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Reaction of Tp(PPh_3)Ru(η^2-O_2CCHPh_2) with Carbene and Vinylidene Precursors

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Tp(PPh_3)Ru(η^2-O_2CCHPh_2) (**1**) [Tp = tris(pyrazolyl)borate] has been prepared by the reaction of TpRu(Cl)(PPh_3)$_2$ with 1.2 equiv of NaO_2CCHPh_2. Complex **1** reacts with diphenylcyclopropene to generate the metallacycle Tp(PPh_3)Ru[κ^2-(C,O)-C(=CHCHPh$_2$)OC(CHPh$_2$)=O] (**2**). A trace of the carbene Tp(PPh_3)(η^1-O_2CCHPh_2)Ru=CHCH=C(Ph)$_2$ (**3**) is also observed in the crude reaction mixture. Compound **1** reacts with phenyldiazomethane to form the benzylidene Tp(PPh_3)(η^1-O_2CCHPh_2)Ru=CHPh (**4**). A similar species is also available by the reaction between AgO_2CCHPh_2 and Tp(PCy_3)(Cl)Ru=CHCH=C(CH_3)$_2$ (**5**), which affords Tp(PCy_3)(η^1-O_2CCHPh_2)Ru=CHCH=C(CH_3)$_2$ (**6**). With the addition of an excess of HCl, complexes **4** and **6** release free HO_2CCHPh_2 and are converted to Tp(PPh_3)(Cl)Ru=CHPh (**7**) and complex **5**, respectively. The reaction of **1** with phenylacetylene yields the five-membered chelate Tp(PPh_3)Ru[κ^2-(C,O)-C(=CHPh)OC(CHPh$_2$)=O] (**8**). Complex **8** is also formed in the reaction of Tp(PPh_3)(Cl)Ru=C=CHPh with 1.2 equiv of AgO_2CCHPh_2. Compounds **1**, **2**, and **8** have been characterized by X-ray crystallography. Complexes **2**, **5**, **6**, **7**, and **8** do not catalyze olefin metathesis reactions, while **4** is an active initiator for the ring-opening metathesis polymerization of norbornene.

Introduction

Tris(pyrazolyl)borate ruthenium complexes have been well studied over the past five years.[1] A wide variety of Tp[Ru] species containing ruthenium−carbon bonds including vinylidene,[2−4] allenylidene,[2,5] alkylidene,[5,6] and alkyl[7] ligands have been prepared, and these compounds have proven useful for carbon−carbon bond forming reactions including alkyne−alkyne[3a,8] and alkyne−olefin[9] couplings and olefin metathesis.[6,10] Due to our ongoing research program involving the preparation of new ruthenium carbene complexes for applications in olefin metathesis,[11] we became interested in the reactions of carbene precursors with Tp[Ru] fragments. Our group and others have reported that cyclopropene derivatives,[12] diazo compounds,[13,14] and terminal alkynes[2,3,15] can react with transition metals to generate

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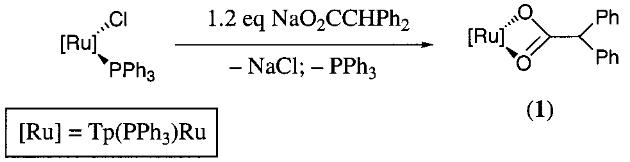
Scheme 1



alkylidene and vinylidene complexes. The use of alkynes for the preparation of Tp[Ru] vinylidenes has been well explored by a number of groups.[2-4] However, the reaction of Tp[Ru] complexes with cyclopropenes or diazo compounds has not been described in the literature.

We report here the first example of an isolable Tp[Ru] η^2-carboxylate complex, $Tp(PPh_3)Ru(\eta^2\text{-}O_2CCHPh_2)$ (**1**) (Scheme 1). This compound reacts cleanly with several carbene precursors to form new ruthenium−carbon bonds where the carboxylate shifts from η^2 to η^1 coordination and, in some cases, couples to the incoming ligand. For example, the reaction of **1** with diphenylcyclopropene results in the generation of the five-membered chelate $Tp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHCHPh_2)OC(CHPh_2){=}O]$ (**2**) (Scheme 2). Complex **1** reacts with phenylacetylene to produce the related metallacycle $Tp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHPh)OC(CHPh_2){=}O]$ (**8**) (Scheme 4). The η^2-carboxylate complex also undergoes reaction with phenyldiazomethane, yielding the new ruthenium benzylidene $Tp(PPh_3)(\eta^1\text{-}O_2CCHPh_2)Ru{=}CHPh$ (**4**) (Scheme 3). This paper describes the synthesis and characterization of these new compounds as well as several related species. The olefin metathesis activities of these Tp[Ru] complexes have also been preliminarily explored.

Results and Discussion

Synthesis of $Tp(PPh_3)Ru(\eta^2\text{-}O_2CCHPh_2)$ (1). The reaction of NaO_2CCHPh_2 with $TpRu(Cl)(PPh_3)_2$ for 24 h in refluxing THF results in clean displacement of one chloride and one PPh_3 ligand to afford $Tp(PPh_3)Ru(\eta^2\text{-}O_2CCHPh_2)$ (**1**) in 82% isolated yield (Scheme 1). In contrast to the formyl complex $Tp(PPh_3)Ru(\eta^2\text{-}O_2CH)$, which was reported by Hill and co-workers,[2b] complex **1** is thermally stable and is readily purified by recrystallization from CH_2Cl_2/pentane.

The product is isolated as an air-stable light yellow solid which is insoluble in pentane, slightly soluble in benzene, and soluble in chlorinated solvents and THF. ^1H NMR spectroscopy of complex **1** shows six resonances for the pyrazolyl protons, indicating that the carboxylate is bound to the metal center in a symmetrical η^2 fashion. The η^2 binding mode is confirmed by IR spectroscopy, which shows the OCO asymmetric stretch at 1526 cm^{-1}. This value is slightly higher than that in $Cp(PPh_3)Ru[\eta^2\text{-}O_2C(t\text{-}Bu)]$ (1495 cm^{-1})[16] and $Cp(PPh_3)Ru(\eta^2\text{-}O_2CCH_3)$ (1490 cm^{-1}),[16] and the difference in IR stretching frequencies in these otherwise similar complexes may be due to the increased electron-donating ability of the Tp ligand relative to the Cp ligand.[17] The solid-state structure of complex **1** was determined by X-ray crystallography. Large orange-yellow crystals were grown by vapor diffusion of pentane into a concentrated CH_2Cl_2 solution of **1** at room temperature. A labeled view of the complex is shown in Figure 1, collection and refinement data are summarized in Table 1, and selected bond lengths and bond angles are reported in Table 2. The Ru−O bond lengths in complex **1** are 2.1481(14) and 2.1631(16) Å. These distances are in the range of other crystallographically characterized ruthenium η^2-carboxylates, such as $Cp(PPh_3)Ru[\eta^2\text{-}O_2C(t\text{-}Bu)]$ (d(Ru−O) = 2.200(3) and 2.202(4) Å),[16] [(*S*)-BINAP]$Ru[\eta^2\text{-}O_2C(t\text{-}Bu)]_2$ (d(Ru−O) = 2.216(8) and 2.137(6) Å),[18] and $(PPh_3)_2(CO)(Cl)Ru(\eta^2\text{-}O_2CMe)$ (d(Ru−O) = 2.152(6) and 2.144(6) Å).[19] In general, the structure of **1** exhibits no unusual features compared to these and other related ruthenium adducts.

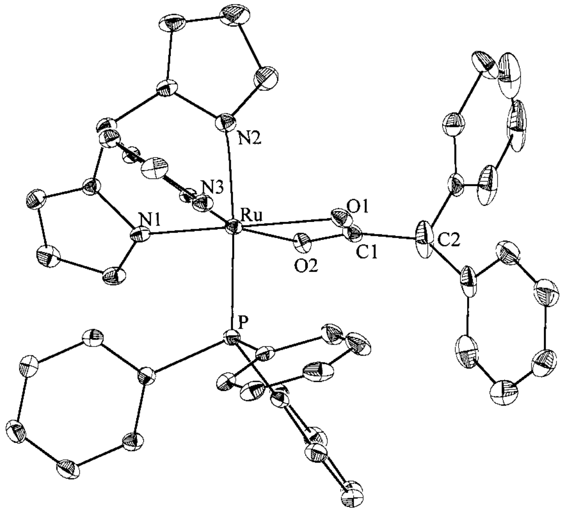


Figure 1. Labeled view of complex **1** with 50% probability ellipsoids.

Reaction of 1 with 3,3-Diphenylcyclopropene. Complex **1** serves as a versatile starting material for ruthenium−carbon bond forming reactions, because the carboxylate ligand undergoes facile η^2 to η^1 interconversion to open up a coordination site at the metal center. For example, complex **1** reacts slowly with diphenylcyclopropene in toluene over 24 h to produce the metallacyclic species $Tp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHCHPh_2)OC(CHPh_2){=}O]$ (**2**) in 48% isolated yield (Scheme 2). Complex **2** is isolated as an orange powder and forms light yellow crystals upon recrystallization from toluene/pentane. This compound is air-stable indefinitely in the solid state, but decomposes in air when in solution to form an intractable dark red mixture.

The ^1H NMR spectrum of **2** shows nine separate resonances for the pyrazolyl protons, indicating that the metal is a stereogenic center. The protons attached to the β- and γ-carbons appear as doublets (J_{HH} = 9 Hz)

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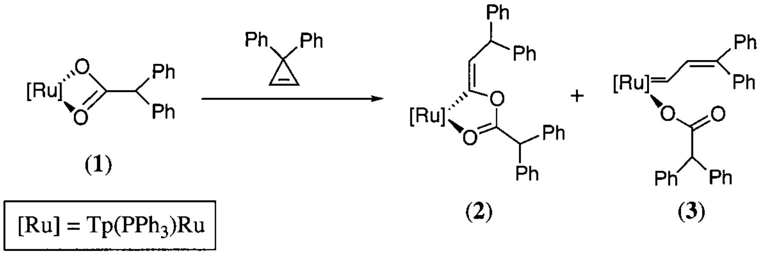
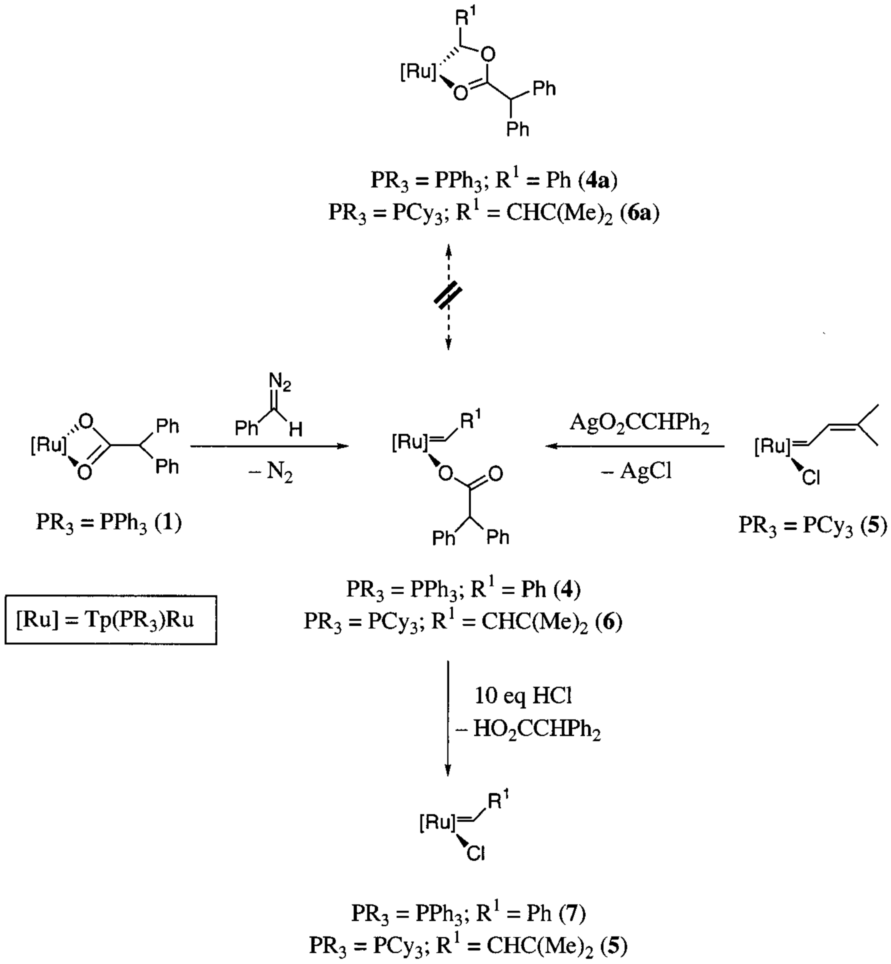
Scheme 2



Scheme 3



at 5.42 and 4.81 ppm, respectively, and show no coupling to the remote ^{31}P nucleus. ^{13}C NMR spectroscopy of complex **2** shows C_α as a doublet ($J_{CP} = 17$ Hz) at 203.97 ppm and C_β as a singlet at 118.97 ppm. The downfield shift of C_α, as well as the observed carbon–phosphorus coupling, indicate that this carbon is sp^2 hybridized and is bound to the metal center. However, this peak is significantly upfield of a typical Ru vinylidene or alkylidene carbon resonance.[20]A small amount of the analogous carbene complex Tp(PPh$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHCH=C(Ph)$_2$ (**3**) (<3%) is also observed if this reaction is monitored by ^{1}H NMR spectroscopy. The α-proton of the alkylidene appears as an overlapping doublet of doublets (apparent triplet) at 18.56 ppm.[21] Unfortunately, this product could not be characterized by any other spectroscopic methods due to its low concentration in solution. Attempts to improve the yield of complex **3** by changing the reaction conditions (solvent, temperature, time) were unsuccessful, and complexes **2** and **3** do not appear to interconvert upon exposure to heat or UV irradiation.[22] In general, these data suggest that complexes **2** and **3** are formed independently and that **3** is not an intermediate in the generation of **2**. Complex **3** is the product of a well-precedented ring opening of diphenylcyclopropene at a Ru(II) center.[12] In contrast, the mechanism of formation of **2** (which requires a formal 1,3-hydrogen shift within the cyclopropene-derived fragment) is not well understood at this time.[23]

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[20] Carbon-13 NMR shifts between 350 and 300 ppm are typical of ruthenium vinylidenes (for examples see ref 2 and ref 3) and alkylidenes (for example see ref 5).

[21] Proton NMR shifts between 18 and 21 ppm are typical of ruthenium alkylidenes. For examples see ref 5.

[22] After 2 days at 45 °C both species decompose entirely. The identity of the multiple decomposition products is unknown at this time.

Scheme 4

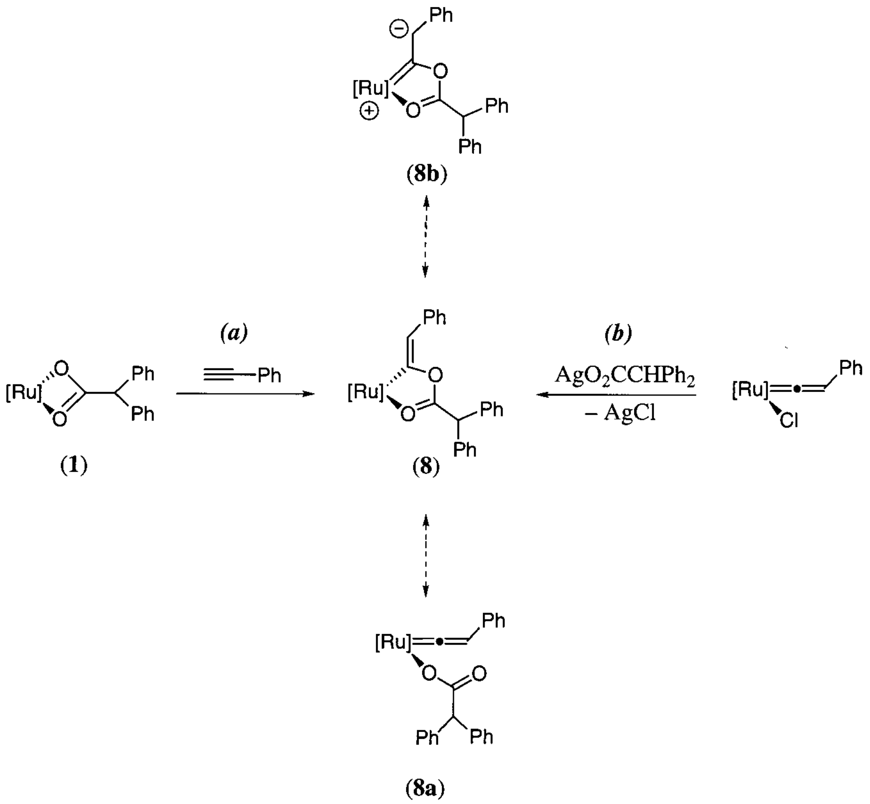

Table 1. X-ray Experimental Data

	$\mathbf{1}\cdot CH_2Cl_2$	$\mathbf{2}\cdot 1/3(C_5H_{12})\cdot 1/6(C_7H_8)$	$\mathbf{8}\cdot 1/2(CH_2Cl_2)$
formula	$C_{42}H_{38}BCl_2N_6O_2PRu$- $[C_{41}H_{36}BN_6O_2PRu\cdot CH_2Cl_2]$	$C_{58.83}H_{53.33}BN_6O_2PRu$- $[C_{56}H_{48}BN_6O_2PRu\cdot 1/3\ (C_5H_{12})\cdot$ $1/6(C_7H_8)]$	$C_{49.50}H_{43}BClN_6O_2PRu$- $[C_{49}H_{42}BN_6O_2PRu\cdot 1/2(CH_2Cl_2)]$
fw	872.56 [787.63 × 84.93]	1019.26 [979.89 × 1/3(72.15) × 1/6(92.14)]	932.23 [889.77 × 1/2 (84.93)]
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$ (# 14)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
a, Å	15.112(3)	14.146(5)	15.573(4)
b, Å	14.287(3)	21.309(8)	18.179(7)
c, Å	19.039(4)	25.345(8)	18.245(5)
α, deg	90	84.57(3)	98.75(3)
β, deg	105.32(3)	79.86(3)	113.89(2)
γ, deg	90	87.45(3)	105.27(2)
volume, Å^3	3964.6(14)	7484(5)	4355(2)
Z	4	6	4
ρ_{calc}, g/cm^3	1.462	1.357	1.422
μ, mm^{-1}	0.62	0.40	0.51
F_{000}	1784	3170	1916
cryst shape	plate	wedge	wedge
cryst color	yellow	canary yellow	yellow
cryst size, mm	0.07 × 0.28 × 0.35	0.11 × 0.33 × 0.44	0.20 × 0.25 × 0.44
T, K	84	84	84
θ range, γ	1.8, 25.0	1.5, 25.0	1.5, 25.0
h,k,l limits	0, 17; −16, 16; −22, 22	−16, 16; −25, 25; −29, 30	−18, 18; −21, 21; −21, 21
no. of data measd	15 540	53 947	31 982
no. of unique data	6953	26 257	15 315
R_{int}[b]	0.016	0.031	0.024
data, $F_o > 4\sigma(F_o)$	6231	21 442	13 208
no. of params/restraints	703/0	2302/12	1360/0
R1,wR2; all data	0.032, 0.060	0.057, 0.082	0.044, 0.074
R1,wR2; $F_o > 4\sigma(F_o)$	0.026, 0.058	0.041, 0.078	0.035, 0.072
GOF on F^2	1.78	1.57	1.70
$\Delta\rho_{max,min}$, e Å^{-3}	0.39, −0.41	1.54, −1.06	1.52, −1.23

[a] All data were collected on a CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). [b] $R_{int} = \sum|\Delta F_o^2| / \sum 2[F_o^2]$ for reflections measured exactly twice with each $F_o > 0$.

The structure of complex **2** was confirmed by X-ray crystallography. Suitable crystals were grown by vapor diffusion of pentane into a concentrated toluene solution at room temperature. A labeled view is shown in Figure 2, and the collection and refinement data are summarized in Table 1. Complex **2** crystallizes with three

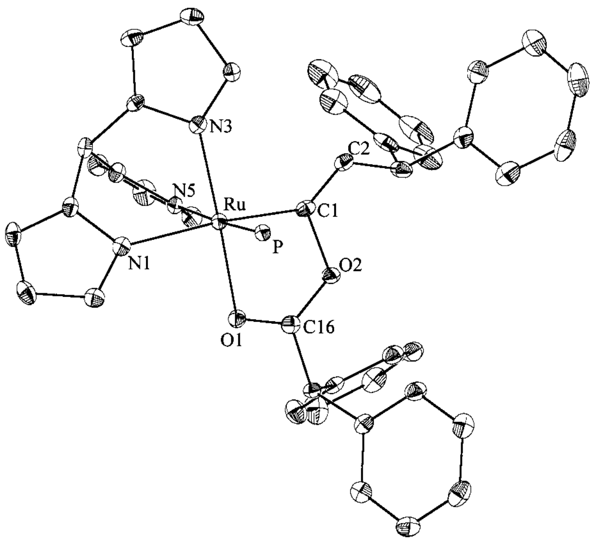

Figure 2. Labeled view of complex **2** with 50% probability ellipsoids (phenyl groups on phosphine ligand omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Bond Lengths			
Ru−N(1)	2.0359(18)	Ru−O(1)	2.1481(14)
Ru−N(2)	2.0584(17)	Ru−O(2)	2.1631(16)
Ru−N(3)	2.1361(16)	O(1)−C(1)	1.271(2)
Ru−P	2.2795(7)	O(2)−C(1)	1.263(2)
Bond Angles			
N(1)−Ru−O(2)	103.44(6)	O(2)−Ru−P	95.66(4)
N(3)−Ru−O(2)	164.64(6)	O(1)−Ru−P	92.55(4)
N(2)−Ru−O(2)	87.98(6)	O(2)−Ru−O(1)	60.95(5)
N(1)−Ru−O(1)	164.02(6)	C(1)−O(1)−Ru	89.44(12)
N(3)−Ru−O(1)	105.26(6)	C(1)−O(2)−Ru	90.32(12)
N(2)−Ru−O(1)	90.96(6)	O(2)−C(1)−O(1)	119.26(19)

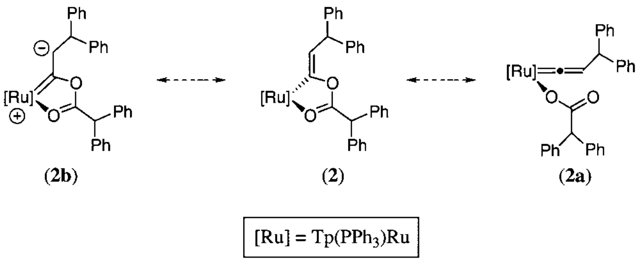

Figure 3. Tautomeric forms of complex **2**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 2 (Molecule A)

Bond Lengths			
Ru−C(1)	2.005(3)	Ru−P	2.2820(12)
Ru−N(1)	2.152(3)	O(1)−C(16)	1.242(4)
Ru−N(3)	2.052(3)	O(2)−C(16)	1.302(4)
Ru−N(5)	2.129(3)	O(2)−C(1)	1.526(3)
Ru−O(1)	2.098(2)	C(1)−C(2)	1.327(4)
Bond Angles			
N(1)−Ru−O(1)	91.67(9)	O(1)−Ru−P	96.28(6)
N(3)−Ru−O(1)	171.63(9)	Ru−O(1)−C(16)	112.49(19)
N(5)−Ru−O(1)	87.32(9)	Ru−C(1)−O(2)	108.64(18)
N(1)−Ru−C(1)	169.05(10)	Ru−C(1)−C(2)	141.7(2)
N(3)−Ru−C(1)	97.51(11)	N(5)−Ru−C(1)	87.06(11)
O(1)−C(16)−O(2)	123.1(3)	O(2)−C(1)−C(2)	108.8(3)

independent molecules (which are very similar in structure) in the asymmetric unit, and the bond distances and bond angles for molecule A are reported in Table 3. The average Ru−C(1) distance of 1.997 Å is intermediate between that in the Ru(II) benzylidene [Tp(PCy$_3$)(H$_2$O)Ru=CHPh]BF$_4$ (d(Ru−C) = 1.878(4) Å)[6] and that in the Ru(II) vinyl species Cp(CO)(PPh$_3$)Ru−C(O^{i}Pr)=CHPh (d(Ru−C) = 2.130(6) Å).[24] In related compounds, Werner and co-workers have suggested that this type of intermediate bond distance indicates significant contribution of a zwitterionic alkylidene complex (**2b**) (Figure 3) to the solid-state structure of the metallacycle.[25,26] The average C(1)−O(2) distance of 1.516 Å in complex **2** is much longer than a typical C−O single bond. (For example, the C$_\alpha$−O bond length in Cp(CO)(PPh3)Ru−C(O^{i}Pr)=CHPh is 1.381(7) Å.)[24] Additionally, the average Ru−C(1)−C(2) angle is 140.6°, while the average O(2)−C(1)−C(2) angle is 109.2°, which are both significant distortions from the ideal sp^2 angles of 120°. Taken together, these data reflect a contribution of the tautomeric vinylidene (**2a**) (Figure 3) to the solid-state structure of complex **2**.[26]

Reaction of 1 with Phenyldiazomethane. Complex **1** reacts with an excess of phenyldiazomethane to generate Tp(PPh$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHPh (**4**) in 78% yield (Scheme 3). The reaction can be followed by observing a dramatic color change from light yellow to dark green and is complete within 3 h. ^{1}H and ^{13}C NMR spectroscopy clearly confirm the identity of complex **4** as a transition metal carbene and *not* its metallacyclic tautomer **4a** (Scheme 3). The α-proton of the carbene appears as a doublet (J_{HP} = 15 Hz) at 19.06 ppm, while the α-carbon appears as a doublet (J_{HP} = 11 Hz) at 339.63 ppm. Interestingly, a number of similar compounds of the general formula Cp(PPh$_3$)(η^1-O$_2$CR^1)Ru(CR$_2$) [R = Ar; R^1 = CH$_3$, ^{t}Bu] have been reported,[16] and their ^{13}C NMR spectra show *no* downfield resonance for C$_\alpha$. As a result, the authors have suggested that these complexes are better described as the tautomeric metallacycles Cp(PPh$_3$)Ru[κ^2-(C,O)-C(R)$_2$OC(CR^1)=O].[16] This is yet another example underlying the inherent reactivity differences between Cp[Ru] compounds and the analogous Tp[Ru] species.[27]

A complex similar to **4** can also be prepared by the reaction of 1.2 equiv of AgO$_2$CCHPh$_2$ with Tp(PCy$_3$)(Cl)Ru=CHCH=C(CH$_3$)$_2$ (**5**) (Scheme 3). This reaction proceeds instantaneously to afford Tp(PCy$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHCH=C(CH$_3$)$_2$ (**6**) in 61% isolated yield.

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(23) Low-temperature ^{1}H, ^{13}C, or ^{31}P NMR studies of this reaction reveal that no long-lived intermediates are generated during the formation of complex **2**, and, with the exception of traces of carbene **3**, only starting material and product can be observed as the reaction progresses. Several additional experiments provide preliminary insights into the mechanism of this reaction. First, the rate of formation of **2** is not affected by the addition of up to 10 equiv of free PPh$_3$. Second, the rate remains constant as the solvent is changed from C$_6$D$_6$ (ϵ = 2.3) to CD$_2$Cl$_2$ (ϵ = 8.9), which represents a significant change in the dielectric constant of the reaction medium. The former result indicates that phosphine dissociation is not required for this reaction to proceed and suggests that the carboxylate ligand undergoes interconversion between an η^2 and an η^1 geometry to generate an open coordination site for olefin binding. The latter result suggests that highly charged intermediates are not involved in the formation of **2**. Further investigations on this topic are ongoing.

(24) Bruce, M. I.; Duffy, D. N.; Humphrey, M. G.; Swincer, A. G. *J. Organomet. Chem.* **1985**, *282*, 383.

(25) Daniel, T.; Mahr, N.; Braun, T.; Werner, H. *Organometallics* **1993**, *12*, 1475.

(26) In solution, the chemical shift of the α-carbon of complex **2** is more consistent with its formulation as a ruthenium vinyl adduct than as the tautomeric alkylidene or vinylidene structures [ref 24].

(27) For a review of the unique chemistry of the Tp ligand see: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

Again, ^{1}H and ^{13}C NMR spectroscopy verify the identity of this complex as a transition metal alkylidene and not a metallacyclic species. The α-proton appears as an apparent triplet ($J_{HP} = J_{HH} = 13$ Hz) at 19.26 ppm by ^{1}H NMR, while the α-carbon appears as a doublet ($J_{CP} = 14$ Hz) at 324.65 ppm by ^{13}C NMR spectroscopy.

Both complexes **4** and **6** react rapidly and quantitatively with an excess of HCl to liberate HO_2CCHPh_2 and generate the appropriate complex $Tp(PR_3)(Cl)Ru{=}CHR^1$ [R = Cy; $R^1 = CH{=}C(CH_3)_2$ (**5**) or R = Ph; R^1 = Ph (**7**)] (Scheme 3). Complex **7** is analogous to the previously reported species $Tp(PCy_3)(Cl)Ru{=}CHPh$; however, it was not available by the same synthetic methodology.[6] This compound is a light green solid that can be separated from the free acid by several washes with toluene at −10 °C. NMR spectroscopy shows the α-proton of the carbene as a doublet ($J_{HP} = 12$ Hz) at 19.40 ppm, while the α-carbon appears as a doublet ($J_{CP} = 19$ Hz) at 340.57 ppm.[28] Interestingly, Werner has reported that the metallacycles $Cp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C(Ar)_2OC(CMe){=}O]$ react in a similar fashion with the chloride sources, such as Et_3NHCl and Al_2O_3/Cl^- (although HCl was not reported), to generate the corresponding alkylidenes $Cp(PPh_3)(Cl)Ru{=}CAr_2$.[16]

Reaction of 1 with Phenylacetylene. Complex **1** reacts rapidly with an excess of phenylacetylene to produce the metallacycle $Tp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHPh)OC(CHPh_2){=}O]$, **8**, in 53% isolated yield (Scheme 4). The identity of complex **8** as the five-membered chelate as opposed to the tautomeric vinylidene structure (**8a**) can be confirmed by NMR spectroscopy. ^{1}H NMR shows nine separate resonances for the pyrazolyl protons, and the proton attached to the β-carbon appears as a singlet at 5.16 ppm. ^{13}C NMR shows the α-carbon as a doublet at 210.44 ppm ($J_{HP} = 13$ Hz), significantly upfield of a typical vinylidene ^{13}C chemical shift.[20] Complex **8** is spectroscopically similar to **2**, as well as to the previously reported metallacycles $Cp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHCO_2Me)OC(Me){=}O]$[25] ($C_\alpha$ = 227.9 ppm) and $(CO)[\eta^1\text{-}O{=}C(Me_2)](P^iPr_3)_2Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHPh)OC(Me){=}O]BF_4$[29] ($C_\alpha$ = 204.7 ppm), which are the products of attack of coordinated carboxylates on vinylidene or alkynyl ligands.

In an attempt to generate the η^1-carboxylate, vinylidene complex $Tp(PPh_3)(\eta^1\text{-}O_2CCHPh_2)Ru{=}C{=}CHPh$ (**8a**) $Tp(PPh_3)(Cl)Ru{=}C{=}CHPh$[8d] was reacted with 1.2 equiv of AgO_2CCHPh_2 (Scheme 4). The reaction mixture instantaneously changed color from light red to yellow with the precipitation of AgCl. However ^{1}H, ^{31}P, and ^{13}C NMR analysis indicated the quantitative formation of chelate **8**, rather than vinylidene **8a**. Notably, Hill and co-workers have reported a similar reaction between $Tp(PPh_3)(Cl)Ru{=}C{=}CHAr$ and $[Et_2NH_2][S_2C(NMe_2)]$, resulting in coupling of the dithiocarbamate to the vinylidene moiety to generate the metallacycle $Tp(PPh_3)Ru[\kappa^2\text{-}(C,S)\text{-}C({=}CHAr)SC(NEt_2){=}S]$.[2] The α-carbon of this complex appears at a comparable chemical shift (201.2 ppm) by ^{13}C NMR spectroscopy.

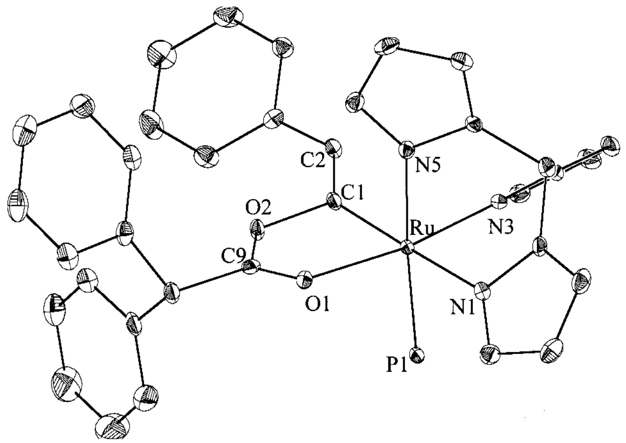

Figure 4. Labeled view of complex **8** with 50% probability ellipsoids (phenyl groups on phosphine ligand omitted for clarity).

On the basis of the above evidence, we believe that the formation of **8** by paths ***a*** and ***b*** (Scheme 4) proceeds through the unstable vinylidene complex **8a**. This proposed intermediate cannot be observed by NMR or IR spectroscopy but undergoes rapid nucleophilic attack to produce the metallacycle **8**. The propensity of vinylidenes to undergo attack by intramolecular nucleophiles has been well documented in the literature. A variety of groups have recently observed similar metallacycle formation with ligand nucleophiles including alcohols,[4b] amides,[4c] and pyrazole[7a] in Tp[Ru] vinylidene systems. Intramolecular nucleophilic attack on a vinylidene by an adjacent carboxylate oxygen has also been reported in a Cp[Ru] system.[25] However, it is interesting to note that the O−O chelate complex Tp(acac)Ru=C=CHPh[4a] is completely stable to this type of intramolecular attack. This is presumably because reaction of an acac oxygen with the vinylidene ligand would result in an unstable, coordinatively unsaturated species.

As further confirmation of its connectivity, the solid-state structure of complex **8** was obtained. Suitable crystals were grown by vapor diffusion of pentane into a concentrated CH_2Cl_2 solution of **8** at room temperature. The collection and refinement data are summarized in Table 1, and a labeled view of **8** is shown in Figure 4. Notably, this complex crystallizes with two similar but independent molecules in the asymmetric unit, and the bond lengths and angles for molecule A are reported in Table 4. The average Ru−C(1) distance of 1.992 Å is comparable to that in complex **2** (d(Ru−C) = 1.997 Å) as well as to that in the related metallacycles $Cp(PPh_3)Ru[\kappa^2\text{-}(C,O)\text{-}C({=}CHCO_2Me)OC(Me){=}O]$[25] ($d$(Ru−C) = 2.002(2) Å) and $(CO)(\eta_1\text{-}OC(Me_2)(P^iPr_3)_2Ru\text{-}[\kappa^2\text{-}(C,O)\text{-}C({=}CHPh)OC(Me){=}O]BF_4$[29] ($d$(Ru−C) = 1.967(8) Å). As described earlier for complex **2**, this short Ru−C distance points to a contribution from the zwitterionic resonance form **8b** to the solid-state structure of **8**.[30] Additionally, the relatively long average C−O distance of 1.495 Å and the distorted average Ru−C(1)−

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[28] The connectivity of complex **7** has been determined by X-ray crystallography; however, the refined model is of low quality due to a large region of disordered solvent. Crystal data for **7**: $C_{38.69}H_{36.69}BCl_{1.77}N_6PRu$, fw = 791.33, monoclinic, $P2_1/n$ (# 14), a = 10.0980(6) Å, b = 30.0953(17) Å, c = 11.9758(7) Å, β = 90.225(1)°, V = 3639.4(4) Å^3, Z = 4, r_{calc} = 1.439 g/cm^3, m = 0.64 mm^{-1}, F_{000} = 1609, T = 98 K. More information is provided in the Supporting Information.

[29] Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669.

[30] In solution, the chemical shift of the α-carbon of complex **8** is more consistent with its formulation as a ruthenium vinyl adduct than as the tautomeric alkylidene or vinylidene structures [ref 24].

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 8 (Molecule A)

Bond Lengths			
Ru−C(1)	1.989(3)	Ru−P	2.2918(14)
Ru−N(1)	2.191(2)	O(1)−C(9)	1.238(3)
Ru−N(3)	2.049(2)	O(2)−C(9)	1.310(3)
Ru−N(5)	2.122(2)	O(2)−C(1)	1.491(3)
Ru−O(1)	2.1223(19)	C(1)−C(2)	1.343(4)
Bond Angles			
N(1)−Ru−O(1)	97.89(8)	N(5)−Ru−O(1)	89.52(8)
N(3)−Ru−O(1)	171.71(8)	Ru−O(1)−C(9)	111.60(17)
Ru−C(1)−O(2)	110.64(17)	O(2)−C(9)−C(10)	114.6(2)
O(2)−C(1)−C(2)	111.1(2)	O(1)−C(9)−C(10)	122.4(2)
O(1)−C(9)−O(2)	123.1(2)	Ru−C(1)−C(2)	138.1(2)

C(2) and C(2)−C(1)−O(2) angles of 138.1° and 110.7°, respectively, suggest that the η^1-carboxylate, vinylidene tautomer **8a** may also play a role in the solid-state bonding of this molecule.[30]

Investigation of the Olefin Metathesis Activities of Complexes 2−8. The activities of complexes **2**−**8** for both ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) reactions were investigated. Compounds **2**−**8** do not to react with diethyl diallylmalonate or other common RCM substrates even after several days at elevated temperatures.[31] Complexes **2** and **8** also fail to react with norbornene and merely decompose in the presence of this substrate after 2 days at 45 °C. This lack of olefin metathesis activity is consistent with the formulation of **2** and **8** as metallacycles rather than the tautomeric vinylidene species. After a week at 45 °C, **5**, **6**, and **7** also fail to polymerize norbornene. Notably, the recently reported Tp[Ru] benzylidenes Tp(PCy$_3$)(X)Ru=CHPh [X = Cl, pyridine, CH$_3$CN, H$_2$O] are similarly unreactive toward norbornene and strained cyclic olefins.[6]

In contrast, complex **4** exhibits low activity as a single-component catalyst for the ROMP of norbornene. After 24 h at 45 °C, ^{1}H NMR shows approximately 5−15% of ROMP product relative to the norbornene starting material. No propagating species can be observed during this polymerization (presumably due to poor initiation), and the catalyst decomposes completely after 24 h of reaction. Attempts to precipitate the resulting poly(norbornene)s into methanol were unsuccessful, suggesting that the products are low molecular weight and oligomeric in nature.

Notably, complexes **4** and **7** exhibit significantly lower activity for the ROMP of norbornene than the previously reported vinylidene adduct, Tp(PPh$_3$)(Cl)Ru=C=CHPh.[8d,10] The dramatic differences in reactivity between these apparently similar compounds are currently under investigation in our laboratory.

Summary

A new complex, Tp(PPh$_3$)Ru(η^2-O$_2$CCHPh$_2$) (**1**), has been prepared and has proven a versatile precursor for the preparation of new Tp[Ru] organometallics. Complex **1** reacts with 3,3-diphenylcyclopropene and phenylacetylene to generate the metallacyclic species Tp(PPh$_3$)Ru[κ^2-(C,O)-C(=CHCHPh$_2$)OC(CHPh$_2$)=O] (**2**) and Tp(PPh$_3$)Ru[κ^2-(C,O)-C(=CHPh)OC(CHPh$_2$)=O] (**8**), respectively. Complex **1** also reacts cleanly with phenyldiazomethane to form the new transition metal benzylidene Tp(PPh$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHPh (**4**). Preliminary results show that the carbene complex **4** is active as a single-component catalyst for the ring-opening metathesis polymerization of norbornene. The product polymer is obtained in low yield and is of low molecular weight, suggesting that the active catalyst has a relatively short lifetime under the polymerization conditions.

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 the tris(pyrazolyl)borate protons were about 2 Hz. Elemental analyses were performed at the Caltech Analytical Facility or at Midwest Microlabs (Indianapolis, IN). High-resolution mass spectral data were obtained from UCLA.

Materials. Toluene, benzene, pentane, and methylene chloride were dried by passage through solvent purification columns.[32] Deuterated solvents were vacuum transferred from the appropriate drying agents, degassed by three consecutive freeze−pump−thaw cycles, and stored in the drybox. Diethyl diallylmalonate (Aldrich) and phenylacetylene (Aldrich) were passed through a plug of activated alumina and degassed by three consecutive freeze−pump−thaw cycles. Norbornene was sublimed prior to use and was stored in the drybox freezer. HO$_2$CCHPh$_2$ and KTp were obtained from commercial sources and used as received. NaO$_2$CCHPh$_2$ was prepared by the reaction of the free acid with NaOH, and AgO$_2$CCHPh$_2$ was prepared by the reaction of the sodium salt with AgNO$_3$ in H$_2$O. (PCy$_3$)$_2$(Cl)$_2$Ru=CHCHC(CH$_3$)$_2$,[15b] TpRuCl(PPh$_3$)$_2$,[33] Tp(PPh$_3$)(Cl)Ru=C=CHPh,[8d] diphenylcyclopropene[34] and phenyldiazomethane[35] were prepared according to literature procedures.

Tp(PPh$_3$)Ru(η^2-O$_2$CCHPh$_2$) (1). TpRu(PPh$_3$)$_2$Cl (2.4 g, 2.7 mmol) and NaO$_2$CCHPh$_2$ (0.77 g, 3.3 mmol) were combined in THF (50 mL), and the resulting suspension was refluxed for 24 h. The THF was removed under vacuum, and the solids were washed with pentane (4 × 25 mL). The resulting yellow product was dissolved in a 3:1 mixture of CH$_2$Cl$_2$ to pentane, filtered through a plug of Celite, and concentrated to dryness to give 1.75 g (82% yield) of a yellow powder. Analytically pure samples were obtained by recrystallization from CH$_2$Cl$_2$/pentane. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 63.7 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.83 (s, 1H, Tp), 7.65 (s, 2H, Tp), 7.35−7.11 (multiple peaks, 26H, P*Ph*$_3$, CH*Ph*$_2$, Tp), 6.84 (s, 2H, Tp), 6.19 (s, 1H, Tp), 5.75 (s, 2H, Tp), 4.56 (s, 1H, C*H*Ph$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 186.97 (*C*=O), 147.90, 139.56, 139.03, 136.34, 135.11, 128.93, 128.36, 126.72, 105.82, 105.22, 60.62. IR (C$_6$H$_6$): 2468 cm^{-1} (B−H), 1526 cm^{-1} (OCO). Anal. Calcd for C$_{41}$H$_{36}$N$_6$BO$_2$PRu: C, 62.52; H, 4.61; N, 10.67. Found: C, 62.79; H, 4.70; N, 11.00.

Tp(PPh$_3$)Ru[κ^2-(C,O)-C(=CHCHPh$_2$)OC(CHPh$_2$)=O] (2). Complex **1** (300 mg, 0.38 mmol) and diphenylcyclopropene (300

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[31] RCM is generally a more challenging reaction than ROMP for olefin metathesis catalysts. For example (PPh$_3$)$_2$Cl$_2$Ru=CHPh is an active catalyst for the ROMP of norbornene and cyclobutene, but is completely unreactive toward RCM substrates such as diethyl diallylmalonate. Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. 1996, unpublished results.

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mg, 1.56 mmol) were dissolved in toluene (20 mL). The resulting solution was stirred for 18 h, during which time it changed color from yellow to light orange. The reaction mixture was evaporated to dryness, and the solids were washed with cold (−10 °C) pentane (3 × 15 mL). The resulting yellow-orange solid was dried in vacuo to give 180 mg (48%) of product. Analytically pure samples were obtained by recrystallization from toluene/pentane. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 61.3 (s). $^{1}\mathrm{H}$ NMR ($\mathrm{CD_2Cl_2}$): δ 7.71 (s, 1H, Tp), 7.67 (s, 1H, Tp), 7.56 (s, 1H, Tp), 7.3−6.75 (multiple peaks, 36 H, $\mathrm{C}Ph_2$, $\mathrm{P}Ph_3$, $\mathrm{CH}Ph_2$, Tp), 6.45 (s, 1H, Tp), 6.41 (s, 1H, Tp), 5.90 (s, 1H, Tp), 5.84 (s, 1H, Tp), 5.78 (s, 1H, Tp), 5.42 (d, 1H, $J_{\mathrm{HH}} = 9$ Hz, Ru−C=C*H*CH(Ph)$_2$), 4.86 (s, 1H, C*H*Ph$_2$), 4.81 (d, 1H, $J_{\mathrm{HH}} = 9$ Hz, CHC*H*(Ph)$_2$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 203.97 (d, Ru−*C*, J_{CP} = 17 Hz), 180.43 (*C*=O), 147.15, 146.57, 146.12, 144.05, 140.73, 138.09, 137.89, 135.74, 135.01, 134.65, 134.55, 134.01, 133.91, 129.55−127.76 (multiple peaks), 127.03, 125.47, 125.30, 118.97, 105.45, 104.93, 104.42, 56.47, 47.76. IR ($\mathrm{CD_2Cl_2}$): 2477 cm^{-1} (B−H), 1618 cm^{-1} (OCO). Anal. Calcd for $\mathrm{C_{56}H_{48}N_6BO_2PRu}$: C, 68.64; H, 4.94; N, 8.58. Found: C, 68.43; H, 4.58; N, 8.84.

Observation of Tp(PPh$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHCH=C(Ph)$_2$ (3). Complex **1** (30 mg, 0.038 mmol) and diphenylcyclopropene (30 mg, 0.16 mmol) were combined in an NMR tube in the drybox. $\mathrm{CD_2Cl_2}$ (0.75 mL) was added, and the reaction was shaken for 24 h at room temperature. $^{1}\mathrm{H}$ NMR after 24 h showed a trace of the alkylidene product as an apparent triplet at 18.56 ppm.

Tp(PPh$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHPh (4). To a solution of **1** (500 mg, 0.635 mmol) in $\mathrm{CH_2Cl_2}$ (25 mL) was added phenyldiazomethane (150 mg, 1.27 mmol). The resulting solution was stirred for 3 h at room temperature, during which time it changed color from yellow to red to brown-green, and finally to dark green. The volatiles were removed in vacuo, and the solids were washed with 3 × 20 mL of pentane and dried under vacuum to leave 435 mg (78%) of a dark green powder. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 44.8 (s). $^{1}\mathrm{H}$ NMR ($\mathrm{CD_2Cl_2}$): δ 19.01 (d, 1H, $J_{\mathrm{HP}} = 15$ Hz, Ru=C*H*Ph), 7.92 (s, 1H, Tp), 7.78 (s, 1H, Tp), 7.67 (s, 1H, Tp), 7.62−7.03 (multiple peaks, 31H, P*Ph*$_3$, CH*Ph*$_2$, CH*Ph*, and Tp), 6.61 (s, 1H, Tp), 6.11 (s, 1H, Tp), 5.73 (s, 1H, Tp), 5.61 (s, 1H,Tp), 5.58 (s, 1H, Tp), 4.80 (s, 1H, C*H*Ph$_2$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 339.63 (d, Ru=*C*HPh, $J_{\mathrm{CP}} = 11$ Hz), 177.22 (*C*=O), 149.48, 145.87, 145,16, 144.40, 142.76, 142.52, 136.27, 135.55, 134.21, 134.02, 133.93, 132.50, 132.41, 132.09, 131.14, 129.70, 129.11, 128.84, 128.34, 127.99, 127.90, 127.62, 125.89, 125.53, 105.68, 105.62, 104.96, 60.90. IR ($\mathrm{CD_2Cl_2}$): 2480 cm^{-1} (B−H), 1614 cm^{-1} (OCO). Anal. Calcd for $\mathrm{C_{48}H_{42}N_6BO_2PRu}$: C, 65.68; H, 4.82; N, 9.57. Found: C, 65.87; H, 4.80; N, 9.54.

Tp(PCy$_3$)(Cl)Ru=CHCH=C(CH$_3$)$_2$ (5). (PCy$_3$)$_2$Cl$_2$Ru=CHCH=C(CH$_3$)$_2$ (1.0 g, 0.13 mmol) and KTp (0.32 g. 0.13 mmol) were dissolved in $\mathrm{CH_2Cl_2}$ (20 mL), and the reaction was stirred for 5 h, over which time a color change from purple to light green was observed. Pentane (50 mL) was added, and the reaction was filtered through a plug of Celite. The resulting solution was concentrated to 5 mL, and pentane (70 mL) was added to precipitate the bright green product. The solids were collected on a frit, washed with pentane (4 × 20 mL), and dried under vacuum to provide 0.63 g (72%) of product. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 35.02 (s). $^{1}\mathrm{H}$ NMR ($\mathrm{CD_2Cl_2}$): δ 19.53 (d of d's, 1H, $J_{\mathrm{HP}} = 9$ Hz, $J_{\mathrm{HH}} = 13$ Hz, Ru=C*H*CH), 8.42 (s, 1H, Tp), 7.84 (s, 1H, Tp), 7.77 (s, 1H, Tp), 7.53 (s, 1H, Tp), 7.24 (d, 1H, J_{HH} = 13 Hz, Ru=CHC*H*), 6.74 (s, 1H, Tp), 6.71 (s, 1H, Tp), 6.39 (s, 1H, Tp), 6.12 (s, 1H, Tp), 5.95 (s, 1H, Tp), 1.88−0.96 (multiple peaks, 33H, P*Cy*$_3$), 1.64 (s, 3H, C*Me*), 1.21 (s, 3H, C*Me*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 332.62 (d, Ru=*C*HPh, J_{CP} = 14 Hz), 147.86, 145.68, 144.79, 142.57, 139.59, 136.57, 135.40, 133.68, 105.96, 105.78, 104.71, 34.56, 34.38, 29.16, 28.51, 28.10, 28.01, 27.99, 28.92, 27.57, 26.46, 21.00. IR ($\mathrm{CD_2Cl_2}$): 2478 cm^{-1} (B−H). Anal. Calcd for $\mathrm{C_{32}H_{51}N_6BClPRu}$: C, 55.06; H, 7.36; N, 12.04. Found: C, 54.91; H, 7.22; N, 12.08.

Tp(PCy$_3$)(η^1-O$_2$CCHPh$_2$)Ru=CHCH=C(CH$_3$)$_2$ (6). Complex **5** (200 mg, 0.29 mmol) and AgO$_2$CCHPh$_2$ (110 mg, 0.32 mmol) were combined in $\mathrm{CH_2Cl_2}$ (15 mL). The reaction was stirred for 3 h and then filtered through a plug of Celite. The solvent was removed under vacuum to afford 150 mg (61%) of a dark green product. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 39.19 (s). $^{1}\mathrm{H}$ NMR ($\mathrm{CD_2Cl_2}$): δ 19.26 (t, 1H, $J_{\mathrm{HP}} = J_{\mathrm{HH}} = 13$ Hz, Ru=C*H*CH), 7.97 (s, 1H, Tp), 7.87 (s, 1H, Tp), 7.77 (s, 1H, Tp), 7.55 (s, 1H, Tp), 7.37−7.25 (multiple peaks, 3H, P*Ph*$_3$, Tp), 7.04−6.72 (multiple peaks, 14H, P*Ph*$_3$, Ru=CHC*H*), 6.52 (s, 1H, Tp), 6.29 (s, 1H, Tp), 6.05 (s, 1H, Tp), 5.84 (s, 1H, Tp), 4.74 (s, 1H, C*H*Ph$_2$), 1.84−0.82 (multiple peaks, 33H, P*Cy*$_3$), 1.75 (s, 3H, C*Me*), 1.30 (s, 3H, C*Me*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 324.65 (d, Ru=CHPh, J_{CP} = 14 Hz), 177.21 (*C*=O), 145.82, 145.19, 144.85, 144.77, 143.62, 143.02, 140.09, 136.65, 134.65, 133.28, 129.00, 128.96, 127.69, 127.51, 125.44, 125.13, 105.78, 105.29, 104.24, 61.62, 34.12, 33.94, 28.76, 27.97, 27.87, 27.75, 26.48, 20.69. IR ($\mathrm{CD_2Cl_2}$): 2475 cm^{-1} (B−H), 1617 cm^{-1} (OCO). Anal. Calcd for $\mathrm{C_{46}H_{62}N_6BO_2PRu}$: C, 63.22; H, 7.15; N, 9.62. Found: C, 63.33; H, 7.00; N, 9.29.

Tp(PPh$_3$)(Cl)Ru=CHPh (7). To a solution of **6** (190 mg, 0.22 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added HCl (1 mL of a 1.0 M solution in diethyl ether, 1.0 mmol). An immediate color change from dark to light green was observed, and the reaction was stirred for 30 min. The solvents were removed under vacuum, and the resulting green residue was washed with −10 °C toluene (3 × 10 mL) and then with a 3:1 mixture of pentane/toluene (2 × 15 mL). The solids were redissolved in $\mathrm{CH_2Cl_2}$ (15 mL), filtered through a plug of Celite, and concentrated under vacuum to afford 49 mg (33%) of the light green product. Satisfactory elemental analyses could not be obtained; however the structure of this complex was confirmed by X-ray crystallography (see Supporting Information) and by mass spectrometry. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 39.74 (s). $^{1}\mathrm{H}$ NMR ($\mathrm{CD_2Cl_2}$): δ 19.40 (d, 1H, $J_{\mathrm{HP}} = 12$ Hz, Ru=C*H*Ph), 7.93 (s, 1H, Tp), 7.78 (s, 1H, Tp), 7.73 (s, 1H, Tp), 7.56 (s, 1H, Tp), 7.40−6.95 (multiple peaks, 19H, P*Ph*$_3$, Ru=CH*Ph*), 6.50 (s, 1H, Tp), 6.13 (s, 1H, Tp), 5.92 (s, 1H, Tp), 5.56 (s, 2H, Tp). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 340.57 (d, Ru=*C*HPh, J_{CP} = 19 Hz), 135.95, 134.67, 134.28, 134.11, 132.37, 132.16, 131.95, 131.79, 129.84, 128.73, 127.88, 127.72, 106.06, 105.60, 105.35. IR ($\mathrm{CD_2Cl_2}$): 2480 cm^{-1} (B−H). Anal. Calcd for $\mathrm{C_{34}H_{31}N_6BClPRu}$: C, 58.17; H, 4.45; N, 11.97. Found: C, 59.46; H, 4.69; N, 11.18. FAB-HRMS: *m/z* calcd for M^{+} 702.1173; *m/z* found 702.1184.

Tp(PPh$_3$)Ru[κ^2-(C,O)-C(=CHPh)OC(CHPh$_2$)=O] (8). (a) To a solution of **1** (150 mg, 0.19 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added phenylacetylene (84 μL, 0.76 mmol). The reaction was stirred for 30 min, during which time a color change from orange to light yellow was observed, and the volatiles were removed under vacuum. The resulting solids were washed with 3 × 15 mL of pentane, then dissolved in 10 mL of $\mathrm{C_6H_6}$ and filtered through a plug of Celite. The light yellow solution was concentrated in vacuo to give 90 mg (53%) of product. Analytically pure samples were obtained by recrystallization from $\mathrm{CH_2Cl_2}$/pentane. (b) TpRu=C=CHPh(PPh$_3$)(Cl) (15 mg, 0.021 mmol) and AgO$_2$CCHPh$_2$ (8 mg, 0.025 mmol) were combined in an NMR tube. $\mathrm{CD_2Cl_2}$ was added, and the reaction was shaken for 5 min. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 62.12 (s). $^{1}\mathrm{H}$ NMR ($\mathrm{CD_2Cl_2}$): δ 7.76 (s, 1H, Tp), 7.71 (s, 1H, Tp), 7.61 (s, 1H, Tp), 7.31−6.76 (multiple peaks, 32H, CH*Ph*, P*Ph*$_3$, CH*Ph*$_2$, Tp), 6.49 (s, 1H, Tp), 5.99 (s, 1H, Tp), 5.95 (s, 1H, Tp), 5.85 (s, 1H, Tp), 5.16 (s, 1H, Ru−C=C*H*Ph), 4.93 (s, 1H, C*H*Ph$_2$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): δ 210.44 (d, Ru−*C*=CHPh, J_{CP} = 13 Hz), 181.40 (*C*=O), 145.93, 144.27, 140.26, 137.74, 137.54, 137.47, 136.03, 134.76, 134.39, 134.21, 134.12, 133.91, 129.35, 129.11, 128.87, 127.75, 127.70, 127.60, 127.26, 123.15, 117.03, 105.60, 105.12. IR ($\mathrm{CD_2Cl_2}$): 2479 cm^{-1} (B−H), 1612 cm^{-1} (OCO). Anal. Calcd for $\mathrm{C_{49}H_{42}N_6BO_2PRu}$: C, 66.14; H, 4.76; N, 9.45. Found: C, 66.21; H, 4.18; N, 9.18.

Polymerization of Norbornene with Complex 4. Complex **4** (5.0 mg, 0.0057 mmol) and norbornene (30 mg, 0.31

mmol, 53 equiv) were combined in an NMR tube. CD_2Cl_2 (1 mL) was added, and the reaction mixture was shaken for 1 min. The reaction was allowed to stand at room temperature for 2 h and was then heated to 45 °C and monitored every 12 h by ^{1}H NMR spectroscopy. After 24 h, the carbene resonance had completely disappeared, and traces (approximately 5−10%) of polynorbornene (approximately 1:1 cis/trans) were observed by ^{1}H NMR. The reaction mixture was poured into methanol; however no polymer precipitated, suggesting that a very low molecular weight product is formed.

Crystal Structures of 1, 2, and 8. General. Crystal, intensity collection, and refinement details are summarized in Table 1 for complexes **1**, **2**, and **8**.[28,36]

Data Collection and Processing. All data were collected at low temperature with ω-scans on a Nonius CAD-4 serial diffractometer equipped with a Crystal Logic CL24 low-temperature device using graphite-monochromated Mo Kα radiation with $\lambda = 0.71073$ Å. The crystals were mounted on glass fibers with Paratone-N oil. The unit cell was calculated from 25 centered reflections. Two sets of data were collected with ω-scans. CRYM[37] programs were used to apply Lorentz and polarization factors and to merge the multiples in the appropriate point group, $2/m$ for **1** and $P\bar{1}$ for **2** and **8**. No absorption corrections were applied for any complex. For **2** and **8**, the individual backgrounds were replaced by a background function of 2θ derived from weak reflections. Small decay corrections (0.33% for **1**, 0.51% for **2**, and 0.40% for **8**) were based on three check reflections measured every 75 min. 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, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$.

Structure Analysis and Refinement. SHELX97[38] was used to solve and to refine (using full-matrix least-squares) all structures. The structure of **1** was determined by the Patterson method and successive structure factor−Fourier calculations. The asymmetric unit consists of one molecule of **1** and one dichloromethane. The CH_2Cl_2 is disordered over two sites (0.500(1):0.500(1)) as is one of the phenyl groups (C(3)−C(8)) of the carboxylate (0.505(6):0.495(6)). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to disordered carbons (C(3)−C(8), C(3A)−C(8A), C(50), and C(60)) were placed in idealized positions with U_{iso} 1.2 times the U_{eq} of the attached carbon atom; all other hydrogen atoms were refined isotropically.

Direct methods were used in the structure solution of **2**. There are three molecules (A, B, and C) in the asymmetric unit, with slightly different orientations of some of the phenyl groups. Molecules B and C are most similar. Also present are one molecule of *n*-pentane and a toluene molecule disordered on a center of symmetry. This was not the typical toluene on a center, but a much less tractable example requiring a total of 12 restraints to keep it geometrically reasonable: nearest neighbor (1.39(0.001), 1.54(0.001)), next-nearest neighbor (2.55(0.01), flat (0.001); all carbon atoms were given equal anisotropic displacement parameters. The largest excursions in the final difference map were near this molecule (1.54 e Å^{-3} at 0.70 Å from H(7E) and −1.6 e Å^{-3} at 0.34 Å from H(5)). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms for both solvent molecules were placed at calculated positions; the coordinates of the other hydrogen atoms were refined with a U_{iso} 1.2 times the U_{eq} of the attached atom.

The structure of **8** was also determined via direct methods and subsequent difference maps. The two molecules in the asymmetric unit have essentially the same conformation, as does the single independent molecule in the toluene solvate.[39] Also present is one somewhat-disordered molecule of dichloromethane with large U_{eq}'s. The largest excursions in the final difference map are near this molecule (1.52 e Å^{-3} at 1.02 Å from Cl(1) and −1.23 e Å^{-3} at 0.43 Å from Cl(1), −1.19 e Å^{-3} at 0.70 Å from Cl(2), and −1.05 e Å^{-3} at 0.57 Å from Cl(1)). The hydrogen atoms of the dichloromethane were placed at calculated positions; the coordinates of the other hydrogen atoms were refined with a U_{iso} 1.2 times 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 figures showing the complete atom-labeling schemes for complexes **1**, **2**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) The Crystallographic Information Files (CIF) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications for complexes **1** (CCDC 133555), **2** (CCDC 164301), **7** (CCDC 165163), **8**·C_7H_8 (CCDC 133554), and **8**·(CH_2Cl_2) (CCDC 164302). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Structure factors are available from the authors via e-mail: xray@caltech.edu.

(37) Duchamp, D. J. American Crystallographic Association Meeting, Bozeman, MT, Paper B14, 1964; pp 29−30.

(38) Sheldrick, G. M. *SHELX97*: Program for Structure Refinement; Universität Göttingen: Germany, 1997.

(39) Crystal data for **8**·C_7H_8: $C_{56}H_{50}BN_6O_2PRu$, fw = 981.91, monoclinic, $P2_1/n$ (# 14), $a = 13.7367(7)$ Å, $b = 19.5683(10)$ Å, $c = 18.5679(10)$ Å, $\beta = 102.091(1)°$, $V = 4880.4(4)$ Å^3, $Z = 4$, $r_{\mathrm{calc}} = 1.336$ g/cm^3, $m = 0.40$ mm^{-1}, $F_{000} = 2032$, $T = 293$ K. More information is provided in the Supporting Information.