) and the amine (**2**) were mixed in ethanol and stirred and heated at 80 °C for a period of 2 h. Thereafter, the reaction mixture was cooled to 0 °C, whereupon a yellow solid precipitated. The solid was filtered, washed with cold ethanol, and then dried under reduced pressure to afford in excellent yields target salicylaldimine (**3a−e**). Modifications preformed on the protocol are described below for each reaction.

(2-[(2,6-Diisopropylphenylimino)methyl]phenol) 3a. Salicylaldehyde (0.611 g, 5.0 mmol), 2,6-diisopropylaniline (0.886 g, 5.0 mmol), and ethanol (25 mL) afforded 1.36 g (97%) of the title compound as a pale yellow solid. A drop of formic acid was used to accelerate the condensation reaction: ^{1}H NMR ($CDCl_3$, 600 MHz) $\delta = 13.10$ (s, 1H), 8.31 (s, 1H), 7.42 (ddd, 8.35, 7.30, 1.70 Hz, 1H), 7.36 (dd, 7.70, 1.70 Hz, 1H), 7.16−7.22 (m, 3H), 7.07 (dd, 8.35, 0.55 Hz, 1H), 6.97 (tdd, 7.50, 1.09 Hz, 1H), 3.00 (sept, 6.88 Hz, 2H), 1.18 (d, 6.88 Hz, 12H).

(2-[(2,6-Diisopropylphenylimino)methyl]-4-nitrophenol) 3b. 5-Nitrosalicylaldehyde (1.00 g, 5.98 mmol), 2,6-diisopropylaniline (1.06 g, 5.98 mmol), and ethanol (15 mL) afforded 1.60 g (82%) of the title compound as a yellow solid: ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 14.29$ (s, 1H), 8.38 (s, 1H), 8.35 (d, 2.75 Hz, 1H), 8.31 (dd, 9.17, 2.75 Hz, 1H), 7.20−7.25 (m, 3H), 7.14 (d 9.17 Hz, 1H), 2.93 (sept, 6.87 Hz, 2H), 1.20 (d, 6.87 Hz, 12H).

(2-[(2,6-Dichloro-4-trifluoromethylphenylimino)methyl]-4-nitrophenol) 3c. 5-Nitrosalicylaldehyde (0.501 g, 3.0 mmol), 2,6 dichloro-4-trifluoromethylaniline (0.690 g, 3.0 mmol), and methanol (10 mL) provided a pale yellow solid, the target compound, in a isolated yield of 1.029 g (90%): ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta =$ 12.94 (s, 1H), 8.67 (s, 1H), 8.43 (d, 2.75 Hz, 1H), 8.36 (dd, 9.17, 2.75 Hz, 1H), 7.70 (s, 2H), 7.18 (d, 9.17 Hz, 1H).

(2-[(4-Bromo-2,6-dimethylphenylimino)methyl]-4-nitrophenol) 3d. 5-Nitrosalicylaldehyde (0.668 g, 4.0 mmol), 4-bromo-2,6-dimethylaniline (0.800 g, 4.0 mmol), and ethanol (15 mL) provided 1.21 g (87%) of the title compound as a yellow solid: ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 13.94$ (s, 1H), 8.40 (s, 1H), 8.35 (d, 2.75 Hz, 1H), 8.31 (dd, 9.16, 2.75 Hz, 1H), 7.28 (s, 2H), 7.14 (d, 9.16 Hz, 1H), 2.19 (s, 6H).

(2-[(Adamantan-2-ylmethylimino)methyl]-4-nitrophenol) 3e. 5-Nitrosalicylaldehyde (0.501 g, 3.0 mmol), 1-adamantanemethylaniline (0.496 g, 3.0 mmol), and ethanol (15 mL) afforded 0.88 g (93%) of the title compound as a yellow solid: ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 15.18$ (s, 1H), 8.24 (d, 2.76 Hz, 1H), 8.21 (s br, Hz, 1H), 8.18 (dd, 9.34, 2.76 Hz, 1H), 6.91 (d, 9.34 Hz, 1H), 3.31 (s, 2H), 2.03 (t, br, 2.59, 3H), 1.66, 1.75 (AB system, $J_{AB} = 12.00$ Hz, 6H), 1.58 (d, 2.59 Hz, 6H).

General Procedure for the Preparation of Schiff Base Substituted Ru Complexes 6a−e. Grubbs first-generation catalyst, the corresponding Schiff base ligand (**3a−e**), silver(I) carbonate, and a catalytic quantity silver(I) chloride[15] were added to a Schlenk flask (50−250 mL). The flask was evacuated and backfilled with argon. Dry THF (20 mL) was then transferred to the Schlenk flask (still under argon) and then heated (40 °C) and stirred for a period of 6 h. The reaction temperature was then lowered to room temperature and allowed to stir overnight. The reaction mixture was cooled at 0 °C whereas the white precipitate of PCy_3AgCl (byproduct) was removed by filtration. The filtrate was collected in a Schlenk flask (250 mL), and the solvent was removed by evaporation under reduced pressure. The isolated solid residue was recrystallized from pentane at a temperature of −84 °C[16] to provide the Schiff-base-substituted Ru complexes **6b−e** in good to excellent yields. Any deviation from this general protocol is provided for each single complex.

Complex 6a. Grubbs first-generation catalyst (0.009 g, 0.012 mmol), 2-[(2,6-diisopropylphenylimino)methyl]phenol **3a** (0.0034 g, 0.012 mmol), silver(I) carbonate (0.0017 g, 0.006 mmol), silver(I) chloride (0.0005 g, 0.004 mmol), and THF (1 mL) were reacted as described above except for the reaction time (3 h). The reaction mixture was investigated on ^{1}H NMR, which revealed only a very small quantity, namely only 2%, of title complex **6a**.

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[15] The presence of silver chloride from the start of the reaction appears to increases the reaction rate.

[16] A sludge of ethyl acetate and liquid nitrogen was used as cooling medium.

Complex 6b. Grubbs first-generation catalyst (0.300 g, 0.3645 mmol), 2-[(2,6-diisopropylphenylimino)methyl]-4-nitrophenol **3b** (0.120 g, 0.3645 mmol), silver(I) carbonate (0.05 g, 0.1823 mmol), silver(I) chloride (0.0005 g, 0.004 mmol), and THF (20 mL) were mixed and reacted as described above to provide title complex **6b**, which was isolated as a brown solid (266 mg) in a yield of 87%: ^{1}H NMR (CD_2Cl_2, 500 MHz) $\delta = 19.77$ (d, 3.61 Hz, 1H), 8.25 (d, 2.93 Hz, 1H), 8.13 (d, 5.45 Hz, 1H), 8.09 (dd, 9.49, 2.93 Hz, 1H), 7.92 (dd, 8.45, 1.10 Hz, 2H), 7.58 (tt, 7.35, 1.10 Hz, 1H), 7.28 (t, 7.82 Hz, 2H), 7.15−7.24 (m, 2H), 7.07 (dd, 7.35, 1.63 Hz, 1H), 6.96 (d, 9.49 Hz, 1H), 3.23 (sept, 6.80, 1H), 2.49 (q, 12.19, 3H), 2.09 (sept, 6.80, 1H), 1.48−2.01 (m, 20H), 1.39 (d, 6.80 Hz, 3H), 1.16−1.36 (m, 10H), 1.13 (d, 6.80 Hz, 3H), 0.78(d, 6.80 Hz, 3H), 0.73 (d, 6.80 Hz, 3H). In addition, a side product, a white solid $(ClAgPCy_3)_2$, was isolated by filtration in a quantity of 147 mg, this corresponding to a side product yield of 95%. ^{1}H NMR of the reaction mixture revealed that the Grubbs catalyst was quantitatively converted, and only 2% of the ligand was still present in the reaction mixture.

Complex 6c. Grubbs first-generation catalyst (0.300 g, 0.3645 mmol), 2-[(2,6-dichloro-4-trifluoromethylphenylimino)methyl]-4-nitrophenol **3c** (0.138 g, 0.3645 mmol), silver(I) carbonate (0.050 g, 0.1823 mmol), silver(I) chloride (0.0005 g, 0.004 mmol), and THF (20 mL) afforded a yield of 289 mg of reddish-brown solid (89%) of the title complex **6c**: ^{1}H NMR (CD_2Cl_2, 500 MHz) $\delta = 19.42$ (d, 4.54 Hz, 1H), 8.25 (d, 2.93 Hz, 1H), 8.09 (dd, 9.54, 2.93, 1H), 8.02 (d, 5.52 Hz, 1H), 7.98 (dd, 7.35, 1.09 Hz, 2H), 7.74 (dd 1.84, 0.72 Hz, 1H), 7.67 (dd 1.84, 0.72 Hz, 1H) 7.58 (tt, 7.35, 1.09 Hz, 1H), 7.28 (t, 7.80 Hz, 2H), 7.04 (d, 9.54 Hz, 1H), 2.47 (q, 12.12, 3H), 1.12−1.96 (m, 30H). In addition, a side product, a white solid $(ClAgPCy_3)_2$, was isolated by filtration in a quantity of 149 mg, this corresponding to a side product yield of 96%.

Complex 6d. Grubbs first-generation catalyst (0.300 g, 0.3645 mmol), 2-[(4-bromo-2,6-dimethylphenylimino)methyl]-4-nitrophenol **3d** (0.127 g, 0.3645 mmol), silver(I) carbonate (0.050 g, 0.1823 mmol), silver(I) chloride (0.0005 g, 0.004 mmol), and THF (20 mL) were mixed and reacted as described above to provide the title complex **6d** (302 mg of a brown solid) in a yield of 96%: ^{1}H NMR (CD_2Cl_2, 500 MHz) $\delta = 19.49$ (d, 4.75 Hz, 1H), 8.23 (d, 2.94 Hz, 1H), 8.07 (dd, 9.52, 2.94, 1H), 8.03 (d, 5.69 Hz, 1H), 7.99 (d, 7.72 Hz, 2H), 7.58 (t, 7.44 Hz, 1H), 7.28 (t, 7.72 Hz, 2H), 7.28 (d, 2.19 Hz, 1H), 7.19 (d, 2.19 Hz, 1H), 7.02 (d, 9.52 Hz, 1H), 2.48 (q, 12.17, 3H), 2.38 (s, 3H), 1.52−2.04 (m, 18 H), 1.49 (s, 3H), 1.06−1.44 (m, 12H). In addition, a side product, a white solid $(ClAgPCy_3)_2$, was isolated by filtration in a quantity of 127 mg, this corresponding to a side product yield of 82%.

Complex 6e. Grubbs first-generation catalyst (0.300 g, 0.3645 mmol), 2-[(adamantan-2-ylmethylimino)methyl]-4-nitrophenol **3e** (0.1146 g, 0.3645 mmol), silver(I) carbonate (0.050 g, 0.1823 mmol), silver(I) chloride (0.0005 g, 0.004 mmol), and THF (1 mL) were mixed and reacted as described above to provide the title complex **6e** (233 mg of greenish solid) in a yield of 78%: ^{1}H NMR (CD_2Cl_2, 500 MHz) $\delta = 18.70$ (d, 13.46 Hz, 1H), 7.95 (dd, 9.38, 2.94, 1H), 7.89 (d, 7.50, 2H), 7.79 (d, 2.94, 1H), 7.64 (t, 7.50 Hz, 1H), 7.39 (d, 7.50 Hz, 1H), 7.30 (t, 7.78 Hz, 2H), 6.97 (d, 9.38 Hz, 1H), 6.10 (d, 10.67, 1H), 3.01 (dd, 10.67, 2.26, 1H), 2.31 (q, 11.67, 3H), 1.09−2.11 (m, 45 H). In addition, a side product, a white solid $(ClAgPCy_3)_2$, was isolated by filtration in a quantity of 140 mg, corresponding to a side product yield of 91%.

Complex 7 [(μ_2-chloro)(tricyclohexylphosphine)silver 7 ($AgClPCy_3)_2$]: ^{1}H NMR ($CDCl_3$) δ (ppm) 1.95−1.66 (m, 18H), 1.43−1.14 (m, 15H). Anal. Calcd for $C_{18}H_{33}AgClP$: C, 51.0; H, 7.85. Found: C, 50.7; H, 7.51.

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Supporting Information Available: ^{1}H NMR spectra for the compounds **3a**−**e**, **6b**−**e**, and **7**. Moreover, various X-ray diffraction analysis data is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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