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Synthesis and Reactivity of Ruthenium Phosphite Indenylidene Complexes

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Supporting Information

ABSTRACT: The synthesis of the four olefin metathesis precatalysts **Caz-1a**–**d**, featuring the NHC ligand N,N'-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes) and four different phosphites (P(O'Pr)₃, P(OPh)₃, P(OEt)₃, and P(OMe)₃), is reported. The complexes are readily synthesized from commercially available [RuCl₂(3-phenylinden-1-ylidene)-(pyridine)(SIMes)] (**Ind-III**) in yields of up to 88%. These complexes adopt an unusual cis configuration between the phosphite and the NHC ligands. NMR experiments and computational studies confirm that the cis complexes are thermodynamically favored in comparison to their trans



counterparts. In addition, the isomerization from trans to cis occurs via a mononuclear and non-dissociative mechanism. Among the four precatalysts, *cis*-**Caz**-1a, featuring a $P(O^{i}Pr)_{3}$ ligand, displays the highest activity in ring-closing metathesis and cross-metathesis transformations. Experiments at low catalyst loadings demonstrated the potential of this catalyst, allowing better conversions than with commonly used commercially available precatalysts.

INTRODUCTION

Olefin metathesis is now considered among the most powerful tools in organic and organometallic chemistry.¹ Its importance was recognized by the 2005 Nobel Prize in chemistry to Grubbs, Schrock, and Chauvin.² The efficiency of metathesis catalysts is also highlighted by the ever-increasing number of applications spanning from the synthesis of biologically active compounds to that of novel polymers.³ Dating back to 1992, when Grubbs reported the first-generation ruthenium catalyst $[RuCl_2(PCy_3)_2(=CHPh)]^4$ numerous studies have targeted the development of longer-living and more active precatalysts.⁵ The replacement of a labile phosphine ligand by a strongly σ donating N-heterocyclic carbene (NHC) afforded the corresponding $[RuCl_2(NHC)PCy_3(=CHPh)]$ complexes, which displayed increased reactivity and stability (G-II, Figure 1).^{1f,g,6} The introduction of 1-isopropoxy-2-vinylbenzene to form oisopropoxybenzylidene instead of the benzylidene moiety afforded chelated catalysts,⁷ the best known being the Hoveyda catalyst⁸ (Hov-II, Figure 1). Further modifications of the chelating ligand allowed for the formation of precatalysts recognized as highly efficient systems.⁹ More recently, replacing the benzylidene by a 3-phenylinden-1-ylidene has given rise to a new family of complexes.¹⁰ These precatalysts have proven highly stable and efficient in various metathesis transformations. Studies focusing on the variation of the NHC on these architectures have been reported.¹¹ However, G-II and Ind-II



Figure 1. Previously reported ruthenium complexes relevant to the present study.

find their limitations in catalysis involving challenging substrates, where the former does not tolerate harsh conditions and the latter requires $2-5 \mod \%$ of catalyst to perform reactions effectively.

Several studies have been reported on the modulation of ruthenium complexes by replacement of the tricyclohexylphos-

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phine ligand by other phosphines,¹² NHCs,¹³ Schiff bases,¹⁴ and pyridine,¹⁵ in the benzylidene and indenylidene families. Unfortunately, the expensive PCy₃ is generally accepted as the best throwaway ligand to perform exchange reactions and generate novel catalysts motifs. In this context, we recently reported the synthesis of a phosphite-containing ruthenium complex (*cis*-**Caz**-1a, Figure 1).^{16a} This study was based on the known synergistic effect between strongly π acidic phosphites and strongly σ donating NHCs on metals.¹⁷ Such a beneficial effect has already been demonstrated, affording extremely long-lived and highly active precatalysts in Ni- and Pd-catalyzed coupling reactions.¹⁸

cis-Caz-1a^{16a} was readily synthesized by reacting commercially available Ind-III¹⁹ with $P(O^{i}Pr)_{3}$ (Scheme 1). During the

Scheme 1. Synthesis of Phosphite-Containing Ruthenium Indenylidene Complex Caz-1a



exchange reaction, when the reaction was performed at room temperature, two isomers, trans- and cis-dichloro, were observed. The trans isomer was found to be the kinetic product of the reaction, and heating to 40 °C afforded full conversion to the unusual cis isomer, the thermodynamic product. cis-Caz-1a represents a rare example of a Ru metathesis complex adopting a cis configuration while solely bearing monodentate ligands. Indeed, to date, monodentate phosphine containing *cis*-dichloro ruthenium complexes had rarely been observed²⁰ or were formed with the assistance of a hydroxy-substituted NHC.²¹ Furthermore, this represented, to the best of our knowledge, the first example of an indenylidenetype complex displaying such a configuration. However, the cisdichloro geometry has been recently found in a limited number of Hoveyda-type catalysts, with metal centers effectively bearing a bidentate ligand.²² In addition to having a fascinating structure, cis-Caz-1a showed interesting properties in ringclosing metathesis (RCM), especially at low catalyst loadings. Indeed, cis-Caz-1a was found to be latent16a and required thermal activation; complete conversions in RCM could be achieved with catalyst loadings as low as 0.02 mol % with heating in refluxing toluene. Knowing that a synergy between the phosphite and the NHC on the ruthenium could lead to even more promising precatalysts, we proceeded to investigate the potential of phosphites other than $P(O^{i}Pr)_{3}$. These findings are reported in this contribution.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes *cis*-Caz-1a–d. Initial syntheses of complexes Caz-1a–d were performed by reacting Ind-III with the phosphites $P(O^iPr)_3$, $P(OMe)_3$, $P(OEt)_3$, and $P(OPh)_3$ in CH_2Cl_2 at room temperature. In each case, the ³¹P{¹H} NMR spectrum of the crude product showed the formation of two complexes (signals between 110 and 135 ppm, whereas free phosphites appear around 128–145 ppm). Each spectrum showed a significant downfield shift of the phosphorus peak from *trans*-Caz-1a-d to the corresponding *cis*-Caz-1a-d. The electronic parameters of the phosphites appear to have an effect on the reaction; an excess of the less electron donating phosphite $P(OPh)_3$ was required in order to convert all of the Ind-III into the new complex.

As previously demonstrated with $P(O^{i}Pr)_{3}^{16a}$ trans- and cis-Caz-1a-d were found to be kinetic and thermodynamic products, respectively; heating the reaction mixture at 40 °C in CH₂Cl₂ allowed for full conversion to the cis isomers (Table 1).



Reactions were monitored by ¹H and ³¹P{¹H} NMR until full conversion to the cis isomers was achieved. In all cases, the initial formation of *trans*-Caz-1a-d was observed, followed by equilibration to the thermodynamically favored cis isomers.

The trans/cis isomerization is strongly dependent on the phosphite cone angle. Bulky phosphites such as $P(O^{i}Pr)_{3}$ and $P(OPh)_{3}$ required longer reaction times than the smaller phosphites $P(OMe)_{3}$ and $P(OEt)_{3}$ (Table 1).²³ However, complexes *cis*-**Caz**-1**a**-**d** could be isolated in good yields, ranging from 57% for *cis*-**Caz**-1**b** to 88% for *cis*-**Caz**-1**c**. The lower yield for *cis*-**Caz**-1**b** was due to isolation issues, as several MeOH washes were necessary to obtain the analytically pure complex.

In order to fully characterize *cis*-Caz-1a-d. single crystals suitable for X-ray diffraction studies were grown by slow evaporation of solutions of complexes in CH₂Cl₂/n-dodecane or THF/n-dodecane or by recrystallization in nitromethane. Graphical representations of cis-Caz-1a-d are provided in Figure 2 and selected bond lengths and angles in Table 2. Crystallographic data of Ind-III are included in the table for comparison.^{19a} The distances of the carbene to the metal center Ru-C(1) range from 2.063(6) to 2.080(4) Å, which are slightly longer than Ru-C(1) in Ind-III but are in the same range as that of the previously reported [RuCl₂(Ind)(PAr₃)(SIMes)], (Ind = 3-phenylinden-1-ylidene).^{12c} Interestingly, the Ru–C(1) bond was found to be slightly longer in cis-Caz-1d, which features $P(OPh)_{3}$, than in the other phosphites. The C(1)-Ru(1)-P(1) angle between the phosphite and the NHC ranges from 97.88° (for $P(OMe)_3$) to 100.06° (for $P(O'Pr)_3$), giving support that steric repulsion between NHC and $P(OMe)_3$ is less important than with $P(O^{i}Pr)_{3}$.

Mechanistic Investigation. Previous kinetic experiments permitted to obtain the thermodynamic parameters of the trans/*cis* isomerization, $\Delta H^{\ddagger} = 22.6$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -4.2$ cal mol⁻¹ K⁻¹. These data indicated that the isomerization

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cis-Caz-1a

cis-Caz-1b



Figure 2. Graphical representations of cis-Caz-1a-d. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes $[RuCl_2(Ind)(L)(SIMes)]$ (Ind = 3-Phenylinden-1-ylidene, L = P(OR)_3, Pyridine)

			L						
	$P(O^{i}Pr)_{3}$	P(OPh) ₃	P(OEt) ₃	$P(OMe)_3$	pyridine				
Ru(1)-C(24)	1.881(8)	1.866(4)	1.871(6)	1.882(4)	1.911(19)				
Ru(1)-C(1)	2.067(7)	2.080(4)	2.063(6)	2.065(4)	2.051(9)				
Ru(1)-P(1)	2.249(2)	2.2179(12)	2.2273(17)	2.2423(10)	$2.128(8)^a$				
Ru(1)-Cl(1)	2.3974(19)	2.3797(11)	2.3899(15)	2.3774(11)	2.385(4)				
Ru(1)-Cl(2)	2.4036(18)	2.3868(11)	2.3972(15)	2.4287(9)	2.385(4)				
C(24)-Ru(1)-C(1)	98.7(3)	98.74(17)	98.2(2)	96.64(15)	98.3(8)				
C(24)-Ru(1)-P(1)	90.5(2)	88.98(13)	90.20(18)	88.60(11)	$95.3(7)^{b}$				
C(1)-Ru(1)-P(1)	100.06(19)	99.17(11)	98.58(16)	97.88(10)	$166.4(7)^{c}$				
N(2)-C(3)-C(4)-N(5)	6.7(7)	2.5(4)	4.6(6)	7.1(4)	0.0				
The distance Ru–N _{Py} is given. ^b The angle C(24)–Ru–N _{Py} is given. ^c The angle C(1)–Ru-N _{Py} is given.									

Table 3. Comparison of the X-ray and DFT Ru-X Bond Distances in Selected Complexes^a

	1	1a		1b		1c		1d	
	X-ray	DFT	X-ray	DFT	X-ray	DFT	X-ray	DFT	
Ru-P	2.249	2.276	2.242	2.253	2.227	2.259	2.218	2.247	
Ru-NHC	2.067	2.057	2.065	2.056	2.063	2.054	2.080	2.066	
Ru–Ind	1.881	1.897	1.882	1.898	1.871	1.897	1.866	1.899	
$Ru-Cl^b$	2.404	2.433	2.429	2.428	2.397	2.433	2.387	2.420	
Ru-Cl ^c	2.397	2.398	2.377	2.397	2.390	2.398	2.380	2.396	

^aAll distances in Å. ^bRu–Cl bond trans to the P(OR)₃. ^cRu–Cl bond trans to the NHC.

Table 4. DFT Calculated	Bond Dissociation E	inergy of the Ligand	L in the Cis Isomer	(BDE) and Energy	Difference between
the BDE of the Cis and T	Γrans Isomers, $\Delta E_{c/t'}$, of a Series of Liga	nds L in [RuCl ₂ (Ind)	(L)(SIMes)] Com	plexes ^a

			$\Delta E_{ m c/t}$			В	DE
L	gas	toluene	CH ₃ NO ₂	toluene ^b	CH ₃ NO ₂ ^b	toluene	toluene ^b
P(OMe) ₃	7.6	7.3	8.0	6.4	7.2	21.8	40.3
$P(OEt)_3$	6.8	6.7	7.7	7.9	8.9	21.0	42.7
$P(O^{i}Pr)_{3}$	4.0	3.5	4.2	7.2	7.7	15.3	44.0
$P(OCy)_3$	4.6	4.2	4.8	7.9	8.3	15.2	46.7
$P(OPh)_3$	4.7	4.6	5.3	7.1	7.8	12.1	38.1
PMe ₃	-3.5	-1.8	1.8	-0.1	3.7	20.5	38.1
PEt ₃	-6.1	-4.4	-1.3	-2.6	0.8	14.7	36.0
P ⁱ Pr ₃	-16.4	-14.7	-11.9	-13.8	-10.8	-2.9	23.8
PCy ₃	-15.7	-14.5	-11.9	-7.9	-7.9	-3.9	29.3
PPh ₃	-5.9	-6.6	-3.9	-3.4	-0.7	3.5	32.6
Py	-6.1	-4.7	-1.9	-4.5	-1.3	9.2	21.4

"All values in kcal/mol. Positive $\Delta E_{c/t}$ values imply that the cis isomer is favored. "M06 calculated values."

followed a mononuclear and nondissociative mechanism,^{16a} which is further supported by the fact that the reaction rate remained unaltered in the presence of an excess of free phosphite. DFT calculations were undertaken to gain insight into the unusual preference of the **Caz-1a-d** systems to form the cis isomer. These results are summarized in Tables 3 and 4.

Before discussing the relative stability of the cis and trans isomers, we briefly focus on the ability of the selected computational recipe to reproduce correctly the coordination distance of the various ligands around the Ru center (see Table 3). The data reported in Table 3 indicate that the combination of the BP86 functional together with the SDD effective core potential for Ru and the SVP basis set for main-group atoms reproduces the experimental distances with an absolute mean error of only 0.019 Å, which can be considered as a more than satisfactory agreement, and it is consistent with previous work.²⁴ More specifically, the DFT geometries nicely reproduce the experimental evidence that the Ru–Cl bond trans to the P(OR)₃ ligand is slightly longer than the Ru–Cl bond trans to the NHC ligand (on average, by 0.018 Å in the experimental structures versus 0.031 Å in the DFT structures).

Moving to the relative energy of the cis and trans isomers, the cis isomer is calculated to be more stable than the trans isomer for all the P(OR)₃-based systems considered, in agreement with the experimental findings, independent of the solvent considered (see the positive $\Delta E_{c/t}$ of Table 4). This is in contrast to the pyridine- and the PR₃-based complexes where, with the exception of PMe₃ in CH₃NO₂, the trans isomer is preferred instead (see the negative $\Delta E_{c/t}$ of Table 4). This difference is not sensitive to the nature of the R group for P(OR)₃, with $\Delta E_{c/t}$ spanning the rather small window of roughly 3.5 kcal/mol in the gas phase, while the bulkiness of R group has a major role in the case of PR₃. The $\Delta E_{c/t}$ values show a fairly good linear correlation with the Tolman cone angle for P(OR)₃ and PR₃, respectively (Figure 3).

Figure 3 also indicates that the different behavior between $P(OR)_3$ and PR_3 is entirely electronic in nature, since the trend observed for $P(OR)_3$ is clearly shifted at higher $\Delta E_{c/t}$ relative to the trend observed of PR_3 . Furthermore, it indicates that smaller ligands can be accommodated slightly better than larger ligands in the rather hindered position cis to the SIMes ligand. Finally, the solvent effect was evaluated, and in agreement with previous results,²⁵ for both $P(OR)_3$ and PR_3 , the cis isomer is stabilized more than the trans isomer in a high-polarity solvent such as nitromethane than in low-polarity solvents such as



Figure 3. Plot of the gas-phase DFT calculated $\Delta E_{\rm c/t}$ versus the Tolman cone angle. 23

toluene: i.e. polar solvents favor the cis isomer due to its higher dipole moment. The relative stabilities of the cis and trans isomers scarcely depend on the specific functional used (compare the $\Delta E_{c/t}$ values in toluene calculated with the BP86 and M06 functionals in Table 4), although the M06 functional is slightly biased toward the cis isomer. This is reasonable, considering that the M06 functional was fitted to reproduce a large data set which includes also dispersion stabilized systems and the cis isomer presents the bulkier NHC and P(OR)₃ ligands in a relative cis orientation, which maximizes dispersion interaction between them.

Focusing on the absolute BDE, we next compared $P(OMe)_3$ and PMe₃, since steric effects should be minimal. The values in toluene reported in Table 4 indicate that the BDE of $P(OMe)_3$ in the trans isomer (14.6 kcal/mol) is 7.7 kcal/mol smaller than the BDE of PMe₃ (22.3 kcal/mol). This difference can be easily rationalized, considering the lower basicity of phosphites relative to that of phosphines. Conversely, in the cis isomer the BDE of P(OMe)₃ (21.8 kcal/mol) is 1.3 kcal/mol greater than the BDE of PMe₃ (20.5 kcal/mol), indicating that in the cis isomer $P(OMe)_3$ binds more strongly than PMe_3 to the Ru center, despite its reduced basicity. Structural analysis indicates that the $Ru-P(OMe)_3$ bond length in the cis isomer, 2.26 Å, is 0.07 Å shorter than in the trans isomer, 2.33 Å, whereas the Ru–PMe₃ bond length in the cis isomer, 2.34 Å, is only 0.05 Å shorter than in the trans isomer, 2.39 Å. Furthermore, the average P-O bond in the cis isomer, 1.66 Å, is 0.01 Å longer than in the trans isomer, 1.65 Å, which is a classical sign of

Entry	Substrate	Product	Pre-catalyst	Cat. loading (mol%)	t (h)	Conv. (%) ^b			
1			cis-Caz-1a		0.5	> 99			
2			sis Car 1h		0.5	78			
3	EtO ₂ CCO ₂ Et	EtO ₂ C CO ₂ Et	cis-Caz-1D		1	> 99			
4	\sim	()	via Can 1a	1	0.5	35			
5	2 🔶	3	cis-Caz-ic		1	73			
6			ais Car 1d		0.5	98			
7			cis-Caz-Iu		1	>99			
8			ais Cor 1a		0.5	72			
9	Ph		C15-Caz-1a		1.75	> 99			
10			cis-Caz-1b	5	1.75	5			
11	4	5	5	s	 ✓ ✓ 5 	cis-Caz-1c		1.75	10
12			cis-Caz-1d		1.75	91			
13			ais Car 1a		0.5	90			
14	*	,CO₂Me	cis-Caz-la		1.75	97			
15	>	×	aia Can 1h		0.5	6			
16			CIS-Caz-10	2	1.75	38			
17	6 + <i>≥</i> CO ₂ Me	> 8	ais Coz 1a	2	0.5	13			
18	> 7	>	C13-Ca2-10		1.75	67			
19		TBDMSO	cis-Caz-1d		0.5	60			
20					1 75	94			

^{*a*}Reaction conditions: substrate (0.25 mmol), precatalyst (0.5 to 5 mol %), toluene (0.1 M), 80 °C. ^{*b*}Conversions were determined by ¹H NMR based on substrates 2, 4 and 6 average of 2 reactions. TBDMS = *tert*-butyldimethylsilyl.



Figure 4. Comparative catalytic studies at low catalyst loading. Reaction conditions: 9 (0.5 mmol), precatalyst (0.5 mol %), toluene (0.1 M, 5 mL) 80 °C.³³

back-donation from the metal into the empty π^* orbitals corresponding to P–O bonds.^{26,27} The strength of the Ru– P(OMe)₃ bond in the various isomers was evaluated with the Mayer bond order (MBO),²⁸ which is a valuable tool in the analysis of the bonding in main-group compounds and has also been used to characterize transition-metal systems.^{29,30} The Ru–P(OMe)₃ MBO in the cis isomer, 0.98, is 0.21 greater than in the trans isomer, 0.77, whereas the Ru–PMe₃ MBO in the cis isomer, 0.78, is only 0.12 greater than in the trans isomer, 0.66, supporting the idea of a back-donation from the metal to the phosphites.

As a final remark, the absolute BDE strongly depends on the specific functional used. A simple comparison of the BDE in toluene calculated with the BP86 and M06 functionals indicates that the M06 functional, as expected, shows much stronger binding in all cases. However, the M06 functional predicts that the bulky and more basic PCy_3 , with a BDE of 37.2 kcal/mol, binds to the trans isomer similarly to the small PMe_3 , with a BDE of 38.2 kcal/mol, which is somewhat surprising considering the steric encumbrance of PCy_3 . In this regard, the BP86 functional predicts that PMe_3 , with a BDE of 22.3 kcal/mol, binds much better than PCy_3 , with a BDE of 10.6

kcal/mol. A recent benchmark study has indicated that both functionals in combination with the solvation model adopted here are probably underestimating and overestimating, respectively, the relative BDE of small and large phosphines.³¹

Precatalyst Activity Comparison. The new complexes were evaluated in diene and enyne ring-closing metathesis (RCM) and cross-metathesis (CM) of benchmark substrates (Table 5). Preliminary experiments showed that cis-Caz-1a displayed a latent character.^{16a} Thus, reactions were performed at 80 °C in toluene. A general trend was found between reactivity and phosphite substitution. Triisopropyl phosphite and triphenyl phosphite containing precatalysts cis-Caz-1a,d exhibited comparable efficiency, the former being slightly more active. Indeed, in the presence of 1 mol % of precatalyst, after 30 min, complete conversion of 2 was achieved with cis-Caz-1a, while traces of 2 could still be detected with cis-Caz-1d (Table 5, entries 1 and 6). Even clearer evidence of cis-Caz-1a being faster than cis-Caz-1d was found when reactions with substrates 4 and 6 were carried out (Table 5, entries 8 and 13 versus 12 and 19). Finally, cis-Caz-1b,c, featuring trimethyl and triethyl phosphite, respectively, were similarly active but less so than cisCaz-1a,d, requiring longer reaction times to reach full conversions.

The activity of cis-Caz-1a-d was also compared to those of commercially available precatalysts in the RCM of hindered N,N-dimethallyltosylamine 9 at relatively low catalyst loading (Figure 4).³² The commercially available Ind-II, Ind-III, G-II, and Hov-II were not able to achieve more than 60% conversions in the benchmark transformation. Due to their increased stability, Ind-II and Hov-II were the most efficient of the "traditional" precatalysts. G-II initiated as fast as the other precatalysts but did not permit more than 17% conversion; Ind-III gave no conversion. In comparison, phosphitecontaining precatalysts *cis*-Caz-1b,c (bearing $P(OMe)_3$ and $P(OEt)_{3}$, respectively) displayed a very slow rate of conversion in addition to an activation period of approximately 1.75 h. The contrast is striking with cis-Caz-1a,d, featuring $P(O^{i}Pr)_{3}$ and $P(OPh)_{3}$, respectively; these precatalysts were able to reach full conversions in less than 7 h. In these cases, an induction period was also observed, confirming the latent character of such complexes. Catalyst efficiency can thus be classified as follows: cis-Caz-1a (P(OⁱPr)₃) > cis-Caz-1d (P(OPh)₃) \gg cis-Caz-1b $(P(OMe)_3) \approx cis-Caz-1c (P(OEt)_3).$

The influence of the concentration was investigated in the RCM of **9** with precatalyst *cis*-**Caz**-**1a**.³⁴ The reaction was conducted at three different concentrations: 0.05, 0.1, and 1 M. The rate of the reaction appeared similar whatever the concentration, indicating that concentrated reactions could be carried out without affecting the reaction outcome.

The reactivity trend observed above could be put in direct relation with the affinity of the different phosphites to the metal center (Table 4). Indeed, whether in the cis or trans complexes, the binding energies of the phosphites to the ruthenium follow the opposite trend: $P(OMe)_3 > P(O'Pr)_3$. In addition, regardless of the phosphite used, the binding is stronger in the cis than in the trans configuration, suggesting that, during the mechanism, decoordination of the phosphite in a trans position should be more facile.³⁵

To obtain more insight into the activation/initiation steps, additional DFT calculations were performed (Figure 5). Considering that recent results indicate that in the case of Hoveyda–Grubbs catalysts the activation step could have an associative-displacement character,³⁶ which suggests that olefin



Figure 5. (top) Energies (kcal/mol) of various isomers of Caz-1a with an ethylene coordinated molecule. Reported energies are in toluene with *cis*-Caz-1a + C_2H_4 taken as reference at 0 kcal/mol (top). M06 values are reported in parentheses. (bottom) Schematic representation of relevant angles in Ru–indenylidene and Ru–methylidene isomers of *trans*-Caz-1a.

coordination to the ruthenium could promote simultaneous dissociation of the labile ligand, we investigated if the smallest olefin, ethylene, could coordinate to **Caz-1a**. However, calculations indicate that, in the presence of a Ru–indenylidene bond, only isomer **A** of Figure 5 is stable, even if it is very high in energy. The other isomers tested, **B** and **C**, are not stable, and ethylene detached from the ruthenium during geometry optimization.

In the case of the Ru-methylidene bond that should be formed when $P(O'Pr)_3$ coordinates back to the ruthenium center after some productive metathesis events, the energies of all isomers A-C were located. Isomer C, which derives from a trans coordination of ethylene to the methylidene moiety, is the most stable isomer. The difference in behavior in comparison to trans-Caz-1a can be attributed to the different bulkiness of the indenylidene and methylidene groups, which is evidenced in the rather larger Cl-Ru-C(indenylidene) angles in trans-Caz-1a relative to those in the methylidene analogue (Figure 5). The bulky indenylidene moiety pushes the Cl atoms toward the vacant coordination position around the Ru atom, preventing olefin coordination as the sixth ligand. This suggests that the mechanism of activation of Caz-1a, with olefins bulkier than ethylene, could proceed via dissociation of $P(O^iPr)_3$. In contrast, in the case of the Ru-methylidene complex an associative mechanism of activation cannot be excluded.

Reaction Scope. In order to explore the tolerance of cis-Caz-1a to different functionalities, a wide range of substrates in various metathesis transformations was studied. The reactions were performed in toluene at 80 °C in the presence of 1-5 mol % of cis-Caz-1a, the higher catalyst loading being only necessary for the formation of 14 and 22 featuring a tetrasubstituted double bond (Table 6). The RCM of unhindered malonate derivatives was achieved in short reaction times (less than 1 h) and in good yields. Indeed, di- and trisubstituted cyclopentenes 12 and 3 were obtained in quantitative yields. Nonetheless, highly constrained substrate 13 could not be fully cyclized, even after 24 h at 80 °C, and was isolated in 70% yield (Table 6, entry 3). Six- and seven-membered rings 16 and 18 were obtained in excellent yields; interestingly, no increase in the reaction time was required in comparison to five-memberedring formation. Of note, a concentration of 0.05 M was necessary to obtain 18 without parasitic polymerization.

The RCM of nitrile-containing substrates 19 and 21 (Table 6, entries 6 and 7) was also studied. Nonhindered cyclopentene 20 was isolated in good yield; however, *cis*-Caz-1a was unable to achieve complete conversion of 21, and only a 55% yield of 22 was obtained. The cyclization of tosylamine-based olefins was found to be very efficient regardless of steric hindrance and ring size (Table 6, entries 8–12); a small increase in the reaction time was needed for larger ring sizes, and a catalyst loading of only 2 mol % was necessary to achieve the cyclization of 9 and 29 to obtain tetrasubstituted five- and sixmembered rings in good yields.

Amide- and ether-based substrates were also efficiently cyclized, with yields spanning from 80% to 99%. Increasing the ring size from six to seven members proved routine, as products **34**, **36**, **38**, and **40** were obtained in excellent yields in less than 1 h (Table 6, entries 14–17).

Enyne ring-closing metathesis is a powerful tool enabling the synthesis of dienes that can undergo further Diels-Alder reaction and thus readily furnish bicyclic compounds. Substrates 4 and 41 were fully converted after 30 min; however, 5 was isolated in only 75% yield (Table 7, entries 1

Table 6. Ring-Closing Metathesis Behavior of cis-Caz-1a^a

Entry	Substrate	Product	t (h)	conv. (%) ^b
1	EtO ₂ C CO ₂ Et	EtO ₂ C LO ₂ Et 12	0.5	>99 (99)
2	etO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	0.5	>99 (99)
3 ^{<i>c</i>}		EtO ₂ C CO ₂ Et	24	82 (70)
4	EtO ₂ C CO ₂ Et	EtO ₂ C _{CO2} Et	0.5	>99 (96)
5^d	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	1	>99 (87)
6	NC		0.5	>99 (88)
7^c		NC CN 22	24	60 (55)
8	∏s № 23	∑N 24	0.5	>99 (97)
9	∑N № 25	∑N № 26	1.25	>99 (99)
10	∑N ≥7	N 28	1	>99 (88)
11 ^e	↓ ^{Ţs} ↓ N ↓ 9	∑N № 10	5	>99 (95)
12 ^e		Ts N 30	1.5	>99 (99)
13	0 Ph N 31	$\sim \sim $	0.5	>99 (99)
14		34	0.75	>99 (99)
15	35		0.75	>99 (80)
16	37	38	0.5	>99 (94)
17^{d}	1 9	40 K	0.75	>99 (99)

^{*a*}Reaction conditions: substrate (0.25 mmol), *cis*-Caz-1a (1 mol %), toluene (0.1 M), 80 °C. ^{*b*}Average of two runs. Conversions were determined by ¹H NMR based on diene. Isolated yields are given in parentheses. ^{*c*}5 mol % of precatalyst was used. ^{*d*}0.05 M concentration was used. ^{*e*}2 mol % of precatalyst was used. Ts = tosylate.

and 2). A longer reaction time was necessary to convert hindered compound 43. Once again, a relatively low isolated yield of 71% was obtained; such behavior could result from parallel polymerization reactions that can easily occur at elevated temperature. While substrate 45 remained unchanged after 24 h, more hindered enyne 47 was efficiently cyclized in 3 h (Table 7, entries 4 and 5).³⁷ In conclusion, precatalyst *cis*-**Caz-1a** allowed the formation of dienes from enynes in short reaction times with acceptable yields.

Finally, the ability of precatalyst *cis*-**Caz-1a** to promote intermolecular cross-metathesis (CM) was investigated (Table 8). CM reactions are more difficult than their RCM counterparts, as side-formation of self-metathesis products may occur. Several substrates were reacted in the presence of 2 mol % of *cis*-**Caz-1a** and 2 equiv of alkene partners in toluene at 80 °C. Silylated compound **6** was efficiently coupled with various olefins (Table 8, entries 1-4). The use of methyl acrylate 7, acrolein **49**, and diallylic acetate **53** as alkene

Table 7. Enyne Ring-Closing Metathesis Behavior of cis-Caz-1a^a

Entry	Substrate	Product	t (h)	$\frac{\text{conv.}}{(\%)^b}$
1	Ph + Q	Ph-Lo 5	0.5	>99 (75)
2	Ph Ph Q 41	Ph Q 42	0.5	>99 (99)
3 ^{<i>c</i>}		Ph+0 44	19	>99 (71)
4	↓ N 45	^{Ts} → 46	24	0
5	↓ N 47		3	>99 (81)

^{*a*}Reaction conditions: substrate (0.25 mmol), *cis*-Caz-1a (1 mol %), toluene (0.1 M), 80 °C. ^{*b*}Average of two runs. Conversions were determined by ¹H NMR based on enyne. Isolated yields are given in parentheses. ^{*c*}5 mol % of precatalyst was used. Ts = tosylate.

partners allowed the isolation of the desired products, in good yields compared to previously reported results;^{11c} thus proving once more that *cis*-Caz-1a displays good tolerance toward a variety of functional groups. However, allyltosylamine 51 was found to be incompatible with the catalytic system, as no conversion to 52 was observed.

Ester-containing substrates **55** and **57** bearing varied chain lengths were also coupled with methyl acrylate 7 in good yields (Table 8, entries 5 and 6). Both products were isolated as the *E* isomers, identified by ¹H NMR. Reaction of eugenol **59** (essential oil of clove) with acrolein **49** was found to be efficient and did not require protection of its phenolic moiety (Table 8, entry 7). Finally, *p*-chlorostyrene **61** reacted well with methyl acrylate 7 and gave **62** in 81% yield with an E/Z ratio of 20:1 (Table 8, entry 8). It is worth noting that no formation of self-metathesis compounds was observed during the screening of substrates.

Evaluation at Low Catalyst Loading. Low catalyst loading experiments in RCM, enyne metathesis, and CM were performed to study the limitations of cis-Caz-1a. Easily cyclized substrates in RCM, i.e. affording di- or trisubstituted cyclic olefins, were accessed with excellent conversions with as low as 0.02 mol % catalyst (Table 9, entries 1-8); increasing the ring size to form six- or seven-membered rings did not require higher loading than 0.05 mol %, while increasing the steric hindrance to form trisubstituted olefins required slightly higher catalyst loadings. Tetrasubstituted olefins 10 and 30 were formed using as little as 0.1 mol % of cis-Caz-1a (Table 9, entries 10 and 11), whereas only 75% conversion of malonate derivative 13 was achieved using 0.5 mol % of precatalyst (Table 9, entry 9). To the best of our knowledge, these results represent the lowest catalyst loadings affording complete conversion of substrates 10 and 30. While more active catalysts for the ring-closing metathesis of less hindered olefins have been reported, ^{15b,32} only a few examples of catalysts as robust as cis-Caz-1a have been described in the literature, ^{13d,e,32a} making it an excellent compromise between reaction condition harshness and tolerance to steric hindrance. For this reason, it represents a superior choice to more popular commercially available catalysts.38

Table 8. Cross-Metathesis Behavior of cis-Caz-1a^a

Entry	Substrate	Alkene partner	Product	t (h)	Yield (%) (<i>E/Z</i>) ^b
1		CO ₂ Me	TBDMSO 8	2	81 (> 20:1)
2	TBDMSO,	СНО 49	TBDMSOCHO 50	2	57 (> 20:1)
3	6	NHTs 51	TBDMSONHTs 52	3.5	0
4^c		Aco 53	TBDMSOOAc 54	3.5	59 (6:1)
5	Ph 0 55	CO₂Me	Ph 0 CO ₂ Me	2.5	85 (> 20:1)
6	Ph 0	7	Ph CO ₂ Me	2.5	75 (> 20:1)
7	MeO HO 59	сно 49	HO CHO	5	62 (6:1)
8	CI 61	CO ₂ Me	CI 62	3	81 (> 20:1)

^{*a*}Reaction conditions: substrate (0.25 mmol), alkene partner (0.5 mmol), *cis*-Caz-1a (2 mol %), toluene (0.1 M), 80 °C. ^{*b*}Average of two runs; isolated yields. *E/Z* ratios were determined by ¹H NMR. ^{*c*}Only 1 equiv of alkene partner was used.

In CM it was found that a loading of 0.1-0.2 mol % was required to achieve good conversions. Compounds **56** and **58** could be isolated in comparable yields than with 2 mol % of catalyst (Table 9, entries 14 and 15 and Table 8, entries 5 and 6). However, in order to limit self-metathesis of the substrate under the slightly harsher reaction conditions, 5 equiv of the less electron rich alkene partner was required. In addition, for **59** and **61**, a lower concentration of 0.1 M was required. The use of acrolein **49** seemed detrimental to the metathesis reaction, as only 12% of CM product **60** was isolated.

CONCLUSION

The family of mixed NHC-phosphite complexes has been extended, and the synthesis and characterization of the three new catalysts cis-Caz-1b-d, bearing phosphites featuring various electronic and steric properties, has been reported. All complexes present an unusual cis configuration between the NHC and the phosphite ligand. Mechanistic and computational studies confirmed that the cis isomer is more stable than the trans form for all the $P(OR)_3$ -based systems considered and indicated that the different behavior between $P(OR)_3$ and PR_3 is entirely electronic in nature. Additionally, experimental and computational studies support a mononuclear nondissociative mechanism for the isomerization from trans-Caz-1 to cis-Caz-1. Catalytic studies demonstrated that precatalysts cis-Caz-1a-d are able to promote ring-closing, cross, and enyne metatheses in excellent yields even at low catalyst loading. Indeed, in RCM, catalyst loadings as low as 0.02 mol % for "easily cyclized substrates" and 0.1 mol % for more challenging ones, leading to tetrasubstituted olefins, were enough to reach full conversions, demonstrating the robust character of the cis-Caz-1 family of catalysts.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. ¹H, ¹³C{¹H}, and ³¹P{¹H} 1D and 2D nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer using the residual solvent peak as reference (CHCl₃, $\delta_{\rm H}$ 7.26 ppm, $\delta_{\rm C}$ 77.16 ppm; CH₂Cl₂, $\delta_{\rm H}$ 5.32 ppm, $\delta_{\rm C}$ 53.80

ppm) at 298 K. Elemental analyses were performed by the University of St Andrews Analytical Service. Calorimetric studies were performed on a CALVET C80 solution calorimeter. The complexes *cis*-Ca2-1a and *trans*-Ca2-1a were synthesized according to literature procedures.^{16a}

Synthesis of Complexes *cis*-Caz-1b–d: General Procedure. Under an inert atmosphere, phosphite (1–4 equiv) was added to a solution of Ind-III in dichloromethane (0.05 M). The mixture was stirred for the appropriate time at 40 °C, cooled to room temperature, and concentrated in vacuo (1 mL). Pentane (10 mL) was added, and the precipitate was collected by filtration and washed with pentane (3 \times 5 mL).

Dichloro[N,N'-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene](3phenylinden-1-ylidene)(trimethyl phosphite)ruthenium (cis-Caz-1b). According to the general procedure, 1 equiv of trimethyl phosphite was used and the reaction mixture was stirred for 3 h at 40 °C. Additional washes of the solid with cold MeOH $(3 \times 5 \text{ mL})$ afforded the product as a brown solid (366 mg, 57%). ¹H NMR $(CD_2Cl_2, 400 \text{ MHz}): \delta$ (ppm) 8.84 (dd, 1H, ${}^{3}J_{HH} = 7.3 \text{ Hz}, {}^{4}J_{HH} = 0.8 \text{ Hz}$, indenylidene CH⁷), 7.66–7.88 (m, 2H, indenylidene CH⁹), 7.53–7.41 (m, 3H, indenylidene CH¹⁰ and CH¹¹), 7.34 (ddd, 1H, ${}^{3}J_{HH} = 7.3 \text{ Hz}, {}^{4}J_{HH} = 0.8 \text{ Hz}$, indenylidene H⁵), 7.27 (ddd, 1H, ${}^{3}J_{HH} = 7.3 \text{ Hz}, {}^{4}J_{HH} = 0.8 \text{ Hz}$, indenylidene H⁵), 7.27 (ddd, 1H, ${}^{3}J_{HH} = 7.3 \text{ Hz}, {}^{4}J_{HH} = 0.8 \text{ Hz}, {}^{4}J_{HH$ ${}^{4}J_{\rm HH} = 0.8$ Hz, indenylidene H⁶), 7.06 (d, ${}^{3}J_{\rm HH} = 7.3$ Hz, 1H, indenylidene H⁴), 7.03 (s, 1H, mesityl CH), 7.02 (s, 1H, mesityl CH), 6.38 (s, 1H, indenylidene H²), 6.28 (s, 1H, mesityl CH), 6.23 (s, 1H, mesityl CH), 4.03-3.63 (m, 4H, carbene H4' and H5'), 3.23 (d, 9H, ${}^{3}J_{PH} = 10.7$ Hz, POCH₃), 2.68 (s, 3H, mesityl CH₃), 2.62 (s, 3H, mesityl CH₃), 2.37 (s, 3H, mesityl CH₃), 2.35 (s, 3H, mesityl CH₃), 1.99 (s, 3H, mesityl CH₃), 1.71 (s, 3H, mesityl CH₃). ¹³C{¹H} NMR $(CD_2Cl_2, 100.6 \text{ MHz}): \delta \text{ (ppm)} = 292.7 \text{ (d, } {}^2J_{CP} = 23.9 \text{ Hz},$ (CIV), 141.2 (d, ${}^{3}J_{CP} = 2.5$, Hz, indenylidene C¹), 208.5 (d, ${}^{2}J_{CPcis} = 14.6$ Hz, carbene C²), 144.0 (s, C^{IV}), 141.2 (d, ${}^{3}J_{CP} = 2.5$ Hz, indenylidene C^{7a}), 140.4 (d, ${}^{3}J_{CP} = 13.5$ Hz, indenylidene C²H), 139.2 (s, C^{IV}), 139.1 (s, C^{IV}), 138.8 (s, C^{IV}), 138.3 (s, C^{IV}), 137.0 (s, C^{IV}), 136.5 (s, C^{IV}), 136.4 (s, C^{IV}), 135.3 (s, U^{IV}), 135.3 (s, U^{IV} C^{IV}), 135.1 (s, C^{IV}), 130.6 (s, mesityl CH), 130.1 (s, indenylidene C⁷), 130.0 (s, mesityl CH), 129.7 (s, mesityl CH), 129.5 (s indenylidene C⁶), 129.3 (indenylidene C⁵), 129.3 (s, indenylidene C¹⁰), 129.0 (s, indenylidene C¹¹), 127.3 (s, indenylidene C⁹), 117.3 (s, indenylidene C⁴H), 53.4 (br s, OCH₃), 52.6 (s, carbene C⁵'H₂), 51.9 (s, carbene C⁴'H₂), 21.5 (s, mesityl CH₃), 21.1 (s, mesityl CH₃), 20.9 (s, mesityl CH₃), 19.4 (s, mesityl CH₃), 19.1 (s, mesityl CH₃), 18.3 (s, mesityl CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ (ppm) 132.2. Anal. Calcd for C39H45Cl2N2O3PRu: C, 59.09; H, 5.72; N, 3.53. Found: C, 59.38; H, 6.07; N, 3.37.

Dichloro[N,N'-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene](3phenylinden-1-ylidene)(triethyl phosphite)ruthenium (cis-**Caz-1c**). According to the general procedure, 1 equiv of triethyl phosphite was

Tab	ole	9.	Experiments	at	Low	Catal	yst	Loading	g with	cis-C	Caz-1a	ľ
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Entry	Substrate	Product	Catalyst loading (mol%)	Reaction time (h)	conv.[%] ^b (yield [%])
1	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et 12	0.05	15	97 (91)
2	EtO ₂ C CO ₂ Et	EtO ₂ C LO ₂ C 16	0.05	15	>99 (93)
3 ^{<i>c</i>}	EtO ₂ C CO ₂ Et		0.05	15	>99 (96)
4	√ ^{Ts} 23	∑ [™] > 24	0.02	15	94 (84)
5	∑ ^{¶s} N 25	∑s № 26	0.05	15	>99 (91)
6	37	38	0.05	15	>99 (67)
7	etO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	0.075	15	>99 (>99)
8	35		0.05	15	>99 (95)
9		EtO ₂ C CO ₂ Et	0.5	24	75 (74)
10	J N 9	∑N 10	0.1	8	96 (94)
11	↓ ^{Ţs} N 29	Jo 30	0.1	8	>99 (98)
12	Ph Ph 41	Ph Ph 42	0.075	15	>99 (68)
13		Ph + 0 44	0.1	24	90 (67)
14	Ph 0 55	Ph O CO ₂ Me	0.2	15	81 (> 20:1) ^d
15		Ph 0 ~ CO ₂ Me	0.2	15	$66 (> 20:1)^d$
16 ^e	HO 59	MeO HO 60 H	0.2	15	$12 (> 9:1)^d$
17^e	CI 61	CI 62	0.1	15	$59 (> 20:1)^d$

^{*a*}Reaction conditions for RCM (entries 1–11): substrate (0.25 mmol), *cis*-Caz-1a, toluene (0.5 M), reflux, or neat, 120 °C for substrates 2, 11, 13. Reaction conditions for enyne-RCM (entries 12 and 13): substrate (0.25 mmol), *cis*-Caz-1a, toluene (0.1 M), reflux. Reaction conditions for CM (entries 14–17): substrate (0.25 mmol), alkene partner (1.25 mmol), *cis*-Caz-1a, toluene (0.5 M), reflux. ^{*b*}Average of two runs. Conversions were determined by ¹H NMR based on substrates. Isolated yields are given in parentheses. ^{*c*}A concentration of 0.05 M was used. ^{*d*}Isolated yields are given. E/Z ratios are given in parentheses. ^{*c*}A concentration of the substrate.

used and the reaction mixture was stirred for 5 h at 40 $^\circ\text{C}.$ The product was obtained as a brown solid (617 mg, 53%). ¹H NMR $(CD_2Cl_2, 400 \text{ MHz}): \delta \text{ (ppm) } 8.85 \text{ (dd, 1H, } {}^3J_{HH} = 7.3 \text{ Hz}, {}^4J_{HH} = 0.8$ Hz, indenylidene H⁷), 7.65 (m, 2H, indenylidene H⁹), 7.52-7.42 (m, 3H, indenylidene H¹¹ and H¹⁰), 7.34 (ddd, 1H, ${}^{3}J_{HH} = 7.3$ Hz, ${}^{4}J_{HH} =$ 0.8, indenylidene H⁶), 7.28 (ddd, 1H, ${}^{3}J_{HH}$ = 7.3 Hz, ${}^{4}J_{HH}$ = 0.8 Hz, indenylidene H⁵), 7.08 (d, 1H, ${}^{3}J_{HH} = 7.3$ Hz, indenylidene H⁴), 7.03 (s, 1H, mesityl CH), 7.01 (s, 1H, mesityl CH), 6.56 (s, 1H, indenylidene H²), 6.31 (s, 1H, mesityl CH), 6.20 (s, 1H, mesityl CH), 4.01-2.99 (m, 10H, carbene H⁴, H⁵ and CH₂CH₃), 3.55-3.26 (br s, 3H, CH₂CH₃), 2.68 (s, 3H, mesityl CH₃), 2.67 (s, 3H, mesityl CH₃), 2.42 (s, 3H, mesityl CH₃), 2.34 (s, 3H, mesityl CH₃), 1.98 (s, 3H, mesityl CH₃), 1.71 (s, 3H, mesityl CH₃), 1.05 (br s, 9H, CH₂CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz): δ (ppm) = 292.5 (d, ²J_{C-P} = 23.9 Hz, indenylidene C¹), 208.7 (d, ${}^{2}J_{CPcis}$ = 14.6 Hz, carbene C²'), 143.5 (s, C^{IV}), 141.2 (d, ${}^{3}J_{CP}$ = 3.1 Hz, indenylidene C^{7a}), 140.4 (d, ${}^{3}J_{CP}$ = 14.6 Hz, indenylidene C²H), 139.1 (s, C^{IV}), 138.8 (s, C^{IV}), 138.3 (s, C^{IV}), 138.2 (s, C^{IV}), 137.0 (s, C^{IV}), 136.6 (s, C^{IV}), 136.5 (s, C^{IV}), 135.5 (s, C^{IV}), 135.2 (s, C^{IV}), 130.4 (s, mesityl CH), 130.1 (s, indenylidene C⁷H), 130.0 (s, mesityl CH), 129.8 (s, mesityl CH),

129.5 (s, indenylidene C⁶H), 129.3 (s, indenylidene C⁵H), 129.2 (s, indenylidene C¹⁰H), 128.9 (s, indenylidene C¹¹H), 127.3 (s, indenylidene C⁹H), 117.3 (s, indenylidene C⁴H), 62.5 (br s, CH₂CH₃), 52.5 (s, carbene C⁵'H₂), 51.9 (s, carbene C⁴'H₂), 21.5 (s, mesityl CH₃), 21.1 (s, mesityl CH₃), 20.9 (s, mesityl CH₃), 19.4 (s, mesityl CH₃), 19.4 (s, mesityl CH₃), 19.4 (s, mesityl CH₃), 19.2 (s, mesityl CH₃), 16.4 (s, CH₂CH₃), 16.3 (s, CH₂CH₃). ³¹P-{¹H} NMR (CD₂Cl₂, 162 MHz): δ (ppm) 127.5. Anal. Calcd for C₄₂H₅₁Cl₂N₂O₃PRu: C, 60.43; H, 6.16; N, 3.36. Found: C, 60.57; H, 6.57; N, 3.60.

Dichloro[N,N'-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene](3phenylinden-1-ylidene)(triphenylphosphite)ruthenium (cis-**Caz-1d**). According to the general procedure, 4 equiv of triphenyl phosphite was used and the reaction mixture was stirred for 15 h at 40 °C. The product was obtained as a brown solid (500 mg, 76%). ¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) 8.72 (d, 1H, ³J_{HH} = 7.3 Hz, indenylidene H⁷), 7.52–7.43 (m, 1H, indenylidene H⁹), 7.42–7.28 (m, 5H, indenylidene H⁶, H¹⁰, and H¹¹), 7.23 (ddd, 1H, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 0.9 Hz, indenylidene H⁵), 7.14–6.59 (br m, 18H, P(OPh)₃ CH, mesityl CH and indenylidene H⁴), 6.32 (s, 1H, indenylidene H²), 6.24 (br s, 2H, mesityl CH), 4.09–3.71 (m, 4H, carbene H⁴' and H^{5'}), 2.81 (s, 3H, mesityl CH₃), 2.70 (s, 3H, mesityl CH₃), 2.46 (s, 3H, mesityl CH₃), 2.12 (s, 3H, mesityl CH₃), 2.04 (s, 3H, mesityl CH₃), 1.63 (s, 3H, mesityl CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz): δ (ppm) 293.2 (d, ²J_{CP} = 24.7 Hz, indenylidene C¹), 207.2 (d, ²J_{CP} = 13.5 Hz, carbene C^{2'}), 151.6 (d, ³J_{CP} = 13.2 Hz, P(OPh)₃ C^{IV}), 143.9 (s, C^{IV}), 141.3 (d, ³J_{CP} = 2.0 Hz, indenylidene C^{7a}), 140.3 (d, ³J_{CP} = 14.6 Hz, indenylidene C²H), 139.7 (s, C^{IV}), 139.1 (s, C^{IV}), 138.5 (s, C^{IV}), 138.4 (s, C^{IV}), 136.6 (s, C^{IV}), 136.3 (s, C^{IV}), 135.7 (s, C^{IV}), 134.3 (s, C^{IV}), 130.8 (s, mesityl CH), 130.7 (s, mesityl CH), 130.4 (s, indenylidene C⁵H), 129.3 (s, indenylidene C⁶H), 129.3 (s, indenylidene C⁶H), 129.3 (s, indenylidene C⁶H), 129.3 (s, indenylidene C⁶H), 129.4 (s, C^{IV}), 52.1 (s, carbene C^{4'}H₂), 21.6 (s, mesityl CH₃), 20.9 (s, mesityl CH₃), 20.8 (s, mesityl CH₃), 19.6 (s, mesityl CH₃), 19.6 (s, mesityl CH₃), 20.9 (s, mesityl CH₃), 19.2 (s, mesityl CH₃), 19.6 (s, mesityl CH₃), 19.6 (s, mesityl CH₃), 20.9 (s, mesityl CH₃), 19.2 (s, mesityl CH₃), 3¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ (ppm) 113.2. Anal. Calcd. for C₅₄H₅₁Cl₂N₂O₃PRu (978.94): C, 66.25; H, 5.25; N, 2.86. Found: C, 66.39; H, 5.15; N, 2.99.

Calorimetric Measurements. Two separate solutions containing the complex and the ligand were prepared: stock solution A, containing 30 mg (0.048 mmol) of $[\text{Ru}(\mu\text{-Cl})\text{Cl}(\eta^6\text{-cymene})]_2$ in CH₂Cl₂ (0.75 mL), and stock solution B, containing the ligand P(OR)₃ (0.293 mmol, 6 equiv) in CH₂Cl₂ (2 mL). The first container of the cell was charged with stock solution B (0.75 mL) and the second container with stock solution A (0.3 mL). The cell was placed in the calorimeter and the temperature stabilized at 30 °C. The solutions were then mixed, and a thermogram was recorded. The reported enthalpy of reaction is based on an average of three consistent measurements. $-\Delta H_{rm}$ (kcal/mol): P(OPh)₃, 34.1 ± 0.4; P(OMe)₃, 42.8 ± 0.6; P(OEt)₃, 42.9 ± 0.5; P(OⁱPr)₃, 43.2 ± 0.4. Relative bond dissociation energies (BDE) (kcal/mol): P(OPh)₃, 17.05; P(OMe)₃, 21.40; P(OEt)₃, 21.45; P(OⁱPr)₃, 21.60.³⁴

Computational Details. All calculations were performed with the Gaussian09 package (Revision A.1)³⁹ at the BP86 GGA level⁴⁰ using the SDD ECP on Ru⁴¹ and the split-valence plus one polarization function SVP basis set on all main-group atoms during geometry optimizations.⁴² The reported energies have been obtained via single point calculations on the BP86 geometries with triple- ζ valence plus polarization function TZVP basis set for main group atoms using the M06 functional.⁴³ Solvent effects, toluene and nitromethane, were included with the PCM model.⁴⁴

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving detailed experimental procedures for catalysis, for DFT calculations and calorimetric studies, UV–vis spectra of *cis*-Caz-1a and *trans*-Caz-1a, NMR spectra of complexes and metathesis products, and crystallographic data for *cis*-Caz-1b–d. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files of crystal structures for *cis*-Caz-1b-d have also been deposited with the CCDC (nos. 862342–862344, respectively). These data can be obtained free of charge from http://www.ccdc.cam. ac.uk.

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Notes

The authors declare no competing financial interest.

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(33) Conversions were determined by GC analysis based on substrate 9. An excess of ethyl vinyl ether was used to quench the reaction in each GC sample.

(34) See the Supporting Information for details.

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This paper was inadvertently published on the web on October 16, 2012, before all author corrections were applied. Corrections were made to Scheme 1, Table 1, and experimental section and the corrected version reposted on October 22, 2012.