Indenylidene−Imidazolylidene Complexes of Ruthenium as Ring-Closing Metathesis Catalysts

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Summary: The indenylidene−imidazolylidene complexes of ruthenium (IMes)(PR$_3$)Cl$_2$Ru(3-phenylindenylid-1-ene) and (IPr)(PR$_3$)Cl$_2$Ru(3-phenylindenylid-1-ene) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, and R= Ph, Cy) were prepared and found to be efficient catalyst precursors for ring-closing metathesis.

Introduction

Olefin metathesis reactions have proven to be a powerful technique for the formation of C−C bonds.[2] The development of ruthenium complexes bearing sterically demanding phosphines such as the well-defined, neutral 16-electron complex RuCl$_2$(=C(H)Ph)(PCy$_3$)$_2$ as an efficient catalyst system has allowed significant progress in the field of olefin metathesis.[3] Since at elevated temperatures phosphines suffer from significant P−C degradation,[4] the development of sterically demanding ligands that can mimic the phosphine behavior and at the same time show stability at higher temperatures would prove useful.[5] Imidazolylidene ligands with sterically demanding groups substituted in the 1 and 3 positions of the five-membered ring have been used to generate very effective catalysts for Suzuki cross-coupling[6] and ring-closing metathesis reactions.[4a,7,8] Recent studies have shown that complexes of unsaturated "C$_\alpha$" ligands other than the alkylidenes, such as allenylidenes, are also efficient catalyst precursors in the olefin metathesis reactions.[8b] As part of our ongoing research directed toward the development of olefin metathesis catalyst precursors incorporating the sterically demanding substituted imidazolylidene ligand (phosphine mimics), we set out to prepare the imidazolylidene analogues of the previously synthesized Ru−allenylidene complexes RuCl$_2$(=C=C=CPh$_2$)(PR$_3$)$_2$, R = Ph and Cy, via substitution reactions. The examination of the X-ray crystal structure of one of the complexes (RuCl$_2$(=C=C=CPh$_2$)(PPh$_3$)(IPr), IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) showed that the "C$_\alpha$" unsaturated moiety in this complex is not an allenylidene but rather a cyclized vinyl carbene, "an indenylidene".[10] Further investigations of the spectroscopic data for RuCl$_2$(=C=C=CPh$_2$)(PCy$_3$)$_2$ proved this compound to be an indenylidene complex, as well.[11]

We now report the synthesis and characterization of Cl$_2$Ru(imidazolylidene)(PR$_3$)(3-phenylindenylid-1-ene) (imidazolylidene = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; R = Ph and Cy). The thermal stability of the above-mentioned compounds and their role as catalyst precursors in RCM reactions are also presented.

Results and Discussion

The novel complexes (imidazolylidene)(PPh$_3$)Cl$_2$Ru-(3-phenylindenylid-1-ene) (imidazolylidene = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene), IMes, and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr, were synthesized by the addition of imidazolylidene to Cl$_2$-Ru(PPh$_3$)$_2$(3-phenylindenylid-1-ene)[12] (**1**) in toluene at room temperature. The removal of volatiles resulted in the formation of orange microcrystalline solids that were formulated as (IMes)(PPh$_3$)Cl$_2$Ru(3-phenylindenylid-1-ene) (**3**) and (IPr)(PPh$_3$)Cl$_2$Ru(3-phenylindenylid-1-ene) (**4**); see Scheme 1.

The ^{31}P NMR spectra show singlets at 29.00 and 30.51 ppm for **3** and **4**, respectively. The signal for the single

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(11) Due to the lack of X-ray crystal structure for the complex **2** and ambiguity of the spectroscopic evidence, the real nature of the unsaturated "C$_\alpha$" ligand could not be determined. In this paper, in analogy with the closely related complex Cl$_2$Ru(PPh$_3$)$_2$(3-phenylindenylid-1-ene) (**3**), whose structure was unambiguously identified from the spectroscopic evidence, **2** is referred to as an indenylidene complex.

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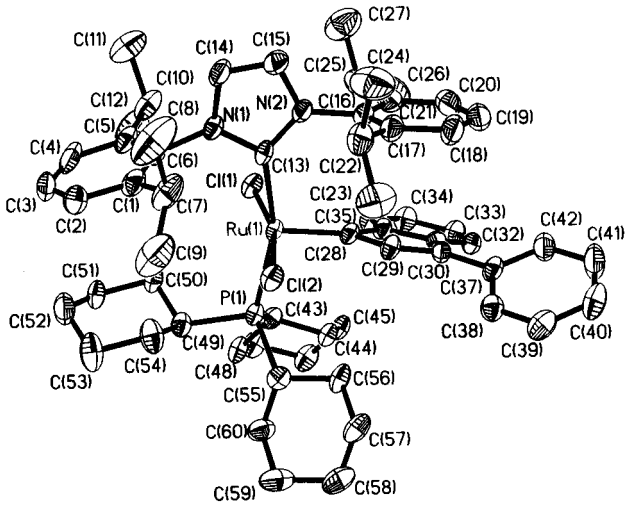
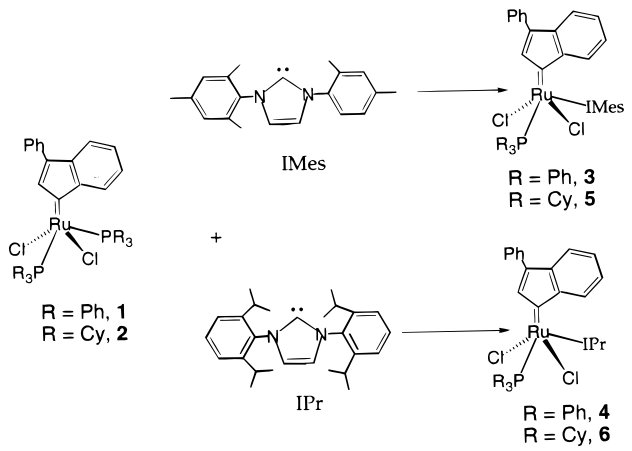


Figure 1. ORTEP of (IPr)(PCy_3)Cl_2Ru(3-phenylindenylid-1-ene), **6**. Hydrogen atoms have been omitted for clarity.

Scheme 1



proton on C_β of indenylidene appears as a singlet at 7.49 and 7.33 ppm in the ^{1}H NMR spectra of **3** and **4**, respectively. The X-ray crystal structure of **4** confirmed that the complex bears an indenylidene ligand.[10]

When (PCy_3)$_2Cl_2$Ru(3-phenylindenylid-1-ene) (**2**) reacts with imidazolylidene ligands IMes and IPr, orange-brown microcrystalline solids (IMes)(PCy_3)Cl_2Ru(3-phenylindenylid-1-ene) (**5**) and (IPr)(PCy_3)Cl_2Ru(3-phenylindenylid-1-ene) (**6**) are formed; see Scheme 1. The reaction conditions are the same as those for the synthesis of **3** and **4**; however, **5** can also be prepared in hot hexanes, which results in the easier isolation of the product (simple filtration vs evaporation of the solvent, washing with hexanes, and drying). Simple phosphine exchange (PCy_3 for PPh_3) in **3** also results in the formation of **5**, whereas the same reaction with **4** produces a mixture of unidentifiable compounds. The ^{31}P NMR spectra of **5** and **6** showed singlets at 31.60 and 32.81 ppm, respectively. The diagnostic singlet of the indenylidene C_β proton appeared at 7.80 and 7.99 ppm in the ^{1}H NMR spectra of **5** and **6**, respectively.

The X-ray crystal structure of **6** has been determined (Figure 1) and clearly shows the coordination of Ru to an indenylidene moiety. The coordination geometry around the ruthenium center is distorted square pyramidal, with the strongest π-acidic ligand (indenylidene) assuming the unique apical site. The square base is defined by the two chlorides and the donor atoms of the phosphine and the imidazolylidene ligands with the ruthenium center lying 0.3443(12) Å above this plane. The Ru−C_α(indenylidene) bond distance is significantly shorter than the bond length between the ruthenium and the weaker π-acid imidazolylidene (1.861(4) vs 2.113(4) Å); both bond distances are identical (within experimental error) to their counterparts in **4**.[10] Crystallographic data are reported in Table 1, and selected bond lengths and bond angles are presented in Table 2.

Table 1. Crystallographic Data for (IPr)(PCy_3)Cl_2Ru(3-phenylindenylid-1-ene), 6

formula	$C_{60}H_{79}Cl_2N_2PRu$
fw	1130.36
color	brown
space group	*Pbcn*
a, Å	27.2154(16)
b, Å	23.4559(14)
c, Å	20.6314(13)
α, deg	90
β, deg	90
γ, deg	90
volume (Å^3), Z	13170.3(13), 8
density (calcd) (g/cm^3)	1.140
R	0.0542
R_w	0.1434
no. of refined params	928
no. of data collected	90581
no. of unique data, $I > 3\sigma$	11594
goodness of fit, F^2	1.032

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for (IPr)(PCy_3)Cl_2Ru(3-phenylindenylid-1-ene), 6

Ru(1)−C(28)	1.861(4)	C(34)−C(35)	1.387(7)
Ru(1)−C(13)	2.113(4)	C(35)−C(36)	1.378(6)
Ru(1)−Cl(1)	2.3833(11)	C(28)−C(36)	1.494(6)
Ru(1)−Cl(2)	2.3903(11)	C(30)−C(37)	1.473(6)
Ru(1)−P(1)	2.4264(12)	C(31)−C(36)	1.423(6)
C(28)−C(29)	1.474(6)	C(28)−Ru(1)−C(13)	102.12(17)
C(29)−C(30)	1.350(6)	C(28)−Ru(1)−Cl(1)	100.13(14)
C(30)−C(31)	1.484(6)	C(13)−Ru(1)−Cl(2)	90.16(11)
C(31)−C(32)	1.381(6)	C(28)−Ru(1)−P(1)	96.59(13)
C(32)−C(33)	1.406(7)	C(13)−Ru(1)−P(1)	161.29(12)
C(33)−C(34)	1.379(7)	Cl(1)−Ru(1)−Cl(2)	164.50(4))

Table 3. Thermal Stability of Catalyst Precursors 1−6[a] at 80 °C

entry	compound	start of decomposition (h)
1	**1**	4
2	**2**	>256
3	**3**	2
4	**4**	42
5	**5**	>256
6	**6**	>256

[a] See text for details.

Thermal Stability Studies. The thermal stability studies have been performed in NMR tubes by dissolving ca. 5 mg of each compound in 0.4 mL of toluene-d_8 and heating the solution to 80 °C. The onset of decomposition was noted by examining the ^{31}P NMR spectra taken at certain intervals (2, 4, ..., 2^n h). The results are reported in Table 3. The compounds containing PPh_3 were the least stable and decomposed on heating; the least stable was (PPh_3)$_2Cl_2$Ru(3-phenylindenylid-1-ene) (**1**), which decomposed after 2 h at 80 °C (Table 3, entry 1), and the most stable was (IPr)(PPh_3)Cl_2Ru(3-phenylindenylid-1-ene) (**4**) (Table 3, entry 4), which showed

Table 4. Ring-Closing Metathesis Results Using Catalyst Precursors 1−6[a]

entry	substrate	catalyst precursor	solvent	temp (°C)	time (min)	yield (%)[b]
1	**7**	**1**	CD_2Cl_2	40	25	0
2	**7**	**2**	CD_2Cl_2	RT	25	84
3	**7**	**3**	CD_2Cl_2	40	25	65
4	**7**	**4**	CD_2Cl_2	40	25	56
5	**7**	**5**	CD_2Cl_2	RT	25	88
6	**7**	**6**	CD_2Cl_2	RT	25	75
7	**8**	**2**	CD_2Cl_2	RT	25	96
8	**8**	**3**	CD_2Cl_2	40	25	94
9	**8**	**4**	CD_2Cl_2	RT	25	94
10	**8**	**5**	CD_2Cl_2	RT	25	30
11	**8**	**6**	CD_2Cl_2	RT	25	89
12	**9**	**2**	d_8−toluene	80	120	0
13	**9**	**3**	d_8−toluene	80	120	66
14	**9**	**4**	d_8−toluene	80	120	17
15	**9**	**5**	d_8−toluene	80	120	20
16	**9**	**6**	d_8−toluene	80	120	19

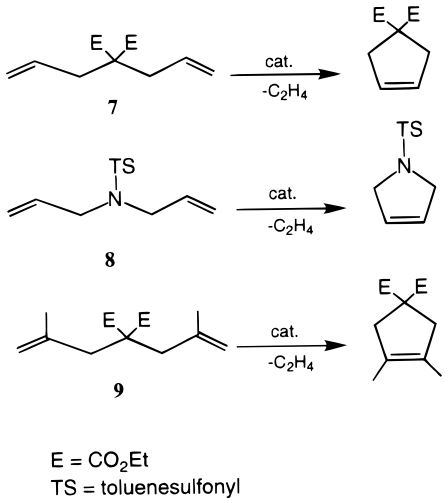
[a] Experimental protocol is described in the text. [b] Determined by ^{1}H NMR; see text for details.

decomposition after 42 h at the same temperature. It can be concluded that the presence of the nucleophilic carbene ligand IPr in the coordination sphere of ruthenium stabilizes the complex significantly. The complexes incorporating PCy_3 were more robust and did not decompose at elevated temperatures even after about 10 days (256 h) (Table 3, entries 2, 5, and 6). This result is hardly surprising because if the decomposition pathway involves the dissociation of phosphines (other ligands are less likely to dissociate), the less electron-releasing and hence the less tightly bound PPh_3 ligand should undergo dissociation faster than the more tightly bound PCy_3 moiety.

Ring-Closing Metathesis Reactions. The role of complexes **1**−**6** as catalyst precursors in the ring-closing metathesis reactions was investigated. Three different diene substrates diethyldiallylmalonate (**7**), diallyltosylamine (**8**), and diethyldi(2-methylallyl)malonate (**9**) were added to the NMR tubes containing a solution of 5 mol % of catalyst precursor in an appropriate deuterated solvent. The NMR tubes were then kept at the temperatures reported in Table 4. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks in the ^{1}H NMR spectra; the results are presented in Table 4, and the catalytic transformations are depicted in Scheme 2.

The compound $(PPh_3)_2Cl_2Ru$(3-phenylindenylid-1-ene) (**1**) did not show any catalytic activity with **7** (Table 4, entry 1) and therefore was eliminated from the list of catalyst precursors in this study. The ruthenium−indenylidene−imidazolylidene complexes that contained PPh_3, $(IMes)(PPh_3)Cl_2Ru$(3-phenylindenylid-1-ene) (**3**) and $(IPr)(PPh_3)Cl_2Ru$(3-phenylindenylid-1-ene) (**4**), showed good catalytic activity with diethyldiallylmalonate (**7**) and diallyltosylamine (**8**) as substrates (Table 4, entries 3, 4, 8, and 9). It should be noted that **3** catalyzes this reaction only when heated to 40 °C, whereas **4** does so at room temperature. Sterically hindered diethyldi(2-methylallyl)malonate (**9**) does not easily undergo ring-closing metathesis reaction; catalyst precursor **3** can convert 60% of this substrate into the product after 2 h, and this is only achieved when the reaction is heated to 80 °C. The rate of conversion with **4** is only 17% at this temperature. Heating the reaction mixtures for longer periods of time does not increase the yields of the reactions; it can be inferred that the catalyst is disabled after a certain period of time at higher temperatures (Table 4, entries 12−16).

Scheme 2



The compound $(PCy_3)_2Cl_2Ru$(3-phenylindenylid-1-ene) (**2**) exhibited high reactivity when used with substrates **7** and **8** but was not effective with substrate **9** (Table 4, entries 2, 7, and 12). The indenylidene derivatives of $(PCy_3)Ru$(imidazolylidene), compounds $(IMes)(PCy_3)Cl_2Ru$(3-phenylindenylid-1-ene) (**5**) and $(IPr)(PCy_3)Cl_2Ru$(3-phenylindenylid-1-ene) (**6**), were comparable to **2** in their reactivity toward **7** (Table 4, entries 5 and 6). The IPr analogue (**6**) converted **8** with a very high yield (comparable to **2**), whereas the IMes compound (**5**) was much less reactive toward the same substrate (Table 4, entries 10 and 11). The yields of the reactions with **9** were low for both compounds (Table 4, entries 15 and 16).

The indenylidene complexes **2**−**6** are shown to be good catalyst precursors in the RCM of sterically unhindered substrates (**7** and **8**), comparable to the alkylidene complexes developed by Grubbs[2] and Herrmann.[7c] They show much higher catalytic activity compared to their allenylidene analogues.[12] The reasons behind this behavior are under investigation.

Conclusion

We have shown that the indenylidene−imidazolylidene complexes of ruthenium $(IMes)(PR_3)Cl_2Ru$(3-phenylindenylid-1-ene) and $(IPr)(PR_3)Cl_2Ru$(3-phenylindenylid-1-ene) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, and R = Ph, Cy) are active catalyst precursors in the ring-closing metathesis of dienes. The compounds incorporating a PCy_3 ligand are very stable thermally and do not decompose even after heating to 80 °C for 10 days.

Experimental Section

General Considerations. All synthesis and kinetic studies were performed under inert atmospheres of argon using standard high-vacuum or Schlenk tube techniques, or in a MBraun glovebox containing less than 1 ppm oxygen and

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water. Solvents including deuterated solvents for NMR analysis were dried and distilled under argon before use employing standard drying agents.[13] The carbene ligands IMes[14] and IPr[15] and compounds $(PPh_3)_2Cl_2Ru$(3-phenylindenylid-1-ene) (**1**),[9] $(PCy_3)_2Cl_2Ru$(3-phenylindenylid-1-ene) (**2**),[9] diallyltosylamine (**8**),[16] and diethyldi(2-methylallyl)malonate (**9**)[17] were prepared according to literature. PCy_3 was purchased from Aldrich and used as received. Diethyldiallylmalonate (**7**) was purchased from Aldrich, dried over P_2O_5, and vacuum distilled prior to use. NMR spectra were recorded using a Varian Gemini 300 or Oxford 400 MHz spectrometer. Elemental analyses were performed by Desert Analysis, Tucson, AZ. Experimental synthetic procedures, leading to isolation of previously unreported complexes, are described below.

Synthesis of (IMes)$(PPh_3)Cl_2Ru$(3-phenylindenylid-1-ene), 3. To an intimate mixture of **1** (0.90 g, 1.02 mmol) and IMes (0.33 g, 1.06 mmol) was added toluene (20 mL) at room temperature. The reaction mixture, which turned orange-brown immediately, was stirred for 4 h. The solvent was then removed in vacuo, and the residue was washed with hexanes (2 × 10 mL) and was dried to afford an orange microcrystalline compound in 83% (0.78 g) yield.^{31}P NMR (121.4 MHz, 25 °C, C_6D_6) δ: 29.0 (s). ^{1}H NMR (300.1 MHz, 25 °C, C_6D_6) δ: 1.78 (s, 3 H, IMes CH_3), 1.92 (s, 3 H, IMes CH_3), 2.09 (s, 3 H, IMes CH_3), 2.23 (s, 3 H, IMes CH_3),2.60 (s, 3 H, IMes CH_3), 2.62 (s, 3 H, IMes CH_3), 6.03 (s, 1 H), 6.07 (s, 1 H), 6.17 (s, 1 H), 6.38 (s, 1 H), 6.79−6.99 (m, 11 H, all phenyl-H + 2 IMes-H), 7.46 (m, 6 H), 7.49 (s, 1 H, Ru=CC*H*), 7.61 (m, 2 H), 8.31 (m, 1 H). Anal. Calcd for $C_{54}H_{49}Cl_2N_2PRu$: C, 69.45; H, 5.55; N, 2.81. Found: C, 69.82; H, 5.32, N, 3.02.

Synthesis of (IPr)$(PPh_3)Cl_2Ru$(3-phenylindenylid-1-ene), 4. To an intimate mixture of **1** (0.5 g, 0.56 mmol) and IPr (0.24 g, 0.62 mmol) was added toluene (20 mL) at room temperature. The reaction mixture, which turned orange-brown immediately, was stirred for 4 h. The solvent was then removed in vacuo, and the residue was washed with hexanes (2 × 10 mL) and was dried to afford an orange microcrystalline compound in 70% (0.40 g) yield. ^{31}P NMR (121.4 MHz, 25 °C, C_6D_6) δ: 30.51 (s). ^{1}H NMR (400.1 MHz, 25 °C, C_6D_6) δ: 0.76 (d, J = 6.4 Hz, 3 H, CH(CH_3)$_2$), 0.78 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.96 (d, J = 6.4 Hz, 3 H, CH(CH_3)$_2$), 1.03 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 1.13 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 1.39 (d, J = 6.4 Hz, 3 H, CH(CH_3)$_2$), 1.45 (d, J = 6.4 Hz, 3 H, CH(CH_3)$_2$), 1.64 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 3.12 (sep., J = 6.4 Hz, 1 H, CH(CH$_3$)$_2$), 3.20 (sep., J = 6.4 Hz, 1 H, CH(CH$_3$)$_2$), 3.68 (sep., J = 6.4 Hz, 1 H, CH(CH$_3$)$_2$), 4.08 (sep., J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$), 6.57 (s, 2 H, NC*H*C*H*N), 6.91−7.24 (all m, 3 H, Ph CH + 15 H, PPh_3 CH + 6 H IPr−Ph), 7.33 (d, J = 7.6 Hz, 1 H, indenylidene CH), 7.35 (s, 1 H, Ru=CCH), 7.38 (m, 1 H, indenylidene CH), 7.40 (m, 1 H, indenylidene CH), 7.67 (d, J = 7.2 Hz, 2 H, Ph CH), 8.02 (d, J = 7.2 Hz, 1 H, indenylidene CH). Anal. Calcd for $C_{60}H_{61}Cl_2N_2PRu$: C, 71.13; H, 6.07; N, 2.77. Found: C, 70.85; H, 5.96, N, 2.50.

Synthesis of (IMes)$(PCy_3)Cl_2Ru$(3-phenylindenylid-1-ene), 5. (a) IMes (0.23 g, 0.76 mmol) was suspended in hexanes (40 mL) before compound **2** (0.69 g, 0.75 mmol) was added in one portion. The mixture was heated for 2.5 h with stirring at 60 °C. In this period the formation of a purple-brown precipitate was observed. After filtration at room temperature the residue was washed with pentane (3 × 10 mL), and 0.5574 g (79%) of pure compound was obtained after drying for 30 min in vacuo.

(b) Compound **3** (1.00 g, 1.08 mmol) was dissolved in toluene (30 mL) before PCy_3 (0.33 g, 1.17 mmol) was added in one portion. The mixture was heated to 40 °C for 16 h. The solvent was removed under reduced pressure, and the residue was suspended in pentane (40 mL). After refluxing for 3 h, the suspension was filtered and the residue was washed with pentane (3 × 5 mL). Drying the residue in vacuo for 30 min afforded 0.88 g (86%) of pure compound **5**. ^{31}P NMR (121.4 MHz, 25 °C, C_6D_6) δ: 31.6 (s). ^{1}H NMR (300.1 MHz, 25 °C, C_6D_6) δ: 1.00−1.41 (m, 18 H, PCy_3), 1.51 (m, 3 H, PCy_3), 1.54 (m, 3 H, PCy_3), 1.74 (m, 3 H, PCy_3), 1.76 (s, 3 H, IMes−CH_3), 1.85 (m, 3 H, PCy_3), 2.00 (s, 3 H, IMes−CH_3), 2.17 (s, 3 H, IMes−CH_3), 2.19 (s, 3 H, IMes−CH_3), 2.47 (m, 3 H, PCy_3), 2.62 (s, 3 H, IMes−CH_3), 2.63 (s, 3 H, IMes−CH_3), 5.98 (s, 1 H), 6.10 (s, 2 H), 6.42 (s, 1 H), 6.91 (s, 2 H), 7.05−7.30 (m, 6 H, phenyl−H), 7.80 (s, 1H, Ru=CC*H*), 7.85 (m, 2 H), 9.08 (m, 1 H). Anal. Calcd for $C_{54}H_{67}Cl_2N_2PRu$: C, 68.48; H, 7.13; N, 2.96. Found: C, 68.32; H, 6.91; N, 3.09.

Synthesis of $Cl_2Ru(IPr)(PCy_3)$(3-phenylindenylid-1-ene), 6. To a mixture of **2** (0.5 g, 0.54 mmol) and IPr (0.25 g, 0.65 mmol) was added toluene (20 mL) at room temperature. The reaction mixture, which turned orange-brown immediately, was stirred for 4 h. The solvent was then removed in vacuo, and the residue was washed with hexanes (2 × 10 mL) and dried to afford an orange microcrystalline compound in 75% (0.42 g) yield. ^{31}P NMR (121.4 MHz, 25 °C, C_6D_6) δ: 32.81 (s). ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ: 1.00−2.20 (broad unresolved m, 24 H, CH(CH_3)$_2$ + 33 H, PCy_3), 2.86 (broad m, 4 H, CH(CH$_3$)$_2$), 7.0−7.22 (broad m, 5 H, Ph CH + 6 H IPr ph + 2 H NC*H*C*H*N), 7.60 (m, 1 H, indenylidene CH), 7.86 (d, J = 7.6 Hz, 1 H, indenylidene CH), 7.88 (m, 1H, indenylidene CH), 7.99 (s, 1H, Ru=CCH), 9.21 (d, J = 7.2 Hz, 1H, indenylidene CH). Anal. Calcd for $C_{60}H_{79}Cl_2N_2PRu$: C, 69.88; H, 7.72; N, 2.72. Found: C, 70.11; H, 7.90, N, 2.78.

General Procedure for Ring-Closing Metathesis. In the drybox catalyst precursor (5 mol %) was accurately weighed in a Wilmad screw-capped NMR tube and dissolved in CD_2Cl_2 or toluene-d_8 (0.4 mL). Diethyldiallyl malonate (**7**), diallyltosylamine (**8**) (0.1 mmol), or diethyl(2-methylallyl)malonate (**9**) (0.1 mmol) was added to the solution, and the NMR tube was heated under Ar to temperatures shown in Table 4. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks.[2c]

X-ray Diffraction Measurements. A single crystal of **6** was coated with paratone oil and then sealed in a glass capillary tube. The X-ray data were collected at low temperature using graphite-monochromated Mo Kα radiation on a Siemens P4 automated X-ray diffractometer. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Initial fractional coordinates for the Ru atom were determined by heavy-atom methods, and the remaining non-hydrogen atoms were located by successive difference Fourier calculations, which were performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Crystallographic data can be found in Table 1, and selected bond distances and bond angles are presented in Table 2.

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Supporting Information Available: Details of crystal structure determinations for **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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