Synthesis and Reactivity of Neutral and Cationic Ruthenium(II) Tris(pyrazolyl)borate Alkylidenes

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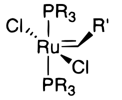
A series of neutral and cationic ruthenium(II) alkylidenes containing the hydrotris(pyrazolyl)borate (Tp) ligand have been prepared. The complex $Tp(PCy_3)(Cl)Ru{=}CHPh$ (**2**) was obtained by the reaction of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**) and KTp. Treatment of **2** with $AgBF_4$ or $AgSbF_6$ in the presence of a variety of coordinating solvents afforded $[Tp(PCy_3)(L)Ru{=}CHPh]^+$ ($L = H_2O$, CH_3CN, pyridine) in high yield. The dynamic NMR behavior of these new complexes is discussed, and the X-ray crystal structure of $[Tp(PCy_3)(H_2O)Ru{=}CHPh]BF_4$ (**3**) is reported. Alkylidenes **2**−**5** alone do not catalyze olefin metathesis reactions. However, complex **2** is activated for ring-closing metathesis by the addition of HCl, CuCl, and $AlCl_3$.

Introduction

Transition metal catalyzed olefin metathesis is an important method for the formation of carbon−carbon bonds and has received intensive study over the past four decades.[1] The diverse applications of olefin metathesis include the synthesis of polymers by ring-opening metathesis polymerization (ROMP),[2] the formation of carbocycles and heterocycles by ring-closing metathesis (RCM),[3] and the preparation of new substituted acyclic olefins by cross metathesis.[4] Ruthenium alkylidene **1** and its derivatives (Figure 1) were the first examples of well-defined ruthenium catalysts for the olefin metathesis reaction,[5] and these complexes (particularly **1**) have proven useful as initiators for the ROMP of substituted monomers[6] and for the RCM of functionalized dienes to form five-, six-, and seven-membered rings and in some cases larger macrocycles.[3] Most importantly, unlike common early transition metal metathesis catalysts,[7] **1** and its derivatives are tolerant of most functional groups and water,[8] making them useful for a variety of applications in organic and polymer chemistry.



R = PCy_3; R' = Ph (**1**)
R = PPh_3; R' = Ph
R = PCy_3; R' = $CHCPh_2$
R = PPh_3; R' = $CHCPh_2$

Figure 1. Ru-based olefin metathesis catalysts.

Although **1** has proven to be a versatile olefin metathesis catalyst, it still has several important limitations. Most notably, this complex is less active than Mo- and W-based catalyst systems and cannot ring close highly substituted dienes.[3d] Catalyst **1** does not tolerate some important functional groups, including unhindered amines and nitriles, and is moderately O_2 and temperature sensitive in solution. In addition, this catalyst exhibits low cis/trans selectivity in the ring closing of large macrocycles.[3]

In an effort to improve the stability, activity, and selectivity of **1**, recent work in our laboratory has focused on modification of the ligand sphere of this catalyst.[9] As part of this ongoing investigation, we became interested in examining the synthesis and reactivity of ruthenium alkylidene complexes containing the tris(pyrazolyl)borate (Tp) ligand. The Tp ligand has been shown to stabilize early transition metal carbenes. For example, Boncella and co-workers have prepared a series of neutral and cationic Tp alkylidenes of Mo[10] and W[11] which exhibit unprecedented tolerance of air and

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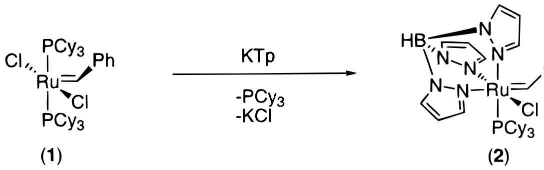
Scheme 1



moisture. Recent reports have shown that both neutral[12] and cationic[13] Tp complexes of Ru(II) are readily available and are generally air stable and thermally robust. In addition, many of these compounds show activity for catalytic reactions including hydrogenation[13d,14] and the dimerization of terminal acetylenes.[15]

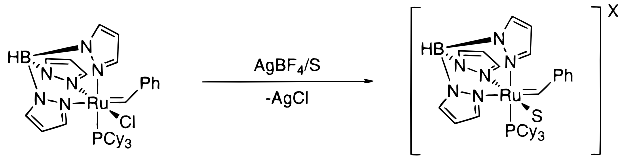
This paper describes the preparation of Tp(PCy$_3$)(Cl)-Ru=CHPh (**2**) by the transmetalation reaction between KTp and alkylidene **1**. In the presence of coordinating solvents, the chloride ligand of **2** can be extracted by AgBF$_4$ or AgSbF$_6$ to generate a series of cationic solvent-bound alkylidene complexes. Some structural aspects and dynamic NMR behavior of the new complexes are described herein. The metathesis activity of these neutral and cationic Tp Ru(II) alkylidenes has also been explored.

Results and Discussion

Synthesis of Tp(PCy$_3$)(Cl)Ru=CHPh (2). The addition of 1.1 equiv of KTp to Ru alkylidene, **1**, results in the clean displacement of one chloride and one PCy$_3$ ligand to afford Tp(PCy$_3$)(Cl)Ru=CHPh in 84% yield (Scheme 1). This reaction can be followed by a dramatic color change from purple to bright green and is complete within 1 h. The product is isolated as an air stable green powder which is insoluble in pentane, slightly soluble in diethyl ether, and soluble in chlorinated solvents, THF, and benzene. Notably, **2** is air stable indefinitely in the solid state and shows no decomposition (by ^{1}H NMR) after a week in reagent grade CD$_2$Cl$_2$ under air.

Alkylidene **2** was characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis. The proton decoupled ^{31}P spectrum of **2** shows a sharp singlet at 33.61 ppm. The ^{1}H NMR spectrum shows the α-proton of the alkylidene as a doublet at 20.01 ppm (J_{HP} = 9.51 Hz). The observed coupling between H$_\alpha$ and the bound

Scheme 2



S = Water; X = BF$_4$ (**3**)
S = Pyridine; X = SbF$_6$ (**4**)
S= Acetonitrile; X = SbF$_6$ (**5**)

^{31}P nucleus suggests that the dihedral angle between the phosphine and the alkylidene (∠P−Ru−C1−H$_\alpha$) is less than 90°.[5] Nine separate resonances are observed for the protons and carbons on the pyrazole rings, indicating that the environment around the ruthenium is asymmetric.

Synthesis of Cationic Analogues of 2. The reaction of **2** with AgBF$_4$ or AgSbF$_6$ in CD$_2$Cl$_2$ results in instantaneous precipitation of AgCl accompanied by a color change from green to brown. In each case, ^{1}H NMR analysis shows complete consumption of the starting material and the formation of at least five new carbene resonances, which remain stable in solution over 24 h at room temperature. Unfortunately the isolation and/or identification of these species has proven impossible due to the complexity of the reaction mixture.

When the same reaction is carried out in the presence of an excess of water, pyridine, or acetonitrile, cationic Ru alkylidenes **3**−**5** form rapidly and cleanly (Scheme 2).[16,17] After filtration to remove AgCl, these compounds can be isolated in 60−77% yield as green microcrystalline solids. The complexes are soluble in chlorinated solvents and THF, slightly soluble in benzene (depending on the counteranion), and insoluble in pentane. Alkylidenes **3**−**5** are moderately air sensitive in solution and are best stored under inert atmosphere.

Complexes **3**−**5** have been characterized by ^{1}H, ^{13}C, and ^{31}P NMR, IR spectroscopy, and elemental analysis. Like alkylidene **2**, these complexes exhibit large J_{HP} coupling constants (between 8 and 11 Hz) for the H$_\alpha$ proton, suggesting that the dihedral angle between the carbene and the phosphine (∠P−Ru−C1−H$_\alpha$) is less than than 90°.[5] The proton and carbon NMR spectra of **3**−**5** show nine separate resonances for the pyrazole protons and carbons, indicating that the Ru is an asymmetric center. IR spectroscopy of complex **3** shows broad υ_{OH} absorptions at 3406 and 3126 cm^{-1} similar to those of the related compounds [TpRu(COD)(H$_2$O)]-[CF$_3$SO$_3$][13e] and [TpRu(H$_2$O)(L)$_2$][CF$_3$SO$_3$].[13a] Complex **5** exhibits a characteristic υ_{CN} absorption at 2287 cm^{-1}, suggesting that minimal back-bonding is involved in the metal−acetonitrile interaction.[13e]

X-ray Diffraction Study of 3. Crystals suitable for X-ray structure determination were obtained by slow diffusion of diethyl ether into an acetone solution of **3** at −30 °C. The collection and refinement parameters for the crystallographic analysis are summarized in

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(12) Recent examples include: (a) Burns, I. D.; Hill, A. F.; White, J. P. A.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552. (b) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1998**, *17*, 827. (c) Slugovc, C.; Sapunov, V. N.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4209. (d) Gemel, C.; Kickelbick; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 2113. (e) Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodrigez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441. (f) Katayama, H.; Yoshida, T.; Ozawa, F. *J. Organomet. Chem.* **1998**, *562*, 203.

(13) Recent examples include: (a) Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186. (b) Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076. (c) Bohanna, C.; Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Martinez, M.-P. *Organometallics* **1997**, *16*, 4464. (d) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34. (e) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Meretier, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998.

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(15) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.

(16) When AgBF$_4$ is added to (PCy$_3$)$_2$Cl$_2$Ru=CHPh (**1**) in the presence of pyridine, acetone, or acetonitrile, the precipitation of AgCl is observed (indicating that Cl$^-$ abstraction is successful), but complete decomposition of all carbene species occurs within minutes at room temperature. Sanford, M. S.; Grubbs, R. H. Unpublished results.

(17) Preparation of analogous cationic alkylidenes containing THF, 2-picoline, 2,6-lutidine, triflate, or PPh$_3$ was attempted, but these complexes did not form cleanly under a variety of conditions.

Table 1. Summary of Crystal Data and Structure Refinement for Complex 3

empirical formula	$C_{40.50}H_{65.75}B_2F_4N_6O_{2.88}PRu$
fw	912.40
crystal habit	flake
crystal size	0.30 × 0.26 × 0.04 mm^3
crystal color	emerald green
diffractometer/wavelength	CAD-4/0.71073 Mo Kα
data collection temp	85 K
unit cell dimens	$a = 20.195(5)$ Å
	$b = 10.629(3)$ Å
	$c = 21.205(7)$ Å
	$\beta = 91.14(2)^o$
volume	4551(2) $Å^3$
Z	4
crystal system	monoclinic
space group	$P2_1/c$
density (calculated)	1.332 mg/m^3
μ	0.44 mm^{-1}
θ range for data collection	1.5−22.5°
h min, max	−21, 21
k min, max	−11, 10
l min, max	0, 22
reflns collected	13 603
independent reflns	5952
GOF merge (mult)	0.96
GOF on F^2	1.322
final R indices $[F_o]$ $[I > 2\sigma(I)]$	0.0446
final weighted R $[F_o^2]$	0.0780

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complex 3

Bond Lengths			
Ru−C1	1.878(4)	Ru−O1	2.143(3)
Ru−N1	2.200(4)	Ru−P1	2.3822(13)
Ru−N3	2.129(3)	C1−C2	1.460(6)
Ru−N5	2.056(4)	C1−H1	0.93(4)
Bond Angles			
C1−Ru−N5	97.65(16)	N3−Ru−N1	82.91(13)
C1−Ru−N3	90.04(16)	O1−Ru−N1	87.34(13)
N5−Ru−N3	86.73(13)	C1−Ru−P	92.40(14)
C1−Ru−O1	86.65(16)	N5−Ru−P	94.45(10)
N5−Ru−O1	172.48(13)	N3−Ru−P	177.12(10)
N3−Ru−O1	87.09(13)	O1−Ru−P	91.53(9)
C1−Ru−N1	170.95(16)	N1−Ru−P	94.51(10)
N5−Ru−N1	87.64(13)	C2−C1−H1	108(2)

Table 1. A labeled view of the cation is shown in Figure 2 and selected bond distances and bond angles in Table 2. Complex **3** cocrystallizes with 1 equiv of acetone and 1 equiv of diethyl ether. The acetone molecule and the BF_4 anion are each hydrogen bound to the H_2O ligand, as reflected by the O1−F2 and O1−O2 distances of 2.738(4) and 2.697(5) Å, respectively. The Ru−O1 distance of 2.143(3) Å is similar to that in $[TpRu(COD)(H_2O)][CF_3SO_3]$ (d(Ru−O) = 2.161(4) Å)[13e] and $[TpRu(THF)(H_2O)_2][CF_3SO_3]$ (d(Ru−O1) = 2.155(5) Å and d(Ru−O2) = 2.151(5) Å).[13a] The Ru−C1 (carbene carbon) distance of 1.878(4) Å is comparable to that of related Ru(II) alkylidenes: $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CPh_2$ (d(Ru−C) = 1.851(21) Å),[5c] $[(P(i\text{-}Pr)_3)_2(CO)(Cl)Ru{=}C(OMe)CH{=}CPh_2][BF_4]$ (d(Ru−C) = 1.874(3) Å),[18] and $(PCy_3)_2(Cl)_2Ru{=}CHC_6H_4Cl$ (d(Ru−C) = 1.838(3) Å).[5a] The three Ru−N bond distances vary from 2.056(4) to 2.200(4) Å and are consistent with the increasing trans influence of the ligands (alkylidene > PCy_3 > H_2O). The torsion angle about P−Ru−C1−C2 is 138.3(4)°. As described earlier, this angle is consistent with the large J_{HP} coupling constant (8.78 Hz) of this complex.

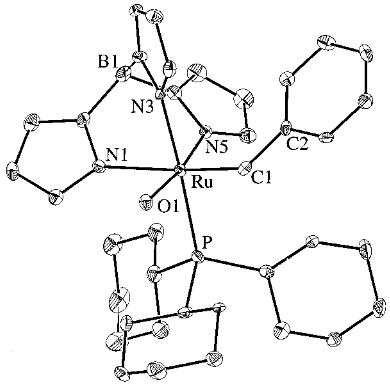

Figure 2. Labeled view of **3** with 50% probability ellipsoids. Hydrogen atoms, solvent molecules, and the BF_4 counteranion are omitted.

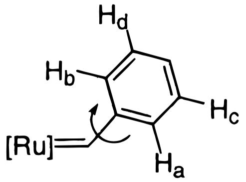

Figure 3. Exchanging phenyl group protons in dynamic NMR experiments.

Table 3. Phenyl Group Rotational Barriers for Complexes 1−5

complex	T (coalescence) (°C)	$G^{\ddagger}$ (kcal/mol)
1	−53	9.71 (±0.60)
2	−15	11.75 (±0.29)
3	−2.5	12.32 (±0.43)
4	12	12.97 (±0.18)
5	2.5	12.60 (±0.80)

Dynamic NMR Behavior of Complexes 2−5. In addition to sharp pyrazole and H_{para} resonances, the aromatic region in the room temperature ^1H NMR spectra of alkylidenes **2**−**5** shows a broad peak at about 7 ppm. This peak integrates to four hydrogens and is assigned as the overlapping ortho and meta protons of the carbene phenyl group in the intermediate exchange regime. Upon warming, this resonance resolves into a virtual doublet and a virtual triplet, which are assigned as the two ortho protons (H_a and H_b in Figure 3) and two meta protons (H_c and H_d) of the carbene phenyl group, respectively. Upon cooling, the broad peak decoalesces into a pair of virtual doublets and a pair of virtual triplets, which correspond to each of the rotationally frozen ortho and meta protons. Notably, the tris(pyrazolyl)borate protons show no exchange within the accessible temperature range (−78 to +100 °C), and a single carbene conformer is observed throughout the experiment.

As shown in Figure 3, this dynamic behavior is the result of rotation about the carbene phenyl bond. Similar phenyl group rotation is also observed for Ru alkylidene **1** but at significantly lower temperatures. The activation barrier for this rotation was calculated for each complex using a modification of the Eyring equation,[19] and the results are summarized in Table 3.

Cationic complexes **3**−**5** have rotational barriers about 1 kcal/mol higher than their neutral analogue (**2**).

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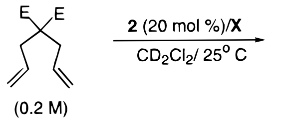
[18] Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258.

[19] Gunther, H. *NMR Spectroscopy*: *An Introduction*; John Wiley & Sons: New York, 1980.

Table 4. RCM Activity of $Tp(PCy_3)(Cl)Ru{=}CHPh$ in the Presence of Various Additives



(*1*)

X	equivalents (vs **2**)	% closed	time (h)
HCl	1	100	4
CuCl	10	100	18
$AlCl_3$	1	82	24

Alkylidenes **3**−**5** are expected to have slightly shorter Ru−N bond lengths than **2** (due to the electrophillicity of the cationic Ru center),[20] and the increased steric crowding at the metal center would account for the observed increase in $\Delta G^{\ddagger}$ of rotation. The lower T_C and rotational barrier of complex **1** most likely reflect lower steric hindrance at this five-coordinate Ru species as opposed to the six-coordinate Tp complexes. However, generalizations about the activity/stability of carbene compounds as a function of this phenyl group rotational barrier cannot be made without further investigation.

Olefin Metathesis Activity of Complex 2. Compound **2** alone shows no activity for olefin metathesis and does not react with common substrates such as norbornene or diethyl diallylmalonate even after several days at 70 °C. (Interestingly, a recent report has shown that a similar compound−$Tp(Cl)(PPh_3)Ru{=}C{=}CHPh$− *is* active for the polymerization of norbornene under similar conditions.[12f]) This lack of reactivity can be attributed to the ability of the Tp ligand to enforce an octahedral coordination geometry and to render the ligands nonlabile.[21] Since alkylidene **2** is coordinatively saturated, ligand dissociation is necessary before olefin coordination and metathesis can take place.[22]

As summarized in Table 4, we have found that a variety of cocatalysts activate alkylidene **2** for the ring-closing metathesis of diethyl diallylmalonate. These cocatalysts, which include Bronstead acids, "phosphine sponges", and Lewis acids, were chosen for their ability to assist in the dissociation of a ligand of complex **2** to generate a 16-electron, coordinatively unsaturated species. HCl has proven the most effective cocatalyst for this reaction, and a 20 mol % solution of **2**/HCl (1 equiv) ring closed the substrate within 4 h at room temperature. No propagating species or free phosphine was observed during this reaction by ^{31}P or ^1H NMR, and the initiator appeared intact at its completion. The lack of an observable propagating species is most likely due to the fact that an undetectable (by ^1H NMR) amount of catalyst initiates and efficiently catalyzes the reaction.[23]

HCl has been shown to activate a variety of Ru alkylidenes for olefin metathesis by protonation of Ru-bound ligands.[24] In the case of complex **2**, it is possible that activation occurs by protonation of a pyrazole arm of the Tp ligand to generate a transient κ^2-coordinated ligand. The protonation of an undetectable amount of phosphine would also explain the observed activity. Unfortunately the stability of complex **2** in the presence of HCl (no decomposition is observed by ^1H or ^{31}P NMR after one week in the presence of 10 equiv of HCl under inert atmosphere) has hampered definitive studies concerning HCl-promoted activation.

The addition of CuCl also induced modest RCM activity in complex **2**. A 20 mol % solution of **5**/CuCl ring closed diethyl diallylmalonate within 18 h at room temperature. Only the parent carbene resonance was observed throughout the reaction, and the catalyst appeared intact at the completion of the ring closure. (Notably alkylidene **2** did decompose after about a week in the presence of excess CuCl.) The role of CuCl in this system has not been established definitively, but this reagent is known to react with phosphines to form ill-defined, marginally soluble complexes.[9c,25] As such, we suggest that CuCl causes an undetectable amount of phosphine dissociation to generate the highly reactive 16-electron species "$Tp(Cl)Ru{=}CHPh$". Interestingly, other phosphine sponges including $[(p\text{-cymene})RuCl_2]_2$ and $Rh(C_2H_4)_2(acac)$ induced little metathesis activity in complex **2**, while no metathesis activity was observed in the presence of $Ni(COD)_2$. This trend is consistent with earlier observations concerning the relationship between electronic and steric properties of phosphine sponges and their ability to activate Ru olefin metathesis catalysts.[9b]

$AlCl_3$ was also an effective cocatalyst for the ring closing of diethyl diallylmalonate. The addition of 1 equiv of $AlCl_3$ to **2** in the presence of the diene substrate resulted in instantaneous conversion to a new carbene species with an H_α signal at 19.8 ppm in the ^1H NMR spectrum. Within 24 h the substrate was 82% ring closed and all carbene resonances had disappeared.[26] Other Lewis acids, including $GaBr_3$ and $B(C_6F_5)_3$, induced less than 10% ring closing before complete decomposition of the alkylidene was observed. The reaction of **2** with weaker Lewis acids such as $MgCl_2$ did not lead to the formation of any detectable new species or cause any RCM activity.

Lewis acids have been used to induce olefin metathesis activity in a number of metal alkylidenes, and their role has never been definitively established.[10a,12f,27] Osborn has suggested that activation can occur by halide abstraction to generate a cationic active species.[27] However, this seems unlikely in the case of complex **2** since its cationic analogues **3**−**5** show no activity for olefin metathesis (vide infra). Boncella has proposed

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(20) For example see ref 13b and the X-ray structures of TpRu(COD)Br versus $[TpRu(COD)(H_2O)]CF_3SO_3$.

(21) For a review of transition metal complexes containing the Tp ligand see: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(22) Olefin metathesis catalyzed by **1** is also approximately 95% dissociative (in PCy_3) (see ref 9c).

(23) A similar phenomenon is exhibited by recently reported Ru alkylidene complexes containing Schiff base ligands (ref 9a). These compounds are active as single-component metathesis catalysts, but no propagating species is observed by NMR at any time during the metathesis reactions. Unfortunately in case of these Schiff base complexes and in the case of complex **2**/HCl, the use of lower catalyst loadings decreases the efficiency of the ring-closing reactions. Chang S.; Grubbs, R. H. unpublished result.

(24) (a) Lynn, D. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1626. (b) Diaz, E. L. Ph.D. Thesis, California Institute of Technology, 1998. (c) Chang, S. B.; Jones, L.; Grubbs, R. H. Unpublished results.

(25) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5.

(26) Notably, preliminary studies show that $AlCl_3$ dramatically increases the activity of complex **1** as well. Sanford, M. S.; Grubbs, R. H. Unpublished results.

(27) (a) Youinou, M. T.; Kress, J.; Fisher, J.; Aguero, A.; Osborn, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1488. (b) Kress, J.; Aguero, A.; Osborn, J. A. *J. Mol. Catal.* **1986**, *36*, 1. (c) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346.

that the $AlCl_3$ activation of Tp[N(2,6-*i*-PrC_6H_3)](CH_3)-MoCH(C(CH_3)$_2$Ph) occurs by cleavage of a pyrazole ring from the Tp ligand to generate a coordinatively unsaturated species.[10a] This mechanism also appears unlikely since no free pyrazole is observed (by ^{1}H NMR) in the reaction of **2** with excess $AlCl_3$. We propose that the $AlCl_3$ may function as a phosphine scavenger in this reaction. The association of the strongly basic phosphine with the strongly Lewis acidic $AlCl_3$ is expected to irreversibly open a coordination site at the metal and enable olefin coordination and metathesis to occur. It is also possible that the $AlCl_3$ associates with a pyrazole arm to generate an active species with a κ^2-coordinated Tp ligand. However, these possibilities could not be distinguished due to the complexity of the reaction mixture.

Metathesis Activity of Cationic Alkylidenes 3−5. Disappointingly, complexes **3**−**5** show no activity for the RCM of diethyl diallylmalonate. Neither heat (50° C for 2 days) nor UV light (broad band irradiation for several hours) induces any metathesis activity in these compounds, and alkylidenes **3**−**5** merely decompose after several days in the presence of the diene substrate. This result is particularly surprising in the case of complex **3**, as studies show that the water ligand is relatively labile. When excess pyridine or acetonitrile is added to a CD_2Cl_2 solution of **3**, liberation of free H_2O and conversion to the appropriate new alkylidene species are observed within seconds at room temperature.[28] In contrast, the bound pyridine in complex **4** does not exchange with free CH_3CN, and the bound CH_3CN of complex **5** does not exchange with an excess of pyridine.

In conclusion, a series of neutral and cationic Ru alkylidenes containing the tris(pyrazolyl)borate ligand have been prepared. These complexes are completely unreactive to olefinic substrates, but the neutral complex **2** can be activated for olefin metathesis by the addition of HCl, CuCl, or $AlCl_3$. Future work in our laboratory will explore the effect of other chelating nitrogen donor ligands on Ru(II) alkylidene complexes. Efforts to prepare new late transition metal alkylidenes containing the Tp ligand are also under way.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solid organometallic compounds were transferred in a nitrogen-filled Vacuum Atmospheres drybox. All NMR spectra were recorded on a JEOL JNM-GX400 (399.8 MHz ^{1}H; 100.5 MHz ^{13}C; 161.9 MHz ^{31}P). When resolved, the coupling constants of all tris(pyrazolyl)borate protons were about 2 Hz. Elemental analysis was performed at the Caltech Analytical Facility by Mr. Fenton Harvey.

Materials. Pentane, methylene chloride, tetrahydrofuran, and diethyl ether were dried by passage through solvent purification columns.[29] Pyridine and acetonitrile were distilled from CaH_2, and acetone was vacuum transferred from $CaSO_4$. All solvents were deoxygenated with a purge of argon. Deuterated solvents were vacuum transferred from the appropriate drying agents, degassed by three continuous freeze−pump−thaw cycles, and stored in the drybox. Diethyl diallylmalonate (Aldrich) was passed through a plug of activated alumina and degassed by three freeze−pump−thaw cycles. CuCl, $AlCl_3$, $AgSbF_6$, and $AgBF_4$ were obtained from Aldrich and used as received. KTp was obtained from Strem and used as received. (PCy_3)$_2$(Cl)$_2$Ru═CHPh was prepared according to literature procedures.[5a]

Tp(PCy_3)(Cl)Ru═CHPh (2). A 200 mL Schlenk flask was charged with KTp (0.505 g, 20.0 mmol) and (PCy_3)$_2$(Cl)$_2$Ru═CHPh (1.5 g, 18.0 mmol). CH_2Cl_2 (20 mL) was added, and the solution was stirred for 1 h, during which time a color change from purple to bright green was observed. The solvent was reduced to 15 mL, and pentane (30 mL) was added to precipitate KCl. The reaction mixture was filtered through a plug of Celite and concentrated in vacuo to about 5 mL. Pentane (60 mL) was added with vigorous stirring to precipitate the product. The green solid was collected on a glass frit, washed with 4 × 20 mL of pentane, and dried in vacuo, to afford 1.1 g (84%) of a light green powder. Analytically pure samples were obtained by recrystallization from CH_2Cl_2/diethyl ether. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 33.64 (s). ^{1}H NMR (CD_2Cl_2): δ 20.01(d, 1H, Ru═C*H*, $J_{HP} = 9.51$ Hz), 8.51 (s, 1H, Tp), 7.86 (s, 2H, Tp), 7.61 (s, 1H, Tp), 7.49 (t, 1H, H_{para}, $J_{HH} = 7.32$ Hz), 7.05 (br s, 4H, H_{ortho} and H_{meta}), 6.42 (s, 1H, Tp), 6.29 (s, 1H, Tp), 6.24 (s, 1H, Tp), 6.04 (s, 1H, Tp), 5.81 (s, 1H, Tp), 1.97−0.85 (m, 33H, $H_{cyclohexyl}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 333.68 (d, Ru═*C*, $J_{CP} = 19.30$ Hz), 150.91, 145.79, 144.79, 143.24, 136.82, 135.49, 134.01, 131.46, 130.73, 128.54, 106.17, 105.99, 104.98, 34.43 (d, $J = 16.5$ Hz), 29.01, 28.81, 28.01 (d, $J = 8.27$ Hz), 27.71 (d, $J = 11.03$ Hz), 26.34. IR (NaCl): 2470 cm^{-1} (B−H). Anal. Calcd for $C_{34}H_{49}N_6BClPRu$: C, 56.71; H, 6.86; N, 11.67. Found: C, 56.46; H, 7.00; N, 11.65.

Ring Closing of Diethyl Diallylmalonate with 2. Alkylidene **2** (15 mg, 0.021 mmol) and the appropriate cocatalyst were combined in a screw cap NMR tube in the drybox. CD_2Cl_2 (1 mL) was added, and the reaction mixture was shaken for 2 min. Diethyl diallylmalonate (23.9 mL, 0.10 mmol) was added, and the reaction was removed from the drybox and monitored by ^{1}H NMR. The catalyst loading of 20 mol % was chosen because it resulted in reaction times on the order of 24 h. The percent ring closure was calculated on the basis of the ratios of the four β hydrogens in the product (H_P) and the starting material (H_S) (% ring closure = H_P/(H_P + H_S)). This calculation assumes that ring closing is the only transformation taking place, which is a reasonable approximation in this system.

[Tp(PCy_3)(H_2O)Ru═CHPh][BF_4] (3). A 50 mL Schlenk flask was charged with **2** (250 mg, 0.35 mmol) and $AgBF_4$ (68 mg, 0.35 mmol). Water (5 mL) was added, followed by 10 mL of THF, and the reaction mixture was stirred for 5 h. The solvents were removed in vacuo, and the resulting dark green solid was dissolved in CH_2Cl_2 and filtered through a plug of Celite. The solvent was then reduced to 5 mL, and pentane (40 mL) was added to precipitate the product. The solids were collected on a glass frit, washed with copious pentane, and dried under vacuum to afford 160 mg (77%) of a green microcrystalline product. Analytically pure samples were obtained by recrystallization from acetone/diethyl ether, and contained 1 equiv of each recrystallization solvent. Elemental analysis was slightly low in C and H due to partial loss of diethyl ether. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 38.11 (s). ^{1}H NMR (CD_2Cl_2): δ 19.80 (d, 1H, Ru═C*H*, $J_{HP} = 8.78$ Hz), 8.31 (s, 1H, Tp), 8.02 (d, 1H, Tp), 7.92 (d, 1H, Tp), 7.73 (s, 1H, Tp), 7.60 (t, 1H, H_{para}, $J_{HH} = 7.32$ Hz), 7.15 (br s, 4H, H_{ortho} and H_{meta}), 6.57 (t, 1H, Tp), 6.37 (s, 1H, Tp), 6.18 (s, 1H, Tp), 6.09 (t, 1H, Tp), 5.93 (s, 1H, Tp), 2.46 (s, 2H, (H_2O)), 2.06−1.21 (m, 33H, $H_{cyclohexyl}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 337.43 (d, $J_{CP} = 12.41$ Hz), 151.70, 146.27, 144.76, 143.57, 138.30, 137.01, 135.37, 132.89, 132.12, 128.84, 107.21, 107.07, 106.50, 33.93 (d, $J = 19.30$ Hz), 29.30, 29.16, 27.85 (d, $J = 8.27$), 27.59 (d, $J = 11.03$), 26.13. IR (NaCl) 3406 cm^{-1} (O−H); 3126 cm^{-1} (O−H); 2482

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[28] Boncella has reported cationic W alkylidenes which have similarly labile solvent ligands but are not active for olefin metathesis (see ref 11a).

[29] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

cm^{-1} (B−H). Anal. Calcd for $C_{41}H_{67}N_6B_2F_4O_3PRu$: C, 53.43; H, 7.33; N, 9.12. Found: C, 52.96; H, 7.22; N, 9.24.

[Tp(PCy$_3$)(C$_5$H$_5$N)Ru═CHPh][SbF$_6$] (4). A 100 mL Schlenk flask was charged with **2** (200 mg, 0.28 mmol) and $AgSbF_6$ (95.4 mg, 0.28 mmol). Pyridine (20 mL) was added, and the reaction was stirred for 90 min. The solvent was removed in vacuo, and the resulting green solid was redissolved in CH_2Cl_2 (15 mL) and filtered through a plug of Celite. The blue/green solution was concentrated to about 5 mL, and the product was precipitated with pentane. The solids were transferred to a frit, washed with copious pentane, and dried in vacuo to give 190 mg (68%) of a green microcrystalline product. Analytically pure samples were obtained by recrystallization from CH_2Cl_2/diethyl ether. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.77 (s). ^1H NMR (CD_2Cl_2): δ 19.96 (d, 1H, Ru═C*H*, $J_{HP} = 10.98$ Hz), 9.81 (br s, 1H, H_{ortho} (pyridine)), 8.13 (d, 1H, Tp), 8.01 (s, 1H, Tp), 7.95 (d, 1H, Tp), 7.84 (s, 1H, Tp), 7.76 (t, 1H, H_{para} (pyridine), $J_{HH} = 7.32$ Hz), 7.62 (t, 1H, H_{para} (carbene), $J_{HH} = 7.32$ Hz), 7.15 (br s, 7H, H_{ortho} and H_{meta} pyridine and carbene), 6.63 (t, 1H, Tp), 6.52 (s, 1H, Tp), 6.10 (t, 1H, Tp), 5.87 (s, 1H, Tp), 5.32 (s, 1H, Tp), 1.67−1.21 (m, 33H, $H_{cyclohexyl}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 339.30 (m, Ru═*C*, $J_{CP} = 14.07$ Hz), 154.29, 152.01, 147.71, 145.32, 143.25, 138.47, 137.70, 136.05, 133.83, 132.41, 129.06, 128.25, 125.10, 108.10, 106.76, 34.90 (d, $J = 17.92$ Hz), 29.77, 29.18, 27.77 (d, $J = 15.16$ Hz), 27.49 (d, $J = 8.27$ Hz), 26.13. IR (NaCl): 2484 cm^{-1} (B−H). Anal. Calcd for $C_{39}H_{54}N_7BF_6PRuSb$: C, 46.87; H, 5.45; N, 9.81. Found: C, 46.91; H, 5.49; N, 9.56.

[Tp(PCy$_3$)(CH$_3$CN)Ru═CHPh][SbF$_6$] (5). (a) A 50 mL Schlenk flask was charged with **2** (200 mg, 0.28 mmol) and $AgSbF_6$ (95.4 mg, 0.28 mmol). CH_3CN (5 mL) was added, followed by 5 mL of CH_2Cl_2. The reaction was stirred for 90 min, and the solvent was removed in vacuo. The resulting olive green solid was redissolved in CH_2Cl_2 (15 mL) and filtered through a plug of Celite. The solution was concentrated to 10 mL, and the product was precipitated with 50 mL of pentane. The resulting solids were transferred to a frit, washed with pentane, and dried under vacuum. Yield = 160 mg (60%).

(b) A 25 mL Schlenk flask was charged with **3** (50 mg, 0.060 mmol). CH_2Cl_2 (5 mL) was added followed by CH_3CN (5 mL). The reaction mixture was stirred for 30 min and then dried in vacuo, leaving the product as a dark green solid. Yield = 49 mg (100%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.09 (s). ^1H NMR (CD_2Cl_2): δ 18.90 (d, 1H, Ru═C*H*, $J_{HP} = 8.05$ Hz), 8.27 (s, 1H, Tp), 7.94 (t, 2H, Tp), 7.73 (s, 1H, Tp), 7.59 (t, 1H, H_{para}, $J_{HH} = 7.32$ Hz), 7.16 (br s, 4H, H_{para} and H_{meta}), 6.53 (s, 1H, Tp), 6.34 (s, 1H, Tp), 6.27 (s, 1H, Tp), 6.14 (s, 1H, Tp), 5.98 (s, 1H, Tp), 2.45 (s, 3H, C*H*$_3$CN), 2.06−1.12 (m, 33H, $H_{cyclohexyl}$). $^{13}C\ \{^1H\}$ (CD_2Cl_2): δ 338.11 (d, $J_{CP} = 12.41$ Hz), 151.01, 145.05, 144.96, 142.79, 137.73, 136.70, 135.30, 133.93, 132.48, 128.91, 126.84, 107.16, 106.96, 106.39, 34.20 (d, $J = 28.95$ Hz), 29.44, 27.59 (d, $J = 13.78$), 27.27 (d, $J = 12.41$), 26.29, 4.26. IR (NaCl): 2484 (B−H); 2287 cm^{-1} (CH_3CN). Anal. Calcd for $C_{36}H_{52}N_7BF_6PRuSb$: C, 44.97; H, 5.45; N, 10.20. Found: C, 44.44; H, 5.44; N, 9.95.

X-ray Structure Determination of 3. Crystals suitable for X-ray structure determination were grown by slow diffusion of diethyl ether into an acetone solution of **3** at −30 °C. An emerald green flake was mounted in Paratone-N oil (Exxon) on a glass fiber and centered in a cold stream (Crystal Logic) on a Nonius CAD-4 diffractometer. Unit cell parameters were determined from 25 reflections with $12° < \theta < 14°$. Table 1 summarizes the crystallographic data. Two equivalent sets of data were collected with 1.15° ω-scans and merged in point group 2/*m* using CRYM programs. Individual backgrounds were replaced by a function of θ based on weak data with $I < 8(\sigma)(I)$. Lorentz and polarization factors were applied; no decay (monitored by three reflections measured every 75 min) or absorption corrections (based on six Ψ-scans) were needed. Weights *w* were calculated as $1/\sigma^2(F_o^2)$; variances $(\sigma^2(F_o)^2)$ were derived from counting statistics plus an additional term $(0.0014I)^2$; variances on the observed data were obtained by propagation of error plus another additional term $(0.0014\langle I\rangle)^2$. The structure was solved by direct methods (SHELXS)[30] and refined by full-matrix least-squares on F^2 (SHELXL).[31] The diethyl ether solvent is slightly disordered and partially present (refined population of 0.872(5)). The hydrogen atoms on the ether were placed at calculated positions; the coordinates of all other hydrogen atoms were refined. The U_{iso} of every hydrogen atom was fixed at 120% of the U_{eq} of the attached atom. All non-hydrogen atoms were refined anisotropically.

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Supporting Information Available: Tables of crystal and intensity collection data, positional and displacement parameters, complete bond distances and bond angles, and a figure showing the complete atom-labeling scheme for **3** (16 pages). See any current masthead page for ordering and Internet access instructions.

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