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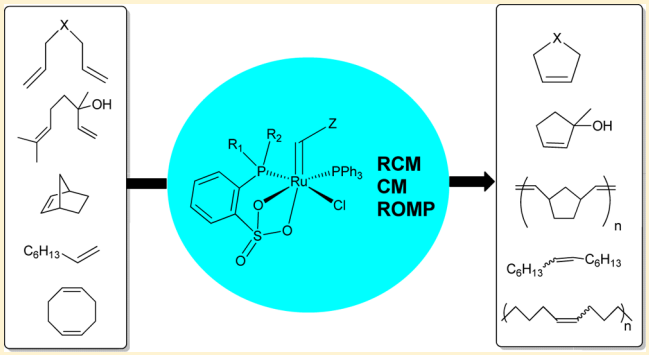
18-Electron Ruthenium Phosphine Sulfonate Catalysts for Olefin Metathesis

Oumar Bashir, Laurence Piche, and Jerome P. Claverie*

Québec Center for Functional Materials, NanoQAM, Department of Chemistry, University of Quebec in Montreal, Succ Centre Ville CP8888, Montreal, Quebec H3C3P8, Canada

Supporting Information

ABSTRACT: The first instances of ruthenium alkylidene complexes based on chelating phosphine sulfonates are presented. Although these complexes are formally 18-electron complexes bearing *cis* phosphines and *cis* one-electron donors (sulfonates and chlorides), they are surprisingly active for ring-closing metathesis, cross-metathesis, and ring-opening metathesis polymerization, thus highlighting the unique potential of the sulfonate ligand in the design of a ruthenium metathesis catalyst.

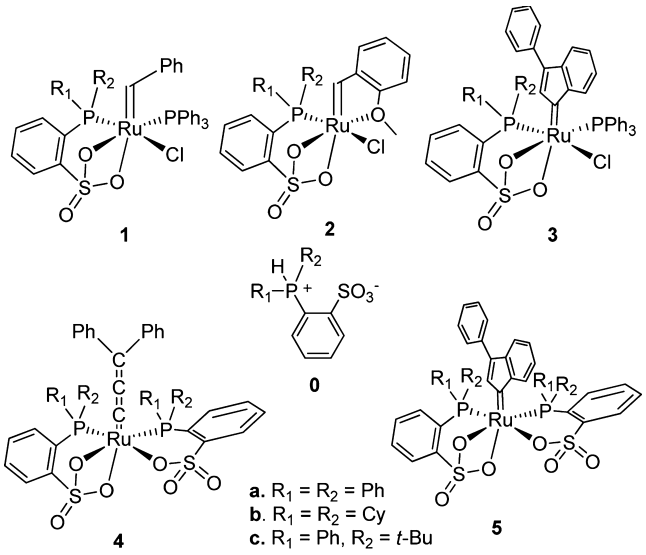


INTRODUCTION

The discovery that well-defined ruthenium alkylidene complexes are active catalysts for the metathesis reaction has attracted considerable attention.[1−5] The structure of these catalysts conforms to the generic formula $RuX_2(=CHR)L_1L_2$, whereby X are halides or pseudo-halides and L_1 and L_2 are 2 e^- σ-donating ligands. Interestingly, catalysts bearing L-X chelating ligands have been scrutinized only very recently. Most of them are based on chelating N-heterocyclic carbenes (NHCs)[6−16] and are found to promote *Z*-selectivity. Ruthenium alkylidenes coordinated by bidendentate amino-benzyloxy ligands[17] were found to be unstable, and only the tridentate amino bis(benzyloxy) complex could be isolated to yield a thermally unstable alkylidene. Alkylidenes of Ru chelated by salicylaldiminates ligands are stable but demonstrate only moderate activity.[18] Surprisingly, catalysts based on chelating phosphines are scarce in the literature. Fogg et al. reacted $RuCl_2(PPh_3)_3$ with the sodium salt of (diphenylphosphino)-1,1′-binaphthyl-2-ol,[19] but $\sigma \rightarrow \pi$ isomerization of the aryloxide moiety prevented the formation of the expected alkylidene.[20,21] Ru alkylidenes bearing a bidentate phosphine phenolate ligand $PR_1R_2(C_6H_4$-*o*-O−), with R_1 and R_2 = ^{t}Bu, adamantyl, and neopentyl, were recently prepared by Torker et al.[22,23] These complexes displayed an interesting *Z*-selectivity for the ring-opening metathesis copolymerization of cyclooctene and norbornene.

We present here the first example of metathesis catalysts based on chelating *ortho* phosphine sulfonate ($\widehat{PSO_3}$) ligands (Chart 1). We found that **1**−**3** are surprisingly active metathesis catalysts despite the fact that they are 18-electron species, the sulfonate and chloride are *cis* to each other, and they are based on phosphines that are less donating than NHCs. The present work is therefore the first illustration of the remarkable potential of sulfonate ligands when incorporated into metathesis catalysts.

Chart 1. Structure of the $\widehat{PSO_3}$ Ligands (0) and Ru Alkylidenes (1−5)



Chelating $\widehat{PSO_3}$ ligands have been extensively scrutinized for the preparation of palladium- and nickel-based polymerization catalysts and were shown to promote main-chain incorporation of a wide range of fundamental polar olefins (such as acrylates, acrylonitrile, vinyl acetate, halogenated monomers) as well as

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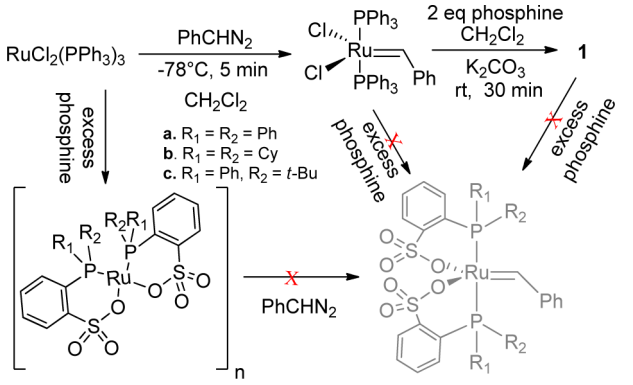
ethylene.[24] When combined with Ru, these versatile ligands are found to be useful for the transfer hydrogenation of ketones,[25] in the regioselective allylation of various substrates,[26] for the insertion polymerization of ethylene,[27] and for the alkylation of amines.[28] The $\widehat{PSO_3}$ ligands present several unique properties. First, it is a highly asymmetrical ligand, containing a strongly donating neutral phosphine (with basicity tunable by changing the nature of the substituents)[29] and very electron-poor anionic sulfonate donor. As the activity of a Ru-based metathesis catalyst increases with the basicity of one of the L ligands, and increases with the acidity of the X ligand,[30,31] the $\widehat{PSO_3}$ ligands should be ideal to form highly active metathesis catalysts. Interestingly, being a very poor donor, the SO_3 can dissociate completely from the metal atom, resulting in the formation of an ion-pair (for L = NHC, M = Pd, Ni).[32,33] Second, the sulfonate ligand can theoretically bind the metal in a κ^1O fashion as a two-electron donor or in a κ^2O,O′ fashion as a four-electron donor, but to our knowledge, prior to this work, phosphine sulfonates having κ^2O,O′ SO_3 groups have not been isolated, except for one intermolecular complex where two of the oxygen atoms of SO_3 are bound to two distinct Pd atoms.[34] For Pd complexes, isomerization between both κ^1O and κ^2O,O′ forms has been shown to be at the origin of a Berry pseudorotation process, which is pivotal to explain the unusual capacity for Pd-based catalysts to polymerize polar olefins.[24]

RESULTS AND DISCUSSION

Compounds **1a**, **1b**, and **1c** were readily prepared by ligand exchange from Grubbs catalyst generation **o**, Ru(=CHPh)-$Cl_2(PPh_3)_2$, with the corresponding $\widehat{PSO_3}$ ligand (Scheme 1).

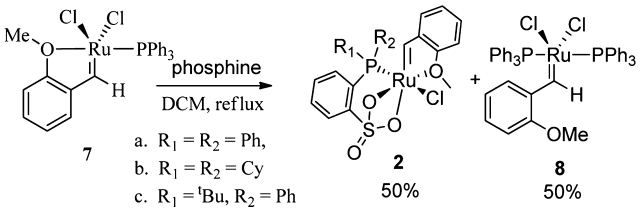
Scheme 1. Formation of Complex 1 and Reactivity with Excess $\widehat{PSO_3}$ Ligand[a]



[a]Yield **1a** = 73%, **1b** = 48%, **1c** = 32%. The grayed structure was not prepared by this route.

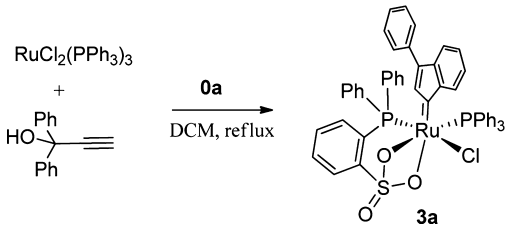
Yields were found to decrease with the steric bulk of the phosphine (**oa** < **ob** < **oc**). Only a single phosphine and chloride substitution occurred, even when the reaction was performed for prolonged time in the presence of excess phosphine. Baffled by the lack of reactivity of **1a** and **1b** toward ligand substitution, several other strategies were attempted to force the formation of a bischelated Ru alkylidene, such as adding K_2CO_3 as HCl trap, starting from a deprotonated phosphine sulfonate (Na, K, and Ag salts), but none succeeded. $Ru(\widehat{PSO_3})_2$ (R = Ph) has been reported by us in the past.[27] This complex, which is polymeric in nature (probably via the intervention of bridging SO_3), was found at that time to readily break up into monomeric 18 e^- $Ru(\widehat{PSO_3})_2L_2$ (L = water, dmso, or acetone) in the presence of the corresponding L.[27] In this study, neither $Ru(\widehat{PSO_3})_2$ nor $Ru(\widehat{PSO_3})_2L_2$ (L = water, dmso, or acetone) was found to react with phenyl diazomethane to form the corresponding bischelated Ru alkylidene: unreacted complex and stilbene were the only isolated products. Single phosphine exchange was also found to occur readily starting from **7**, to yield **2a**, **2b**, and **2c**, which were separated from **8** by column chromatography (Scheme 2). In a similar fashion to **1a** and **1b**, complexes **2a**, **2b**, and **2c** resisted further substitution by a second $\widehat{PSO_3}$ ligand.

Scheme 2. Preparation of Complexes 2



The formation of $\widehat{PSO_3}$ alkylidenes was also probed via the Meyer−Schuster rearrangement of 1,1-diphenyl-2-propyn-1-ol.[35−38] Thus, **3a** was formed upon reaction of $RuCl_2(PPh_3)_3$, the alkyne, and the corresponding $\widehat{PSO_3}$ phosphine, in a one-pot reaction (Scheme 3). Only compound **3a** could be isolated, in agreement with the larger steric bulk of phosphines **ob** and **oc**, despite their greater basicity.

Scheme 3. Preparation of 3a



All compounds were fully analyzed by nuclear magnetic resonance (NMR), mass spectrometry (MS), elemental analysis, and, for **1a**, **1b**, and **3a**, single-crystal X-ray diffraction (Figure 1). These compounds exhibit uncharacteristic features, in comparison to other Ru alkylidenes. First, the two P atoms are *cis* to each other (angle P1−Ru−P2 = 100° ± 5°, Table 1). Second, all the complexes adopt a distorted octahedral geometry, whereby two oxygens of the sulfonate are coordinated to Ru, one (O1) *trans* to P2 and the other one (O2) *trans* to the alkylidene, although O2 is offset from the octahedral coordination site (O2−Ru−C < 180°, and Ru−O2 longer than Ru−O1, Table 1) as expected for a small-size four-member O_1−Ru−O_2−S chelate. Coordination of both O_1 and O_2 is evidenced by the equal bond lengths for S−O1 and S−O2 and longer bond length for S=O3 (Table 1). Thus, these Ru alkylidenes are formally 18-electron octahedral complexes bearing a unique κ^2O,O′ sulfonate ligand.[39] Third, the Ru=C bond length is longer than in active Ru alkylidenes. A literature survey over 31 Ru catalytically active alkylidenes (see Table S1) indicates that the bond length of Ru=CHPh is between 1.818 and 1.854 Å. Longer Ru=CHPh bonds, between 1.859 and 1.879 Å, are found for 18-electron complexes that are catalytically inactive (see Table S2). The

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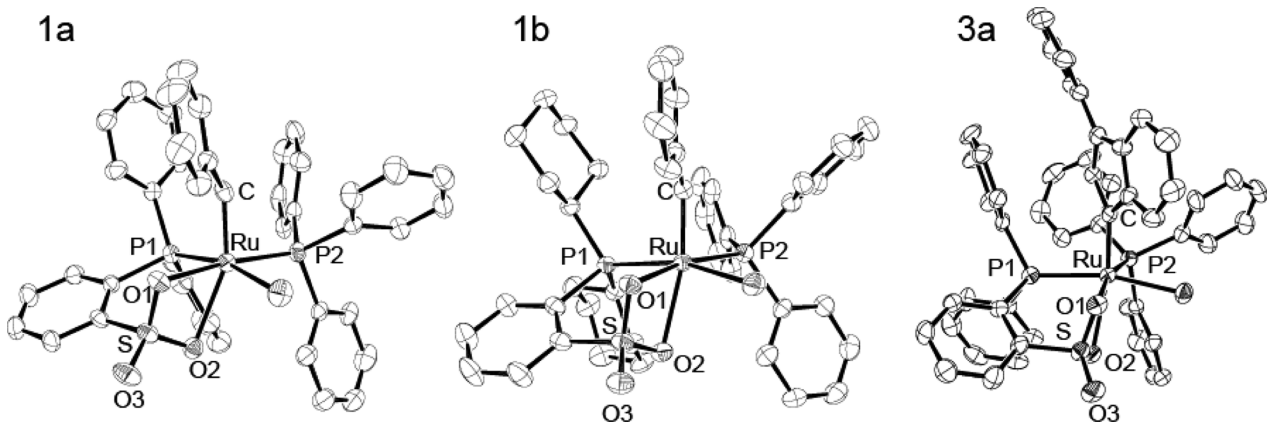


Figure 1. Labeled view of **1a**, **1b**, and **3a** with 50% probability ellipsoids (hydrogen atoms and solvent molecules omitted).

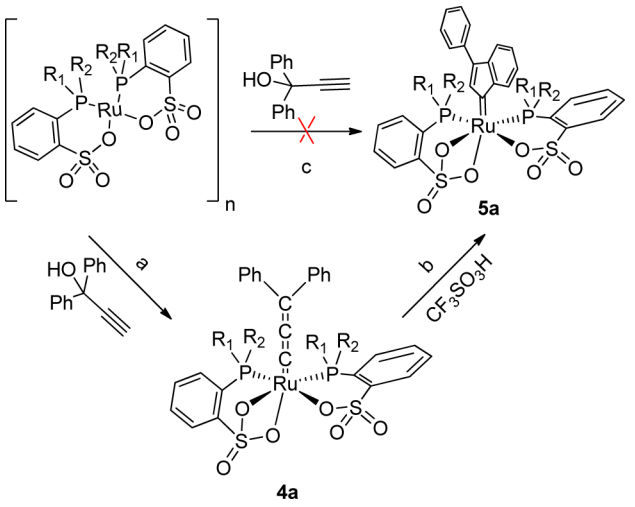
Table 1. Selected Bond Lengths and Bond Angles for Complexes 1a, 1b, and 3a

	1a	1b	3a
	Bond Lengths (Å)		
Ru−C	1.869	1.873	1.884
Ru−P1	2.338	2.413	2.371
Ru−P2	2.295	2.308	2.305
Ru−Cl	2.380	2.369	2.370
Ru−O1	2.226	2.221	2.232
Ru−O2	2.407	2.362	2.403
S−O1	1.490	1.489	1.485
S−O2	1.486	1.477	1.481
S−O3	1.433	1.434	1.435
	Bond Angles (deg)		
P1−Ru−P2	97.44	103.69	100.28
C−Ru−P1	86.91	94.01	93.42
O1−Ru−P2	172.43	167.90	167.61
O2−Ru−C	155.55	163.81	157.10

fact that *d*(Ru=C) is longer in 18-electron complexes may be explained by the presence of a destabilizing *trans* ligand sharing the same metal orbitals as the alkylidene (akin to a *trans* influence). However, complexes **1**−**3**, which are formally 18-electron, as also shown by unusually long Ru=C bond lengths, are catalytically active (see below). For the sake of completion, it should be mentioned that during the course of this study an 18-electron alkylidene complex bearing an unusual nitrato ligand has been reported.[8,11]

Before embarking upon a survey of the catalytic activity of complexes **1**−**3**, it should be noted that the preparation of bischelated Ru alkylidenes was found to be possible using the Meyer−Schuster route (Scheme 4), leading to the formation of a stable allenylidene, **4a**, which was rearranged into an indenylidene, **5a**, upon acidic treatment.[41] Complex **4a** was also characterized by X-ray diffraction (Figure 2), indicating the presence of two inequivalent $\widehat{PSO_3}$ ligands, one bis-coordinated and strongly bound to Ru, as shown by short Ru−P4 and Ru−O4 distances, and one tricoordinated, but less strongly bound, as shown by longer Ru−P1, Ru−O1, and Ru−O2 distances. By ^{31}P NMR, the signal of the two *cis* P appeared as two distinct broad resonances that coalesce into a single resonance at 55 °C in $C_2D_4Cl_2$, indicating the presence of a fluxional process whereby the κ^2O,O′ sulfonate isomerizes into a κ^1O sulfonate, leading to the coordination of the other sulfonate in a κ^2O,O′ fashion. Using band-shape analysis of the ^{31}P NMR data at

Scheme 4. Preparation of 4a and 5a[a]



[a]Conditions: (a) THF reflux, 12 h; (b) −40 °C, 90 min in CH_2Cl_2−basic Al_2O_3; (c) dimethylcarbonate, 70 °C,[40] CH_2Cl_2 reflux overnight.

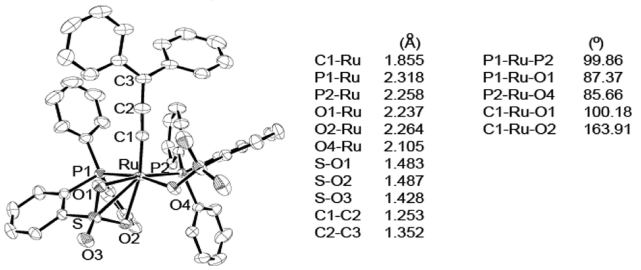


Figure 2. Labeled view of **4a** with 50% probability ellipsoids (hydrogen atoms omitted) with selected bond lengths and angles.

temperatures ranging from 22 to 60 °C, the activation energy for the κ^2O,O′ → κ^1O → κ^2O,O′ process was found to be 16.1 kcal/mol, which is of the same magnitude as the calculated activation barriers for the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization in allyl complexes.[42] In complex **5a**, this isomerization process is also rapid, as shown by the presence of a single sharp resonance by ^{31}P NMR, which splits into two resonances at −50 °C in CD_2Cl_2 (activation energy: 10.6 kcal/mol).

The $\widehat{PSO_3}$ Ru alkylidene complexes **1**−**5** have several common features: the sulfonate ligands (or at least one of them) are in a κ^2O,O′ binding mode, and therefore the

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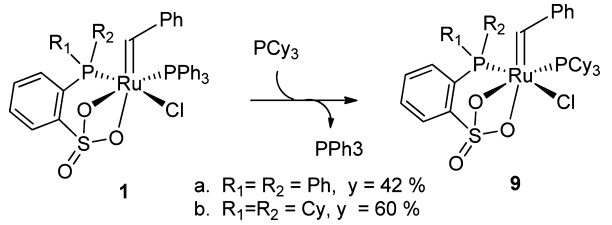
complexes are 18 electron, a fact that is further confirmed by the unusually long alkylidene bond lengths. Furthermore, both phosphines are *cis* to each other. Last, the phosphine forming the strongest Ru−P bond is the nonchelating one (shorter Ru−P2 bond than Ru−P1), i.e., PPh_3 in **1**−**3**. The combinations of these structural features would entice us to believe that **1**−**3** are inactive in metathesis. First, Ru 18-electron carbenes are known to promote cyclopropanation instead of metathesis, as the intermediary metallacyclobutane is prone to reductive elimination.[43] Second, complexes bearing *cis* X ligands are often found to be inactive (although an exception[44] was recently reported), but they slowly interconvert to active *trans* X catalysts.[45−47]

It is now well established that the active species in metathesis is the 14 e^- $RuLX_2(=CHR)$, which is generated by dissociation of the phosphine. In complexes bearing *trans* L and *trans* X ligands, this dissociation step is rapid because the *trans* influence of the strongly σ-donating L ligand (a phosphine or a NHC) weakens the Ru−P bond. In our case, unlike conventional Ru metathesis catalysts, we noticed that the Ru−P_2 bond *trans* to the sulfonate is short, and one could question whether dissociation of PPh_3 would in fact occur. PPh_3 substitution by the more basic PCy_3, which most likely occurs via dissociation of PPh_3 first (as the complex is 18 e^-), was found to occur smoothly on **1** (Scheme 5), yielding complexes **9**.

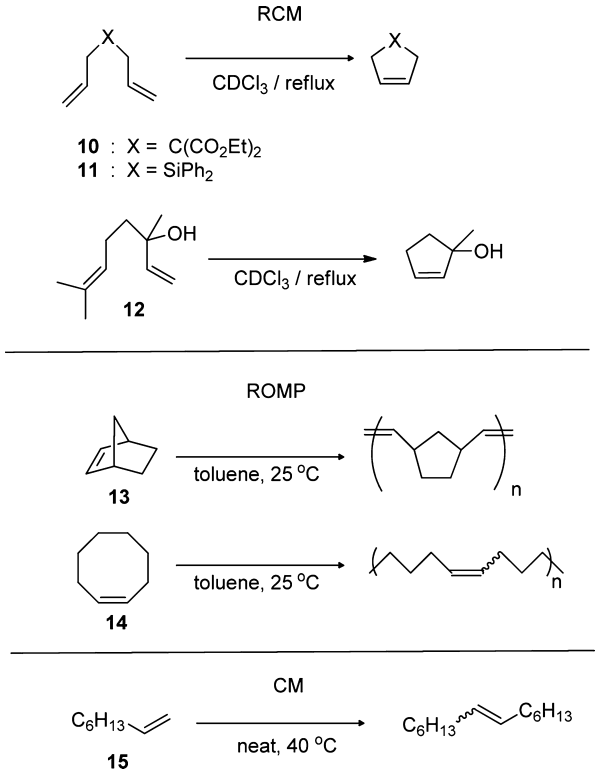
Scheme 5. Phosphine Substitution[a]



[a]Room temperature, 30 min.

The activity of catalysts **1**−**3** and **9a** were assessed in ring-closing metathesis (RCM) of diethyl diallyl malonate (**10**, Scheme 6, Figure 3), diallyldiphenyl silane, **11**, and linalool, **12**, ring-opening metathesis polymerization (ROMP) of norbornene, **13**, and cyclooctene, **14**, and cross-metathesis (CM) of octene, **15**, which are all standard activity beacons for metathesis catalysts (Table 2). These catalysts are all active, with **1b** exhibiting the greatest activity (Figure 3) of all of them, probably due to the greater σ-donating character of the $P\widehat{SO}_3$ phosphine bearing two cyclohexyl groups. Surprisingly, catalyst **9a** is more active than **1a**, which is unexpected, as PCy_3, being more donating than PPh_3, should be a worse leaving group. This may be ascribed to a steric effect resulting from the faster dissociation of PCy_3 in order to reduce steric encumbrance around the metal center. Interestingly, catalyst **1b** exhibits an activity that is superior to Grubbs first-generation catalyst (**G1**) and that approaches Grubbs second-generation catalyst (**G2**),[48] as shown in ring-closing of **10** (entries 4 and 5, 380 turnovers in 45 min) or in cross-metathesis of 1-octene (entry 21, 55 turnovers in 2.7 h). Compound **5a** was found to be inactive despite several attemps to make it react, even at high temperature (for example, ROMP of **13**, [**13**]:[**5**] = 250:1, T = 80 °C in toluene, and RCM of **10**, [**10**]:[**5**] = 100:1, T = 60 °C in $CDCl_3$). These preliminary activity results clearly

Scheme 6. RCM and ROMP Experiments Performed to Assess the Activity of Catalysts 1−3 and 9



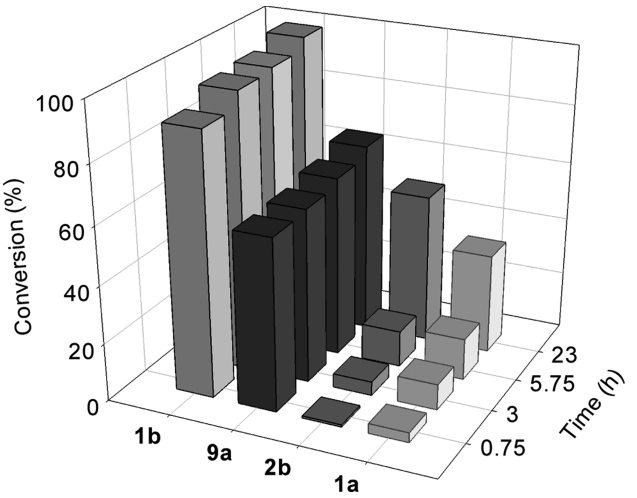


Figure 3. Comparison of the RCM kinetics of **10** with various catalysts. Conditions: **10** = 0.02 M; 1 mol % of catalyst, $CDCl_3$, reflux (^1H NMR measurements).

illustrate the interesting potential of the sulfonate ligand in the design of novel metathesis catalysts.

CONCLUSION

In summary, chelating phosphine sulfonates and more generally chelating sufonated ligands have been exploited with great success for Pd and Ni catalytic chemistry,[24] because of their remarkable electronic asymmetry as well as their geometric flexibility. Their installation on ruthenium alkylidenes has been presented for the first time here, yielding olefin metathesis catalysts with an activity that surpasses the activity of comparable nonchelating phosphine catalysts. It clearly ensues

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Table 2. Survey of the Catalytic Activity of Catalysts 1−3 and 9 with Different Substrates S (Scheme 6)

entry	cat	S	[S]/[cat]	t (h)	yield (%)
1[a]	**1b**	**10**	100	0.75	90
2[a]	**1b**	**10**	100	3	95
3[a]	**1b**	**10**	500	0.75	47
4[a]	**1b**	**10**	500	3	77
5[b]	**1b**	**10**	2000	0.45	19
6[a]	**1a**	**10**	100	5.75	14
7[a]	**1a**	**10**	100	23	35
8[a]	**1a**	**10**	100	72	45
9[a]	**9a**	**10**	100	0.75	59
10[a]	**G1**	**10**	100	0.75	91
11[a]	**G1**	**10**	500	0.75	23
12[a]	**G2**	**10**	100	0.75	99
13[a]	**G2**	**10**	500	0.75	99
14[a]	**2b**	**10**	100	23	52
15[a]	**2b**	**10**	100	72	85
16[a]	**3a**	**10**	100	21	15
17[a]	**1b**	**11**	100	2	18
18[a]	**1b**	**11**	100	20	41
19[a]	**1b**	**11**	20	20	61
20[a]	**1b**	**12**	100	20	35
21[c]	**1b**	**13**	1500	0.15	90
22[d]	**1b**	**13**	17000	0.3	70
23[e]	**1a**	**14**	100	22	33
24[f]	**1b**	**14**	1000	1	55
25[g]	**1b**	**15**	100	2.7	55
26[g]	**1b**	**15**	100	23	62

[a][S] = 0.02 mol/L, reflux, $CDCl_3$. [b][S] = 0.02 mol/L, toluene, 80 °C. [c][S] = 4×10^{-3} mol/L, room temperature, $CDCl_3$ (Z:E = 30:70). [d]S = 1.3 mol/L, room temperature, toluene (Z:E = 28:72). [e][S] = 0.5 mol/L, room temperature, $CDCl_3$ (Z:E = 40:60). [f][S] = 1 mol/L, room temperature, $CDCl_3$ (Z:E = 50:50). [g]Neat, T = 60 °C (Z:E = 30:70).

that sulfonate anionic donors are of interest for the design of highly active metathesis catalysts (sulfonated NHCs are currently under scrutiny in our group). Furthermore, these catalysts are active, despite both X ligands being in a *cis* position and the formal electron count of the catalyst being 18 e^-. Such surprising features are bound to lead to novel mechanistic and structural studies, which should guide the design of more active metathesis catalysts departing from the conventional 16 e^- $RuX_2(=CHR)L_1L_2$ pattern.

EXPERIMENTAL SECTION

General Procedures. All manipulations were done under an inert atmosphere using standard Schlenck and cannula techniques. Dry, oxygen-free solvents were obtained using a solvent purification system. $RuCl_3$, 1,1-diphenyl-2-propyn-1-ol, and trifluoromethanesulfonic acid were bought from Sigma-Aldrich and used without further purification. $[RuCl_2(PPh_3)_3]$,[49] $[RuCl_2(DMSO)]$,[50] phosphines **oa**,[51] **ob**,[52] and **oc**,[29] $(PCy_3)_2Cl_2Ru{=}CHPh$,[53] and $Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)PPh_3$ (**7**)[54] were synthesized according to published procedures. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a 600 or 300 MHz spectrometer at ambient temperature. NMR spectra were reported relative to external 85% H_3PO_4 (^{31}P) or internal TMS (^1H, ^{13}C). Mass spectrometry analyses were performed using a time-of-flight LC/MS liquid chromatography coupled to an MS spectrometer. Data were collected in positive reflection mode. Analyte solutions were prepared in CH_2Cl_2 at concentrations of 1 mg/mL. Elemental analysis was performed by the Service d'Analyses Elementaires, Departement de Chimie, Université de Montréal. Crystallographic analysis was performed at the X-ray crystallography laboratory of the University of Delaware, Department of Chemistry and Biochemistry.

$(PPh_3)[P(\text{-}6\text{-}SO_3\text{-}C_6H_4)(Ph)_2]Cl\text{-}Ru{=}CH\text{-}Ph$ (1a). Inside a drybox, 100 mg (0.127 mmol, 1.0 equiv) of $(PPh_3)_2Cl_2Ru{=}CHPh$ and 87 mg (0.254 mmol, 2.2 equiv) of **oa** were weighed in a vial to which 5 mL of CH_2Cl_2 was added. The solution was first stirred at room temperature for 30 min and then filtered on Celite, and the solvent was evaporated. Methanol was added to wash the crude, the supernatant was removed, and the crude was dried *in vacuo* to give the desired product as a brown solid (76.8 mg, 0.093 mmol, 73%). The product could also be further purified by passing the residue through a column of silica gel (CH_2Cl_2/diethyl ether = 87:13 v/v). The progress of the compound over the column was monitored visually (purple band). Air-stable crystals were obtained by slow diffusion of diethyl ether in CH_2Cl_2. ^1H NMR (300 MHz, $CDCl_3$): δ 15.64 (dd, $^3J_{HP}$ = 15.4, $^3J_{HP}$ = 12.7 Hz, 1H, Ru=CH), 7.83 (dd, $^3J_{HP}$ = 11.5, $^3J_{HH}$ = 8.0 Hz, 5H), 7.58 (dd, $^3J_{HP}$ = 14.2, $^3J_{HH}$ = 6.9 Hz, 3H), 7.49−7.23 (m, 8H), 7.17 (dd, $^3J_{HP}$ = 16.7, $^3J_{HH}$ = 7.6 Hz, 6H), 7.10−6.97 (m, 3H), 6.89 (dt, $^3J_{HH}$ = 9.9, $^3J_{HH}$ = 4.9 Hz, 5H), 6.83−6.75 (m, 2H), 5.84−5.54 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 321.26 (s), 149.96 (s), 145.28 (d), 134.92 (s), 133.08 (m), 132.18 (s), 131.42 (m), 129.84 (d), 128.90 (s), 128.37 (m), 126 (dd). ^{31}P NMR ($CDCl_3$): δ 53.50 (d, $^2J_{PP}$ = 34.8 Hz), 20.42 (d, $^2J_{PP}$ = 34.8 Hz). Anal. Calcd for $RuC_{43}H_{35}P_2SO_3Cl{\cdot}0.82CH_2Cl_2$ (1 molecule of CH_2Cl_2 was found in the solid-state structure of **1a**): C, 58.40; H, 4.18. Found: C, 58.41; H, 4.06. Anal. Calcd for $RuC_{43}H_{35}P_2SO_3Cl{\cdot}0.85CH_2Cl_2$: C, 58.36; H, 4.10. Found: C, 58.41; H, 4.06. HRMS [ESI$^+$] $RuC_{43}H_{35}P_2SO_3Cl$: calcd 795.0903 $[M + H]^+$, found 795.0348 $[M + H]^+$.

$(PPh_3)[P(\text{-}6\text{-}SO_3\text{-}C_6H_4)(Cy)_2]Cl\text{-}Ru{=}CH\text{-}Ph$ (1b). Inside a drybox, 100 mg (0.127 mmol, 1.0 equiv) of $(PPh_3)_2Cl_2Ru{=}CHPh$, 100 mg (0.279 mmol 2.2 equiv) of **ob**, and K_2CO_3 (35 mg, 0.279 mmol, 2.2 equiv) were weighed in a vial, and 5 mL of CH_2Cl_2 was added. The suspension was stirred at room temperature for 60 min. The solution was filtered on basic alumina oxide, and the solvent evaporated. Fresh diethyl ether was added to wash the green solid before drying *in vacuo* (50.9 mg, 0.06 mmol, 48%). The product could be purified by silica gel chromatography (CH_2Cl_2/diethyl ether = 87:13 v/v). Crystals were obtained by slow diffusion of diethyl ether in CH_2Cl_2. ^1H NMR (300 MHz, $CDCl_3$): δ 20.29 (d, $^3J_{HP}$ = 2.6 Hz, 1H), 7.87 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 3.6 Hz, 1H), 7.65 (t, $^3J_{HH}$ = = 6.3 Hz, 3H), 7.59 (dd, $^3J_{HP}$ = 11.0 Hz, $^3J_{HH}$ = 7.7 Hz, 2H), 7.49−7.43 (m, 3H), 7.41−7.33 (m, 10H), 7.32−7.28 (m, 3H), 7.17 (s, 1H), 7.00 (dd, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.4 Hz, 3H), 3.53−3.28 (m, 2H), 1.97−1.20 (m, 16H), 1.21−1.08 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 443.88 (s), 134.75 (s), 133.34 (s), 132.56−131.57 (m), 130.33 (s), 128.42 (t, J = 13.7 Hz), 30.93 (s), 26.31 (s). ^{31}P NMR (122 MHz, $CDCl_3$): δ 30.69 (d, $^2J_{PP}$ = 268.7 Hz), 11.83 (d, $^2J_{PP}$ = 268.7 Hz). Anal. Calcd for $RuC_{43}H_{47}P_2SO_3Cl{\cdot}0.3CH_2Cl_2{\cdot}0.1Et_2O$: C, 59.97; H, 5.60. Found: C, 59.95; H, 5.61. HRMS [ESI$^+$] $RuC_{43}H_{47}P_2SO_3Cl$: calcd 807.1764 $[M - Cl]^+$, found 807.1223 $[M - Cl]^+$.

$(PPh_3)[P(\text{-}6\text{-}SO_3\text{-}C_6H_4)(Ph)(^tBu)]Cl\text{-}Ru{=}CH\text{-}Ph$ (1c). Inside a drybox, 130 mg (0.164 mmol, 1.0 equiv) of $(PPh_3)_2Cl_2Ru{=}CHPh$, 56 mg (0.180 mmol, 1.1 equiv) of ligand **oc**, and K_2CO_3 (35 mg, 0.279 mmol, 2.2 equiv) were weighed in a vial, and 5 mL of CH_2Cl_2 was added. The suspension was stirred at room temperature for 30 min. The solution was filtered on basic alumina oxide, and the solvent evaporated. The resulting brown solid was found to be partially soluble in diethyl ether and in pentane, which rendered further purification difficult. The spectroscopic data obtained here are for the crude product. ^1H NMR (300 MHz, CD_2Cl_2): δ 15.73 (t, $^3J_{HP}$ = 16.3 Hz, 1H), 7.8−6.4 (m, 30H), 1.3−1.1 (m, 9H), ^{31}P NMR (122 MHz, CD_2Cl_2): δ 53.67 (d, $^2J_{PP}$ = 41.5 Hz), 20.11 (d, $^2J_{PP}$ = 41.5 Hz).

$[P(\text{-}6\text{-}SO_3\text{-}C_6H_4)(Cy)_2]Cl\text{-}Ru(=CH\text{-}O\text{-}Me\text{-}C_6H_4)$ (2b). Inside a glovebox, $Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)PPh_3$ (**7**) (40 mg, 0.073 mmol, 1.0 equiv) and **ob** (61.5 mg, 0.173 mmol, 2.4 equiv) were added in a Schlenk flask containing 4 mL of $CHCl_3$. The flask was equipped with a condenser, and the mixture was heated at 60 °C for 24 h. The solvent was evaporated, and the crude was passed through a silica gel column using CH_2Cl_2/CH_3OH = 10:1 v/v as eluent to yield a green solid (17.3 mg, 0.029 mmol, yield = 40%). ^1H NMR (300 MHz,

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acetone): δ 18.08 (d, $^3J_{HP}$ = 6.4 Hz, 1H), 7.82 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.72 (d, $^3J_{HP}$ = 11.9 Hz, 1H), 7.66−7.58 (m, 1H), 7.38 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.35−7.27 (m, 2H), 7.16 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 4.27 (s, 3H), 1.83−0.46 (m, 22H). ^{31}P NMR (122 MHz, acetone): δ 54.77 (s). Anal. Calcd for $RuC_{26}H_{34}PSO_4Cl{\cdot}0.2CH_2Cl_2$: C, 50.17; H, 5.48. Found: C, 50.19; H, 4.42. HRMS [ESI$^+$] $RuC_{26}H_{34}PSO_4Cl$: calcd 575.0905 [M − Cl]$^+$, found 575.0958 [M − Cl]$^+$.

[P(-6-SO$_3$-C$_6$H$_4$)(Ph)(^{t}Bu)]Cl-Ru(=CH-*O*-Me-C$_6$H$_4$) (2c). Inside a glovebox, $Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)PPh_3$ (40 mg, 0.073 mmol, 1.0 equiv) and **oc** (56 mg, 0.173 mmol, 2.4 equiv) were added to a Schlenk flask containing 4 mL of $CHCl_3$. The flask was equipped with a condenser, and the mixture was heated at 60 °C for 24 h. The solvent was evaporated, and the crude was passed through a silica gel column using CH_2Cl_2/CH_3OH = 10:1 v/v as eluent to yield a green solid (25 mg, 0.030 mmol, yield = 41%). ^{1}H NMR (300 MHz, acetone) δ 16.75 (ddd, $^3J_{HP}$ = 4.1, $^3J_{HH}$ = 2.3 Hz, 1H), 7.82 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.72 (d, $^3J_{HP}$ = 11.9 Hz, 1H), 7.66−7.58 (m, 1H), 7.38 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.35−7.27 (m, 2H), 7.16 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 4.27 (s, 3H), 1.83−0.46 (m, 22H). ^{31}P NMR (122 MHz, acetone): δ 65.11.

(PPh$_3$)[P(-6-SO$_3$-C$_6$H$_4$)(Ph)$_2$]Cl-Ru=(Ind) (3a). Inside a glovebox, $[RuCl_2(PPh_3)_3]$ (100 mg, 0.104 mmol, 1 equiv), 1,1-diphenyl-2-propyn-1-ol (33 mg, 0.156 mmol, 1.5 equiv), and 43 mg (0.125 mmol 1.2 equiv) of ligand **oa** were weighed in a 50 mL Schlenk flask. After adding 10 mL of CH_2Cl_2, the mixture was brought to reflux for 60 min. The solvent was evaporated, and the green crude (73 mg, 0.079 mmol, 75%) was purified through column chromatography on silica gel (CH_2Cl_2/diethyl ether = 87:13 v/v) (63 mg, 65%). Crystals were obtained by slow diffusion of diethyl ether in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.27 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 8.26−8.17 (m, 2H), 7.95 (dd, $^3J_{HH}$ = 6.4, $^3J_{HH}$ = 4.4 Hz, 1H), 7.69−7.34 (m, 19H), 7.29−6.95 (m, 13H), 6.62 (ddd, $^3J_{HP}$ = 29.0, $^3J_{HP}$ = 14.8, $^3J_{HH}$ = 6.2 Hz, 3H), 5.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.92−147.39 (m), 135.51−134.76 (m), 134.41−134.03 (m), 133.50−133.11 (m), 131.48 (s), 130.14 (s), 129.80−129.62 (m), 129.28 (s), 128.75 (s), 128.68−128.58 (m), 128.56−128.48 (m), 127.91 (d, J = 9.8 Hz), 126.94 (s), 118.43 (s), 68.37−62.15 (m), 17.17−14.06 (m). ^{31}P NMR (122 MHz, $CDCl_3$): δ 48.87 (d, $^2J_{PP}$ = 34.6 Hz), 19.90 (d, $^2J_{PP}$ = 34.6 Hz). Anal. Calcd for $RuC_{51}H_{39}P_2SO_3Cl{\cdot}0.5Et_2O{\cdot}0.5H_2O$ (1 molecule of Et_2O was found in the solid-state structure of **1a**): C, 65.19; H, 4.61. Found: C, 65.18; H, 4.62. HRMS [ESI$^+$] $RuC_{51}H_{39}P_2SO_3Cl$: calcd 895.940632 [M − Cl]$^+$, found 895.05554 [M − Cl]$^+$.

[P(-6-SO$_3$-C$_6$H$_4$)(Ph)$_2$]$_2$Ru=C=C=CPh$_2$ (4a). $RuC_{36}H_{28}P_2S_2O_6$ (100 mg, 0.127 mmol) and 1,1-diphenyl-2-propyn-1-ol (39.9 mg, 0.191 mmol, 1.5 equiv) were weighed inside a glovebox in a 50 mL Schlenk flask. A 10 mL amount of THF was added, and the reaction mixture was heated overnight under reflux under N_2. The solvent was evaporated, and the crude was purified through column chromatography on silica gel (CH_2Cl_2/diethyl ether = 87:13 v/v) to give the desired product as a red compound (106.7 mg, 0.109 mmol, 86%). Crystals were obtained by slow diffusion of diethyl ether in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.24 (s, 1H), 7.98 (s, 1H), 7.79−7.38 (m, 10H), 7.36−6.94 (m, 14H), 6.91−5.86 (m, 11H). ^{31}P NMR (122 MHz, $CDCl_3$): δ 44.58−42.18 (m), 40.88 (s), 38.62 (s), 26.63−23.90 (m). Anal. Calcd for $RuC_{51}H_{38}P_2S_2O_6{\cdot}0.55CH_2Cl_2$: C, 62.89; H, 3.93. Found: C, 60.66; H, 3.86. Anal. Calcd for $RuC_{51}H_{38}P_2S_2O_6{\cdot}0.6CH_2Cl_2{\cdot}0.4Et_2O$: C, 60.59; H, 4.13. Found: C, 60.59; H, 4.14. HRMS [ESI$^+$] $RuC_{51}H_{38}P_2S_2O_6$: calcd 975.0706 [M + H]$^+$, found 975.0681 [M + H]$^+$.

[P(-6-SO$_3$-C$_6$H$_4$)(Ph)$_2$]$_2$Ru=(Ind) (5a). In a 50 mL round-botton flask, 132 mg (0.168 mmol) of **4a** was added to 10 mL of CH_2Cl_2. The mixture was cooled to −78 °C, and CF_3SO_3H (126 mg, 0.841 mmol, 5 equiv) was added. The mixture was stirred for 2 h at −78 °C. Alumina oxide basic grade I (0.5 g) was added, the mixture was stirred for another 10 min, and the solution was filtered off. The crude was concentrated and passed through a silica gel column (CH_2Cl_2/ether: 100/15) to yield a green solid (161.3 mg, 0.165 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.03 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 8.02 (d, $^3J_{HH}$ = 6.7 Hz, 2H), 7.53 (d, $^3J_{HP}$ = 13.2 Hz, 4H), 7.45 (dd, $^3J_{HP}$ = 15.3, $^3J_{HH}$ = 7.6 Hz, 4H), 7.27 (q, $^3J_{HH}$ = 7.5 Hz, 5H), 7.21−7.11 (m, 8H), 7.05 (dd, $^3J_{HP}$ = 13.9, $^3J_{HH}$ = 7.2 Hz, 4H), 6.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.81 (dt, $^3J_{HP}$ = 18.4, $^3J_{HH}$ = 9.8 Hz, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.39−136.85 (m), 134.65 (s), 133.91 (s), 133.65 (s), 133.49−133.37 (m), 130.87 (s), 130.33 (s), 130.02 (s), 128.64 (d, J = 9.2 Hz), 128.00−127.58 (m), 127.17 (s), 118.98−118.52 (m), 62.10 (s), 29.10 (s). ^{31}P NMR (122 MHz, $CDCl_3$): δ 35.54 (s). Anal. Calcd for $RuC_{51}H_{38}P_2S_2O_6{\cdot}Et_2O$: C, 62.41; H, 4.35. Found: C, 61.74; H, 4.56. Anal. Calcd for $RuC_{51}H_{38}P_2S_2O_6{\cdot}0.35CH_2Cl_2{\cdot}1.05Et_2O$: C, 61.69; H, 4.59. Found: C, 61.74; H, 4.56. HRMS [ESI$^+$] $RuC_{51}H_{38}P_2S_2O_6$: calcd 975.0706 [M + H]$^+$, found 975.0782 [M + H]$^+$.

(PCy$_3$)[P(-6-SO$_3$-C$_6$H$_4$)(Ph)$_2$]Cl$_2$Ru=CH-Ph (9a). Inside a drybox, 100 mg (0.123 mmol) of $(PCy_3)_2Cl_2Ru{=}CHPh$[5] and 63 mg (0.183 mmol 1.5 equiv) of 2-(diphenylphosphanyl)benzenesulfonic acid[3] were weighed in a vial, and 5 mL of CH_2Cl_2 was added. The solution was stirred at room temperature for 30 min. The solution was filtered on Celite, and the solvent evaporated. Ether was then added on the crude, and the solution was stirred for another 60 min. The mother liquid was taken off, and the crude was dried *in vacuo* to yield the desired product as a green solid (42.5 mg, 0.0502 mmol, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 17.40 (dd, $^3J_{HP}$ = 16.3, $^3J_{HH}$ = 9.7 Hz, 1H), 8.06−7.89 (m, 5H), 7.51−7.30 (m, 5H), 7.25 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.07 (dd, $^3J_{HP}$ = 16.8, $^3J_{HH}$ = 7.9 Hz, 4H), 6.98−6.88 (m, 2H), 6.53 (t, $^3J_{HH}$ = 8.6 Hz, 1H), 2.02 (dd, $^3J_{HP}$ = 22.7, $^3J_{HP}$ = 11.3 Hz, 3H), 1.82 (s, 4H), 1.74 (d, $^3J_{HP}$ = 11.3 Hz, 4H), 1.65−1.41 (m, 13H), 1.33 (s, 4H), 1.24−0.91 (m, 8H), 0.79 (d, $^3J_{HP}$ = 12.7 Hz, 1H). ^{31}P NMR (122 MHz, $CDCl_3$): δ 49.17 (d, $^2J_{PP}$ = 29.4 Hz), 15.73 (d, $^2J_{PP}$ = 29.4 Hz). Anal. Calcd for $RuC_{43}H_{53}P_2SO_3Cl{\cdot}CH_2Cl_2$: C, 56.62; H, 5.94. Found: C, 56.43; H, 6.01. HRMS [ESI$^+$] $RuC_{43}H_{53}P_2SO_3Cl$: calcd 813.2234 [M − Cl]$^+$, found 813.2199 [M − Cl]$^+$.

(PCy$_3$)[P(-6-SO$_3$-C$_6$H$_4$)(Cy)$_2$]Cl$_2$Ru=CH-Ph (9b). Inside a drybox, 90 mg (0.108 mmol, 1.0 equiv) of catalyst **1b** and 67 mg (0.238 mmol, 2.2 equiv) of PCy_3 were weighed in a vial, and 5 mL of CH_2Cl_2 was added. The suspension was stirred at room temperature for 60 min. The solution was filtered on Celite and the solvent evaporated. The resulting green solid was found to be a mixture of catalyst **1b** and **9b**, which were not readily separated by column chromatography (^{1}H NMR yield 60%). ^{31}P NMR (122 MHz, $CDCl_3$): δ 26.37 (d, $^2J_{PP}$ = 239.8 Hz), 7.65 (d, $^2J_{PP}$ = 239.8 Hz).

General Procedure for RCM Tests. Inside a drybox, 1.7 mg of catalyst **1b** was weighed in a vial, and 1 mL of $CDCl_3$ added ($c = 2 \times 10^{-3}$ mol/L). In a separate vial, **10** (48 mg, 0.2 mmol) was added to 1 mL of $CDCl_3$. The combined solutions ([**10**]:[**1b**] = 100) were stirred at 60 °C on a "Heat on Block" System carousel 12 Plus from Radleys Technologies. The conversion of **10** into diethyl-3-cyclopentene-1,1-dicarboxylic acid was followed by ^{1}H NMR. The conversion was calculated by integrating the ^{1}H resonance corresponding to the product at 2.94 ppm and the resonance of the starting material at 2.58 ppm.

General Procedure for ROMP Tests. Inside a vial, 1 mg of catalyst **1b** (0.0012 mmol, 1 equiv) was dissolved in 1 mL of $CDCl_3$. In a 10 mL round-bottom flask, 130 mg of **14** (1.2 mmol, 1000 equiv) was combined with the catalytic solution, and the mixture was heated for 1 h at 60 °C. The reaction was stopped by adding 1 mL of ethyl vinyl ether. The polymer was collected by methanol precipitation.

General Procedure for CM Tests. Inside a vial, 1.1 mg of catalyst **1b** (0.0012 mmol, 1 equiv) was dissolved in 1 mL of $CDCl_3$. In a small vial, 20 μL of **15** (0.127 mmol, 100 equiv) was stirred at 60 °C on "Heat on Block" System carousel 12 Plus. The conversion was measured by ^{1}H NMR analysis of the mixture.

■ ASSOCIATED CONTENT

Supporting Information

Procedure for variable-temperature NMR experiments, NMR spectra, MS spectra, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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AUTHOR INFORMATION

Corresponding Author

*E-mail: claverie.jerome@uqam.ca.

Notes

The authors declare no competing financial interest.

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