A New, Highly Active Bimetallic Grubbs–Hoveyda–Blechert Precatalyst for Alkene Metathesis

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A new Grubbs−Hoveyda−Blechert alkene metathesis catalyst, in which the benzylidene ligand has been coordinated to a highly electron-withdrawing tricarbonylchromium moiety, is presented. The structure of the complex provides evidence for a so far unreported attractive interaction between the benzylidene hydrogen atom and one of the mesityl substituents at the Arduengo carbene ligand. Screening of the catalytic properties shows that the activity of the new catalyst in ring-closing, enyne, cross, and homo metathesis of alkenes is comparable and in some cases better than that of known catalysts.

Introduction

The development of efficient catalysts compatible with numerous functional groups has caused metathesis to become a powerful method for the construction of carbon−carbon bonds.[1–6] The metathesis catalysts frequently used predominantly include ruthenium and molybdenum carbene complexes, the latter ones usually being more sensitive as compared to the ruthenium systems. In addition to improvements in the efficiency of the catalysts, a number of other variations such as catalyst immobilization[7,8] or the introduction of chirality[9–18] adapted the catalyst properties to demands of practicability or asymmetric catalysis. In this rapidly developing field the design of new catalysts with improved application profiles continues to be an important challenge (Chart 1).

While **1** (Grubbs I) is among the first catalysts being routinely used for alkene metathesis, ruthenium phosphane complexes **2** and **3** bearing Arduengo carbene ligands instead of one of the phosphane ligands have been shown to be more efficient.[19,20] Phosphane-free isopropoxy chelate complexes **4**−**6** and double chelates **7** and **8**, a group of catalysts introduced by Hoveyda, Blechert, and Grela, show an expanded application profile associated with enhanced catalytic activity and stability.[21–24] Carbene complexes **6** and **8** show a significant increase in catalytic activity as compared to **4**, **5**, and **7**, because of a weakened coordination of the oxygen atom positioned *para* to the nitro group.

The electron-withdrawing effect of the nitro substituent in **6** is mainly directed to the *ortho* and *para* positions, and consequently the benzylidene carbon atom, which is coordinated to ruthenium, should be comparatively less affected. This is nicely reflected by inspection of the NMR properties of the benzylidene moiety, indicating rather similar benzylidene proton chemical shifts for **4** (δ = 16.56 ppm) and for **6** (δ = 16.42 ppm).[24–26]

(Arene)tricarbonylchromium complexes have been known for decades and are among the most important arene complexes

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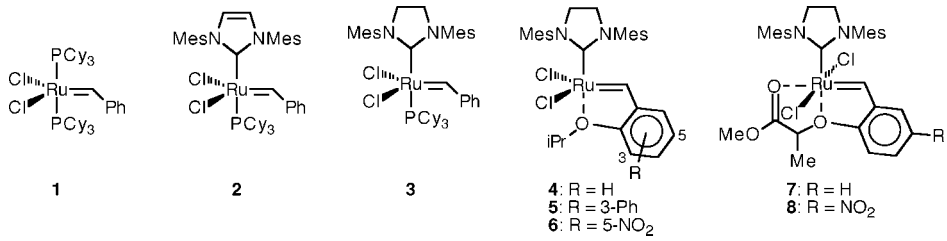
Chart 1. Alkene Metathesis Catalysts (Mes = 2,4,6-trimethylphenyl)

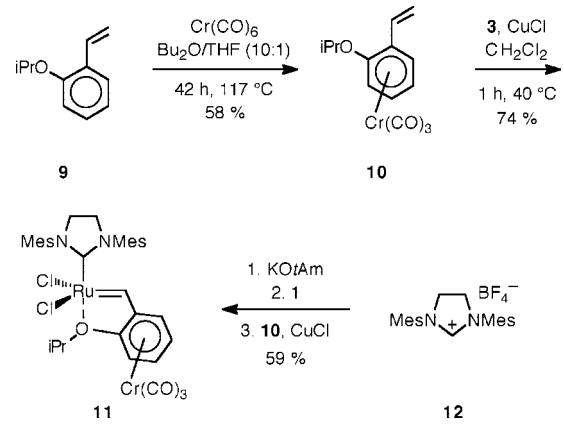


with respect to organic synthesis. Among other features the facial differentiation at the coordinated arene and the electron withdrawal of the tricarbonylchromium moiety have been exploited for stereoselective synthesis, dearomatization, and many other reactions not possible in the absence of the tricarbonylchromium group.[27–45] The extent of its electron withdrawal is comparable to that of a *para* nitro group, as indicated by pK_a comparison of the respective phenylacetic acids.[46]

In contrast to an electron-withdrawing substituent such as a nitro group at an arene, its coordination at tricarbonylchromium causes the electron withdrawal to affect all six carbon atoms of the arene ring and the groups attached to them. In order to reduce the electron density in **6** not only at the chelating oxygen atom but also at the benzylidene moiety, we envisaged the bimetallic precatalyst **11** with a π-coordinated tricarbonylchromium group at the benzylidene ligand.[47] In addition to its electron withdrawal the steric bulk of the tricarbonylchromium group due to its proximity to the ruthenium atom in **11** might have some influence in its catalytic properties. Here we present the synthesis and full spectroscopic and structural characterization of **11** as well as an investigation of the catalytic profile of this bimetallic complex with respect to alkene metathesis.

Results and Discussion

Treatment of *ortho*-isopropoxystryrene (**9**) with hexacarbonylchromium in dibutyl ether/THF (10:1)[34] afforded chromium complex **10** in racemic form in 58% yield as a bright yellow powder after purification by column chromatography. The constitution of **10** was confirmed by characteristic IR absorptions at 1941 and 1837 cm^{-1} as well as by fully consistent ^1H and ^{13}C NMR spectra. The mass spectrum shows the molecular ion peak and the fragmentation pattern typical for (arene)tricarbonylchromium complexes. Reaction of **10** with Grubbs catalyst **3** in the presence of CuCl as a tricyclohexylphosphane scavenger gave the racemic bimetallic complex **11** in 74% yield as a dark red powder.[48] Alternatively, **11** was obtained in 59% overall yield by a one-pot procedure from the commercially available Grubbs I catalyst **1**: 1,3-dimesitylimidazolium tetrafluoroborate (**12**) was treated with potassium *tert*-amylate, followed by addition of **1** and then by addition of **10** and CuCl.



11 was characterized spectroscopically. The ^1H NMR chemical shift of the signal assigned to the benzylidene H atom is δ = 15.49 ppm, a value considerably different from those of **4** and **6** (*vide supra*). The effect of the tricarbonylchromium moiety on the benzylidene part of the ligand system is also reflected by the ^{13}C NMR data of the benzylidene carbon atom. While the respective resonance is observed at δ = 297.3 ppm for **4** and at δ = 289.1 ppm for **6**, it appears at δ = 285.4 ppm for **11** if measured in CD_2Cl_2 and at δ = 283.5 ppm in C_6D_6.

Another unusual observation is the fact that in the ^1H NMR spectra the signals assigned to the mesityl protons appear as a broadened singlet when the spectrum was recorded in CD_2Cl_2, whereas there are two singlet signals when deuterated benzene was used as the solvent. In addition, the signal assigned to the *ortho*-methyl groups of the mesityl substituents is a sharp singlet in CD_2Cl_2, whereas it is significantly broadened in C_6D_6 (Figure 1). ^1H NMR measurements in C_6D_6 do not show coalescence up to 345 K.

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(48) The synthesis of enantiomerically pure **11** would start from enantiomerically pure **10**, which might be obtained by resolution of **10** by chiral HPLC. However, as the planar chiral (*o*-isopropoxybenzylidene)tricarbonylchromium moiety is separated from the catalytically active ruthenium part in the catalytic cycle, we refrained from preparing **11** in enantiomerically pure form.

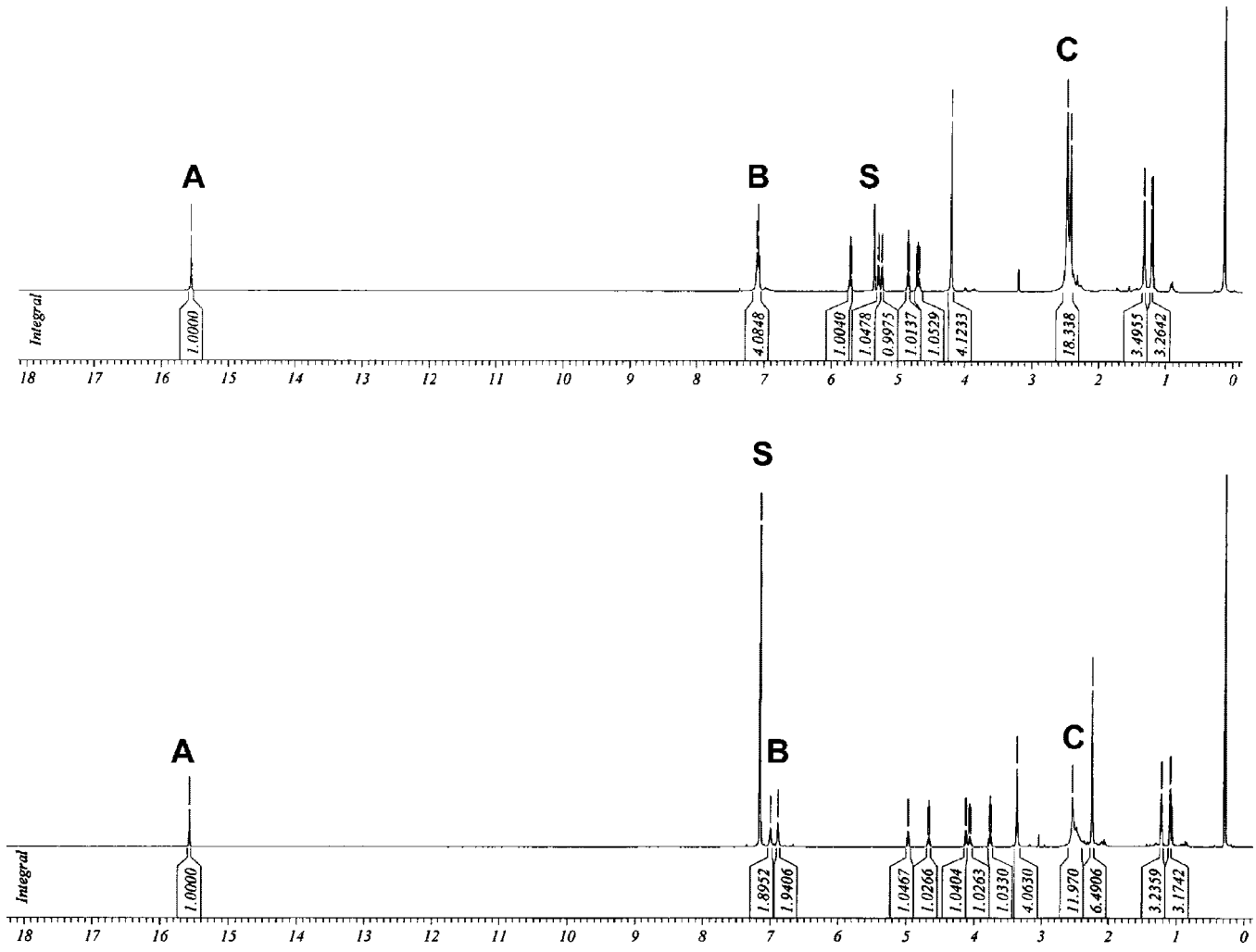

Figure 1. ^{1}H NMR spectra (400 MHz) of **11** in CD_2Cl_2 (top) and in C_6D_6 (bottom). Selected signal assignments: (A) benzylidene proton, (B) mesityl protons, (C) mesityl *ortho*-methyl protons, (S) residual solvent signal.

These observations indicate a hindered rotation of one of the mesityl substitutents around the C−N bond in **11** in deuterated benzene, whereas this appears not to be the case in deuterated dichloromethane. Such an observation has not been reported for **4**[24,25] or for **6**[26] and suggests that the molecular dynamics is reduced in C_6D_6 as compared to CD_2Cl_2, a trend opposing that reported by Fürstner[19] and Grela.[49]

Crystallization by slow evaporation from a solvent mixture (2:1) of hexane and *tert*-butyl methyl ether (TBME) afforded crystals suitable for a single-crystal X-ray structure analysis (Figure 2). **11** displays a strongly distorted trigonal bipyramidal coordination geometry at ruthenium with the isopropoxy ligand in an axial position and the chlorine atoms as well as the benzylidene ligand in equatorial positions. One face of the benzylidene ligand moiety is efficiently blocked by the tricarbonylchromium group, which, for obvious steric reasons, adopts a staggered conformation with one carbonyl ligand pointing away from the chlororuthenium part of the complex. Compared to the Hoveyda−Grubbs catalyst **4**,[24] a decreased Ru−C14 bond length is observed in **11** [198.1(5) vs 195.6(5) pm]. As the heterocyclic carbene ligand is identical in both compounds, its σ-donor or π-acceptor properties are unlikely to be the reason for the observed difference. Instead, the $Cr(CO)_3$ coordination

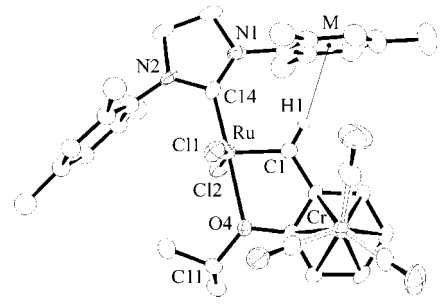

Figure 2. Structure of **11** in the crystal. Only one enantiomer is shown. Selected bond lengths [pm], angles [deg], and dihedral angles [deg]: Ru−C1 180.7(5), Ru−C14 195.9(6), Ru−O4 229.8(4), Ru−Cl1 231.8(2), Ru−Cl2 233.7(2), C14−N1 136.1(7), C14−N2 137.1(6), Cr-*C*2 224.9(6), Cr−C3 218.9(6), Cr−C4 218.6(7), Cr−C5 218.5(6), Cr−C6 222.9(6), Cr−C7 226.3(5); C1−Ru−O4 79.5(2), C1−Ru1−C14 101.9(2), C14−Ru−O4 178.38(18), Cl1−Ru−Cl2 160.16(6); N1−C14−Ru−C1 3.5(6), N2−C14−Ru−C1 −177.8(5), C14−Ru−C1–C2 −179.3(5); C−H···π hydrogen bond (M denotes the centroid of the mesityl substituent): C1···M 344.9, C1−H1 93, H1···M 253, C1−H1···M 170.

makes the benzylidene ligand a stronger acceptor ligand, thereby leading to a stronger and shorter Ru−C14 bond. The Ru−O4 bond, which is decoordinated in metathesis catalysis, is slightly longer than in **4** [229.8(3) vs 226.1(3) pm],[24] possibly indicating

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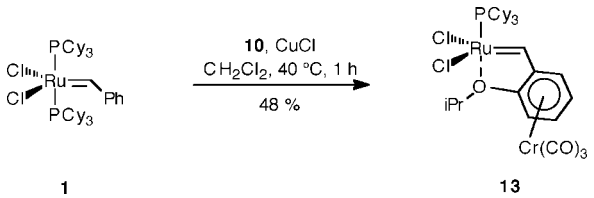
a somewhat weaker bond in **11** as a result of a reduced donor ability of the isopropoxy group.

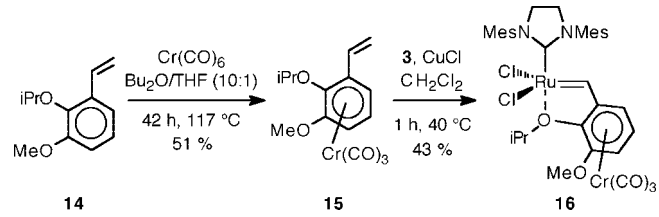
Another interesting observation is the short distance between the benzylidene proton H1 and the center of the mesityl ring attached at N1 (253 pm), suggesting an interaction with the π system (C–H$\cdots\pi$ hydrogen bond),[50] which is in line with the differentiation of the mesityl groups by ^{1}H NMR. It is interesting to note that the location of the benzylidene proton directly below the mesityl ring in Hoveyda–Grubbs type precatalysts has previously been observed,[19,51–54] but for **11** this distance is shorter, presumably as a result of the strongly electron-withdrawing $Cr(CO)_3$ group rendering H1 more electrophilic. Recently, the precedent of a $\pi-\pi$ stacking of the two perpendicularly arranged aromatic rings in Grubbs-type complexes has been documented.[19]

In addition to **11** two related complexes were prepared. Treatment of Grubbs I catalyst **1** with tricarbonyl(*ortho*-isopropoxystyrene)chromium(0) (**10**) in the presence of copper(I) chloride afforded the bimetallic derivative **13** in 48% yield as a brown-red powder after purification by column chromatography. While the presence of a phosphane ligand was confirmed by ^{31}P NMR, the resonance assigned to the benzylidene proton appears as a doublet at $\delta = 16.58$ ppm ($^3J_{P,H} = 4.2$ Hz). This contrasts with the corresponding resonance of the respective catalyst not coordinated at tricarbonylchromium, which is observed at $\delta = 17.44$ ppm ($^3J_{P,H} = 4.4$ Hz)[55] with similar coupling constants, indicating a similar dihedral angle.[56] In the ^{13}C NMR spectrum the benzylidene carbon atom resonates at $\delta = 274.5$ ppm as compared to $\delta = 280.63$ ppm for the corresponding chromium-free complex.[55]



1 **13**

Next we attempted to synthesize the 3-methoxy-substituted analogue of **11**. The chromium-free catalyst had earlier been prepared and investigated by Blechert.[47,57] Complexation of 2-isopropoxy-2-methoxystyrene (**14**) with $Cr(CO)_6$ under standard reaction conditions afforded complex **15** in 51% yield as a yellow powder. Subsequent treatment with **3** in the presence of CuCl afforded **16** in 43% yield as a brown-red powder. **16** is rather sensitive, difficult to purify, and unfortunately underwent partial decomposition. However, the IR and ^{1}H NMR data obtained clearly identify the product obtained as **16**. IR absorptions at 1955 and at 1874 (br) cm^{-1} indicate the $Cr(CO)_3$ group, and the ^{1}H NMR signal of the benzylidene proton is observed as a singlet at $\delta = 15.72$ ppm, a value that compares very well with the corresponding absorption in **11**.



14 **15** **16**

As complex **11** was the least sensitive and best characterized one in the series, we decided to screen the catalytic properties of this compound. Indeed, **11** proved to be stable in air at 25 °C for at least two months without significant loss of catalytic activity. The results of ring-closing metathesis experiments are listed in Table 1 in comparison to corresponding reactions with catalysts **3**–**6** and **8**, which are among the most advanced catalysts known today.

RCM (entries 1–4) was performed starting from dienes **17**, **19**, **21**, and **23** with monosubstituted double bonds at 25 and at 0 °C with 1 mol % of catalyst **11**, giving cyclic products **18**, **20**, **22**, and **24** in very good yields. The new catalyst showed a catalytic activity comparable to that of Hoveyda–Grubbs catalysts **5** and **6**. In addition, experiments with a 10-fold reduced catalyst loading of 0.1 mol % of **11** showed that RCM works even at this low catalyst concentration, albeit with somewhat reduced yields, as indicated by GC. RCM with more highly substituted alkenes (entries 5–7) was possible with substrates **25** and **27**, giving **26** and **28** in 99% and 49% yield, respectively, which is again comparable to the efficiency of the best catalysts known today. However, the experiment with **29** failed, and the known catalysts also gave very poor yields of RCM product **30**.

rac-**13** performed very well in enyne metatheses (Table 2), the reaction of enyne **31** afforded **32** in almost quantitative yield, and even with 0.1 mol % of catalyst 86% yield was achieved (entry 1). The reaction of enyne **33** to diene **34** showed a significantly higher activity of **11** as compared to the other catalysts, as indicated by a much higher yield, lower catalyst loading, and lower reaction temperature (entry 2). When performed in benzene instead of dichloromethane as the solvent, however, the yield dramatically decreased to 8%. As a possible explanation, we consider the reduced molecular dynamics in **11** in benzene as compared to dichloromethane, which has been indicated by NMR (*vide supra*). This might render conformations favorable for the metathesis catalysis less accessible.

CM catalyses (Table 3) were performed with **11** using **35**, **38**, and **48** as coupling partners for α,β-unsaturated ester **36**, ketone **40**, sulfone **42**, nitrile **44**, and phosphane oxide **46**. The yields are very high and compare very well to those of the other catalysts. The selectivity of cross-metathesis reactions with vinyl phosphaneoxide **46** and sulfone **42** led exclusively to *E*-isomers; only experiments involving methyl acrylate (**36**, entries 1, 2) or acrylonitrile (**44**, entry 5) showed a tendency toward increased amounts of the *Z*-isomer. **11** is active even over extended heating in dichloromethane, as indicated by the reaction of **48** giving **49** in 83% yield (entry 7). Overall the experiments show that not only a nitro group as in catalyst **6** but also coordination at an electron-withdrawing tricarbonylchromium group gives a metathesis catalyst of good stability and extremely high catalytic activity.

Recently we reported the homometathesis of the *P*-chiral phosphane oxide (S_P)-**50**, which gave *trans* product (S_P,S_P)-**51** in 80% yield in the presence of 5 mol % of nitro-substituted

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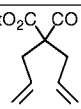
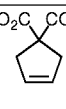
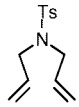
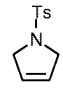
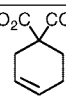
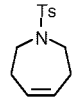
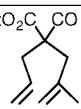
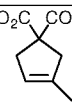
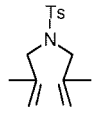
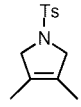
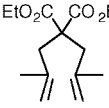
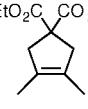
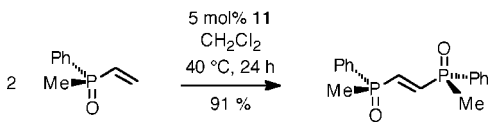
Table 1. Ring-Closing Metathesis Catalyzed by 11 in Comparison to Other Catalysts [solvent CH_2Cl_2, yields of isolated product unless otherwise indicated]

Entry	Substrate	Product[a]	Yield (conditions) using 11	Yield (conditions) using known catalysts
1	 **17**	 **18**	99 % (1 mol%, 25 °C, 10 min)	**6**: 78 % (1 mol%, 0 °C, 8 h)[22]
2	 **19**	 **20**	99 % (1 mol%, 25 °C, 10 min) 96 % (1 mol%, 0 °C, 2 h) 85 %[b] (0.1 mol%, 25 °C, 2 h)	**5**: 97 % (1 mol%, 0 °C, 2 h)[22] **6**: 92 % (1 mol%, 0 °C, 2 h)[22]
3	 **21**	 **22**	99 % (1 mol%, 25 °C, 12 min)	**5**: 99 % (1 mol%, 25 °C, 10 min)[21]
4	 **23**	 **24**	99 % (1 mol%, 25 °C, 8 min) 98 % (1 mol%, 0 °C, 1 h) 85 %[b] (0.1 mol%, 25 °C, 2 h)	**5**: 99 % (1 mol%, 25 °C, 10 min)[21] **6**: 99 % (1 mol%, 0 °C, 1 h)[22] **8**: 65 % (0.06 mol%, 25 °C, 36 min)[23]
5	 **25**	 **26**	99 % (1 mol%, 25 °C, 50 min) 59 %[b] (0.1 mol%, 25 °C, 3 h)	**4**: 50 % (2.5 mol%, 25 °C, 18 h)[58] **5**: 99 % (1 mol%, 25 °C, 40 min)[22] **6**: 99 % (1 mol%, 25 °C, 2 h)[22]
6	 **27**	 **28**	49 %[b] (5 mol%, 40 °C, 24 h)	**3**: 52 %[b] (5 mol%, 40 °C, 20 h)[22] **4**: 45 %[b] (5 mol%, 40 °C, 20 h)[22] **6**: 42 %[b] (5 mol%, 40 °C, 24 h)[22]
7	 **29**	 **30**	0 %[b] (5 mol%, 40 °C, 24 h)	**3**: 14 %[b] (5 mol%, 40 °C, 8 h)[22] **4**: 2 %[b] (5 mol%, 40 °C, 16 h)[22] **5**: 1 %[b] (5 mol%, 40 °C, 16 h)[22] **6**: 0 %[b] (5 mol%, 40 °C, 24 h)[22]

[a] Identified by comparison of ^1H and ^{13}C NMR data with literature data. [b] Yield determined by gas chromatography without product isolation.

catalyst **6** in dichloromethane at 40 °C over 24 h.[59] We now were pleased to find that replacement of **6** by **11** under otherwise unchanged reaction conditions afforded (S_P,S_P)-**51** in an improved yield of 91%.



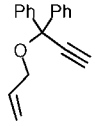
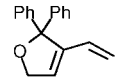
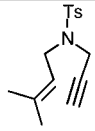
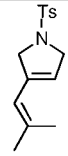
(S_P)-**50** (S_P,S_P)-**51**

In order to open a different pathway to *P*-chiral diphosphanes by homometathesis of vinyl derivatives, the homometathesis of borane-stabilized methylphenylvinylphosphane **54**, which was prepared either from methylphenylvinylphosphane[60,61] (**52**) by reaction with borane in 46% yield or alternatively from 2-(boranatomethylphenyl)phosphanylethyl methanesulfonate (**53**) in 86% yield,[62] to **55** was also tried. However, no metathesis was observed with **6** as the catalyst, nor were any other products obtained. Presumably the electron withdrawal of the borane moiety reduces the electron density of the vinyl group to an extent precluding a complexation at ruthenium. Most recently Gouverneur reported related findings using **3** as the catalyst.[63]

Conclusions

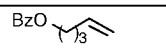
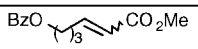
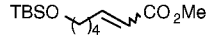
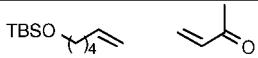
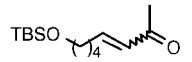
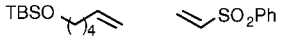
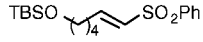
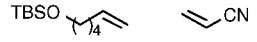
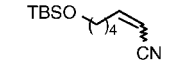
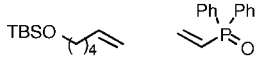
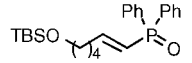
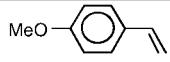
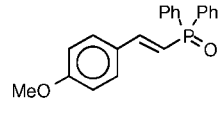
11 proved to be an air-stable precatalyst for ring-closing, enyne, cross, and homo metathesis with an efficiency that very well compares to those of the most advanced catalysts for these reactions. In particular, in the homometathesis of *P*-chiral vinylphosphane oxide (S_P)-**50** catalyst **11** came out to be significantly more efficient that the so far best catalyst **6**. The

Table 2. Enyne Metathesis Catalyzed by 11 in Comparison to Other Catalysts [solvent CH_2Cl_2 unless otherwise indicated, yields of isolated product]

Entry	Substrate	Product[a]	Yield (conditions) using 11	Yield (conditions) using known catalysts
1	 **31**	 **32**	99 % (1 mol%, 25 °C, 10 min) 99 % (1 mol%, 0 °C, 1 h) 86 % (0.1 mol%, 25 °C, 2 h)	**2**: 85 % (1 mol%, 80 °C, 1 h)[19] **6**: 99 % (1 mol%, 0 °C, 1 h)[22] **8**: 85 % (0.2 mol%, 25 °C, 1.5 h)[23]
2	 **33**	 **34**	99 % (1 mol%, 25 °C, 20 min) 8 % (1 mol%, C_6H_6, 25 °C, 30 min)	**2**: 89 % (5 mol%, 80 °C, 30 min)[19]

[a] Identified by comparison of ^1H and ^{13}C NMR data with literature data.

Table 3. Cross Metathesis Catalyzed by 11 in Comparison to Other Catalysts [solvent CH_2Cl_2, yields of isolated product unless otherwise noted]

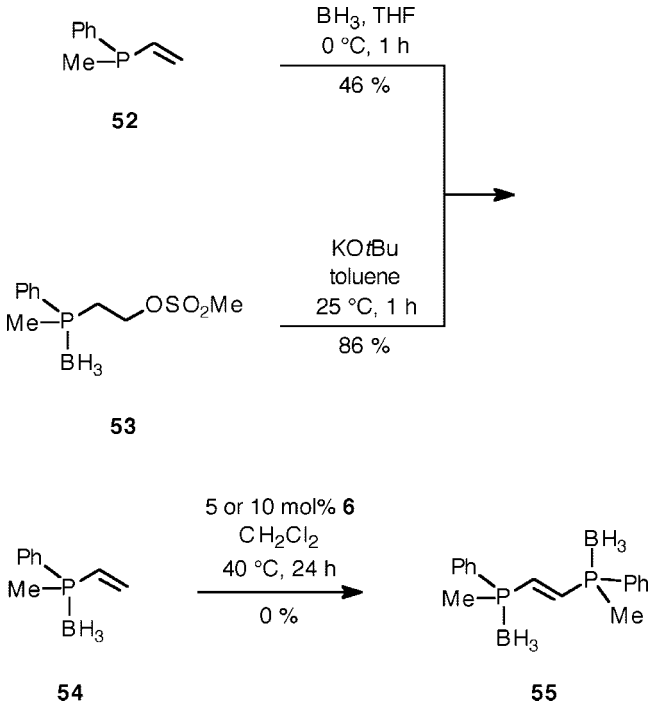
Entry	Substrate	Product[a]	Yield (conditions) using 11	Yield (conditions) using known catalysts
1	 **35** **36**	 **37** (*E*:*Z* = 9.7:1)	99 % (1 mol%, 25 °C, 30 min)	**5**: 99 % (1 mol%, 25 °C, 30 min) (*E*/*Z* = 97:3)[21]
2	 **38** **36**	 **39** (*E*:*Z* = 3.7:1)	99 % (1 mol%, 25 °C, 25 min)	**6**: 95 % (1 mol%, 25 °C, 30 min) (*E*/*Z* = 95:5)[22]
3	 **38** **40**	 **41** (*E*:*Z* = 99:1)	93 % (2.5 mol%, 20 °C, 3 h)	**5**: 90% (1 mol%, 20 °C, 40 min) (*E*/*Z* = 99:1)[21] **6**: 95 % (2.5 mol%, 25 °C, 3 h) (*E*/*Z* = 99:1)[22]
4	 **38** **42**	 **43**	89 % (2.5 mol%, 20 °C, 16 h)	**3**: 85 % (5 mol%, 40 °C, 16 h)[22] **6**: 90 % (2.5 mol%, 25 °C, 16 h) (*E*)[22]
5	 **38** **44**	 **45** (*E*:*Z* = 1:2.6)	76.5 % (5 mol%, 20 °C, 3 h)	**3**: 68 %[b] (5 mol%, 80 °C, 16 h)[22] **6**: 83 %[b] (5 mol%, 25 °C, 2 h) (*E*/*Z* = 1:2.7)[22] **7**: 70 % (3 mol%, 25 °C, 5 h) (*E*/*Z* = 1:2.7)[23]
6	 **38** **46**	 **47**	87 % (5 mol%, 40 °C, 16 h)	**3**: 82 % (5 mol%, 40 °C, 16 h) (*E*)[22] **6**: 82 % (5 mol%, 40 °C, 16 h) (*E*)[22]
7	 **48** **46**	 **49**	83 % (5 mol%, 40 °C, 24 h)	**3**: 78 % 5 mol%, 40 °C, 24 h) (*E*)[59] **6**: 81 % 5 mol%, 40 °C, 16 h) (*E*)[59]

[a] Identified by comparison of ^1H and ^{13}C NMR data with literature data. [b] Yield determined by gas chromatography without product isolation.

structure of **11** indicates an attractive benzylidene C−H···π interaction to one of the mesityl substituents. Further investigations directed to broadening the application profile of bimetallic precatalysts of this type are underway in our laboratories.

Experimental Section

General Procedures. All operations involving air-sensitive materials were performed under argon using standard Schlenk techniques. Diethyl ether, THF, and benzene were dried over Na/K−benzophenone; petroleum ether (PE) and *tert*-butyl methyl ether (TBME) were dried over $CaCl_2$; dibutyl ether and dichloromethane were dried over CaH_2 and distilled under Ar prior to use. Starting materials were either purchased or prepared according to literature procedures. IR: Perkin-Elmer 2000, FT 1170 (ATR). ^{1}H NMR: Bruker AVS 400 (400.1 MHz), AVB 500 (500.1 MHz). Chemical shifts refer to $\delta_{TMS} = 0$ ppm or to residual solvent peaks. br: broad, unresolved signal. ^{13}C NMR: Bruker AVS 500 (125 MHz). Chemical shifts refer to $\delta_{TMS} = 0$ ppm or to residual solvent peaks. MS (EI, LSIMS): AMD 604 Inectra, Finnigan MAT 112, MAT 312, 70 eV. HRMS (ESI): Finnigan MAT 312, VG Autospec. Melting points: Electrothermal IA 9200. GC: Hewlett-Packard HPGC, SE-54 capillary column, FID detector 19231 D/E. Each metathesis experiment was checked at least two times.



Tricarbonyl(2-isopropoxystyrene)chromium(0) (10). 2-Isopropoxystyrene[24] (**9**, 1.000 g, 6.2 mmol) in 3 mL of THF was added to $Cr(CO)_6$ (1.765 g, 8.0 mmol) in 440 mL of Bu_2O/THF (10:1), and the mixture was heated at reflux for 42 h. In the first 2 h the color of the reaction mixture turned to orange. The reaction mixture was cooled to 25 °C and filtered under argon through silica gel. Solvent evaporation at reduced pressure gave an orange residue, which was purified by column chromatography [SiO_2, PE/TBME (2:1), $R_f = 0.42$] to give 1.050 g (3.5 mmol, 58%) of **10** as a yellow powder (mp 63.5–64.0 °C).

IR (KBr): $\tilde{\nu}$ 2981 (w) cm^{-1}, 1941 (s, CO), 1837 (s, CO), 1626 (w), 1532 (w), 1461 (s), 1424 (s), 1375 (w), 1335 (w), 1280 (w), 1249 (s), 1157 (w), 1107 (s), 993 (w), 949 (w), 918 (s), 816 (w), 667(s), 625 (s). ^{1}H NMR (400 MHz, C_6D_6): δ 6.64–6.71 (dd, 1H, J = 17.6 Hz, J = 11.1 Hz, C*H*=CH$_2$), 5.32 (d, 1H, J = 17.6 Hz, −CH=C*H*H), 5.27 (dd, 1H, J = 6.6 Hz, J = 1.2 Hz, arom. H), 4.92 (d, 1H, J = 11.1 Hz, CH=CH*H*), 4.75–4.78 (dt, 1H, J = 7.0 Hz, J = 1.1 Hz, arom. H), 4.22 (d, 1H, J = 6.8 Hz, arom. H), 4.14 (t, 1H, J = 6.3 Hz, arom. H), 2), 3.71 [sept, 1H, J = 6.1 Hz, C*H*(CH$_3$)$_2$], 1.09 (d, 3H, J = 6.2 Hz, CH$_3$), 0.77 (d, 3H, J = 6.0 Hz, CH$_3$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ 233.8 (CO), 139.9 (*C*OiPr), 129.7 (−*C*H=CH$_2$), 114.9 (=CH$_2$), 94.7 (*C*CH=CH$_2$), 93.8 (arom. CH), 92.7 (arom. CH), 84.8 (arom. CH), 75.8 (arom. CH), 72.0 [*C*H(CH$_3$)$_2$], 22.1 (CH$_3$), 21.5 (CH$_3$) ppm. MS (EI): *m*/*z* (%) 298 (42) [M$^+$], 242 (19) [M$^+$ − 2CO], 215 (28), 214 (89) [M$^+$ − 3 CO], 173 (8), 172 (29), 171 (98) [M$^+$ − 3 CO − H$_3$CCH=CH$_2$], 162 (6), 145 (7), 143 (22) [M$^+$ − 3 CO − H$_3$CCH=CH$_2$ − HCCH], 120 (20), 91 (14), 52 (100) [Cr$^+$]. HR-MS (EI): ($C_{14}H_{14}O_4{}^{52}Cr$) calcd 298.0297, found 298.0297. Anal. ($C_{14}H_{14}O_4Cr$) Calcd: C 56.38, H 4.73. Found: C 56.43, H 4.61.

Precatalyst 11. 10 (88 mg, 0.3 mmol) in 3 mL of dichloromethane was added dropwise via syringe to benzylidene complex **3** (250 mg, 0.3 mmol) and CuCl (30 mg, 0.3 mmol) in 5 mL of dichloromethane. The mixture was heated at reflux for 1 h, the reaction progress being monitored by TLC ($R_f = 0.13$, hexane/EtOAc, 5:2). After solvent removal at reduced pressure the residue was dissolved in 35 mL of benzene and carefully filtered under argon through silica gel to remove residual **10**. Subsequent elution with hexane/TBME (2:1) gave 168 mg (0.2 mmol, 74%) of **11** as an air-stable dark red solid (mp 176 °C, dec).

IR (KBr): $\tilde{\nu}$ 2925 (w) cm^{-1}, 2847 (w), 2052 (w), 1963 (s, CO), 1903 (s, CO), 1867 (s, CO), 1739 (w), 1605 (w), 1484 (w), 1448 (w), 1382 (w), 1296 (w), 1260 (s), 1208 (w), 1098 (w), 1016 (b), 928 (w), 854 (w), 822 (w), 674 (w), 661 (w), 620 (w). ^{1}H NMR (400 MHz, C_6D_6): δ 15.49 (s, 1H, Ru=CH), 7.00 (s, 2H, mesityl-CH), 6.88 (s, 2H, mesityl-CH), 4.97 (dd, 1H, J = 6.5 Hz, J = 1.2 Hz, Ru=CHCC*H*), 4.68 (dt, 1H, J = 7.0 Hz, J = 1.2 Hz, Ru=CHCCHCHC*H*), 4.10 (d, 1H, J = 6.9 Hz, RuCHCCHCH-CHC*H*), 4.01 [sept, 1H, J = 6.2 Hz, OC*H*(CH$_3$)$_2$], 3.74 (t, 1H, J = 6.2 Hz, Ru=CHCCHC*H*), 3.36 (s, 4H, CH$_2$), 2.54 (bs, 12H, *o*-CH$_3$), 2.25 (s, 6H, *p*-CH$_3$), 1.21 (d, 3H, J = 6.2 Hz, OCHC*H*$_3$), 1.08 (d, 3H, J = 6.0 Hz, OCHC*H*$_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 15.49 (s, 1H, Ru=CH), 7.03 (4H, br, mesityl-CH), 5.65 (1H, dt, J = 7.0 Hz, J = 1.2 Hz, Ru=CHCCHCHC*H*), 5.23 (1H, d, J = 6.9 Hz, RuCHCCHCHCHC*H*), 5.18 (1H, dd, J = 6.5 Hz, J = 1.2 Hz, Ru=CHCC*H*), 4.79 (1H, t, J = 6.2 Hz, Ru=CHCCHC*H*), 4.62 [sept, J = 6.2 Hz, 1H, OC*H*(CH$_3$)$_2$], 4.15 (4H, s, CH$_2$), 2.37 (18H, br, *o*-CH$_3$, *p*-CH$_3$), 1.26 (d, J = 6.2 Hz, 3H, OCHC*H*$_3$), 1.14 (d, J = 6.0 Hz, 3H, OCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 285.6 (Ru=CH), 233.0 (CrCO), 210.7 (Ru=CNN), 138.6 (arom. C−O), 138.4 (N−C$_q$), 137.2 (mesityl-*o*-C$_q$), 135.5 (mesityl-*p*-C$_q$), 129.9 (mesityl-*m*-CH), 129.5 (*p*-C$_q$), 107.3 (Ru=CH*C*$_q$), 91.6 (Ru=CHCC-HCH*C*H), 91.5 (Ru=CHC*C*H), 83.8 (RuCHCCH*C*H), 77.2 (OCH), 76.1 (Ru=CHCCHCHCH*C*H), 51.2 (br, CH$_2$), 21.6 (CH*C*H$_3$), 21.4 (CH*C*H$_3$), 21.1 (*o*-CH$_3$), 17.9 (*p*-CH$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 285.4 (Ru=CH), 232.7 (CrCO), 208.8 (Ru=CNN), 138.7 (arom. C−O), 138.6 (N−C$_q$), 136.8 (mesityl-*o*-C$_q$), 129.3 (mesityl-*m*-CH), 128.5 (mesityl-*p*-C$_q$), 107.3 (Ru=CH*C*$_q$), 92.3 (Ru=CHCCHCH*C*H), 92.2 (Ru=CHC*C*H), 85.2 (RuCHCCH*C*H), 77.7 (OCH), 77.05 (Ru=CHCCHCHCH*C*H), 51.5 (br, CH$_2$), 21.4 (CH*C*H$_3$), 21.4 (CH*C*H$_3$), 21.0 (br, *o*-CH$_3$ + *p*-CH$_3$). ESI-HRMS (CH$_3$CN, $C_{36}H_{41}ClCrN_3O_4Ru$ [M − Cl + CH$_3$CN]$^+$): calcd 768.1234, found 768.1250.

One-Pot Synthesis of 11 from Grubbs I (1). At 25 °C 0.23 mL (0.39 mmol, 1.7 M in toluene) of potassium *tert*-amylate was

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added to 158 mg (0.4 mmol) of 1,3-dimesitylimidazolinium tetrafluoroborate in 7 mL of hexane, and the mixture was stirred for 1 h. Then 300 mg (0.36 mmol) of Grubbs I catalyst (**1**) was added as a solid, and the reaction mixture was heated at reflux for 40 min, being monitored by TLC (hexane/EtOAc, 9:1). Thereafter the reaction mixture was cooled to 25 °C, and 37 mg (0.38 mmol) of CuCl and 113.3 mg (0.37 mmol) of **10** in 7 mL of dichloromethane were added. After stirring the reaction mixture at reflux for 1 h, solvents were removed at reduced pressure and the residue was purified as described previously. Yield: 161 mg (0.21 mmol, 59%) of **11**.

Bimetallic Complex 13. Tricarbonyl(2-isopropoxystyrene)chromium(0) (**10**) (145.0 mg, 0.49 mmol) in dichloromethane (6 mL) was added via syringe to benzylidene complex **1** (200 mg, 0.25 mmol) and CuCl (24.1 mg, 0.24 mmol) in dichloromethane (12 mL). The reaction mixture was heated at 40 °C for 1 h, the reaction progress being monitored by TLC (R_f = 0.13, hexane/TBME, 15:1). After solvent removal at reduced pressure the residue was purified by column chromatography under argon, leading to **13** as a brown-red powder, 85.6 mg (0.11 mmol, 48%).

IR (ATR): $\tilde{\nu}$ 2922 (w) cm $^{-1}$, 2849 (w), 1957 (s, CO), 1882 (s, br, CO), 1518 (w), 1444 (w), 1261 (w), 1102 (w), 949 (w), 801 (w), 725 (w), 658 (w), 622 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.7–2.24 (m, 33H, PCy_3; d, J = 6.0 Hz, 3H, CHCH_3; d, J = 6.0 Hz, 3H, CHCH_3), 4.90 (t, J = 6.1 Hz, 1H, Ru=CHCCHC*H*), 5.02 [sept, J = 6.0 Hz, 1H, C*H*(CH_3)$_2$], 5.47 (d, J = 6.9 Hz, 1H, Ru=CHCCHCHCHC*H*), 5.74 (dt, J = 6.9 Hz, J = 1.0 Hz, 1H, Ru=CHCCHCHC*H*), 5.97 (dd, J = 6.5 Hz, J = 1.2 Hz, 1H, Ru=CHCC*H*), 16.58 (d, J = 4.2 Hz, 1H, 1-H) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ 21.9 (CH*C*H_3), 22.7 (CH*C*H_3), 26.2 ($PCHCH_2CH_2CH_2$), 27.6 (d, $^2J_{PC}$ = 12.3 Hz, PCH*C*H_2), 29.9 (d, $^1J_{PC}$ = 31.1 Hz, P*C*H), 35.6 (d, $^3J_{PC}$ = 25.6 Hz, $PCHCH_2CH_2$), 77.2 (Ru=CHCCHCHCH*C*H), 77.8 [*C*H(CH_3)$_2$], 84.3 (Ru=CHCCH*C*H), 91.8 (Ru=CHC*C*H), 91.9 (Ru=CHCCHCH*C*H), 105.7 (Ru=CH*C*), 137.5 (Ru=CHC*C*O), 232.2 (CO), 274.01 (Ru=*C*) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ +64.1 ppm. ESI-HRMS (CH_3CN, $C_{33}H_{48}{}^{37}Cl^{52}CrNO_4P^{102}Ru$ [M − Cl + CH_3CN]$^+$): calcd 742.1458, found 742.1459.

Tricarbonyl(η^6-2-isopropoxy-3-methoxystyrene)chromium(0) (15). 2-Isopropoxy-3-methoxystyrene[47] (0.470 g, 2.4 mmol) in THF (3 mL) was added to $Cr(CO)_6$ (0.59 g, 2.7 mmol, 1.1 equiv) in Bu_2O/THF (10:1, 175 mL) and heated at reflux for 42 h. In the first 2 h the color of the reaction mixture turned orange. The reaction mixture was cooled to 25 °C and filtered under argon through silica gel. Solvent evaporation at reduced pressure gave a yellow residue, which was purified by column chromatography (SiO_2, PE/TBME, 2:1) to give 0.46 g (1.3 mmol, 51%) of **15** as a light yellow powder. Mp = 99 °C.

IR (ATR): $\tilde{\nu}$ 2978 (w) cm $^{-1}$, 1950 (s, CO), 1869 (s, CO), 1844 (s, CO), 1518 (w), 1411 (w), 1376 (w), 1276 (w), 1205 (w), 1097 (w), 1047 (w), 996 (w), 916 (w), 855 (w), 797 (w), 735 (w), 708 (w), 665 (w), 628 (s). ^{1}H NMR (400 MHz, C_6D_6): δ 1.09 (d, J = 6.2 Hz, 3H, 1-H), 1.23 (d, J = 6.1 Hz, 3H, 2-H), 2.97 (s, 3H, 13-H), 4.11 (m, 1H, 6-H), 4.28 (sept, J = 6.1 Hz, 1H, 3-H), 4.51 (m, 2H, 7-H; 8-H), 5.08 (d, J = 11.0 Hz, 1H, 11′-H), 5.29 (d, J = 17.8 Hz, 1H, 11-H), 6.52–6.78 (dd, J = 17.8 Hz, J = 11.0 Hz, 1H, 10-H) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC, HMBC, C_6D_6): δ 22.5 (C-2), 22.3 (C-1), 55.9 (C-13), 74.2 (C-6), 79.6 (C-3), 81.9 (C-8), 90.2 (C-7), 104.5 (C-9), 117.4 (C-11), 127.1 (C-5), 130.4 (C-10), 136.8 (C-4), 234.3 (C-12) ppm. MS (EI) *m*/*z* (%): 328 (31) [M$^+$], 272 (12), 244 (92), 216 (26), 202 (82), 186 (82), 150 (11). Anal. ($C_{15}H_{16}O_5Cr$) Calcd: C 54.88, H 4.91. Found: C 54.81, H 5.21.

Bimetallic Complex 16. Tricarbonyl(2-isopropoxy-3-methoxystyrene)chromium(0) (**15**) (38.6 mg, 0.12 mmol) in dichloromethane (2 mL) was added via syringe to benzylidene complex **3** (100 mg, 0.12 mmol) and CuCl (11.6 mg, 0.12 mmol) in dichloromethane (5 mL). The reaction mixture was heated at 40 °C for 1 h. After solvent removal at reduced pressure the residue was dissolved in benzene (10 mL) and carefully filtered under argon through silica gel to remove residual **15**. Subsequent elution with diethyl ether afforded 40.1 mg (0.05 mmol, 43%) of **16** as a purple solid, which decomposed during the NMR measurement. Mp = 109–110 °C.

IR (ATR): $\tilde{\nu}$ 2924 (w) cm $^{-1}$, 2845 (w), 2363 (w), 2052 (w), 1955 (s, CO), 1874 (s, br, CO), 1479 (w), 1443 (w), 1262 (s), 1173 (w), 1099 (w), 887 (w), 851 (w), 806 (w), 674 (w), 657 (w). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.35 (d, J = 6.0 Hz, 6H, 2 CHCH_3), 2.71 (br, 18H, mesityl-CH_3), 3.42 [sept, 1H, C*H*(CH_3)$_2$], 2.79 (s, 3H, OCH_3), 3.68 (s, 4H, CH_2), 3.88 (t, 1H, Ru=CHCCHC*H*), 4.25 (d, 1H, Ru=CHCC*H* or RuCHCCHCHC*H*), 4.69 (d, 1H, Ru=CHCC*H* or RuCHCCHCHC*H*), 7.05 (s, 4H, mesityl-C*H*), 15.72 (s, 1H, Ru=C*H*) ppm.

Methylphenylvinylphosphane Borane Adduct (53). (a) Potassium *tert*-butoxide (30 mg, 0.3 mmol) was added as a powder to a stirred solution of 2-(boranatomethylphenyl)phosphanylethyl methanesulfonate[62] (60 mg, 0.2 mmol) in toluene (2 mL). The mixture was stirred for 1 h at 25 °C. After quenching the reaction by addition of water the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with aqueous $NaHCO_3$ (20 mL) and brine (30 mL) and dried with $MgSO_4$, and the solvents were removed at reduced pressure. The crude product was purified by flash chromatography (SiO_2, 25 × 4 cm, ethyl acetate) to afford pure product as an oil, 37.9 mg (0.20 mmol, 86%). To prevent decomposition, **53** was stored as a solution in dichloromethane at −25 °C.

(b) To a stirred solution of methylphenylvinylphosphane[60,61] (**52**, 200 mg, 1.3 mmol) in THF (2 mL) was added at 0 °C BH_3 (115 mg, 1.4 mL, 1.4 mmol, 1.0 M in THF). The mixture was allowed to reach 20 °C over 2 h. The reaction was quenched by addition of 2 N HCl (3 mL). The organic layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with aqueous $NaHCO_3$ (20 mL) and brine (30 mL) and dried with $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 25 × 4 cm, ethyl acetate/cyclohexane, 2:5) to afford pure product as a colorless viscous oil, 101 mg (0.6 mmol, 46%). To prevent decomposition, **127** was stored as a solution in dichloromethane at −25 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.48 (m, 3H, BH_3), 1.61 (d, $^2J_{PH}$ = 10.3 Hz, 3H, CH_3), 6.04 (m, 2H, P−CH=CH_2), 6.29 (m, 1H, P−C*H*=), 7.43 (m, 3H, *m*-, *p*-H), 7.66 (m, 2H, *o*-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 11.1 (d, $^1J_{PC}$ = 40.8 Hz, CH_3), 128.7 (d, $^3J_{PC}$ = 9.9 Hz, *m*-CH), 129.1 (d, $^1J_{PC}$ = 57.3 Hz, P-C_q), 129.3 (d, $^1J_{PC}$ = 52.2 Hz, P−*C*H=CH_2), 131.1 (d, $^4J_{PC}$ = 2.3 Hz, *p*-CH), 131.3 (d, $^2J_{PC}$ = 9.4 Hz, *o*-CH), 133.1 (d, $^2J_{PC}$ = 3.8 Hz, P−CH=*C*H_2) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 7.1–8.2 (m) ppm.

General Procedure for Ring-Closing (Table 1) and Enyne Metathesis (Table 2). A solution of **11** in dichloromethane [0.00050 mmol (0.1%), 0.00500 mmol (1%), or 0.02500 mmol (5%)] was added to a solution of the substrate (0.5 mmol, 0.02 M) in dichloromethane at 0 or at 25 °C. The mixture was stirred at this temperature, and the reaction was monitored by TLC (hexane/ethyl acetate). After the reaction was complete cold vinyl ethyl ether (0.5 mL, 2 M in CH_2Cl_2) was added to the reaction mixture. The solvent was removed at reduced pressure, and the product was isolated by column chromatography (SiO_2, hexane/ethyl acetate). Product identification was based on literature data.[19,21–23,58]

General Procedure for Cross Metathesis (Table 3). 11 in dichloromethane [(0.00500 mmol (1%), 0.0125 mmol (2.5%), or 0.02500 mmol (5%)] was added to the substrate (0.5 mmol, 0.125 or 0.2 M) at 25 °C. The mixture was stirred at this temperature or at 40 °C, and the reaction was monitored by TLC (hexane/ethyl

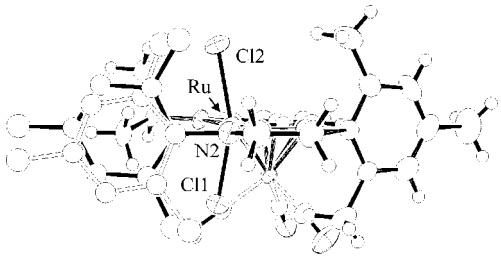

Figure 3. ORTEP diagram of **11** illustrating the two orientations of the trimethylphenyl group attached to N2.

acetate). After the reaction was complete cold vinyl ethyl ether (0.5 mL, 1 M in CH_2Cl_2) was added. The solvent was removed at reduced pressure, and the product was isolated by column chromatography (SiO_2, hexane/ethyl acetate). Product identification was based on literature data.[21–23,59]

Crystal Structure Analysis of 11.[64] Crystals were obtained by slow evaporation from hexane/TBME (2:1) under argon. Empirical formula $C_{34}H_{27}Cl_2CrN_2O_4Ru$, formula weight 751.54 g/mol, crystal system monoclinic, space group $P2_1/c$ (14), unit cell dimensions $a = 9.996(4)$ Å, $b = 23.873(8)$ Å, $c = 15.218(6)$ Å, $\beta = 99.64(5)°$, $V = 3580(2)$ Å^3, $Z = 4$, $d_{calc} = 1.394$ g/cm^3, $\mu = 0.911$ mm^{-1}, crystal size $0.33 \times 0.07 \times 0.07$ m^3, STOE IPDS one-axis diffractometer with imaging plate detector, $T = 298$ K, Mo Kα radiation ($\lambda = 0.71073$ Å), $\theta_{max} = 25.90°$, 51 080 (6712) measured (unique) reflections, R(int) = 0.076, direct methods, full-matrix least-squares refinement on F^2 including all data (SHELXL-97),[65] the mesityl group attached to N2 treated as 2-fold positionally disordered rigid group (Figure 3), anisotropic displacement parameters for all non-H atoms with the exception of the C atoms of the disordered mesityl group, for which isotropic displacement parameters were used, H atoms geometrically placed and allowed to ride on the respective C atoms, H atoms of the disordered mesityl group were not considered, 294 parameters in final refinement, $R_1 = 0.044$ ($I > 2\sigma_I$, 2594 reflections), $wR_2 = 0.072$ (all reflections), largest peak (hole) in final difference electron density map 0.43 (−0.50) e Å^{-3}.

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Supporting Information Available: NMR spectra of new compounds and the .cif file of **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701242T

(64) Crystallographic data (without structure factors) have been deposited as supplementary publication no. CCDC 635880 at the Cambridge Crystallography Data Centre. Copies can be obtained free of charge by contacting the CCDC: deposit@ccdc.cam.ac.uk.

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