Ruthenium Metathesis Catalysts Containing Chelating Aryloxide Ligands

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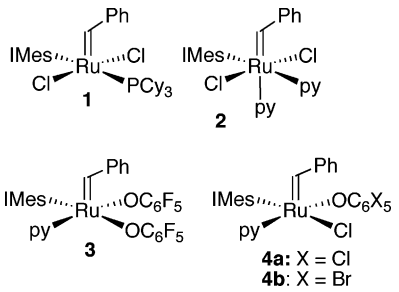
Olefin metathesis catalysts containing chelating aryloxide donors, RuXX′(IMes)(py)(=CHPh) (**5**, XX′ = 3,5-dichloro-2-oxidobenzenesulfonate; **6**, XX′ = catecholate), are accessible in high yield by reaction of *o*-sulfonato aryloxide or catecholate salts, respectively, with $RuCl_2(IMes)(py)_2$(=CHPh). Isomerization to π-bound aryloxides, as found with phenoxide ion or 2′-(diphenylphosphino)-1,1′-binaphthyl-2-olate, is suppressed by use of these smaller, more rigid, chelate rings. Preliminary investigations indicate that the catecholato derivative exhibits metathesis activity approaching that of the recently reported, highly active catalyst $RuCl(OC_6Br_5)(IMes)(py)$(=CHPh).

Introduction

Substituted aryloxide ligands offer considerable promise as sterically and electronically tunable anionic donors in transition metal catalysis. In the area of olefin metathesis, remarkable activity and selectivity are exhibited by group 6 complexes containing alkoxide, biphenolate, and binaphtholate ligands.[1,2] We recently demonstrated that ruthenium alkylidene complexes bearing monodentate, electron-deficient aryloxides (Chart 1) exhibit metathesis efficiencies comparable or superior to those of the "second-generation" catalysts **1** and **2**, in some cases at significantly lower catalyst loadings.[3] Our motivation for use of perhaloaryloxide ligands in **3** and **4** stems from insights obtained from model reactions of $RuXCl(PPh_3)_3$ (X = H, Cl) with phenoxide ion, which afforded only piano-stool, π-phenoxide complexes (Scheme 1).[4] While we were able to curb the tendency toward $\sigma \rightarrow \pi$ isomerization of the aryloxide ligand by depleting the electron-donor ability of the aromatic ring,[3,5] this appears to exact a price in terms of the lability of the pyridine donor (and hence initiation efficiency)[6] and severely restricts one of the major potential assets of the aryloxide platform, its ease of electronic and steric tuning.

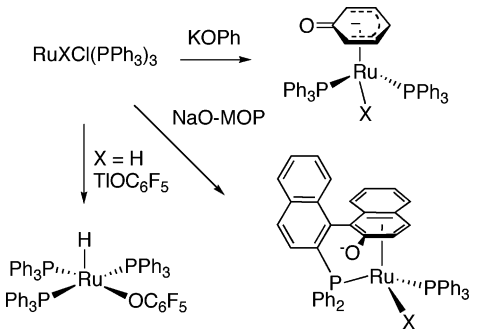
In seeking alternatives to electronic stabilization of the Ru-(σ-OAr) bond, we had considered the possibility that isomerization could be restricted through the chelate effect. (As an ancillary advantage, we anticipated that catalytic activity might be enhanced by the reduced steric congestion at the metal.) However, chelation of the aryloxide donor within a seven-membered ring proved insufficient to prevent isomerization, as indicated by reaction of $RuXCl(PPh_3)_3$ with sodium 2′-(diphenylphosphino)-1,1′-binaphthyl-2-ol (NaO-MOP; Scheme 1).[7] In the present study, we explored the potential of smaller, less flexible chelate rings. We now report that stable, five-coordinate Ru(σ-XX′)(IMes)(py)(=CHPh) complexes are accessible on incorporation of the aryloxide donor into a five- or six-membered chelate ring, irrespective (for the smaller ring) of the electron-deficiency of the aryloxide ligand.

Chart 1[a]



[a] IMes = *N*,*N*′-bis(mesityl)imidazol-2-ylidene.

Scheme 1



Results and Discussion

Ruthenium complexes in which the sulfonate group functions as a robust donor ligand are well established. Most common are simple monodentate tosylate[8−11] or triflate[12−15] derivatives;

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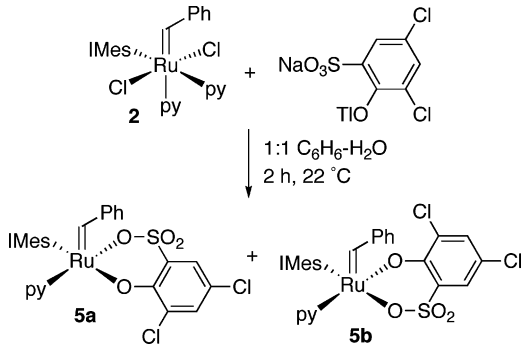
more rarely, sulfonate-bridged complexes have been obtained.[16,17] Ortho-sulfonato aryloxide derivatives are thus potentially attractive as precursors to six-membered chelate complexes. Among five-membered chelates, catecholates are attractive as planar, tunable ligands. A number of octahedral Ru-catecholato complexes have been reported, including Ru(σ-cat)(ER_3)$_2$(CO)$_2$ (ER_3 = $AsPh_3$,[18] P^iPr_3;[19] cat = catecholate). Although coordinatively unsaturated examples containing labile ligands have not previously been synthesized, we hoped that the small ring size might stabilize such species. The following describes the successful synthesis of both catecholato and *o*-sulfonato aryloxide derivatives of the second-generation Grubbs catalysts, and preliminary explorations of their metathesis activity.

Chelating Sulfonato-aryloxide Derivative. Commercially available sodium 3,5-dichloro-2-hydroxybenzenesulfonate was converted into its thallium salt (in DMF, as the parent phenol was insoluble in aromatic solvents) and reacted with **2** in benzene at 22 °C (Scheme 2). Reaction times could be reduced from >7 days to 2 h by use of degassed water as cosolvent: the dibasic anion is slightly soluble in water, though completely insoluble in organic solvents. The product was isolated as a blue-green precipitate in 72% yield. Complete conversion to **5** was indicated by inert-atmosphere MALDI-TOF MS analysis. A mass ion corresponding to [M − py]$^{+\bullet}$ was observed (Figure 1a): the molecular ion could not be observed, but the isotope pattern confirms complete exchange of the chloride ligands.

Assignment of the product as **5** is supported by spectroscopic data and microanalysis. A strong infrared band at 1262 cm^{-1} is assigned to the ν(S=O) stretch. The ^{1}H NMR spectrum in C_6D_6

Scheme 2



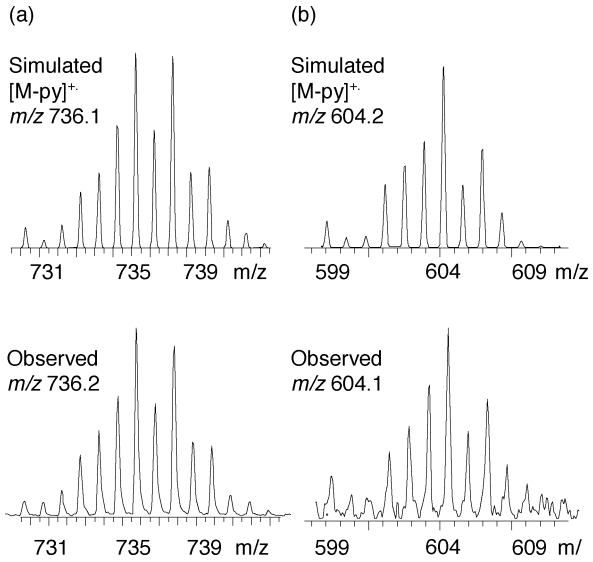


Figure 1. Inert-atmosphere MALDI-TOF mass spectra of [M − py]$^{+\bullet}$ region for (a) **5** (pyrene matrix); (b) **6** (anthracene matrix).

(in which the sample is incompletely soluble) reveals one new alkylidene singlet at 17.68 ppm. However, two such signals (δ_H 17.68, 18.51 ppm; ratio 1:1) are observed in $CDCl_3$. These are assigned to **5a** and **5b**, although we are unable to distinguish which singlet is due to which isomer. In view of the complexity of the overlapping patterns for the two complexes in $CDCl_3$, we highlight the characterization data obtained in C_6D_6. Owing to the low solubility of the complex in this solvent, carbon signals were most conveniently located by HMQC and HMBC correlation experiments. The singlet due to the alkylidene proton at 17.68 ppm correlates with singlets due to the alkylidene carbon (321 ppm, HMQC) and the IMes carbene carbon (182 ppm, HMBC). The HMBC experiment also permitted location of the ortho protons of the benzylidene phenyl group (7.83 ppm), via their correlation with the alkylidene carbon. The meta and para protons could then be located by a ^{1}H−^{1}H COSY experiment. The singlet for the imidazole ring proton at 6.06 ppm correlates with ^{13}C NMR singlets due to the "olefinic" IMes carbon atoms (124.6 ppm, HMQC) and the carbene carbon (182 ppm, HMBC). The aromatic protons of the IMes ligand (6.77, 6.60 ppm) could be assigned on the basis of an HMBC correlation with the methyl carbon signals and their mutual correlation by ^{1}H−^{1}H-COSY. The pyridine and aryloxide protons were distinguished on the basis of the number of ^{1}H−^{1}H-COSY correlations observed for each. The aryloxide signals exhibit the expected two doublets (8.14, 7.53 ppm; $^4J_{HH}$ = 3 Hz), each integrating 1:1 relative to the singlet for the alkylidene proton, in the ^{1}H NMR spectrum. These signals correlate with ^{13}C NMR singlets at 126.0 and 132.5 ppm, respectively, in HMQC experiments. However, the weakness of the HMBC correlations prevents location of the signals due to the quaternary aryloxide carbons. While the absence of the $^2J_{HC}$ correlations was expected, given the small size of the $^2J_{HC}$ coupling constants in aromatic rings (often on the order of 1 Hz),[20] failure to observe the $^3J_{CH}$ coupling, which should be on the order of 4−7 Hz,[20] was somewhat surprising. This is probably an artifact of the low solubility of the complex, which results in poor signal-to-noise ratios in the HMBC spectrum.

The two isomers of **5** equilibrate on the NMR time scale, as indicated by EXSY studies. Unexpectedly, however, isomer-

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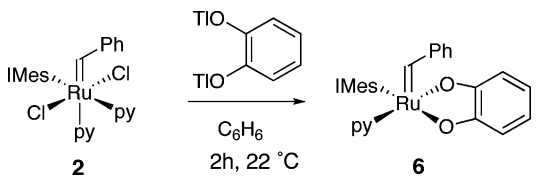
ization does not involve loss and recoordination of the pyridine ligand, as exchange is not suppressed by addition of free pyridine. This treatment gives rise to a new singlet at 18.7 ppm, presumably due to a pyridine adduct, which correlates (EXSY) with the singlet at 18.5 ppm; the **5a**−**5b** correlation is also retained. Similar behavior resulted from addition of acetonitrile; importantly, the pyridine ligand is not displaced, suggesting that this ligand is very nonlabile, as also borne out by the metathesis data (vide infra). Taken together, these data suggest that isomerization involves decoordination of the sulfonate group, rather than pyridine, but that chelation is thermodynamically favored. Given the established correlation between M−OR bond strengths and H−OR bond energies,[21] we presume that the exchange proceeds via cleavage of the Ru−OSO_2R bond. The relative polarity of the charge-separated intermediate may account for the failure to observe the isomerization in benzene. The possibility of selective dissolution of one isomer in benzene was eliminated on the basis of an experiment in which we extracted a sample of solid **5** with benzene and then took the residue up in $CDCl_3$: the 1:1 ratio of isomers was unperturbed, indicating that the sample was not enriched in a benzene-insoluble constituent.

Catecholato Derivative. Reaction of **2** with 1 equiv of Tl_2-(*o*-$O_2C_6H_4$) in benzene effected complete conversion to **6** within 2 h at 22 °C (Scheme 3). The identity of the compound is supported by inert-atmosphere MALDI-TOF mass spectrometry (Figure 1b), NMR, and elemental analysis. As with **5**, only the $[M - py]^{+\bullet}$ radical cation is evident in the MALDI mass spectrum. NMR analysis reveals singlets for the benzylidene proton and carbon at 16.99 and 287 ppm, respectively, significantly further upfield (2.5−3 ppm (^{1}H); ca. 25 ppm (^{13}C)) than the corresponding signals for $RuCl_2(PCy_3)_2$(=CHPh),[22] $RuCl_2$(NHC)(PCy_3)(=CHPh),[23,24] or $RuCl_2$(NHC)(py)$_2$(=CHPh)[3,25] (NHC = IMes, H_2IMes). The "olefinic" singlet for the IMes ring protons is shifted downfield by nearly 1 ppm, relative to **2**:[3] it appears in the aromatic region, but is located from its long-range coupling with the singlet for the carbene carbon at 189.0 ppm (HMBC). Signals for the pyridine and benzylidene phenyl protons are readily differentiated on the basis of the three-bond coupling between the phenyl ortho protons and the benzylidene carbon. The remaining aromatic signals are assigned on the basis of ^{1}H−^{1}H COSY analysis, enabling full assignment of the signals due to the catecholate ring.

Scheme 3



Unambiguous identification of the catecholate signals is important in confirming the coordination mode of this potentially π-coordinating ligand. Diagnostic for π-bound aryloxide rings are upfield shifts of 0.5−3 ppm for ^{1}H nuclei and up to 30 ppm for ^{13}C nuclei.[7,26−28] The ortho and meta nuclei for the catecholate ligand in **6** show a very minor coordination shift to higher field, relative to the free ligand (0.15−0.5 ppm, ^{1}H NMR; 2−6 ppm, ^{13}C NMR). The ipso carbons exhibit a significant downfield shift of ca. 20 ppm, as also reported for the six-coordinate catecholato complexes Ru(σ-cat)(ER_3)$_2$(CO)$_2$ described above,[18,19] in which only a Ru(σ-OAr) bond is present. The "normal", aromatic location of the signals for the catecholate ligand in **6** is unequivocal evidence for the proposed κ^2-O,O-C_6H_4 structure, versus a piano-stool complex. The small size and rigidity of the chelate ring in **6** is evidently sufficient to inhibit $\sigma \rightarrow \pi$ isomerization, despite the reservoir of electron density in the aromatic ring. The implication that electron deficiency is not essential to stabilize the Ru−aryloxide bond significantly expands the range of (chelating) aryloxide ligands that can potentially be deployed in Ru-catalyzed olefin metathesis, a finding that will facilitate tuning of catalyst properties.

Screening for Metathesis Activity. Complexes **5** and **6** were tested for ring-closing metathesis (RCM) activity using the benchmark substrate diethyl diallylmalonate (DEDAM), as well as more challenging disulfide[29] and ene-yne substrates. The low lability of the pyridine ligand at room temperature is implied by the requirement for elevated temperatures in order to achieve high activity, as we earlier found for pseudohalide catalysts **3** and **4**.[3,5] Catalyst **5** is lower in activity than either **6** or perfluorophenoxide catalyst **3**, the latter of which is the least reactive of the aryloxide catalysts previously studied. It achieves 95% RCM of diethyldiallyl malonate **7** within 15 min under our standard conditions (refluxing $CDCl_3$, 0.5 mol % Ru; Table 1), while catalysts **1**−**4** and **6** effect complete RCM within this period. However, a much greater discrimination in activity is found in RCM of diallyl sulfide **9**, toward which **5** and **3** exhibit very low activity, while **6** (and **4b**) effect quantitative RCM within 15 min. We speculate that the near-zero activity of **5** is due to poisoning by coordination of the sulfide to the metal center: the electron-deficiency suggested by the low pK_a of the parent SO_3H group (Table 2) may enhance binding of the sulfur donor. Consistent with this interpretation is the strong binding of the pyridine ligand suggested by the characterization data discussed above and inferred from the generally lower reactivity of **5**. Finally, while **5** exhibits modest activity for RCM of ene-yne substrate **11**, the activity of catalyst **6** approaches that of **4**[3] and significantly exceeds that found for either **3** or the second-generation catalyst **1**, for which conversions of 85% were achieved after heating at 80 °C for 1 h, at a catalyst loading of 5 mol %.[30]

Conclusions

The foregoing demonstrates that incorporating aryloxide donors into small, rigid chelate rings can be a successful strategy for formation of stable, coordinatively unsaturated Ru(σ-OAr) structures, irrespective of the electron-deficiency of the aryloxide

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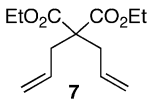
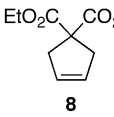
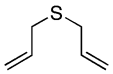
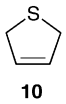
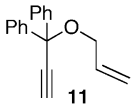
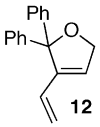
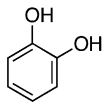
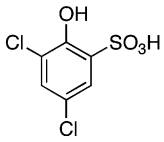
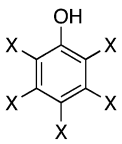
Table 1. Benchmarking RCM Activity of 5 and 6[a]

Substrate	Product	Catalyst	% Conversion
 7	 8	**1**	100[3]
		2	100[3]
		3	100[3]
		4a	100[3]
		4b	100[3]
		5	95
		6	100
 9	 10	**3**	29
		4b	100
		5	5
		6	100
 11	 12	**3**	15
		4b	100
		5	13
		6	90

[a] Conditions: 0.5 mol % Ru, $CDCl_3$, Δ, 15 min. Conversions determined by GC-FID and confirmed by NMR; ±2% in replicate runs.

Table 2. Relative Acidity of Protonated Aryloxide Ligands

Parent phenol	pK_a	Reference
	9.36	31
	(a) SO_3H: -1.29 (b) OH: 7.7	(a) 32 (b) 33
	X = F: 5.52 X = Cl: 4.70 X = Br: 4.57	34 35 31

ring. Five- and six-membered chelate complexes were prepared in which the aryloxide donor formed part of a O,OSO_2-bound or O,O-bound aromatic ring, respectively. The stability of these new complexes, and particularly that of the comparatively electron-rich catecholate derivative, has important implications for the range of phenols that can be considered as candidate ligands for new Ru-pseudohalide catalysts. Of interest is the low lability of the pyridine ligand within the sulfonato-aryloxide derivative, which significantly depresses catalyst activity. If, as this finding suggests, the sulfonato group enhances the binding affinity of other donor groups present on the metal center, pseudohalide ligands incorporating this group may be of limited utility for the purpose of olefin metathesis. More generally, these findings point toward a correlation between high catalyst activity, and minimal electron deficiency within the pseudohalide ligand. The high activity of the catecholato derivative **6** is noteworthy in this context: this ligand class offers considerable opportunity for modification of catalyst properties, including modulation of the electronic properties of the catecholate ligand itself, without necessarily perturbing the steric characteristics of the catalyst. Such studies are presently under way and will be reported in due course.

Experimental Section

General Procedures. Reactions were carried out at room temperature (RT, 22 °C) under N_2 using standard Schlenk or drybox techniques. Dry, oxygen-free solvents were obtained using a Glass Contour or Anhydrous Engineering solvent purification system and stored over Linde 4 Å molecular sieves. Pyridine and acetonitrile were distilled from CaH_2. $CDCl_3$ and C_6D_6 were dried over activated sieves (Linde 4 Å) and degassed by consecutive freeze/pump/thaw cycles. Water was degassed by multiple freeze/pump/thaw cycles. Anhydrous *N*,*N*-dimethylformamide, sodium-3,5-dichloro-2-hydroxybenzosulfonate, catechol, and thallium ethoxide (Aldrich) were used without purification. Complex **2** was prepared as previously described.[3] ^1H NMR (300 or 500 MHz) and ^{13}C (75 MHz) spectra were recorded on a Bruker Avance-300 or Avance-500 spectrometer. NMR spectra are reported relative to TMS (^1H, ^{13}C) at 0 ppm. IR spectra were measured on a Bomem MB100 IR spectrometer. Inert-atmosphere MALDI-TOF MS analyses were performed using a Bruker OmniFlex MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm) and interfaced to an MBraun glovebox. Data were collected in positive reflectron mode, with the accelerating voltage held at 20 kV. Matrix (anthracene or pyrene) and analyte solutions were prepared in CH_2Cl_2 at concentrations of 20 and 1 mg/mL, respectively. Samples were mixed in a matrix:analyte ratio of 20:1. Microanalyses were carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Note: The toxicity of thallium (particularly in the +1 oxidation state) is well established, and the subject has been recently reviewed.[36] Care must be taken to prevent introduction into the body by inhalation, by ingestion via contaminated hands or gloves, or through the skin. All thallium reagents and wastes, including contaminated solvents, were handled using double-glove and secondary containment procedures, with separate disposal of all wastes in accordance with government regulations.

Representative Procedure for Synthesis of Catecholate Salts. $Tl_2(o\text{-}O_2C_6H_4)$. Addition of a solution of thallium ethoxide (1.14 g, 4.6 mmol) in 3 mL of diethyl ether to a solution of catechol (251 mg, 2.3 mmol) in 10 mL of diethyl ether resulted in an instantaneous precipitation of an orange solid. The suspension was stirred at RT for 7 h, following which the product was collected by filtration, washed with diethyl ether (15 mL), then hexanes (10 mL), and dried under vacuum. Yield: 1.1 g (93%).

$[C_6H_2(3,5\text{-}Cl_2)(2\text{-}OTl)(SO_3Na)]$. The thallium salt was prepared in DMF, owing to the low solubility of the ligand precursor in all other solvents except water, which would decompose the TlOEt reagent. Addition of TlOEt (0.954 g, 3.82 mmol) to a rapidly stirred, colorless solution of $[C_6H_2(3,5\text{-}Cl_2)(2\text{-}OH)(SO_3Na)]$ (1.00 g, 3.77 mmol) in 20 mL of DMF caused a white powder to deposit within

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5 min. Stirring was continued for 20 min, after which the product was collected by filtration, washed with diethyl ether (10 mL), and dried in vacuo. Yield: 1.61 g (91%).

Ru[κ^2-OSO$_2$-2-O-C$_6$H$_2$(3,5-Cl$_2$)](IMes)(py)(=CHPh), 5. A solution of **2** (299 mg, 0.41 mmol) in 5 mL of benzene was added to a rapidly stirred suspension of [C$_6$H$_2$(3,5-Cl$_2$)(2-OTl)(SO$_3$Na)] (193 mg, 0.41 mmol) in 5 mL of H$_2$O. The mixture was stirred vigorously for 2 h, over which time a green-blue suspension formed. This material was filtered off and washed with ether (10 mL), then redissolved in 10 mL of THF and filtered through Celite to remove TlCl. Concentration, addition of hexanes, and cooling to −35 °C precipitated a blue-green powder, which was filtered off and dried under vacuum. Yield: 242 mg (72%). ^{1}H NMR (C$_6$D$_6$, 298 K): δ 17.68 (s, 1H, Ru=C*H*), 8.46 (d, $^3J_{HH}$ = 5 Hz, 2H, py *o*-C*H*), 8.14 (d, $^4J_{HH}$ = 3 Hz, 1H, Ar, aryloxide C*H*), 7.83 (d, $^3J_{HH}$ = 7 Hz, 2H, Ph, *o*-C*H*), 7.53 (d, $^4J_{HH}$ = 3 Hz, 1H, Ar, aryloxide C*H*), 7.23 (t, $^3J_{HH}$ = 7 Hz, 1H, Ph, *p*-C*H*), 6.99 (t, $^3J_{HH}$ = 8 Hz, 2H, Ph, *m*-C*H*), 6.77 (s, 2H, Ar, Mes C*H*), 6.60 (s, 2H, Ar, Mes C*H*), 6.49 (t, $^3J_{HH}$ = 8 Hz, 1H, py, *p*-C*H*), 6.12 (t, $^3J_{HH}$ = 7 Hz, 2H, py, *m*-C*H*), 6.06 (s, 2H, IMes =C*H*), 2.13 (s, 6H, Mes *p*-C*H*$_3$), 1.99 (s, 6H, Mes *o*-C*H*$_3$), 1.66 (s, 6H, Mes *o*-C*H*$_3$). ^{13}C NMR signals could not be directly observed, as the solubility of the complex in C$_6$D$_6$ is very low, but the majority of the signals could be located via HMQC and HMBC experiments (see text). ^{13}C NMR (C$_6$D$_6$, 298 K): δ 320.9 (Ru=*C*H), 182.0 (IMes N*C*N), 154.0 (py, *o*-*C*H), 152.5 (Ph *C*$_i$), 139.4 (Ar, Mes *p*-*C*Me), 136.0 (Ar, Mes *C*$_i$), 135.0 (py, *p*-*C*H), 132.5 (Ar, aryloxide *C*H) 130.9 (Ph *o*-*C*H), 129.6 (Ar, Mes *C*H), 129.3 (Ar, Mes *C*H), 128.3 (Ph, *m*-*C*H), 128.1 (Ph, *p*-*C*H), 126.0 (Ar, phenoxide *C*H), 124.6 (Ar, IMes =*C*H), 123.9 (py, *m*-*C*H), 20.8 (Mes, *o*-*C*H$_3$), 17.8 (Mes, *p*-*C*H$_3$). Anal. Calcd for C$_{39}$H$_{37}$Cl$_2$N$_3$O$_4$RuS: C, 57.42; H, 4.57; N, 5.15. Found C, 57.77; H, 4.17; N, 4.92. IR (KBr): ν(S=O) 1262 cm^{-1}. MALDI-TOF MS, *m*/*z*: calcd for [M − py]$^{+\bullet}$ 736.1; found, 736.2.

Ru(κ^2-O$_2$C$_6$H$_4$)(IMes)(py)(=CHPh), 6. A solution of **2** (300 mg, 0.41 mmol) in 20 mL of benzene was treated with solid Tl$_2$(*o*-O$_2$C$_6$H$_4$) (216 mg, 0.42 mmol) and stirred vigorously for 2 h, over which time it turned brown from green. The mixture was then filtered through Celite to remove TlCl, and the filtrate was stripped off to give a green solid, which was taken up in hexanes. The suspension was chilled at −35 °C, and the solid was collected by filtration, washed with diethyl ether (10 mL) and hexanes (5 × 10 mL), then dried in vacuo. Yield: 218 mg (77%). ^{1}H NMR (CDCl$_3$, 298 K): δ 16.99 (s, 1H, Ru=C*H*), 8.36 (d of d, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, py, *o*-C*H*), 7.45 (t of t, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, py, *p*-C*H*), 7.28 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ph, *o*-C*H*), 7.17 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ph, *p*-C*H*), 7.08 (s, 2H, IMes =C*H*), 6.96−6.85 (m, 6H, Ph, *m*-C*H*; py, *m*-*CH*; Ar, Mes C*H*), 6.71 (d of d, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, Ar, catechol *o*-C*H*), 6.70 (d of d, $^3J_{HH}$ = 7.0, $^4J_{HH}$= 2.0 Hz, 1H, Ar, catechol *o*-C*H*), 6.58 (br s, 2H, Mes C*H*), 6.49 (t of d, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, Ar, catechol *m*-C*H*), 6.36 (t of d, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, Ar, catechol *m*-C*H*), 2.22 (s, 6H, Mes *p*-C*H*$_3$), 2.16 (s, 6H, Mes *o*-C*H*$_3$), 1.88 (s, 6H, Mes *o*-C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ 287.42 (Ru=*C*H), 189.60 (IMes N*C*N), 164.09 (Ar, catechol O-*C*), 160.51 (Ar, catechol O-*C*), 154.68 (py, *o*-*C*H), 152.56 (Ph *C*$_i$), 138.99 (Ar, Mes *p*-*C*Me), 136.58 (Ar, Mes *o*-*C*Me), 135.62 (Ar, Mes *o*-*C*Me), 135.14 (Ar, Mes *C*$_i$), 134.03 (py *p*-*C*H), 129.13 (Ar, Mes *m*-*C*H), 128.00 (Ph *m*-*C*H), 127.73 (Ph *o*-*C*H), 126.48 (Ph *p*-*C*H), 124.02 (IMes =*C*H), 123.70 (py, *m*-*C*H), 116.13 (Ar, catechol *C*H), 114.77 (Ar, catechol *C*H), 114.17 (Ar, catechol *C*H), 113.76 (Ar, catechol *C*H), 21.06 (Mes *p*-C*C*H$_3$), 17.82 (Mes *o*-C*C*H$_3$), 17.69 (Mes *o*-C*C*H$_3$). Anal. Calcd for C$_{39}$H$_{39}$N$_3$O$_2$Ru: C, 68.60; H, 5.76; N, 6.15. Found C, 69.03; H, 5.38; N, 6.14. MALDI-TOF MS, *m*/*z*: calcd for [M − py]$^{+\bullet}$ 604.2; found, 604.1.

General Procedure for Ring-Closing Metathesis. In a typical experiment, **6** (10 mg, 14.6 μmol) and diethyl diallylmalonate (38.5 mg, 0.16 mmol) were weighed into separate vials. The catalyst was dissolved in 1.00 mL of CDCl$_3$, and 54.7 μL of this stock solution was added to a solution of the substrate in 1.6 mL of solvent (final [S] = 100 mM). The reaction was divided between two sealed vials and heated to reflux in a pierced aluminum block. Each experiment was carried out in duplicate (total 4 runs), measuring conversions by GC and NMR analysis.

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Supporting Information Available: ^{1}H, ^{1}H−^{13}C HMQC, and ^{1}H−^{13}C HMBC NMR spectra for **5**; ^{1}H and ^{13}C NMR spectra of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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