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Mixed N-Heterocyclic Carbene/Phosphite Ruthenium Complexes: The Effect of a Bulkier NHC.

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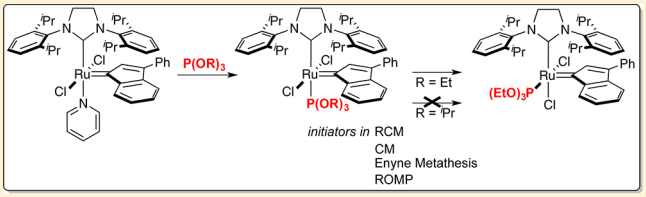
Supporting Information

ABSTRACT: The synthesis, characterization, and catalytic activity of two new complexes, **2a**,**b**, featuring a sterically demanding NHC and two different phosphites are described. Complexes **2a**,**b** display a mutually trans arrangement of the π-acidic phosphite and the strong σ-donor SIPr ligand (SIPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). The synergy between the phosphite and the NHC ligand was revealed in the RCM of challenging substrates leading to tetrasubstituted olefins where, in comparison to their phosphine-containing analogues, **2a**,**b** allowed higher conversions of these challenging substrates.



INTRODUCTION

Olefin metathesis catalysts bearing bulky N-heterocyclic carbene (NHC) ligands often display rapid initiation,[1] which in many cases translates into good catalytic activity and short reaction times. However, there is, with this increased activity, a concomitant increase in the decomposition rate, and usually these catalysts are less stable than complexes bearing SIMes (*N*,*N*′-bis[2,4,6-(trimethyl)phenyl]imidazolin-2-ylidene) (Figure 1).[2] For these reasons, olefin metathesis catalysts featuring bulky NHCs are mainly used for the synthesis of less hindered olefins,[3] as in general their reactivity toward the formation of tetrasubstituted bonds is poor.[4] In contrast, catalysts featuring less hindered NHCs such as *o*-SITol (*N*,*N*′-bis(2-methylphenyl)imidazolin-2-ylidene)[2a,5] display much better reactivity toward the synthesis of tetrasubstituted olefins; however, the activity in these complexes is affected by decomposition via C−H activation of the N-aryl substituents and in general the complexes are less active toward the synthesis of di- or trisubstituted double bonds than the SIMes or SIPr analogues.[2a,6]

It has previously been demonstrated that the stability of second-generation olefin metathesis catalysts, and therefore their activity in several metathesis transformations, can be easily tuned by substitution of the ligand trans to the NHC.[7] As part of recent efforts toward developing ever more active and robust olefin metathesis catalysts, our group developed a new strategy, replacing the commonly used tricyclohexylphosphine with a phosphite. This small modification led to the isolation of ***cis*-Caz-1**,[8] a latent catalyst at room temperature, which is extremely efficient when thermal activation is applied (Figure 2). ***cis*-Caz-1** is one of the most effective catalysts reported to date for the synthesis of tetrasubstituted double bonds[9] and is able to achieve turnover numbers (TONs) of up to 1000 for the synthesis of challenging olefins and up to 4700 for the synthesis of disubstituted double bonds.[8a,c] In contrast, specialized complexes for the synthesis of tetrasubstituted double bonds such as $[RuCl_2(Ind)(o\text{-SITol})PCy_3]$ and $[RuCl_2(=CHPh)(o\text{-SITol})PCy_3]$ are only able to achieve TONs of up to 196 and 138, respectively,[2a] while complexes bearing two NHCs are able to achieve TONs of up to 200.[7b,10]

The high activity of ***cis*-Caz-1** comes from its unusual structure; it was proposed that during the course of the reaction the cis species isomerizes to its trans isomer and then undergoes olefin metathesis,[8] which renders the cis complex a stable reservoir of active species during the reaction. This, together with a stronger bond between the phosphite and the Ru center, due to the strong π acidity of the phosphite, slows significantly the initiation rates of the complex, which renders it more stable than its PCy_3 analogue.[8] Further development of the NHC−phosphite combination led to the discovery of ***cis*-Caz-1$^+$**,[11] one of the rare examples of active cationic ruthenium precatalysts and by far the most active of this family.[12] ***cis*-Caz-1$^+$** is able to achieve TONs of up to 900 and TOFs of up 3600 for the synthesis of tetrasubstituted olefins.[11] As a continuation of this research theme, and with a view to find even more powerful catalysts that could be active at lower temperatures, we envisioned the combination of the effectiveness of the SIPr (*N*,*N*′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) ligand with the stability furnished by a phosphite ligand.

RESULTS AND DISCUSSION

Since the electronic and steric interactions between SIPr and the phosphite are difficult to predict, triisopropyl phosphite and

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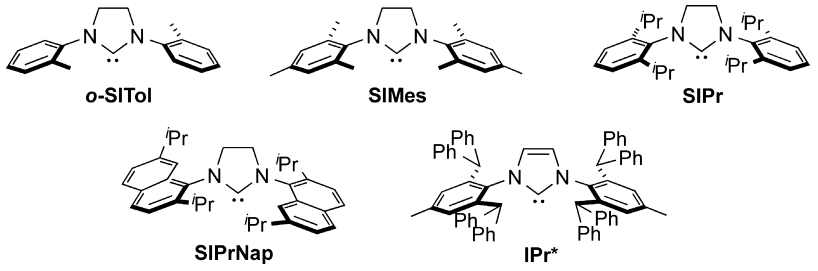


Figure 1. NHCs featured in olefin metathesis catalysts.

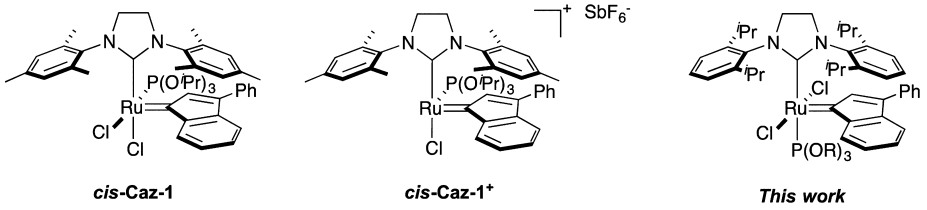
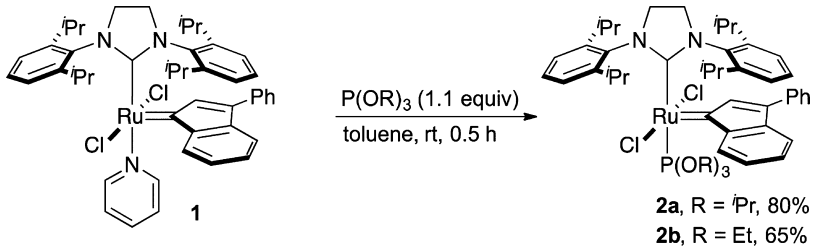


Figure 2. Mixed NHC−phosphite olefin metathesis catalysts.

Scheme 1. Synthesis of 2a,b



triethyl phosphite were chosen as ligands due to the different behavior observed in catalysis when SIMes-bearing complexes were used.[8c] While $P(O^iPr)_3$ afforded the right match between high stability and slow initiation required to achieve complete conversion in challenging transformations at competitive reaction times, the use of $P(OEt)_3$ resulted in a complex that initiates very slowly.

As for the SIMes congeners,[8a,c] the new complexes were synthesized by ligand exchange from the corresponding pyridine-containing complex. The reaction of $[RuCl_2(SIPr)(Ind)(Py)]$ (**1**) (Ind = 3-phenylinden-1-ylidene, Py = pyridine) with 1.1 equiv of the appropriate phosphite in toluene at room temperature afforded the desired complexes $[RuCl_2(Ind)(SIPr)\{P(O^iPr)_3\}]$ (**2a**) and $[RuCl_2(Ind)(SIPr)\{P(OEt)_3\}]$ (**2b**) (Scheme 1). After removal of the volatiles under vacuum and washing the crude material with methanol and pentane, the complexes were isolated as bright orange powders in good yields and excellent purity, as supported by elemental analysis data.

The ^1H NMR spectra of both complexes differ significantly; while the ^1H NMR spectrum of **2a** displays the expected splitting pattern for the nonequivalent isopropyl substituents of the SIPr ligand, in the spectrum of **2b** most signals are reduced to broad singlets, thus highlighting the fluxional behavior of this complex in solution. The $^{31}P\{^1H\}$ NMR spectra of complexes **2a,b** exhibit the expected singlets for the phosphites at 116.7 and 123.7 ppm, respectively. The $^{13}C\{^1H\}$ spectra of **2a,b** display the characteristic downfield doublets for the carbenic carbon of the indenylidene moiety (300.8 ppm ($^2J_{CP}$ = 21.3 Hz) and 301.0 ppm ($^2J_{CP}$ = 20.8 Hz), respectively), with coupling constants characteristic for the cis arrangement between the phosphite and the indenylidene ligand,[8] while the doublets for the carbenic carbon of the NHC (217.3 ppm ($^2J_{CP}$ = 134.8 Hz) and 217.4 ppm ($^2J_{CP}$ = 131.7 Hz), respectively) exhibit coupling constants typical for a trans arrangement between the phosphite and the NHC.[8]

The structure of **2a** was further confirmed by single-crystal X-ray diffraction (Figure 3, Table 1).[13] Suitable crystals were obtained by cooling a saturated solution of the complex in a CH_2Cl_2/MeOH mixture (1/4 v/v).

Complex **2a** exhibits the expected distorted-square-pyramidal geometry around the metal center, with the two chloride ligands and with the SIPr and the phosphite in mutually trans

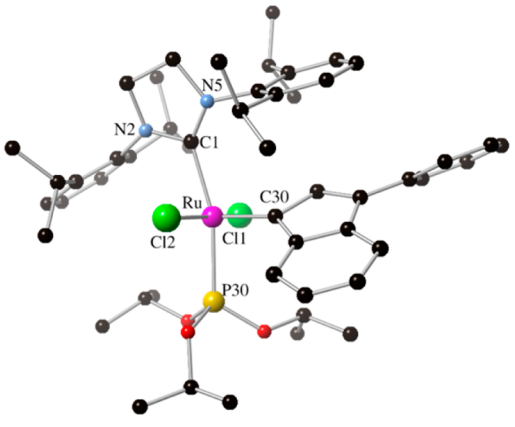


Figure 3. Molecular representation of **2a**. Hydrogen atoms are omitted for clarity.

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Table 1. Selected Bond Distances (Å) and Angles (deg) In Complexes 2a and 3

	[$RuCl_2$(Ind)(SIPr){P(O^iPr)$_3$}] (**2a**)	[$RuCl_2$(Ind)(SIPr)(PCy_3)] (**3**)[4c]
Ru(1)−C(1)	2.130(5)	2.1019(11)
Ru(1)−C(30)	1.854(5)	1.8604(11)
Ru(1)−P(30)	2.3402(15)	2.4446(3)
Ru(1)−Cl(1)	2.3797(13)	2.3890(3)
Ru(1)−Cl(2)	2.3746(13)	2.3885(3)
C(31)−Ru(1)−C(1)	104.3(2)	102.25(4)
C(31)−Ru(1)−P(1)	90.56(15)	95.59(3)
P(30)−Ru(1)−C(1)	164.48(16)	162.13(3)
Cl(1)−Ru(1)−Cl(2)	168.15(5)	164.373(10)
N(2)−C(3)−C(4)−N(5)	−15.8(4)	25.94(12)

arrangements, while the apical position is occupied by the indenylidene ligand. Bond distances and angles were within the expected ranges for Ru−indenylidene complexes such as [$RuCl_2$(SIPr)(Ind)(PCy_3)] (**3**).[1e,4c,d,7d,8,14] Interestingly, the shorter bond distance for Ru(1)−P(30) in **2a** suggests a stronger bond between the phosphite and the metal center which can slow the initiation of the complex, thus rendering it more stable at higher temperatures.

In contrast, with SIMes analogues such as **Caz-1** that undergo relatively easy trans to cis isomerization,[8a,c] the cis configuration in the SIPr-containing congeners appears to be disfavored. This is illustrated by the fact that the cis isomer of **2a** was not observed[15] and that **2b** showed very slow isomerization to the cis isomer. *cis*-**2b** could not be cleanly isolated, as isomerization occurred simultaneously with decomposition.[15] The fact that the SIPr analogues isomerize with difficulty is likely due to the higher steric bulk of the NHC ligand (%V_{bur} = 32.5) in comparison to SIMes (%V_{bur} = 30.0),[15,16] hence impeding the formation of the cis isomer. Steric arguments can also explain the difference in reactivity of **2a** versus **2b**, as the cis isomer is only observed in the system bearing the smallest phosphite ligand, **2b** (Tolman cone angle θ = 109° for P(OEt)$_3$ and 130° for P(O^iPr)$_3$).[17]

The stabilizing effect of phosphites as ligands in second-generation complexes was once more demonstrated with the new complexes **2a**,**b**; while the parent compound bearing tricyclohexylphosphine is almost completely decomposed after 24 h at 40 °C,[4c] the new complexes are very stable and little decomposition is observed after this time interval.

Complexes **2a**,**b** were first evaluated in the ring-closing metathesis (RCM) of diethyl diallylmalonate (**4**) and dimethyl allylmethallylmalonate (**6**). When the reactions were carried out at room temperature with 1 mol % of precatalysts, 2.5−3.5 h was required to reach full conversions (Table 2, entries 1, 2, 10, and 11), while only 30 min was necessary with the parent pyridine-containing complex **1** or the tricyclohexylphosphine-containing complex **3**. Such results highlight the stabilizing effects of the phosphites in this catalysis.

Following our initial goal to reduce the amount of catalyst used, lower catalyst loading experiments were carried out. With 0.1 mol % of **2a** at room temperature, full conversion of **4** was achieved in dichloromethane while only 73% was obtained in toluene (Table 2, entries 3 and 4). The catalyst loading was further decreased to 0.05 mol %, and in that case, at room temperature, 22 h of reaction was necessary to reach 92% conversion (Table 2, entry 5). In order to reduce the reaction time, the temperature was increased to 50 °C, and after 8 h,[18] 93% conversion was obtained (Table 2, entry 6). Changing the solvent to toluene or methyl *tert*-butyl ether (MTBE), which are known to be good alternatives to chlorinated solvents for metathesis,[4c,6b,19] led to similar conversions (Table 2, entries 7 and 8). Complex **2b**, featuring the P(OEt)$_3$ ligand, at 0.05 mol % in dichloromethane at 50 °C allowed for better conversion than **2a** (Table 2, entry 9). A similar trend was observed in the RCM of **6**. For this particular transformation it was possible to further decrease the catalyst loading to 0.025 mol % and achieve excellent conversions, with **2b** showing again a better activity (Table 2, entries 12 and 13). In addition, it was found that only 2 h of reaction was necessary to reach complete conversion with **2b**. Comparison of these data with those reported in the same RCM reaction for ***cis*-Caz-1**[8c] and **3**[4c] shows that while there is a real benefit in using the SIPr ligand in comparison to SIMes with phosphites, complex **3**, bearing tricyclohexylphosphine, is still more active than phosphite analogues for this substrate.

However, when comparison is made in the synthesis of the highly hindered olefin **9**, the superiority of phosphite adducts is evident. Indeed, at 50 °C, using 2 mol % of **2a**,**b** led to good conversion of the challenging substrate **8**, while with the phosphine adduct **3** poor conversions were reported using 5 mol % loading at 80 °C.[4c] On the other hand, comparison with the SIMes analogue of **2**, ***cis*-Caz-1**, is less straightforward, as under similar conditions (50 °C) ***cis*-Caz-1** is less active, a quantitative yield of the desired product can be obtained using 1 mol % of Ru within 1.5 h, but at an operating temperature of 80 °C.[8c] It is worth noting that complexes featuring the less sterically demanding NHC *o*-SITol, [$RuCl_2$(Ind)(*o*-SITol)-PCy_3] and [$RuCl_2$(=CHPh)(*o*-SITol)PCy_3], are able to achieve conversions of 55% for substrate **9** using only 0.5 mol % of catalyst at 60 °C.[2a]

The use of **2a**,**b** at low catalyst loading was next evaluated with benchmark substrates in RCM, enyne metathesis, and cross metathesis (CM). Reactions were performed under the optimized conditions, with the reaction time set to 3 h (Table 3). The five-, six- and seven-membered ring malonates **5**, **11**, and **13** were isolated in excellent yields with catalysts loadings as low as 0.05 mol % (Table 3, entries 1−3). Interestingly, lower catalyst loadings were required for the synthesis of **7** in comparison with those for **5**, and although no explanation has been found, it is a common observation for SIPr-bearing catalysts.[4d,7e] Tosylamine-containing **14** was also cyclized with 0.075 mol % of **2a** (Table 3, entry 4). Slightly more hindered substrates leading to the synthesis of trisubstituted olefins were then tested. Interestingly, malonate **6** required only 0.025 mol % of precatalysts **2a**,**b** (Table 3, entry 5) to reach high conversions, an observation consistent with the literature for SIPr-containing catalysts.[4d,7e] Ether-containing **16** could also be converted to **17** efficiently with 0.075 mol % of catalyst (Table 3, entry 6). Finally, dienes **18** and **8** leading to tetrasubstituted alkenes were evaluated and moderate to good conversions were observed. **2a**,**b** were also found to be efficient in enyne metathesis and achieved complete conversions to dienes **21** and **23**. Complexes **2a**,**b** also proved efficient in cross metathesis, and compounds **25** and **27** were isolated in good yields (Table 3, entries 11 and 12).

Although the complexes [$RuCl_2$(Ind)(*o*-SITol)PCy_3] and [$RuCl_2$(=CHPh)(*o*-SITol)PCy_3] were more efficient for the synthesis of tetrasubstituted olefin **9**, complexes **2a**,**b** are significantly more efficient for the synthesis of compound **21** by enyne metathesis, and while complete conversions were

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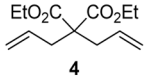
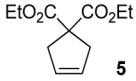
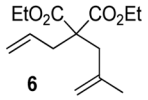
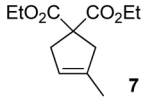
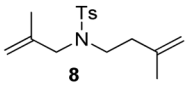
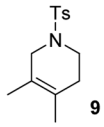
Table 2. Optimization in RCM with 2a,b[a]

	Substrate	Product	[Ru]	mol%	Solvent	T (°C)	t (h)	Conv.(%)[b]
1			**2a**	1	CH_2Cl_2	rt	2.5	>99
2			**2b**	1	CH_2Cl_2	rt	2.5	>99
3			**2a**	0.1	CH_2Cl_2	rt	8	>99
4			**2a**	0.1	toluene	rt	8	73
5	 **4**	 **5**	**2a**	0.05	CH_2Cl_2	rt	22	92
6			**2a**	0.05	CH_2Cl_2	50	8	93
7			**2a**	0.05	toluene	50	8	88
8			**2a**	0.05	MTBE	50	8	90
9			**2b**	0.05	CH_2Cl_2	50	8	99
10			**2a**	1	CH_2Cl_2	rt	3.5	>99
11			**2b**	1	CH_2Cl_2	rt	3.5	>99
12	 **6**	 **7**	**2a**	0.025	CH_2Cl_2	50	2	96
13			**2b**	0.025	CH_2Cl_2	50	2	>99
14[4d]			**3**	0.025	CH_2Cl_2	30	1	99
15[8c]			***cis*-Caz-1**	0.075	toluene	120	15	>99
16			**2a**	2	CH_2Cl_2	50	3	75
17	 **8**	 **9**	**2b**	2	CH_2Cl_2	50	3	61
18[4c]			**3**[c]	5	toluene	80	1	23[d]
19[8c]			***cis*-Caz-1**	1	toluene	80	1.5	>99

[a]Reaction conditions: substrate (0.25 mmol), precatalyst, solvent (0.5 M). [b]Average of two runs; conversions were determined by ^{1}H NMR based on diene. [c]Reaction conditions: substrate (0.5 mmol), precatalyst, solvent (0.1 M). [d]Isolated yield.

achieved using **2a,b** with a catalyst loading of 0.2 mol% at 50 °C, the complex $[RuCl_2(Ind)(o\text{-SITol})PCy_3]$ requires 2 mol % at room temperature to achieve the same conversion.[2a] This shows that, for less challenging transformations, the combination of a bulky NHC and a phosphite is beneficial.

We were next interested in testing the activity of complexes of type **2** in ring-opening metathesis polymerization (ROMP) reactions. Due to the similar catalytic performance of **2a,b** in ring-closing, enyne, and cross-metathesis reactions, only the initiator **2a** was employed for the polymerization studies. The ROMP characteristics of initiator **2a** were investigated on the basis of the polymerization of *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**Mon1**; see Table 4). **Mon1** has been used as the benchmark monomer in previous reports since the resulting polymers, even with number-average molecular weights (M_n) of more than 1000000, are quite soluble in CH_2Cl_2, toluene, or THF and secondary metathesis (so-called back-biting) hardly occurs. Accordingly, data from gel permeation chromatography readily permits the assessment of initiation efficacy of novel initiators. Together with an evaluation of the kinetics of the polymerization, carried out by polymerizing *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-diphenyl ketone (**Mon2**) and monitoring the reaction by NMR spectroscopy, a fast protocol for benchmarking ROMP initiators is available.[4d,7d,16d,20]

Compound **2a** is a slow initiator at room temperature, giving a polymer characterized with a M_n value of 131000 g/mol and a polydispersity index (PDI) of 1.6 (Table 4, entry 1): i.e.,

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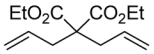
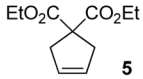
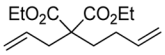
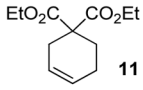
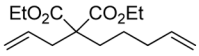
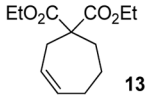
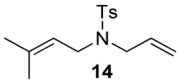
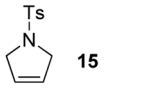
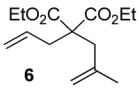
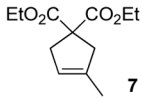
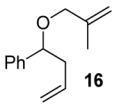
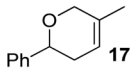
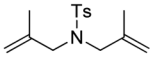
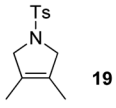
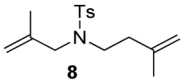
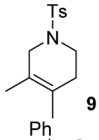
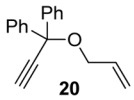
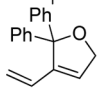
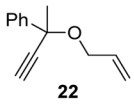
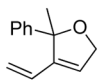
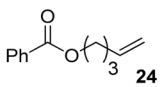
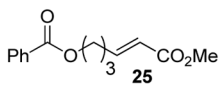
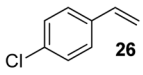
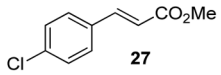
Table 3. Experiments at Different Catalyst Loadings in the Presence of 2a,b[a]

Entry	Substrate	Product	Catalyst	Loading (mol%)	Conv. (Yield)[b] (%)
1	 4	 5	**2a**	0.075	>99 (95)
			2b	0.05	>99 (97)
2	 10	 11	**2a**	0.1	>98 (97)
			2b	0.075	>99 (92)
3[c]	 12	 13	**2a**	0.1	>99 (94)
			2b	0.1	>99 (91)
4	 14	 15	**2a**	0.075	94 (92)
			2b	0.1	95 (88)
5	 6	 7	**2a**	0.025	96 (95)
			2b	0.025	>99 (99)
6	 16	 17	**2a**	0.075	94 (89)
			2b	0.1	>99 (89)
7	 18	 19	**2a**	2	46 (46)
			2b	2	47 (46)
8	 8	 9	**2a**	2	75 (74)
			2b	2	61 (59)
9[d]	 20	 21	**2a**	0.2	>99 (94)
			2b	0.2	>99 (94)
10[d]	 22	 23	**2a**	0.1	>99 (88)
			2b	0.1	>99 (94)
11[e]	 24	 25	**2a**	0.2	80 (>20:1)[f]
			2b	0.2	77 (>20:1)[f]
12[d,e]	 26	 27	**2a**	0.2	69 (>20:1)[f]
			2b	0.2	58 (>20:1)[f]

[a]Reaction conditions: substrate (0.25 mmol), **2a,b**, CH_2Cl_2 (0.5 M), reflux, 3 h. [b]Average of two runs; conversions were determined by ^{1}H NMR based on diene; isolated yields in parentheses. [c]0.05 M. Identity of the product confirmed by HRMS. [d]0.1 M. [e]Reaction conditions: substrate (0.25 mmol), methyl acrylate (1.25 mmol), **2a,b**, CH_2Cl_2 (0.5 M), reflux, 3 h. [f]Isolated yields (*E*/*Z* ratio).

initiation and propagation rate constants are approximately of the same order of magnitude. The M_n value is considerably higher than that of the polymer obtained with initiator **3** (Table 4, entry 2) but polymerization is considerably faster than in the case of using the initiator ***cis*-Caz-1** (Table 4, entry 3). Comparing the performance to other SIMes-based congeners with *trans*-dichloro geometry such as $[RuCl_2(Ind)(SIMes)(PCy_3)]$ (**28**) and $[RuCl_2(Ind)(SIPr)(Py)]$ (**29**) revealed a somewhat better initiation efficacy of **2a** in comparison to **28** (Table 4, entry 4). The result for **29** reflects the case of an initiator providing fast and complete initiation (Table 4, entry 5).[21] For the polymerization of **Mon1** with **2a** at 40 and 80 °C

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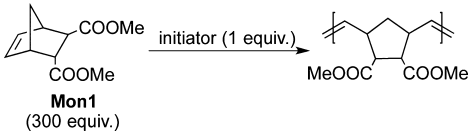
Table 4. Polymerization of Mon1 with Different Initiators[a]



entry	initiator	solvent	temp (°C)	time[b] (h)	M_n[c]	PDI[c]
1	$[RuCl_2(Ind)(SIPr)\{P(O^iPr)_3\}]$ (**2a**)	CH_2Cl_2	20	8	131000	1.6
2	$[RuCl_2(Ind)(SIPr)(PCy_3)]$ (**3**)	CH_2Cl_2	20	2	52000	1.3
3	$[RuCl_2(Ind)(SIMes)\{P(O^iPr)_3\}]$ (***cis*-Caz-1**)	CH_2Cl_2	20	24[d]	n.d.[d]	n.d.[d]
4	$[RuCl_2(Ind)(SIMes)(PCy_3)]$ (**28**)	CH_2Cl_2	20	4	300000	2.0
5	$[RuCl_2(Ind)(SIMes)(Py)]$ (**29**)	CH_2Cl_2	20	0.25	48000	1.05
6	$[RuCl_2(Ind)(SIPr)\{P(O^iPr)_3\}]$ (**2a**)	toluene	40	3	80700	1.5
7	$[RuCl_2(Ind)(SIMes)\{P(O^iPr)_3\}]$ (***cis*-Caz-1**)	toluene	40	50	235000	2.0
8	$[RuCl_2(Ind)(SIPr)\{P(O^iPr)_3\}]$ (**2a**)	toluene	80	0.25	73300	1.3
9	$[RuCl_2(Ind)(SIMes)\{P(O^iPr)_3\}]$ (***cis*-Caz-1**)	toluene	80	1	106000	1.8

[a]Reaction conditions: monomer/initiator = 300/1; concentration of the monomer 0.1 mol/L. [b]Tentative time for complete conversion of the monomer as checked every 30 min by TLC; isolated yields were 75−85%. [c]Determined by gel permeation chromatography in THF, calibrated against poly(styrene) standards. [d]Low conversion, ∼10%.

in toluene, the M_n and PDI values as well as the polymerization time decrease with increasing temperature (Table 4, entries 6 and 8), rendering **2a** more active than ***cis*-Caz-1** (Table 4, entries 7 and 9).

Additionally, kinetic data were obtained by monitoring the progress of the polymerization reaction involving **Mon2** with various initiators via ^1H NMR (Figure 4). For initiator **2a**, a

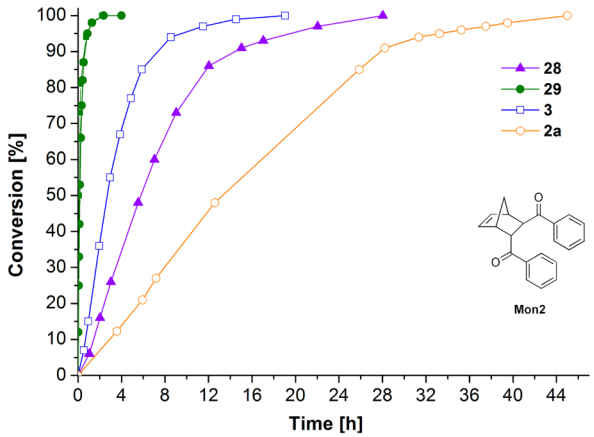


Figure 4. Kinetic plots of the polymerization of **Mon2** with **2a** and its congeners (lines are visual aids and not curve fits). Reaction conditions: monomer/initiator = 50/1, $CDCl_3$, 25 °C, concentration of the monomer 0.1 mol/L.

polymerization half-life of 13.2 h was determined, which is considerably more than the half-life for the polymerization with the SIPr-PCy_3 derivative **3** (2.8 h) or the SIMes-PCy_3 derivative **28** (5.8 h). ***cis*-Caz-1** gives a conversion of less than 10% after 44 h under these conditions (the corresponding curve is not shown in Figure 4). The polymerization experiments can be summarized by the following points: **2a** is a much more active initiator than ***cis*-Caz-1**. The higher activity can be above all attributed to the stereochemistry of **2a**, which has a *trans*-dichloro arrangement, in contrast to ***cis*-Caz-1**, which features a *cis*-dichloro arrangement. **2a** is less active than its PCy_3 congener **3**, which can be explained by a lower initiation efficacy and the higher recoordination tendency of the phosphite in comparison to the phosphine ligand during propagation. The recoordination of the phosphite is also held responsible for the remarkable stability of the propagating polymer chain. Polymerizations with **2a** (and with ***cis*-Caz-1**) can be performed in air, and no detrimental effects of the presence of oxygen on the molecular weight or polydispersity are observed.

CONCLUSION

The synthesis, characterization, and catalytic activity at low loadings of two new complexes featuring a sterically demanding NHC and two different phosphites have been described. In contrast to previously described phosphite-bearing complexes, precatalysts **2a,b** were only cleanly isolated with the phosphite and SIPr ligand in a mutually trans orientation. Nevertheless, for **2b**, the cis isomer could be observed by NMR spectroscopy. **2a,b** proved to be efficient in catalysis, requiring shorter reaction times to achieve complete conversion in comparison to their SIMes-bearing analogue ***cis*-Caz-1**. The improvement due to the introduction of the phosphite ligand was revealed in the RCM of challenging substrates leading to tetrasubstituted olefins. Indeed, in comparison to their phosphine-containing analogues, **2a,b** led to improved isolated yields of challenging compounds. **2a,b** were also found to be highly efficient in enyne and cross metathesis, with good yields obtained at low loadings.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under argon using standard Schlenk or glovebox techniques. Solvents (dichloromethane, toluene) were dried using a Solvent Purification System (SPS). All other reagents and solvents were used without further purification. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer or an AVANCE-300 spectrometer using the residual solvent peak as reference ($CHCl_3$, δ_H = 7.26 ppm, δ_C = 77.16 ppm; CH_2Cl_2, δ_H = 5.32 ppm, δ_C = 53.80 ppm) at 298 K (C^{IV} = quaternary carbon; for multiplets in which $J_1 = J_2$ only one coupling constant is reported).

Synthesis of Complexes 2a,b. *General Procedure.* Inside a glovebox, the phosphite (0.66 mmol) was added to a solution of $[RuCl_2(SIPr)(Py)(Ind)]$ (500 mg, 0.60 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 30 min, and the solvents were removed under vacuum. The resulting solid was washed with cold MeOH (3 × 5 mL) and cold pentane (3 × 5 mL).

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*Dichloro[N,N′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene](3-phenylinden-1-ylidene)(triisopropyl phosphite)ruthenium (**2a**).* The general procedure afforded **2a** as an orange solid (460 mg, 0.48 mmol, 80%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.78 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, H^7), 7.57 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, H^9), 7.51 (dd, $^3J_{HH}$ = 7.5 Hz, 1 H, H$^{9\prime}$), 7.29−7.44 (m, 7 H, H$^{8\prime}$ H^{10} H^{11}), 7.23 (dd, $^3J_{HH}$ = 7.3 Hz, 1 H, H^5), 7.14 (dd, $^3J_{HH}$ = 7.2 Hz, 1 H, H^6), 7.01 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, H^4), 6.74 (d, $^3J_{HH}$ = 7.3, Hz, 1 H, H$^{12\prime}$), 6.63 (dd, $^3J_{HH}$ = 7.7 Hz, 2 H, H$^{12\prime}$ H$^{13\prime}$), 6.28 (s, 1 H, H^2), 4.46 (sept, $^3J_{HH}$ = 6.3, 1 H, CH iPr$_{NHC}$), 3.89−4.15 (m, 3 H, H$^{4/a}$ H$^{4/b}$ H$^{3/a}$), 3.61−3.89 (m, 6 H, H$^{3/b}$ CH ^{i}Pr$_{NHC}$ CH ^{i}Pr$_{phosphite}$), 3.00 (sept, $^3J_{HH}$ = 7.0 Hz, 1 H, CH ^{i}Pr$_{NHC}$), 1.60−1.64 (m, 6 H, CH$_3$ ^{i}Pr$_{NHC}$), 1.54 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH$_3$ ^{i}Pr$_{NHC}$), 1.28−1.29 (m, 3 H, CH$_3$ ^{i}Pr$_{NHC}$), 1.20−1.24 (m, 6 H, CH$_3$ ^{i}Pr$_{NHC}$), 0.95 (d, $^3J_{HH}$ = 6.0 Hz 9 H, CH$_{3phosphite}$), 0.85 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH$_{3phosphite}$), 0.73 (d, $^3J_{HH}$ = 5.9 Hz 9 H, CH$_{3phosphite}$), 0.44 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH$_{3phosphite}$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ (ppm) 300.8 (d, $^2J_{CP}$ = 21.1 Hz, C^1), 217.3 d, ($^2J_{CP}$ = 135.2 Hz, C$^{1\prime}$), 150.3 (s, C^{IV}), 149.9 (s, C^{IV}), 148.3 (s, C^{IV}), 147.6 (s, C^{IV}), 146.8 (s, C^{IV}), 143.5 (s, C^{IV}), 143.4 (s, C^{IV}), 141.3 (s, C^{IV}), 140.7 (s, C^{IV}), 137.7 (s, C^2), 136.9 (s, C^{IV}), 136.8 (s, C^{IV}), 135.9 (s, C^{IV}), 131.5 (s, C^7), 130.2 (s, C^{11} C$^{13\prime}$), 129.5 (s, C^5), 128.9 (s, C^6), 128.2 (C$^{9\prime}$), 127.1 (C^9), 125.6 (s, CH), 125.3 (s, CH), 124.7(s, CH), 124.0 (s, C^{12}), 117.0 (s, C^4), 69.2 (d, $^2J_{CP}$ = 4.3 Hz, CH ^{i}Pr$_{phosphite}$) 55.2 (d, $^4J_{CP}$ = 5.4 Hz, C$^{4\prime}$), 55.0 (d, $^4J_{CP}$ = 3.5 Hz, C$^{3\prime}$), 30.2 (s, CH ^{i}Pr$_{NHC}$), 29.3 (s, CH ^{i}Pr$_{NHC}$), 28.8 (s, CH ^{i}Pr$_{NHC}$), 27.3 (s, CH ^{i}Pr$_{NHC}$), 26.8−27.3 (m, CH ^{i}Pr$_{NHC}$) 23.6−24.4 (m, CH ^{i}Pr$_{NHC}$ CH ^{i}Pr$_{phosphite}$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz): δ (ppm) 116.65 (s). Anal. Calcd for $C_{51}H_{69}Cl_2N_2O_3PRu$: C, 63.74; H, 7.24; N, 2.91. Found: C, 63.73; H, 7.46; N, 3.02.

*Dichloro[N,N′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene](3-phenylinden-1-ylidene)(triethyl phosphite)ruthenium (**2b**).* The general procedure afforded **2b** as an orange solid (358 mg, 0.39 mmol, 65%). ^{1}H NMR (300 MHz, C_6D_6): δ (ppm) 9.41 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, H^7), 7.66 (d, $^3J_{HH}$ = 7.2 Hz, 2 H^9) 7.16 (br m, 9 H, H$_{Ar}$), 6.51−6.88 (m, 4 H, H$_{Ar}$), 4.63 (br s, 1 H, CH$_2$ NHC), 4.06 (br s, 1 H, CH$_2$ NHC), 3.12−3.94 (m, 12 H, H^3 H^4 CH ^{i}Pr CH$_{2phosphite}$), 1.85 (br s, 9 H, CH$_{3phosphite}$), 0.53−1.49 (m, 24 H, CH$_3$ ^{i}Pr). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ (ppm) 301.0 (d, $^2J_{CP}$ = 20.8 Hz, C^1), 217.7 (d, $^2J_{CP}$ = 131.7 Hz, C$^{1\prime}$), 150.5 (s, C^{IV}), 143.5 (s, C^{IV}), 143.4 (s, C^{IV}), 141.1(s, C^{IV}), 140.7 (s, C^{IV}), 137.7 (s, C^2), 136.8(s, C^{IV}), 136.5 (s, C^{IV}), 135.6 (s, C^{IV}), 131.2 (s, C^7), 130.1 (s, C$^{9\prime}$), 130.1(s, C$^{13\prime}$), 129.6 (s, C^5), 128.9 (s, 2C, C^{10}), 128.8 (s, C^6), 128.3 (s, C^{11}), 127.1 (s, C^9), 124.7 (s, C$^{8\prime}$), 124.0 (s, C$^{12\prime}$) 117.2 (s, C^4), 60.8 (d, $^2J_{CP}$ = 3.0 Hz, CH$_{2phosphite}$), 55.2 (d, $^4J_{CP}$ = 5.5 Hz, C$^{4\prime}$), 55.0 (d, $^4J_{CP}$ = 3.4 Hz, C$^{4\prime}$), 27.2 (s, CH$_3$ NHC), 27.0 (s, CH$_3$ NHC), 23.7 (s, CH$_3$ NHC), 16.1 (d, $^3J_{CP}$ = 6.4 Hz, CH$_{3phosphite}$). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ (ppm) 123.7 (s). Anal. Calcd for $C_{48}H_{63}Cl_2N_2O_3PRu$: C, 62.73, H, 6.91, N, 3.05. Found: C, 62.59, H, 6.84, N, 3.22.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and a CIF file giving procedures for catalysis, NMR spectra of complexes and catalysis products, procedure and NMR spectra for the isomerization of **2b**, crystal data and structure refinement details for **2a**, calculations for % V_{Bur}, and topographical steric maps. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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