# Synthesis and Characterization of New Ruthenium-Based Olefin Metathesis Catalysts Coordinated with Bidentate Schiff-Base Ligands

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A novel series of Schiff-base-substituted ruthenium carbene complexes have been prepared by the treatment of $RuCl_2(=CHPh)(PCy_3)_2$ with a variety of Schiff-base ligands as the thallium salts. Modification of the Schiff-base electronic and/or structural substituents allowed for the tuning of the complexes activities in olefin metathesis reactions. The structures of the complexes were unambiguously characterized by NMR studies and X-ray analysis. These newly prepared complexes are highly stable to air, moisture, and temperature and even exhibit catalytic activity in polar protic solvents.



## Introduction

A large number of catalyst systems which can initiate olefin metathesis reactions have been developed.[1] However, most of the early work in olefin metathesis was done using ill-defined multicomponent catalyst systems. It has only been in recent years that well-defined single-component metal carbene complexes have been prepared and extensively utilized in olefin metathesis reactions. With the advent of more efficient catalyst systems, olefin metathesis has emerged as a powerful tool for the formation of C−C bonds in chemistry.[2] Of particular utility among the various well-defined catalyst systems has been the alkoxy imido molybdenum system **1**[3] developed by Schrock and co-workers (Figure 1) and the benzylidene ruthenium carbene complexes **2** and **3** developed in our laboratory.[4,5]

The Ru−carbene systems **2** and **3** have drawn a lot of attention because they both exhibit high reactivity for a variety of metathesis processes under mild conditions and are remarkably tolerant of many organic functional groups such as alcohols, esters, aldehydes, and ketones.[6] To further demonstrate their versatility, polymer-supported[7] and water-soluble[8] versions of these Ru systems have recently been described. To date, the Ru−carbene catalysts **2** and **3** have been widely used in a variety of olefin metathesis reactions with remarkable success.[9] However, further investigation is necessary to develop and explore the feasibility of Ru−carbene chiral catalysts and catalysts which can control cis/trans selectivity in olefin metathesis processes. To facilitate the development of the aforementioned catalysts, Ru−carbene catalysts exhibiting improved thermal stability and catalysts capable of maintaining high activity in polar protic solvents need to be developed. In this report, we disclose our initial efforts toward the preparation and characterization of thermally stable Schiff-base-substituted Ru−carbene complexes which show high metathesis activity in polar protic solvents

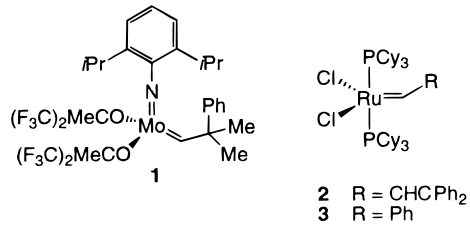


**Figure 1.**

(1) For representative examples, see: (a) Grubbs, R. H.; Pine, S. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A. Eds.; Pergamon: New York, 1991; Vol. 5, Chapter 9.3. (b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997.

(2) For representative examples, see: (a) Novak, B. M.; Risse, W.; Grubbs, R. H. *Adv. Polymer. Sci.* **1992**, *102*, 47. (b) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−552. (c) Hashimi, A. S. K. *J. Prakt. Chem.* **1997**, *339*, 195−199.

(3) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886. (b) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378−8387. (c) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899−6907.

(4) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (c) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511.

(5) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem.* **1995**, *107*, 2197−2181. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(6) (a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (b) Clark, T. D.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1995**, *117*, 12364−12365. (c) Diver, S. T.; Schreiber, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 5106−5109.

(7) (a) Nguyen, S. T.; Grubbs, R. H. *J. Organomet. Chem.* **1995**, *497*, 195−200. (b) Hartley, F. R. In *Supported Metal Complexes*; Ugo, R., James, B. R., Eds.; D. Reidel Publishing Company: Dordrecht, Holland, 1985.

(8) (a) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317−4325. (b) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784−790.

(9) For the detailed mechanism and activity of these catalysts, see: Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897.

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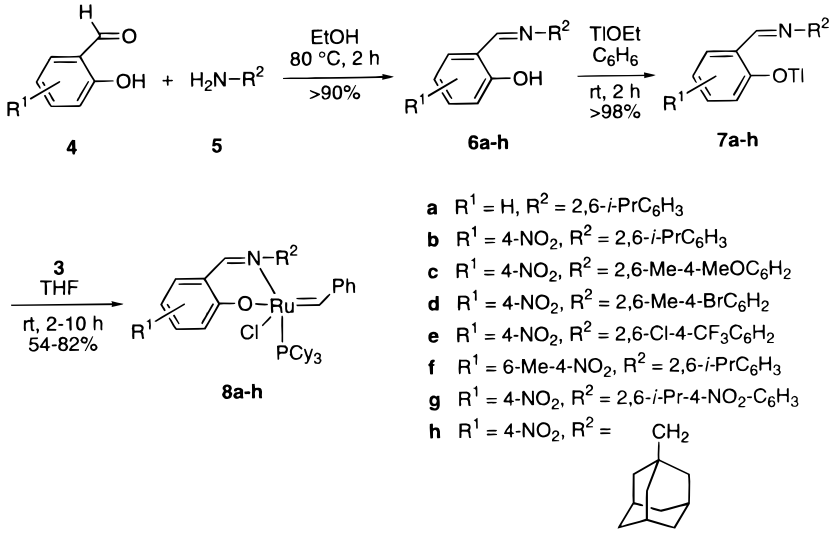
**Scheme 1**






as well as in commonly used organic solvents such as dichloromethane or benzene.

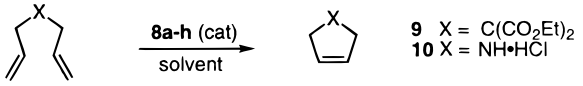
## Results and Discussion

**Synthesis of Ruthenium Schiff-Base Complexes.** The use of bidentate Schiff-base ligands in organometallic chemistry has been extensive because (i) they are easy to prepare and (ii) they exert easily varied steric and/or electronic effects on the resulting complexes.[10] In an attempt to develop new Ru-based complexes that act as efficient olefin metathesis catalysts, we envisioned that bidentate Schiff bases would be suitable for the simultaneous substitution of one neutral phosphine and one anionic chloride ligand in the Ru complexes **2** or **3**. The use of Schiff-base ligands could provide a convenient route into a variety of functionalized complexes such as chiral or cis/trans-selective catalysts,[11] polymer-supported catalysts,[7b] or water-soluble catalysts.[8]

The salicylaldimine ligands **6a**−**h** were easily prepared by simple condensation of salicylaldehydes **4** with aliphatic or aromatic amine derivatives **5** in excellent yields (Scheme 1). The substitution reactions (**7** → **8**) of complex **3** with Schiff bases **6a**−**h** were performed after converting the ligands to the corresponding salts. Among the various salts tested, the thallium salts proved to be the most efficient and were consequently used in all the substitution reactions. Thus, thallium salts **7a**−**h** were quantitatively obtained upon treatment of the Schiff-base ligands **6a**−**h** with thallium ethoxide. Further treatment of **7a**−**h** with **3** at room temperature afforded the desired complexes **8a**−**h** in moderate to good yields as brown solids stable to air and moisture. Despite the quantitative conversion of **3** to the Schiff-base Ru complexes **8a**−**h** by $^1$H NMR, isolated recrystallization yields were lower due to the high solubility of the complexes in most organic solvents. In any case, we found the complexes to be stable to air and moisture after being exposed to air on the benchtop for several days. In addition, we also found the complexes to be stable when heated to 80 °C over several hours in a NMR tube. Under both of the aforementioned conditions, no decomposition was observed by $^1$H or $^{31}$P NMR.

It is worthy of note that the efficiency of the substitution reactions varied depending on the bulk of the substituents on the ligands. For example, while the thallium salts of ligands bearing a methyl group (**7f**) on the 6-position of the phenoxy fragment readily underwent substitution with **3**, the reaction of ligands bearing bulkier substituents (i.e., *t*-Bu group) on the same position gave poor conversion under various substitution conditions. Similarly, ligands bearing highly bulky groups (i.e., triisopropylsilyloxy-) on the 2- and 6-positions of the benzimine fragments exhibited very poor reactivity in the substitution reaction with **3**, presumably due to steric reasons.

**Scheme 2**




**Preliminary Metathesis Activity Studies of Schiff-Base-Substituted Ruthenium Complexes.** As demonstrated in Scheme 2, the Schiff-base-substituted ruthenium carbene complexes **8a**−**h** exhibited catalytic activity in ring-closing metathesis (RCM) reactions. Although the new species are, in general, less reactive at room temperature than the carbene complex **3** for metathesis reactions, *the reactivity increases dramatically at higher temperatures*. For instance, although the ring closure of diethyl diallylmalonate ester **9** proceeds in 12 h at room temperature with complex **8g** (8 mol %, $CH_2Cl_2$), the reaction is completed in 1 h at 70 °C with the same carbene catalyst (3 mol %, $C_6H_6$, 96% yield). This phenomena may prove advantageous in a total synthesis setting, since RCM is favored over competing processes at higher temperatures.[1b]

(10) (a) Blaser, H.-U. *Chem. Rev.* **1992**, *92*, 935−952. (b) Nitta, H.; Yu, D.; Kudo, M.; Mori, A.; Inoue, S. *J. Am. Chem. Soc.* **1992**, *114*, 7969−7975. (c) El-Hendawy, A. M.; Alkybaisi, A. H.; El-Kourasy, A. E.-G.; Shanab, M. M. *Polyhedron* **1993**, *12*, 2343−2350. (d) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1048−1067.

(11) For recent examples of chiral ruthenium Schiff-base complexes in asymmetric reactions, see: (a) Kurseshy, R. I.; Khan, N. H.; Abdi, S. H. R.; Bhatt, K. N. *Tetrahedron: Asymmetry* **1993**, *4*, 1693−1701. (b) Chuard, T.; Gretillat, F.; Bernauer, K. *Chimia* **1993**, *47*, 215−217. (c) Kurseshy, R. I.; Khan, N. H.; Abdi, S. H. R.; Bhatt, A. K. *J. Mol. Catal. A* **1997**, *120*, 101−108.

**Table 1. NMR Data for Ru−Carbene Complexes 8a−h (in $CD_2Cl_2$)**

| entry | compound | $^1H_\alpha$ (ppm) | $J_{HP}$ (Hz) | $^{31}P$ (ppm) |
|---|---|---|---|---|
| 1 | **8a** | 19.68 | 3.6 | 52.23 |
| 2 | **8b** | 19.77 | 3.3 | 52.23 |
| 3 | **8c** | 19.49 | 4.7 | 50.51 |
| 4 | **8d** | 19.48 | 4.8 | 50.62 |
| 5 | **8e** | 19.39 | 4.5 | 50.65 |
| 6 | **8f** | 19.69 | 2.7 | 53.50 |
| 7 | **8g** | 19.72 | 3.3 | 52.54 |
| 8 | **8h** | 18.68 | 13.5 | 38.95 |

In addition to their prolonged stability to air or moisture, another important aspect of these new complexes is their metathesis activities in various organic solvents including protic polar media. Olefin metathesis catalysts which are active in polar protic solvents are needed for certain substrates.[12] As a demonstration of the utility of these complexes, diallylamine·HCl salt **10**, which is not soluble in common nonpolar solvents, was cleanly cyclized *in methyl alcohol* with complex **8a** (5 mol %, 40 °C, 12 h, 95% yield). Further studies are currently in progress to explore the full utility of complexes **8a**−**h** in the olefin methathesis reaction.

**Structural Characterization of the Schiff-Base-Substituted Ru Complexes.** For all the substitution reactions (**7** → **8**, Scheme 1), the substitution of one phosphine and one chloride ligand of **3** with the bidentate Schiff bases **7a**−**h** were unambiguously indicated by characteristic $^1H$ and $^{31}P$ NMR spectral changes. The coupling constants $J$ (Hz) between the carbene proton Hα and the coordinated phosphine has been found to be sensitive to the relative orientation of the plane defined by the atoms of the carbene fragment and that of the P−Ru−P plane in **2** and **3**. When the carbene plane is 90° to the P−Ru−P plane, $J_{PH} = 0$ Hz, and $J_{PH} > 10$ Hz when they are coplanar.[4c,5b,13]

In contrast to complex **3** (singlet, 20.1 ppm in $CD_2Cl_2$), the benzylidene protons in the compounds **8a**−**h** appear between 18.7 and 19.8 ppm as doublets (Table 1). As expected, the carbene protons of the complexes having more electron-withdrawing substituents were shifted further downfield. The proton−phosphorus couplings also varied depending on the nature of the Schiff-base ligands. Especially noteworthy is that the coupling constants $J_{PH}$ are more sensitive to the steric bulk than to the electronic contribution of the substituents on the Schiff-base ligands. This suggests that although the ligand coordination around the ruthenium metal center is similar, the relative geometry of each species varies slightly depending on the steric demands of the ligands. For instance, while sterically crowded ligands give lower $J_{PH}$ coupling constants (i.e., 2.7 Hz in **8f**), those values increase upon reduction of the steric demands in the Schiff bases (i.e., 4.8 Hz in **8d**). As found in the proton NMR spectroscopy, the $^{31}P$ shifts for the coordinated phosphine ligands in **8a**−**h** are also dependent on the electronic nature of the Schiff-base ligands. For instance, while the chemical shift of phosphorus is in the range of 51−54 ppm for aniline derived ligands, it is shifted upfield (39 ppm) for **8h**.

Representative of complexes **8a**−**h**, the structure of the Schiff-base-substituted benzylidene species **8b** was

(12) Miller, S. J.; Blackwell, H. E.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 9606−9614.

(13) Tallarico, J. A.; Bonitatebus, P. P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157−7158.

**Table 2. Summary of Crystal Data and Structure Refinement of 8b**

| | |
|---|---|
| empirical formula | $C_{44}H_{60}ClN_2O_3PRu·0.31CH_2Cl_2·0.17H_2O$ |
| fw | 863.53 |
| cryst syst | monoclinic |
| space group | $P2_1/c$ |
| temp | 160 K |
| unit cell dimens | $a = 9.123(4)$ Å<br>$b = 24.320(7)$ Å<br>$c = 19.863(5)$ Å |
| $Z$ | 4 |
| vol | 4405(3) Å$^3$ |
| $\mu$ | 5.30 cm$^{-1}$ ($\mu r_{max} = 0.13$) |
| $2\theta$ | 3−5° |
| no. of reflns measd | 17 106 |
| no. of indep reflns | 7741 |
| goodness-of-fit on $F^2$ | 1.64 for 658 parameters and 7741 reflections |
| final $R$ indices [$F_o$] | 0.079 for 5735 reflections with $F_o^2 > 2\sigma(F_o^2)$ |
| final weighted $R$ [$F_o^2$] | 0.121 for 7741 reflections |

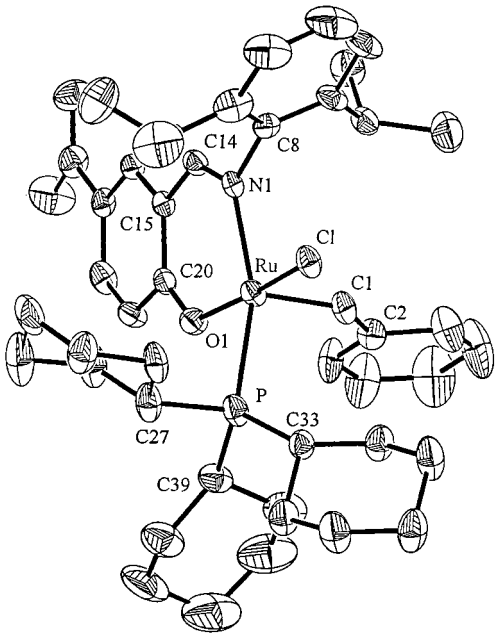



**Figure 2.** ORTEP drawing of **8b** with 50% probability ellipsoids with a few atoms labeled. Hydrogen atoms and the solvent molecules are omitted.

confirmed by single-crystal X-ray analysis. The crystals suitable for X-ray structure determination were isolated from a concentrated diisopropyl ether solution at −20 °C. The collection and refinement data for the crystallographic analysis are summarized in Table 2. The ORTEP diagram is shown in Figure 2, and selected bond distances and angles are listed in Table 3. In the solid state, the molecule adopts a distorted trigonal-bipyramidal coordination geometry. The bulky 2,6-diisopropyl benzimine occupies an axial position trans to the tricyclohexyl phosphine. The phenoxy moiety is positioned at an equatorial position with a nearly linear O1−Ru−Cl angle (173.0°). The two aromatic rings of the Schiff-base ligand are tilted at an angle of 80.1°. While the benzylidene moiety in complex **3** is perpendicular to the P1−Ru−P2 plane,[6b] the angle of the carbene unit to the P−Ru−N1 plane in **8b** is 87.1°. This distortion of the carbene plane is consistent with the nonzero value of $J_{PH}$ for **8b**. The Ru−C1 (carbene carbon) bond distance (1.850(6) Å) is similar to those in related compounds: $RuCl_2(=CHCH=CPh_2)PCy_3$ ($d$(Ru−C), 1.851(21) Å),[4b]

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for 8b**

| | | | |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| Ru−Cl | 1.850 (6) | P−C33 | 1.860 (6) |
| Ru−O1 | 2.055 (4) | P−C39 | 1.862 (6) |
| Ru−N1 | 2.106 (4) | O1−C20 | 1.288 (6) |
| Ru−P | 2.345 (2) | N1−C8 | 1.473 (7) |
| Ru−Cl | 2.382 (2) | N1−C14 | 1.301 (7) |
| C1−C2 | 1.451 (8) | C14−C15 | 1.433 (8) |
| P−C27 | 1.864 (7) | C1−H1(Carbene H) | 0.94 (6) |
| Bond Angles (deg) | | | |
| C1−Ru−O1 | 98.1 (2) | C8−N1−Ru | 121.5 (3) |
| C1−Ru−N1 | 103.5 (2) | C33−P−Ru | 114.2 (2) |
| O1−Ru−N1 | 88.9 (2) | C39−P−Ru | 117.5 (2) |
| C1−Ru−P | 96.8 (2) | C27−P−Ru | 102.4 (2) |
| O1−Ru−P | 88.4 (1) | C33−P−C39 | 111.7 (3) |
| N1−Ru−P | 159.8 (1) | C33−P−C27 | 103.9 (3) |
| C1−Ru−Cl | 88.7 (2) | C39−P−C27 | 105.2 (3) |
| O1−Ru−Cl | 173.0 (1) | O1−C20−C15 | 124.7 (5) |
| P−Ru−Cl | 89.0 (1) | N1−C14−C15 | 129.4 (5) |
| Ru−C1−H1 | 113 (4) | C2−C1−H1 | 112 (4) |

$[RuCl(=C(OMe)(CH=CPh_2)(CO)(P\textit{i}\text{-}Pr_3)_2][BF_4]$ (*d*(Ru−C), 1.874(3) Å)[14] and $RuCl_2(=CH\text{-}\textit{p}\text{-}C_6H_4Cl)(PCy_3)_2$ (*d*(Ru−C), 1.838(3) Å).[5b]

In summary, the new complexes reported in this paper are thermally stable under standard catalytic reaction conditions and exhibit high olefin metathesis activity in RCM reactions at higher temperatures. Moreover, the utility and activity of these complexes in polar protic solvents (such as MeOH) opens significant new avenues to be explored in the area of olefin metathesis. Further detailed studies regarding the mechanistic description, the scope and limitations, and the steric/electronic effects of the substituents on the complex activities will be published in due course.

## Experimental Section

**General.** Unless otherwise noted, all operations were carried out using standard Schlenk techniques or drybox procedures. Argon was purified by passage through a column of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. $^1$H (300.1 MHz) and $^{13}$C NMR (75.49 MHz) spectra were recorded on a General Electric QE-300 spectrometer. $^{31}$P NMR (161.9 MHz) spectra were recorded on a JEOL GX-400 spectrometer. NMR chemical shifts are reported downfield from tetramethylsilane (TMS) ($\delta$ scale), with TMS employed as the internal solvent for proton spectra and phosphoric acid employed as the internal solvent for phosphorus spectra. High-resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California, Riverside). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230−400 mesh) from EM Science. All solvents were rigorously degassed in 18 L reservoirs and passed through two sequential purification columns.[15] Complex **3**[5b] and 2,6-dimethyl-4-methoxyaniline[16] were prepared according to published procedures. Unless otherwise noted, all other compounds were purchased from Aldrich Chemical Co. and used as received.

**General Procedure for the Preparation of Schiff-Base Ligands (6a−h).** The condensation of salicylaldehydes with aliphatic or aromatic amine derivatives was carried out with stirring in ethyl alcohol at 80 °C for 2 h. Upon cooling to 0 °C, a yellow solid precipitated from the reaction mixture. The solid was filtered, washed with cold ethyl alcohol, and then dried in vacuo to afford the desired salicylaldimine ligand in excellent yields. Any modifications are described below for each reaction.

**Schiff-Base Ligand 6a.** Salicylaldehyde (0.37 g, 3.0 mmol), 2,6-diisopropylaniline (0.53 g, 3.0 mmol), and ethanol (15 mL) afforded 0.76 g (90%) of the title compound as a yellow solid. A drop of formic acid was used to accelerate the condensation reaction: mp 60−61 °C; $^1$H NMR ($CDCl_3$) $\delta$ 13.16 (s, 1H), 8.34 (s, 1H), 7.46 (d, $J$ = 7.2 Hz, 1H), 7.40 (t, $J$ = 7.2 Hz, 1H), 7.22 (bs, 3H), 7.10 (d, $J$ = 8.4 Hz, 1H), 6.99 (t, $J$ = 7.5 Hz, 1H), 3.20 (sept, $J$ = 6.6 Hz, 2H), 1.20 (d, $J$ = 6.9 Hz, 12H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.4, 161.0, 145.9, 138.4, 133.0, 132.0, 125.3, 123.0, 118.8, 118.4, 117.1, 27.9, 23.3; HRMS (EI) for $C_{19}H_{23}NO$ $[M]^+$ 281.1780, found 281.1786.

**Schiff-Base Ligand 6b.** 5-Nitrosalicylaldehyde (1.10 g, 6.60 mmol), 2,6-diisopropylaniline (1.20 g, 6.60 mmol), and ethanol (25 mL) afforded 2.0 g (93%) of the title compound as a yellow solid: mp 122−124 °C; $^1$H NMR ($CDCl_3$) $\delta$ 14.35 (s, 1H), 8.43 (s, 1H), 8.38 (d, $J$ = 2.7 Hz, 1H), 8.32 (d, $J$ = 9.3 Hz, 1H), 7.25 (bs, 3H), 7.15 (d, $J$ = 9.0 Hz, 1H), 2.97 (sept, $J$ = 6.9 Hz, 2H), 1.22 (d, $J$ = 6.9 Hz, 12H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.8, 165.2, 144.4, 139.7, 138.4, 128.3, 128.2, 126.1, 123.3, 118.3, 117.3, 28.1, 23.3; HRMS (CI) for $C_{19}H_{23}N_2O_3$ $[M + H]^+$ 327.1709, found 327.1708.

**Schiff-Base Ligand 6c.** 5-Nitrosalicylaldehyde (6.68 g, 40 mmol), 2,6-dimethyl-4-methoxyaniline[16] (6.65 g, 44 mmol), and ethanol (140 mL) afforded 11.52 g (96%) of the title compound as a yellow solid: mp 122−124 °C; $^1$H NMR ($CDCl_3$) $\delta$ 14.67 (s, 1H), 8.41 (s, 1H), 8.33 (d, $J$ = 2.7 Hz, 1H), 8.28 (dd, $J$ = 9.1, 2.7 Hz, 1H), 7.10 (d, $J$ = 9.1 Hz, 1H), 6.68 (s, 2H), 3.81 (s, 3H), 2.24 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 167.6, 165.0, 157.3, 130.2, 128.3, 128.2, 118.5, 117.5, 113.9, 55.4, 18.9; HRMS (CI) for $C_{16}H_{17}N_2O_4$ $[M + H]^+$ 301.1188, found 301.1196.

**Schiff-Base Ligand 6d.** 5-Nitrosalicylaldehyde (0.67 g, 4.0 mmol), 4-bromo-2,6-dimethylaniline (0.80 g, 4.0 mmol) and ethanol (15 mL) afforded 1.41 g (91%) of the title compound as a yellow solid: mp 194−196 °C; $^1$H NMR ($CDCl_3$) $\delta$ 13.96 (s, 1H), 8.41 (s, 1H), 8.35 (d, $J$ = 2.7 Hz, 1H), 8.30 (d, $J$ = 9.0 Hz, 1H), 7.28 (s, 2H), 7.13 (d, $J$ = 9.0 Hz, 1H), 2.19 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.4, 165.5, 145.6, 139.8, 131.0, 130.2, 128.4, 128.2, 118.5, 118.2, 117.3, 18.1; MS (CI) 350 (100), 348 (92), 268 (29), 131 (91), 104 (25), 77 (29).

**Schiff-Base Ligand 6e.** 5-Nitrosalicylaldehyde (1.30 g, 8.0 mmol), 4-amino-3,5-dichlorobenzotrifluoride (1.80 g, 8.0 mmol), and ethanol (25 mL) afforded 2.70 g (90%) of the title compound as a yellow solid: mp 173−174 °C; $^1$H NMR ($CDCl_3$) $\delta$ 12.96 (s, 1H), 8.68 (s, 1H), 8.43 (d, $J$ = 2.7 Hz, 1H), 8.36 (dd, $J$ = 9.3, 2.7 Hz, 1H), 7.70 (s, 2H), 7.17 (d, $J$ = 9.3 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 168.7, 166.1, 145.7, 140.1, 129.4, 129.1, 127.6, 125.8, 125.7, 118.5, 116.9; HRMS (CI) calcd for $C_{14}H_{11}N_2O_3F_3Cl_2$ $[M + H]^+$ 378.9864, found 378.9866.

**Schiff-Base Ligand 6f.** 3-Methyl-5-nitrosalicylaldehyde[17] (0.63 g, 3.40 mmol), 2,6-diisopropylaniline (0.80 g, 3.40 mmol), and ethanol (20 mL) afforded 1.10 g (95%) of the title compound as a yellow solid: mp 120−121 °C; $^1$H NMR ($CDCl_3$) $\delta$ 14.50 (s, 1H), 8.38 (s, 1H), 8.21 (s, 1H), 7.23 (s, 4H), 2.95 (sept, $J$ = 6.9 Hz, 2H), 2.42 (s, 3H), 1.20 (d, $J$ = 6.9 Hz, 12H); $^{13}$C NMR ($CDCl_3$) $\delta$ 165.4, 144.4, 139.1, 138.5, 132.9, 128.5,

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(17) 3-Methyl-5-nitrosalicylaldehyde was prepared in the following manner. *o*-Cresol was treated with anhydrous stannic chloride, paraformaldehyde, 2,6-lutidine, and toluene to afford 3-methylsalicylaldehyde in 40% yield. The corresponding aldehyde was then nitrated using glacial acetic acid and concentrated nitric acid to afford the title compound in 97% yield.

128.2, 126.0, 125.9, 123.2, 116.3, 28.0, 23.3, 15.4; HRMS (DCI) $C_{20}H_{25}N_2O_3$ $[M + H]^+$ 341.1865, found 341.1873.

**Schiff-Base Ligand 6g.** 5-Nitrosalicylaldehyde (1.0 g, 6.0 mmol), 2,6-diisopropyl-4-nitroaniline[18] (1.30 g, 6.0 mmol), and ethanol (20 mL) afforded 2.0 g (91%) of the title compound as a yellow solid: mp 118−120 °C; $^1$H NMR ($CDCl_3$) $\delta$ 13.34 (s, 1H), 8.43 (s, 2H), 8.33 (dd, $J$ = 9.0, 2.4 Hz, 1H), 8.09 (s, 2H), 7.18 (d, $J$ = 9.0 Hz, 1H), 3.00 (sept, $J$ = 6.9 Hz, 2H), 1.23 (d, $J$ = 6.9 Hz, 12H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.0, 165.7, 150.3, 145.8, 140.3, 134.0, 128.8, 128.6, 118.9, 118.1, 117.1, 28.3, 22.6; HRMS (DCI) $C_{19}H_{22}N_3O_5$ $[M + H]^+$ 372.1559, found 372.1560.

**Schiff-Base Ligand 6h.** 5-Nitrosalicylaldehyde (0.84 g, 5.0 mmol), 1-adamantanemethylaniline (0.90 g, 5.0 mmol), and ethanol (15 mL) afforded 1.40 g (92%) of the title compound as a yellow solid: mp 178−180 °C; $^1$H NMR ($CDCl_3$) $\delta$ 15.18 (s, 1H), 8.21 (s, 1H), 8.16 (t, $J$ = 9.0 Hz, 2H), 6.86 (d, $J$ = 9.3 Hz, 1H), 3.29 (s, 2H), 2.00 (s, 3H), 1.65 (m, 6H), 1.55 (bs, 6H); $^{13}$C NMR ($CDCl_3$) 172.9, 164.4, 137.2, 129.1, 128.5, 120.4, 115.1, 68.4, 40.1, 33.9, 27.9; HRMS (DCI) $C_{18}H_{23}N_2O_3$ $[M + H]^+$ 315.1709, found 315.1710.

**General Procedure for the Preparation of Thallium Salts (7a−h).** To a solution of Schiff bases **6a−h** in benzene or THF (10 mL) was added dropwise a solution of thallium ethoxide in benzene or THF (5 mL) at room temperature (note: using a glass pipet, the solution of thallium ethoxide in benzene or THF was filtered through a plug of glasswool to remove any impurities). Immediately after the addition, a pale yellow solid formed and the reaction mixture was stirred for 2 h at room temperature. Filtration of the solid under a nitrogen or argon atmosphere gave the thallium salts **7a−h** in quantitative yields. The salts were immediately used in the next step without further purification.

**General Procedure for the Preparation of Schiff-Base-Substituted Ru Complexes (8a−h).** To a solution of Ru complex **3**[5b] in THF (5 mL) was added a solution of thallium salts **7a−h** in THF (5 mL). The reaction mixture was stirred at room temperature for 3 h. After evaporation of the solvent, the residue was dissolved in a minimal amount of benzene and cooled to 0 °C. The thallium chloride (the byproduct of the reaction) was removed via filtration. The desired complex was then washed with cold benzene (10 mL × 3), and the filtrate was evaporated. The solid residue was recrystallized from pentane (−70 °C) to give the Schiff-base-substituted Ru complexes **8a−h** in moderate to good yields as brown solids. Any modifications are described below for each reaction.

**Complex 8a.** Ru complex **3**[5b] (1.20 g, 1.50 mmol), thallium salt **7a** (0.78 g, 1.60 mmol), and THF (20 mL) afforded 0.89 g (75%) of the title complex as a brown solid: mp 119−122 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.68 (d, $J$ = 3.6 Hz, 1H), 8.06 (d, $J$ = 5.4 Hz, 1H), 7.92 (d, $J$ = 7.5 Hz, 2H), 7.53 (t, $J$ = 7.2 Hz, 1H), 7.33−7.00 (m, 8H), 6.60 (t, $J$ = 7.2 Hz, 1H), 3.36 (sept, $J$ = 6.9 Hz, 1H), 2.51 (q, $J$ = 11.7 Hz, 3H), 2.13 (sept, $J$ = 6.9 Hz, 1H), 1.79−1.52 (m, 20H), 1.38 (d, $J$ = 6.6 Hz, 3H), 1.22 (m, 10H), 1.11 (d, $J$ = 6.9 Hz, 3H), 0.75 (dd, $J$ = 21.3, 6.9 Hz, 6H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 52.23; MS (FAB) 787 (3), 386 (12), 315 (26), 297 (19), 281 (49), 279 (19), 255 (8), 231 (20), 154 (23), 119 (23), 117 (100).

**Complex 8b.** Ru complex **3**[5b] (1.65 g, 2.0 mmol), thallium salt **7b** (1.10 g, 2.10 mmol), and THF (40 mL) afforded 1.40 g (82%) of the title complex as a brown solid: mp 140−145 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.77 (d, $J$ = 3.3 Hz, 1H), 8.27 (d, $J$ = 2.7 Hz, 1H), 8.14 (d, $J$ = 5.4 Hz, 1H), 8.10 (dd, $J$ = 9.6, 2.7 Hz, 1H), 7.94 (d, $J$ = 7.8 Hz, 2H), 7.60 (t, $J$ = 7.2 Hz, 1H), 7.30 (t, $J$ = 7.8 Hz, 2H), 7.21 (m, 2H), 7.09 (dd, $J$ = 6.9, 1.8 Hz, 1H), 6.99 (d, $J$ = 9.3 Hz, 1H), 3.26 (sept, $J$ = 6.6 Hz, 1H), 2.52 (q, $J$ = 11.5 Hz, 3H), 2.11 (sept, $J$ = 6.6 Hz, 1H), 1.73 (bs, 20H), 1.40 (d, $J$ = 6.6 Hz, 3H), 1.23 (m, 10H), 1.15 (d, $J$ = 6.9 Hz, 3H), 0.78 (dd, $J$ = 17.4, 6.9 Hz, 6H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 52.23; HRMS (FAB) $C_{44}H_{60}ClN_2O_3PRu$ $[M]^+$ 832.3074, found 832.3104.

**Complex 8c.** Ru complex **3**[5b] (0.25 g, 0.30 mmol), thallium salt **7c** (0.16 g, 0.32 mmol), and THF (3 mL) afforded 0.13 g (54%) of the title complex as a brown solid: mp 139−142 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.49 (d, $J$ = 4.7 Hz, 1H), 8.22 (d, $J$ = 2.8 Hz, 1H), 8.08−8.04 (m, 3H), 7.98 (d, $J$ = 7.8 Hz, 2H), 7.56 (d, $J$ = 7.4 Hz, 1H), 7.35 (d, $J$ = 1.3 Hz, 1H), 7.27 (t, $J$ = 7.5 Hz, 2H), 7.00 (d, $J$ = 9.6 Hz, 1H), 3.79 (s, 3H), 2.38 (s, 6H), 1.75−1.21 (m, 30H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 50.51; HRMS (FAB) $C_{41}H_{54}ClN_2O_4PRu$ $[M]^+$ 806.2553, found 806.2520.

**Complex 8d.** Ru complex **3**[5b] (0.41 g, 0.50 mmol), thallium salt **7d** (0.32 g, 0.55 mmol), and THF (25 mL) afforded 0.35 g (80%) of the title complex as a brown solid: mp 128−131 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.48 (d, $J$ = 4.8 Hz, 1H), 8.22 (d, $J$ = 2.7 Hz, 1H), 8.07 (dd, $J$ = 9.3, 2.7 Hz, 1H), 8.03 (d, $J$ = 5.7 Hz, 1H), 7.98 (d, $J$ = 7.8 Hz, 2H), 7.58 (t, $J$ = 7.8 Hz, 1H), 7.28 (t, $J$ = 7.8 Hz, 2H), 7.17 (s, 1H), 7.00 (d, $J$ = 9.6 Hz, 1H), 2.47 (q, $J$ = 12.0 Hz, 3H), 2.37 (s, 3H), 1.78−1.63 (bs, 20H), 1.50 (d, $J$ = 13.5 Hz, 3H), 1.30−1.16 (m, 10H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 50.62; HRMS (FAB) $C_{40}H_{51}BrClN_2O_3PRu$ $[M]^+$ 856.1532, found 856.1573.

**Complex 8e.** Ru complex **3**[5b] (0.34 g, 0.40 mmol), thallium salt **7e** (0.26 g, 0.44 mmol), and THF (20 mL) afforded 0.30 g (85%) of the title complex as a brown solid: mp 145−149 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.39 (d, $J$ = 4.5 Hz, 1H), 8.25 (d, $J$ = 2.7 Hz, 1H), 8.09 (dd, $J$ = 9.3, 2.7 Hz, 1H), 7.99 (m, 3H), 7.69 (d, $J$ = 18.0 Hz, 1H), 7.57 (t, $J$ = 7.2 Hz, 1H), 7.35 (s, 1H), 7.28 (t, $J$ = 7.8 Hz, 1H), 7.02 (d, $J$ = 9.6 Hz, 1H), 2.48 (q, $J$ = 11.7 Hz, 3H), 1.73−1.54 (m, 15H), 1.39 (m, 5H), 1.22 (bs, 10H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 50.65; HRMS (FAB) $C_{39}H_{45}Cl_3F_3N_2O_3PRu$ $[M]^+$ 886.1199, found 886.1179.

**Complex 8f.** Ru complex **3**[5b] (0.82 g, 1.0 mmol), thallium salt **7f** (0.60 g, 1.10 mmol), and THF (35 mL) afforded 0.68 g (80%) of the title complex as a brown solid: mp 155−158 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.69 (d, $J$ = 2.7 Hz, 1H), 8.11 (d, $J$ = 4.5 Hz, 2H), 7.89 (d, $J$ = 7.8 Hz, 1H), 7.55 (t, $J$ = 7.2 Hz, 1H), 7.33 (s, 1H), 7.24 (t, $J$ = 7.5 Hz, 2H), 7.17 (m, 3H), 7.07 (d, $J$ = 7.2 Hz, 1H), 3.22 (sept, $J$ = 6.6 Hz, 1H), 2.58 (q, $J$ = 11.4 Hz, 3H), 2.38 (s, 3H), 1.91 (sept, $J$ = 6.6 Hz, 1H), 1.80−1.54 (m, 20H), 1.36 (d, $J$ = 6.6 Hz, 3H), 1.19 (bs, 13H), 1.10 (d, $J$ = 6.6 Hz, 3H), 0.85 (d, $J$ = 6.9 Hz, 3H), 0.72 (d, $J$ = 6.3 Hz, 3H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 53.50; HRMS (FAB) $C_{45}H_{62}ClN_2O_3PRu$ $[M]^+$ 846.3230, found 846.3279.

**Complex 8g.** Ru complex **3**[5b] (0.66 g, 0.80 mmol), thallium salt **7g** (0.51 g, 0.88 mmol), and THF (50 mL) afforded 0.59 g (67%) of the title complex as a brown solid: mp 160−163 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 19.72 (d, $J$ = 3.3 Hz, 1H), 8.30 (d, $J$ = 2.7 Hz, 1H), 8.13 (d, $J$ = 3.0 Hz, 1H), 8.10 (s, 2H), 8.05 (d, $J$ = 2.1 Hz, 1H), 7.95 (d, $J$ = 2.4 Hz, 1H), 7.92 (d, $J$ = 7.8 Hz, 2H), 7.61 (t, $J$ = 7.2 Hz, 1H), 7.30 (t, $J$ = 7.8 Hz, 2H), 7.00 (d, $J$ = 9.6 Hz, 1H), 3.29 (sept, $J$ = 6.6 Hz, 1H), 2.48 (q, $J$ = 11.4 Hz, 2H), 2.18 (sept, $J$ = 6.6 Hz, 1H), 1.72 (bs, 20H), 1.45 (d, $J$ = 6.9 Hz, 3H), 1.20 (m, 13H), 0.80 (dd, $J$ = 21.0, 6.6 Hz, 6H); $^{31}$P NMR ($CD_2Cl_2$) $\delta$ 52.54; HRMS (FAB) $C_{44}H_{59}ClN_3O_5PRu$ $[M]^+$ 877.2924, found 877.2887.

**Complex 8h.** Ru complex **3**[5b] (0.33 g, 0.40 mmol), thallium salt **7h** (0.23 g, 0.44 mmol), and THF (20 mL) afforded 0.18 g (54%) of the title complex as a brown solid: mp 162−166 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 18.68 (d, $J$ = 13.5 Hz, 1H), 7.95 (dd, $J$ = 9.3 Hz, 1H), 7.89 (d, $J$ = 7.5 Hz, 2H), 7.79 (d, $J$ = 3.0 Hz, 1H), 7.64 (t, $J$ = 7.5 Hz, 1H), 7.38 (d, $J$ = 7.5 Hz, 1H), 7.30 (t, $J$ = 7.8 Hz, 1H), 6.97 (d, $J$ = 9.3 Hz, 1H), 6.09 (d, $J$ = 10.8 Hz, 1H), 3.00 (dd, $J$ = 10.8, 2.7 Hz, 2H), 2.29 (q, $J$ = 11.4 Hz, 3H), 1.99 (bs, 3H), 1.84 (bs, 3H), 1.73 (m, 20H), 1.57 (m, 10H), 1.25

(18) 2,6-Diisopropyl-4-nitrobenzene was prepared in an analogous manner to that found in Wepster, B. M. *Recl. Trav. Chim.* **1954**, *73*, 809−818. 2,6-Diisopropylaniline was protected as the sulfonamide using tosyl chloride, pyridine, and dichloromethane in 97% yield. The corresponding sulfonamide was then nitrated using concentrated nitric acid, water, acetic anhydride, and sodium nitrite in 53% yield. Deprotection of the amine was accomplished using a 10:1 mixture of concentrated sulfuric acid:water to afford the title compound in quantitative yields.

(d, $J$ = 8.7 Hz, 9H); $^{31}$P NMR ($CD_2Cl_2$) 38.95; HRMS (FAB) $C_{43}H_{60}ClN_2O_3PRu$ $[M]^+$ 820.3074, found 820.3079.

**General Procedure for the Ring-Closing Metathesis of Diethyl Diallylmalonate Using Catalysts 8a−h.** All reactions were performed on the benchtop in air by weighing 8 mol % of catalysts **8a**−**h** into a dry NMR tube and dissolving the solid in 0.5 mL of $CD_2Cl_2$ or $C_6D_6$. A solution of diethyl diallylmalonate (0.1 mmol) in $CD_2Cl_2$ or $C_6D_6$ (0.5 mL) was added. The tube was then capped, wrapped with Parafilm, and shaken periodically. The studies were run at both ambient temperatures and higher temperatures (~65 °C) to access the activity and stability of the catalysts during the course of the reactions. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks.

**X-ray Structure of the Ruthenium Complex 8b.** Crystals suitable for X-ray structure determination were grown from a solution of isopropyl ether at −20 °C over a few days. The brown crystal used for data collection was 0.10 mm × 0.13 mm × 0.44 mm. Data collection was carried out at 160 K. A total of 17 106 reflections were collected, 7741 of which were independent. Data collection parameters are summarized in the Table 1 (in part) and in the Supporting Information. The structure was solved by direct methods using the Siemens SHELXS-86 program. The molecule was refined isotropically (with riding H atoms on dichloromethane solvent) with a fractional population parameter for each solvent molecule also refined. The hydrogen atoms were originally placed at calculated positions. Eventually, the coordinates of all but two (H38a and H38b) were refined, with $U_{iso}$'s fixed at 1.2 times the $U_{eq}$ of the attached atom. Refinement was full-matrix least-squares using SHELXL-93.

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**Supporting Information Available:** $^1$H NMR spectra for complexes **8a**−**h** and tables of crystal and intensity collection data, positional and displacement parameters, and complete bond distances and angles for **8b** (30 pages). Ordering information is given on any current masthead page.

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