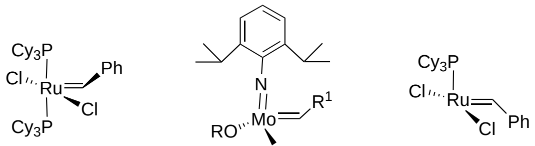
Ruthenium-Based Four-Coordinate Olefin Metathesis Catalysts**

Melanie S. Sanford, Lawrence M. Henling, Michael W. Day, and Robert H. Grubbs*

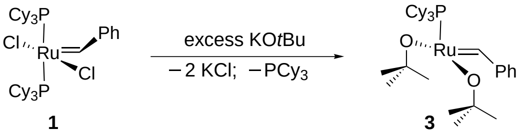
Recent work has shown that the ruthenium alkylidene complex $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (**1**) is a highly efficient catalyst for metathesis of olefins containing most common functional groups, and, as such, this complex has found extensive application in both organic and polymer chemistry.[1] Detailed experimental[2] and theoretical[3] studies have been carried out to elucidate the mechanism of activity of catalyst **1**, and these investigations implicate a 14-electron, mono-phosphane alkylidene, $[(PCy_3)Cl_2Ru{=}CHR]$ (**2**) as a probable intermediate both on the metathesis reaction coordinate and in the decomposition of **1**. Complex **2** is remarkable both for its unusual coordinatively unsaturated structure and for its similarity to the four-coordinate Mo and W olefin metathesis catalysts, $[(ArN)(OR)_2M{=}CHR^1]$, developed by Schrock (Figure 1).[4] Unfortunately, the short lifetime of this proposed intermediate **2** has rendered it elusive to isolation or even observation by spectroscopic methods, presumably a result of its high reactivity in solution with olefinic substrates,[2a] coordinating solvents,[5] and/or a second equivalent of **2**[2b]. Prompted by considerable interest in the nature and structure of this intermediate, we have pursued the preparation of isolable analogues of **2**. We reasoned that complexes such as **2** should be stabilized by more π-donating ligands, which would increase the electron density at the coordinatively unsaturated Ru^{II} center, and by larger ligands, which would drive the equilibrium towards phosphane dissociation and alleviate potential bimolecular decomposition pathways. Herein we report that the replacement of the two halide ligands of **1** with tertiary alkoxides, which possess both π-donor abilities[6] and steric parameters that can be easily modulated, has enabled the first four-coordinate, 14-electron ruthenium alkylidenes $[(PCy_3)(RO)_2Ru{=}CHPh]$ to be isolated.



1 **2**

Figure 1. Olefin metathesis catalysts and the proposed intermediate **2**.

The reaction of **1** with an excess of KO*t*Bu under rigorously anhydrous and air-free conditions proceeds cleanly to form $[(PCy_3)(tBuO)_2Ru{=}CHPh]$ (**3**) and one equivalent of PCy_3 [Eq. (1)]. Both of these products are extremely soluble in pentane and common organic solvents; however, the two can be separated by the addition of CuCl, which reacts with the free phosphane to form an insoluble polymeric material.[2a] The alkylidene product **3** is diamagnetic in solution and the NMR spectrum shows a single resonance signal for the carbene (doublet, $\delta = 15.5$) and alkoxide ($\delta = 1.29$) protons and a single ^{31}P resonance signal for the complex ($\delta = 83.5$). Although it is coordinatively unsaturated, complex **3** is remarkably stable, and solutions of **3** in C_6D_6 can be heated at 75 °C under an inert atmosphere for more than 24 h without significant decomposition (as observed by ^1H NMR spectroscopy).



1 **3** (1)

Single crystals of **3** were grown from a concentrated pentane solution at −30 °C and its highly unusual solid-state structure is shown in Figure 2. Despite the expected steric preference for the four-coordinate Ru^{II} center to adopt a tetrahedral geometry (as is observed in Schrock's Mo and W systems),[4] this complex crystallizes with a slightly distorted trigonal pyramidal ligand array. The phosphane ligand is at the vertex of the pyramid and the angles from the phosphane to the three other ligands are close to 90°. The angles within the trigonal plane are 133.19(6) (O1-Ru-O2), 114.47(9) (O2-Ru-C1), and 112.17(8)° (O1-Ru-C1), which suggests that this geometry may be a sterically induced distortion of the square-pyramidal structure adopted by the ruthenium alkylidene complex **1**.[7] In complex **3** the phenyl substituent of the carbene ligand is rotated away from the bulky phosphane and

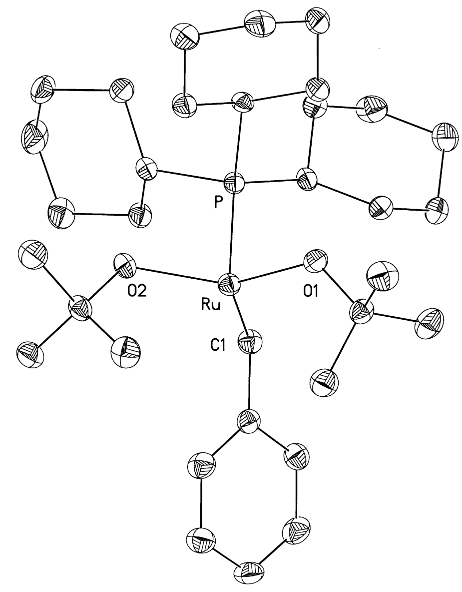


Figure 2. ORTEP plot of complex **3** (50 % probability ellipsoids). Selected bond lengths [Å] and bond angles [°]: Ru-C1 1.850(2), Ru-O1 1.9412(15), Ru-O2 1.9558(15), Ru-P 2.2232(7); C1-Ru-O1 112.17(8), C1-Ru-O2 114.47(9), O1-Ru-O2 133.19(6), C1-Ru-P 92.49(8), O1-Ru-P 93.49(5), O2-Ru-P 88.36(5).

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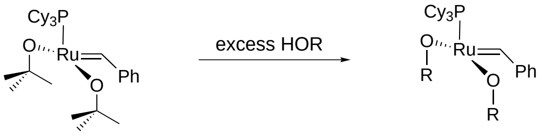
into the space below the trigonal plane which results in a P-Ru-C_α-H_α dihedral angle of 12.2 (14)°. Similar angles have been observed in 16-electron Ru^{II} alkylidene complexes that contain relatively small ligands (e.g. PPh_3);[8] however, complex **1** and its analogues which contain bulky PCy_3 ligands typically have P-Ru-C_α-H_α angles of close to 90°.[7] Notably, mechanistic studies of catalytic reactions with **1** suggest that the rotation of the carbene moiety to the conformation observed in complex **3** may be a crucial step on the pathway to the formation of the metallacyclobutane intermediate.[2a]

Another interesting feature of the structure of complex **3** is that despite the numerous accessible C−H bonds in the empty coordination site below the trigonal plane, the ruthenium center does not appear to be stabilized by agostic interactions. The closest Ru ⋯ C distance (other than C_α) is 3.091 Å and the closest Ru ⋯ H distance (other than H_α) is 2.75 Å, which are both long for agostic contacts.[9, 10] Furthermore, an overlay of the two *t*Bu groups shows that they are identical, which indicates that neither of these ligands is sufficiently distorted so as to interact with the metal center. Both IR spectroscopy and variable temperature ^1H NMR spectroscopy studies (which shows that the resonance signals of the *t*Bu groups are equivalent to −120 °C in C_5D_{12}) suggest that **3** is free of agostic interactions in solution. Only three other four-coordinate 14-electron Ru^{II} complexes have been structurally characterized[10] and all of these are formally 18-electron octahedral species with two agostic CH interactions occupying the two open coordination sites.

Complex **3** reacts readily with Brønsted acids including acidic alcohols and phenols. For example, the combination of **3** with an excess of $HOC(CH_3)(CF_3)_2$ or $HOC(CF_3)_3$ results in the rapid liberation of *t*BuOH and the formation of $[(PCy_3)(CH_3(CF_3)_2CO)_2Ru{=}CHPh]$ (**4**) and $[(PCy_3)((CF_3)_3CO)_2Ru{=}CHPh]$ (**5**), respectively [Eq. (2)].[11] Preliminary (NMR) experiments show that this reaction is equally facile for *ortho*-substituted phenols (e.g. 2,6-diphenylphenol and 2-phenylphenol); however, phenols without *ortho* substitution (e.g. *p*-nitrophenol) do not yield stable products. This is likely because the unsubstituted phenols lack the steric bulk to protect the metal center from bimolecular decomposition.[2b] The use of acidic 1° or 2° alcohols leads to a mixture of ruthenium hydrides, presumably through *β*-hydrogen elimination from the coordinated alkoxide.



3

R = $C(CF_3)_2(CH_3)$ **4**
R = $C(CF_3)_3$ **5**

(2)

The olefin metathesis activities of complexes **3**–**5** for the ring-closing metathesis (RCM) of diethyl diallylmalonate were compared, and the results are summarized in Table 1. Although all of these four-coordinate alkylidene complexes are essentially inactive for RCM at room temperature, **4** and **5** exhibit moderate catalytic activity at 60 °C. However, the activity of these complexes, particularly **5**, is limited by their low thermal stability in the presence of the olefinic substrate, and both decompose before the metathesis reaction reaches completion. Notably no propagating species (which is expected to be a ruthenium methylidene complex) is observed by ^1H NMR spectroscopy in any of these reactions. The results described here are qualitatively similar to earlier studies of complex **1** and its analogues in which it was found that more electron withdrawing ligands afford more active olefin metathesis catalysts.[2a] These results are also consistent with Schrock's early transition metal systems in which catalytic activity increases with the acidity of the parent alcohol.[4] The relatively low reactivities of **3**–**5** for the RCM reaction are likely due to of the same factors which render these species sufficiently stable to be isolated: the large steric bulk of the alkoxides effectively shields the metal from the incoming substrate,[12] while π donation by these ligands discourages olefin binding by decreasing the electrophillicity of the Ru^{II} center.[6]

Table 1. Ring-closing metathesis reactions of diethyl diallylmalonate with complexes **1** and **3**–**5**.[a]

Catalyst	Additive	*T* [°C]	*t* [h]	Yield [%]
3	none	60	96	< 5
4	none	60	96	70
5	none	60	12	40
4	HCl[b]	25	0.65	> 96
1	none	25	1.5	> 96[c]

[a] Reactions of five equivalents of substrate in C_6D_6; [catalyst] = 0.01–0.02 M; yields were estimated by integration of the ^1H NMR spectrum; unless indicated catalyst decomposition terminated the reaction. [b] Two equivalents of HCl were added as a 2 M solution in diethyl ether. [c] Catalyst remains at the end of the reaction.

However, complexes **3**–**5** become excellent catalysts for RCM when activated with HCl, and the representative example of the **4**/HCl system is shown in Table 1. The addition of two equivalents of HCl to a solution of complex **4** in C_6D_6 results in an instantaneous color change from red to brown. Although no new carbene resonance signals can be observed by ^1H NMR spectroscopy, a small amount of a highly metathesis active species is generated. In fact, under otherwise identical conditions, the RCM of diethyl diallylmalonate proceeds *at least twice as fast* with **4**/HCl than with catalyst **1** alone, despite the undetectably small amounts of active catalyst present in the **4**/HCl reaction mixture. By analogy to the ligand exchange reaction of **2** with acidic alcohols, we believe that the HCl serves to protonate the alkoxide ligands of **4**, to generate free $HOC(CF_3)_2CH_3$ (which is the sole species observed by ^{19}F NMR spectroscopy) and the elusive four-coordinate species $[(PCy_3)Cl_2Ru{=}CHR]$ (**2**). Evidence for this proposal is provided by the reaction of **4** with HCl in the presence of one equivalent of PCy_3; this reaction results in the regeneration of catalyst **1**.

In conclusion, a series of four-coordinate ruthenium alkylidene complexes with highly unusual trigonal pyramidal geometries has been prepared as analogues of the proposed olefin metathesis intermediate **2**. The new complexes show moderate activity as single component catalysts for ring-closing metathesis. The RCM reactions can be greatly accelerated by the addition of HCl which is believed to generate the highly reactive complex **2** in solution.

Experimental Section

3: Complex **1** (0.91 mmol) and KO*t*Bu (3.2 mmol) were combined in C_6H_6 (30 mL). The reaction mixture was stirred for 24 h during which time it changed color from purple to brownish red. The solvent was frozen and removed by sublimation under vacuum. The resulting solids were suspended in a mixture of C_6H_6 (0.5 mL) and pentane (50 mL). CuCl (9.1 mmol) was added, and the suspension was stirred for 20 min, and then cooled at −30 °C for 24 h. The supernatant solution was decanted and the solvent removed under vacuum to give **3** as a dark brown foamy solid (52 % yield). This solid is typically about 95 % pure (by ^{31}P NMR), and contains traces of CuCl(PCy_3) polymer. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 15.5$ (d, $^3J_{P,H} = 4.4$ Hz, 1 H, Ru=CH), 7.88 (d, $^2J_{H,H} = 7.3$ Hz, 2 H, *ortho*-H), 7.27 (t, $^2J_{H,H} = 7.3$ Hz, 1 H, *meta*-H), 7.17 (s, 2 H, *para*-H), 2.4–1.1 (m, 33 H, PCy_3), 1.29 (s, 9 H, *t*Bu); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): $\delta = 83.5$ (s); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta = 230.5$ (d, $^2J_{P,C} = 15.2$ Hz, Ru=C), 152.1, 129.9, 125.3, 124.6, 74.50, 36.69, 34.57, 34.48, 34.14, 33.68, 33.44, 31.52, 29.61, 28.84, 28.70, 28.51, 28.37, 27.48, 27.24.

4: Hexafluoro-*tert*-butanol (0.5 mL) was added to a solution of complex **3** (0.41 mmol) in pentane (25 mL). The reaction was stirred for 30 min then cooled to −30 °C for 24 h. The supernatent solution was decanted and the solvents were removed under vacuum to give an oily dark brown solid. The product was recrystallized from a minimum volume of pentane to afford reddish crystals of **4** (40 % yield). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 17.5$ (s, 1 H, Ru=CH), 7.88 (d, $^2J_{H,H} = 5.9$ Hz, 2 H, *ortho*-H), 7.14 (m, 3 H, *meta*-H and *para*-H), 2.4–1.1 (m, 33 H, PCy_3); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): $\delta = 80.1$ (s);. ^{19}F NMR (283 MHz, C_6D_6): $\delta = -77.93$ (s), −79.27 (s); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta = 262.6$ (d, $^2J_{P,C} = 18$ Hz, Ru=C), 150.6, 131.0, 130.4, 126.1 (q, $^1J_{F,C} = 288$ Hz), 125.4 (q, $^1J_{F,C} = 288$ Hz), 124.5, 34.33, 34.00, 29.49, 28.40, 28.26, 27.02, 20.46; elemental analysis calcd (%) for $C_{33}H_{45}F_{12}O_2PRu$: C 47.54, H 5.44; found: C 47.19, H 5.41.

5: The same procedure as for complex **4**, but using perfluoro-*tert*-butanol, afforded **5** as a reddish microcrystalline solid (37 % yield). ^{1}H NMR (400 MHz, C_6D_6): 19.2 (s, 1 H, Ru=CH), 7.72 (d, $^2J_{H,H} = 7.34$ Hz, 2 H, *ortho*-H), 7.14 (m, 3 H, *meta*-H and *para*-H), 2.1–0.8 (m, 33 H, PCy_3); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): $\delta = 75.1$ (s); ^{19}F NMR (283 MHz, C_6D_6): $\delta = -73.55$ (s); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta = 286.5$ (d, $^2J_{P,C} = 15.2$ Hz, Ru=C), 151.4, 130.0, 129.6, 125.6, 123.0 (q, $^1J_{F,C} = 292$ Hz), 35.20, 34.90, 32.23, 31.91, 31.66, 31.63, 29.91, 28.34, 28.21, 27.95, 27.80, 26.94, 26.75; elemental analysis calcd (%) for $C_{33}H_{39}F_{18}O_2PRu$: C 42.09, H 4.17; found: C 41.60, H 4.18.

Crystal Structure of **3**: Dark red-brown blades were grown from pentane: $C_{33}H_{57}O_2PRu$ (617.83), crystal dimensions: $0.21 \times 0.16 \times 0.03$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.0120(7)$, $b = 20.5338(14)$, $c = 15.7802(11)$ Å, $\beta = 92.1300(10)^\circ$, $Z = 4$, $V = 3241.9(4)$ Å^3, $\rho_{calc} = 1.266$ mg m^{-3}, $T = 93$ K, $2\Theta = 57.5^\circ$, 29 820 reflections were measured, 7759 independent reflections were obtained ($R_{int} = 0.0683$) on a Bruker SMART diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods,[13a] with refinement by full-matrix least squares of F^2 [13b]: $R_1 = 0.0328$, $wR_2 = 0.0527$ (for $I > 2\sigma(I)$), $R_1 = 0.0611$, $wR_2 = 0.0569$ (for all data), residual electron density : +0.632/−0.510 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140726. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk), and structure factors are available on request from xray@caltech.edu.

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[11] Complexes **4** and **5** have also been characterized by X-ray crystallography, and their structures are qualitatively similar to that of **3**. However, reliable bond lengths and angles could not be determined because of the extreme disorder of the CF_3 groups in both molecules.

[12] We have attempted to study the binding of other ligands (including THF, PMe_3, and CH_3CN) to these complexes. Complexes **2**–**4** do not appear to bind THF, while the other ligands lead to decomposition or to a mixture of products.

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Calix[6]arene as a Wheel for Rotaxane Synthesis[**]

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Rotaxanes and catenanes[1] are interesting supermolecules that have been extensively studied for their use in the preparation of molecular switches. A possible approach to their synthesis is based on the formation of an axial complex between a molecular wheel that is used as the host and a specific guest that is employed as the axle.

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