

Study Concerning the Effects of Chelation on the Structure and Catalytic Activity of Ruthenium Carbene Complexes

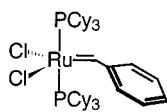
Alois Fürstner,* Oliver R. Thiel, and Christian W. Lehmann

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

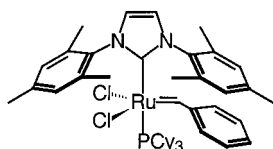
Received September 26, 2001

The ruthenium chelate complexes **4** and **5** were prepared by reaction of the Grubbs catalyst **1** and its second-generation analogue **2** with the 2-vinylbenzoic acid isopropyl ester **3** in the presence of CuCl. The fact that the chelating carbonyl group in these complexes attenuates their catalytic activity sets an experimental basis for the interpretation of reactivity data previously described in the literature.

The tremendous progress in olefin metathesis during the past decade is largely due to the development of well-defined ruthenium carbene complexes which combine high activity and good durability with an excellent functional group tolerance.¹ Following the seminal disclosure of Grubbs on ruthenium complex **1** and



1



2

congeners,² many variants of this catalyst have been described in the literature. Among them, "second generation" catalysts bearing N-heterocyclic carbene (NHC) ligands such as **2** and analogues are most noteworthy, because they exhibit an even more attractive application profile and promise to define new standards in the field.³

Although the mode of action of such complexes is now understood at the molecular level in reasonable detail,⁴ many preparative results which have accumulated over the years still await mechanistic interpretation. Thus, it has been deduced from reactivity data that ruthenium catalysts, in particular complex **1**, respond in a delicate

way to chelation by carbonyl groups in vicinity to the olefins.^{5–8} While some level of Lewis acid/Lewis base interaction seems to be necessary for productive macrocyclization (cf. Scheme 1), *stable* ruthenium chelate complexes must be avoided because they might sequester the catalyst in an unproductive form, as suggested by the data shown in Scheme 2.^{5,9} Addition of an appropriate Lewis acid such as Ti(O*i*Pr)₄, which competes with the Ru center for the coordination site, may help to rectify such a situation.^{10,11}

To corroborate the validity of this analysis, attempts were made to intercept and characterize the assumed ruthenium–carbonyl chelate complexes. With sub-

(1) Reviews: (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (b) Fürstner, A. *Angew. Chem.* **2000**, *112*, 3140; *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (c) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (d) Fürstner, A. *Top. Catal.* **1997**, *4*, 285. (e) Schuster, M.; Blechert, S. *Angew. Chem.* **1997**, *109*, 2124; *Angew. Chem., Int. Ed.* **1997**, *36*, 2037. (f) Schrock, R. R. *Top. Organomet. Chem.* **1998**, *1*, 1.

(2) (a) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(3) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247. (c) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787. (d) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem.* **1999**, *111*, 2573; *Angew. Chem., Int. Ed.* **1999**, *38*, 2416. (e) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (f) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204.

(4) (a) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (b) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.

(5) (a) Fürstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942. (b) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792. (c) Fürstner, A. *Top. Organomet. Chem.* **1998**, *1*, 37.

(6) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324.

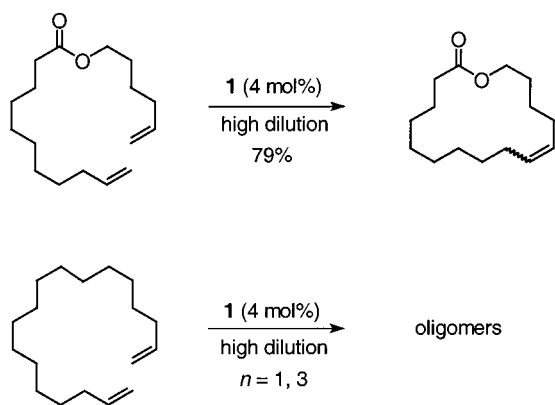
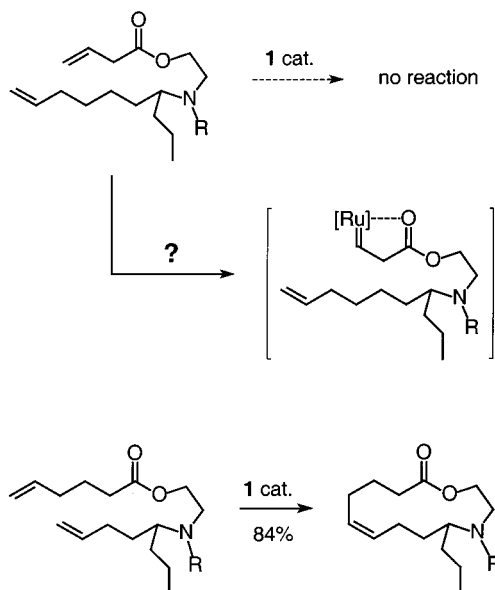
(7) For pertinent examples showing the effect of donor sites other than carbonyls on the outcome of metathesis reactions see, inter alia: Engelhardt, F. C.; Schmitt, M. J.; Taylor, R. E. *Org. Lett.* **2001**, *3*, 2209 and literature cited therein.

(8) Chelation effects have been proven by X-ray crystallography for metathesis catalysts containing metals other than ruthenium; cf.: Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260.

(9) Note that this notion has some predictive power, as it allows us to identify those sites within a given target molecule at which productive macrocyclization can be expected. It has greatly facilitated our synthetic endeavors and has provided safe guidance for retrosynthetic planning in a considerable number of cases. See the following for pertinent examples: (a) Fürstner, A.; Müller, T. *Synlett* **1997**, 1010. (b) Fürstner, A.; Müller, T. *J. Org. Chem.* **1998**, *63*, 424. (c) Fürstner, A.; Gastner, T.; Weintritt, H. *J. Org. Chem.* **1999**, *64*, 2361. (d) Fürstner, A.; Müller, T. *J. Am. Chem. Soc.* **1999**, *121*, 7814. (e) Fürstner, A.; Grabowski, J.; Lehmann, C. W. *J. Org. Chem.* **1999**, *64*, 8275. (f) Fürstner, A.; Thiel, O. R.; Blanda, G. *Org. Lett.* **2000**, *2*, 3731. (g) Fürstner, A.; Grabowski, J.; Lehmann, C. W.; Kataoka, T.; Nagai, K. *ChemBioChem* **2001**, *2*, 60. (h) Fürstner, A.; Radkowski, K. *Chem. Commun.* **2001**, 671.

(10) Fürstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130.

(11) (a) Ghosh, A. K.; Cappiello, J.; Shin, D. *Tetrahedron Lett.* **1998**, *39*, 4651. (b) Dirat, O.; Kouklovsky, C.; Langlois, Y.; Lesot, P.; Courtieu, J. *Tetrahedron: Asymmetry* **1999**, *10*, 3197. (c) Wipf, P.; Weiner, W. S. *J. Org. Chem.* **1999**, *64*, 5321. (d) Winkler, J. D.; Holland, J. M.; Kasperec, J.; Axelsen, P. H. *Tetrahedron* **1999**, *55*, 8199. (e) Cossy, J.; Bauer, D.; Bellosta, V. *Tetrahedron Lett.* **1999**, *40*, 4187. (f) Clive, D. L. J.; Cheng, H. *Chem. Commun.* **2001**, 605. (g) Held, C.; Fröhlich, R.; Metz, P. *Angew. Chem.* **2001**, *113*, 1091; *Angew. Chem., Int. Ed.* **2001**, *40*, 1058. (h) Martin, S. F.; Follows, B. C.; Hergenrother, P. J.; Franklin, C. L. *J. Org. Chem.* **2000**, *65*, 4509. (i) Bourgeois, D.; Mahuteau, J.; Pancrazi, A.; Nolan, S. P.; Prunet, J. *Synthesis* **2000**, 869. (j) Takemoto, Y.; Baba, Y.; Saha, G.; Nakao, S.; Iwata, C.; Tanaka, T.; Ibuka, T. *Tetrahedron Lett.* **2000**, *41*, 3653.

Scheme 1**Scheme 2**

strates containing flexible tethers between the olefin and the ester, we were unable to obtain the desired complexes in pure form. However, reaction of complex **1** with the 2-vinylbenzoic acid ester **3** in the presence of CuCl in CH₂Cl₂ at ambient temperature proceeds cleanly and affords the chelate complex **4** in 82% isolated yield (Scheme 3). The structure of this compound can be inferred from some characteristic spectroscopic data, such as the high-field shift of the benzylic proton from δ 20.02 ppm in **1** to δ 18.76 ppm in **4**. Even more diagnostic is the fact that the signal of this proton appears as a singlet in **1** but as a doublet in **4** ($J_{P,H\alpha} = 8.1$ Hz). This indicates that there is only one PCy₃ group left and shows that the dihedral angle P–Ru–C_α–H_α in **4** must be close to 0°. ¹² If this is the case, the ester group is ideally disposed to occupy the apical coordination site of the ruthenium center. Surprisingly, though, this ligation is hardly reflected in the IR stretching frequency of this group, which shifts only marginally from 1715 cm⁻¹ in the free ester **3** to 1712 cm⁻¹ in complex **4**.

Crystals of **4** suitable for X-ray analysis were grown by slowly diffusing *n*-pentane into a solution of this

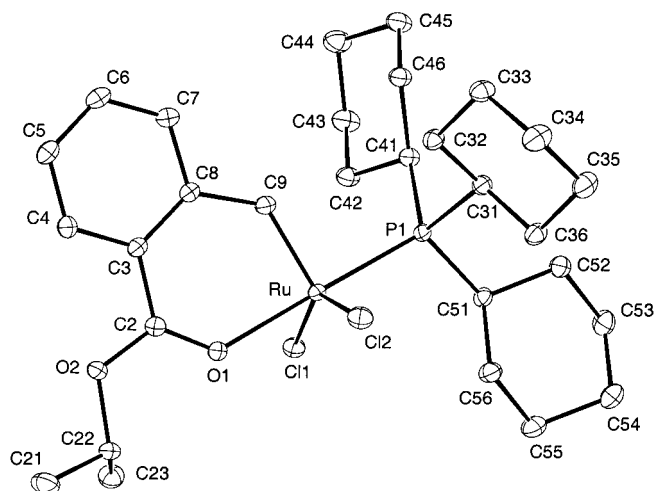


Figure 1. Molecular structure of complex **4** shown with the atomic labeling scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

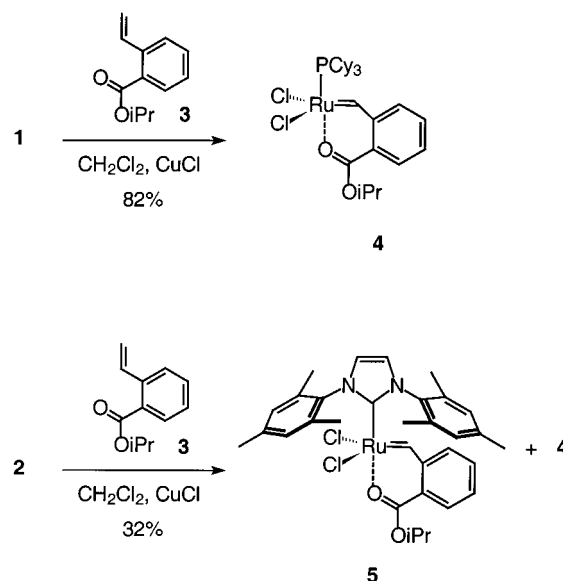
Scheme 3

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **4**

Ru(1)–Cl(1)	1.8311(13)	Ru(1)–O(1)	2.1633(10)
Ru(1)–P(1)	2.2991(4)	Ru(1)–Cl(2)	2.3129(4)
Ru(1)–Cl(1)	2.3207(4)	O(1)–C(2)	1.2267(16)
O(2)–C(2)	1.3305(17)	C(2)–C(3)	1.4789(19)
C(8)–C(9)	1.4637(19)		
C(9)–Ru(1)–O(1)	89.63(5)	C(9)–Ru(1)–P(1)	91.80(5)
O(1)–Ru(1)–P(1)	177.08(3)	C(9)–Ru(1)–Cl(2)	106.95(5)
O(1)–Ru(1)–Cl(2)	85.33(3)	P(1)–Ru(1)–Cl(2)	96.681(14)
C(9)–Ru(1)–Cl(1)	109.47(5)	O(1)–Ru(1)–Cl(1)	83.66(3)
P(1)–Ru(1)–Cl(1)	93.461(14)	Cl(2)–Ru(1)–Cl(1)	141.756(13)
C(2)–O(1)–Ru(1)	128.56(9)	O(1)–C(2)–O(2)	121.50(12)
O(1)–C(2)–C(3)	125.11(12)	O(2)–C(2)–C(3)	113.39(11)
C(8)–C(9)–Ru(1)	128.62(10)		

complex in CH₂Cl₂. The molecular structure in the solid state (Figure 1, Table 1) is in excellent agreement with the solution structure deduced from the NMR data. The coordination sphere around the Ru(II) center is best described as a distorted trigonal bipyramid, with the axial sites being occupied by the PCy₃ ligand and the ester carbonyl group. The Ru–O distance of 2.1633(19) Å compares well with that observed in other metalla-

(12) Grubbs et al. were the first to propose a Karplus-type relation between the dihedral angle P–Ru–C_α–H_α and the observed coupling constant $J_{P,H}$.^{4b}

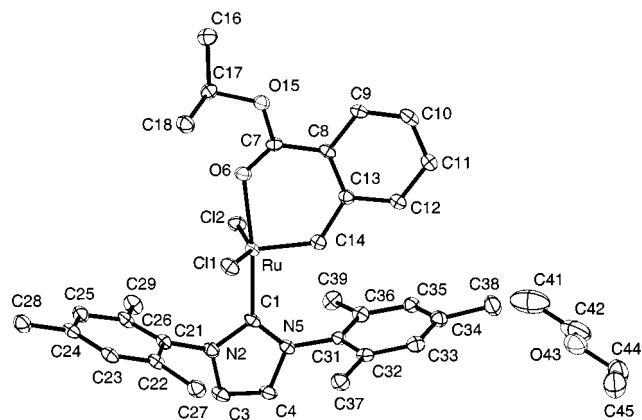


Figure 2. Molecular structure of complex **5** shown with one molecule of cocrystallized diethyl ether and the atomic labeling scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

cyclic ruthenium complexes incorporating ester moieties.¹³ Importantly, the phenyl ring is oriented perpendicularly to the Cl–Ru(–Cl)–C_α plane, thus confirming the interpretation of the coupling constants for P,H_α summarized above.

Although the exposure of the “second generation” metathesis catalyst **2** to vinylbenzoic acid ester **3** also leads to the formation of the expected metallacyclic complex **5**, this reaction is markedly less productive (32% yield). Moreover, complex **4** is formed in almost equal amounts, showing that the NHC is rather labile under these conditions and is released with as much ease as PCy₃. This outcome is somewhat surprising, in view of the widely accepted notion that metal–NHC complexes in general are distinguished by their reluctance for ligand dissociation.¹⁴ It might result from the exceptionally strong σ -donor character of NHC's, which prefer π -acceptor ligands in the trans position (e.g. an olefin substrate) to balance the electron density;^{4a} if a donor substituent is forced to occupy this site, as is the case in **5** owing to the metallacyclic ring, the metal–NHC bond itself may be weakened and rendered kinetically less inert. Alternatively, the admixed Cu(I) salt could intervene at some stage of the reaction by partly pulling off the NHC rather than the PCy₃ from the Ru(II) center in **2**. So far, however, we were unable to detect the Cu–NHC species in solution that should be formed in this case.¹⁵

Crystals of **5** suitable for X-ray analysis have been grown by slowly cooling a saturated solution in Et₂O to –60 °C. The solid-state structure (Figure 2, Table 2) can again be described as a trigonal bipyramid, with the gross features being similar to those observed in com-

(13) (a) Hauptman, E.; Brookhart, M.; Fagan, P. J.; Calabrese, J. C. *Organometallics* **1994**, *13*, 774. (b) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669. (c) Daniel, T.; Mahr, N.; Braun, T.; Werner, H. *Organometallics* **1993**, *12*, 1475. (d) Braunstein, P.; Matt, D.; Dusauso, Y. *Inorg. Chem.* **1983**, *22*, 2043.

(14) (a) For a general treatise see: Herrmann, W. A.; Köcher, C. *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem., Int. Ed.* **1997**, *36*, 2162. (b) See also: Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370.

(15) Attempts to form complex **5** in the absence of CuCl were unsuccessful, as the conversion turned out to be extremely slow in these cases. For literature precedents for stable Cu–NHC complexes see: Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027 and references therein.

Scheme 4

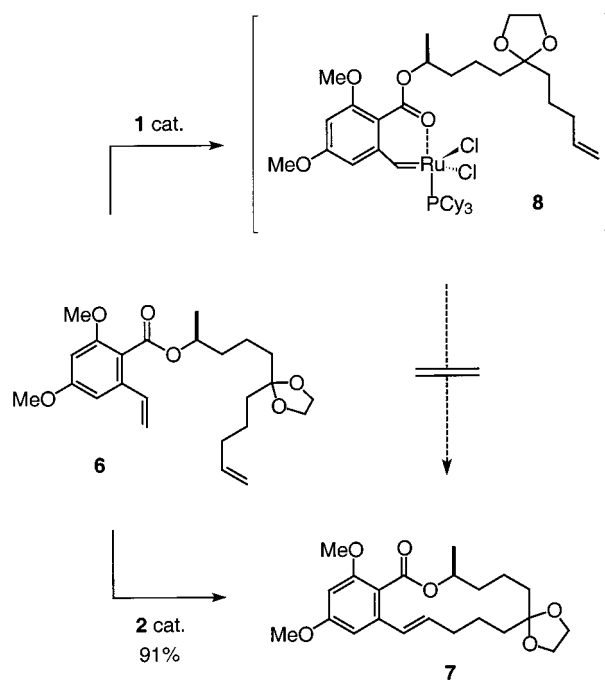


Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Ru(1)–C(14)	1.825(4)	Ru(1)–C(1)	2.034(4)
Ru(1)–O(6)	2.152(3)	Ru(1)–Cl(2)	2.3206(9)
Ru(1)–Cl(1)	2.3244(9)	O(6)–C(7)	1.236(4)
C(7)–O(15)	1.318(4)	C(7)–C(8)	1.470(5)
C(13)–C(14)	1.473(5)		
C(14)–Ru(1)–C(1)	97.70(16)	C(14)–Ru(1)–O(6)	89.05(14)
C(1)–Ru(1)–O(6)	172.95(12)	C(14)–Ru(1)–Cl(2)	104.43(11)
C(1)–Ru(1)–Cl(2)	88.93(10)	O(6)–Ru(1)–Cl(2)	87.43(8)
C(14)–Ru(1)–Cl(1)	100.06(11)	C(1)–Ru(1)–Cl(1)	96.62(10)
O(6)–Ru(1)–Cl(1)	84.11(7)	Cl(2)–Ru(1)–Cl(1)	153.92(4)
C(7)–O(6)–Ru(1)	129.0(3)	O(6)–C(7)–O(15)	121.3(3)
O(6)–C(7)–C(8)	124.3(3)	O(15)–C(7)–C(8)	114.4(3)
C(13)–C(14)–Ru(1)	128.5(3)		

plex **4**. The distance between the Ru atom and the carbonyl oxygen is slightly shorter (2.152(2) Å) than that in **4** (2.1633(10) Å) but is still within the expected range;¹³ in contrast, the Cl(1)–Ru–Cl(2) angle of 153.92(4)° is larger than that observed in complex **4** (141.756(13)°). The C(1)–Ru–O(6) axis is tilted, with the bond angle being 172.95(12)°. This effect is deemed to reflect the steric repulsion between the benzylidene carbene and the perpendicularly oriented mesityl substituent on the NHC. This arrangement is also unfavorable in electronic terms, as it prevents the π -stacking of these groups, which constitutes a highly conserved structural motif in all other Ru–NHC complexes studied so far.¹⁶

From the results summarized above, it must be deduced that the standard Grubbs catalyst **1** is affected more strongly by adjacent donor sites in a given substrate than its “second generation” analogue **2**, which exhibits a markedly reduced bias for chelate complex formation. This explains without difficulty why diene **6** is recovered unchanged if exposed to **1** in refluxing CH₂Cl₂, whereas this substrate cyclizes in almost quantitative yield to the macrocyclic product **7**

(16) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236.

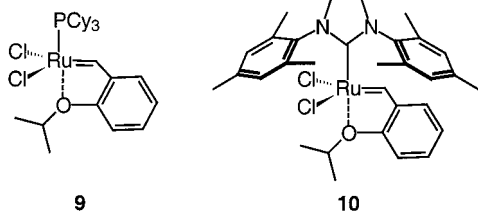
Table 3. Comparison of the Catalytic Activity of Chelate and Nonchelate Ruthenium Carbene Complexes (5 mol %)

Entry	Substrate	Product	Catalyst	Solvent ^a	t(h)	Yield(%)
1			1	CH ₂ Cl ₂	0.5	85
2			2	CH ₂ Cl ₂	0.5	92
3			4	CH ₂ Cl ₂	22	35
4			4	toluene	5	75
5			5	CH ₂ Cl ₂	18	92
6			2	toluene	24	95
7			5	toluene	20	44

^a The reactions in CH₂Cl₂ are carried out at reflux temperature and those in toluene at 80 °C.

in the presence of **2** (Scheme 4).¹⁷ A control experiment was carried out which showed that treatment of diene **6** with stoichiometric amounts of **1** in CH₂Cl₂ leads to the formation of one major new alkylidene complex which hardly evolves with time. Although we were unable to obtain crystals suitable for X-ray analysis, the spectroscopic characteristics of this new species, in particular the high-field shift of its alkylidene H atom (δ 18.89 ppm) together with the diagnostic $J_{P,H\alpha} = 8.0$ Hz, are highly indicative for chelate structure **8**, which likely constitutes an unreactive sink for the catalyst. Moreover, the formation of **8** implies that precoordination of **1** onto a polar group may define the site of initiation of a metathesis reaction within an unsymmetrical diene, a finding which bears considerable significance in retrosynthetic terms. The assumption that the formation of such stable carbonyl chelate complexes attenuates the reactivity of the metathesis catalysts is further supported by the results compiled in Table 3. Thus, **4** and **5** are found to be significantly less active than their parent compounds **1** and **2** in a set of representative RCM reactions.

Complexes **4** and **5** are structurally very reminiscent of catalysts **9** and **10**, incorporating a tethered styrenyl ether ligand, which were originally reported by Hoveyda et al.¹⁸ In this context, however, it is important to note



(17) (a) Fürstner, A.; Thiel, O. R.; Kindler, N.; Bartkowska, B. *J. Org. Chem.* **2000**, *65*, 7990. (b) Fürstner, A.; Kindler, N. *Tetrahedron Lett.* **1996**, *37*, 7005. (c) Fürstner, A.; Seidel, G.; Kindler, N. *Tetrahedron* **1999**, *55*, 8215.

(18) (a) Harrity, J. P. A.; La, D. S.; Cefalo, D. R.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 2343. (b) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791. (c) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168. (d) Dowden, J.; Savovic, J. *Chem. Commun.* **2001**, *37*. (e) Gessler, S.; Randl, S.; Blechert, S. *Tetrahedron Lett.* **2000**, *41*, 9973. (f) Randl, S.; Connon, S. J.; Blechert, S. *Chem. Commun.* **2001**, 1796. (g) Cossy, J.; BouzBouz, S.; Hoveyda, A. H. *J. Organomet. Chem.* **2001**, *624*, 327.

that—in contrast to **4** and **5**—the latter retain appreciable catalytic activity despite their closely related two-point binding motif. One must therefore conclude that different heteroatoms (e.g. ether versus ester) exert rather distinct influences on the reactivity pattern of ruthenium carbene complexes which are far from being comprehensively studied. This notion has strong implications for retrosynthetic planning as well as for catalyst design, which we intend to probe in more detail during our current research program.

Experimental Section

General Considerations. All reactions were carried out under Ar. The solvents were dried by distillation over the following drying agents prior to use and were transferred under Ar: Et₂O (Mg–anthracene), CH₂Cl₂ (P₄O₁₀), toluene (Na). Flash chromatography was carried out on Merck silica gel, type 9385, 230–400 mesh. NMR spectra were recorded on a Bruker AC 200 or DPX 300 spectrometer; chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) in Hz. MS measurements were carried out on a Finnigan MAT 8200 instrument (70 eV), ESI-MS on a Hewlett-Packard HP 5989 B MS-Engine, and HR-MS on a Finnigan MAT 95. IR spectra were recorded on a Nicolet FT-7199 spectrometer. Melting points were determined on a Büchi B-540 instrument (uncorrected). Elemental analyses were carried out by H. Kolbe, Mülheim/Ruhr, Germany. All commercially available reagents were used as received.

2-Vinylbenzoic Acid Isopropyl Ester (3). A solution of 2-propanol (310 μ L, 4 mmol) and PPh₃ (1.05 g, 4 mmol) in Et₂O (3 mL) was added to a solution of 2-vinylbenzoic acid (296 mg, 2.0 mmol) and diethyl azodicarboxylate (DEAD; 630 μ L, 4 mmol) in Et₂O (3 mL), and the resulting mixture was stirred at ambient temperature for 3 h. For workup, the mixture was concentrated to a total volume of ca. 2 mL, the precipitated Ph₃P=O was filtered off, the filtrate was evaporated, and the crude product was purified by flash chromatography (hexanes/ethyl acetate, 20/1) to afford product **3** as a pale yellow syrup (283 mg, 74%). ¹H NMR (CDCl₃, 300 MHz): δ 7.83 (1H, d, $J = 7.7$ Hz), 7.55 (1H, d, $J = 7.8$ Hz), 7.50–7.38 (2H, m), 7.29 (1H, dd, $J = 7.7, 7.5$ Hz), 5.63 (1H, d, $J = 17.4$ Hz), 5.32 (1H, d, $J = 11.0$ Hz), 5.25 (1H, sept, $J = 6.3$ Hz), 1.35 (6H, d, $J = 6.3$ Hz). ¹³C NMR (CDCl₃, 75.5 MHz): δ 167.0, 139.3, 135.9, 131.8, 130.1, 129.4, 127.3, 127.1, 116.2, 68.5, 21.9. IR (film): 3089, 3067, 3028, 2981, 2936, 2876, 1715, 1626, 1600, 1568, 1482, 1467, 1454, 1413, 1386, 1374, 1351, 1335, 1288, 1256, 1201, 1181, 1138, 1108, 1073, 1023, 989, 918, 855, 833, 771, 716 cm⁻¹. MS (EI): m/z (relative intensity) 190 ($[M]^+$, 16), 148 (100), 131 (39), 120 (17), 103 (23), 91 (9), 77 (28), 63 (3), 51 (11), 43 (11). HR-MS (EI): m/z calcd for C₁₂H₁₄O₂ 190.0994, found 190.0994. Anal. Calcd for C₁₂H₁₄O₂ (190.24): C, 75.76; H, 7.42. Found: C, 75.56; H, 7.35.

Complex 4. Ester **3** (114 mg, 0.60 mmol) was added to a solution of the ruthenium complex **1** (448 mg, 0.54 mmol) in CH₂Cl₂ (20 mL). CuCl (53 mg, 0.53 mmol) was then introduced, and the resulting mixture was stirred at ambient temperature for 2 h. After that time, TLC indicated complete conversion of the substrates. Insoluble residues were filtered off, the filtrate was evaporated, the residue was suspended in Et₂O (5 mL), the suspension was again filtered through a pad of silica, the filtrate was evaporated, and the crude product was triturated with pentane (2 \times 20 mL) to afford complex **4** as a pale green solid (277 mg, 82%). Mp: 163–165 °C. ¹H NMR (CD₂Cl₂, 200 MHz): δ 18.76 (1H, d, $J_{PH} = 8.1$ Hz), 8.38–8.28 (1H, m), 7.87–7.77 (3H, m), 5.44 (1H, sept, $J = 6.3$ Hz), 2.48–2.25 (3H, m), 2.17–2.00 (6H, m), 1.96–1.67 (15H, m), 1.48 (6H, d, $J = 6.3$ Hz), 1.38–1.20 (9H, m). ¹³C NMR (CD₂Cl₂, 50.3 MHz): δ 284.9 (d, $J_{PC} = 14.0$ Hz), 173.1, 147.5, 136.7, 133.1, 128.3, 126.1, 122.1, 73.0, 35.3, 30.3 (d, $J_{PC} = 23.3$ Hz), 28.2, 26.7 (d, $J_{PC} =$

9.8 Hz), 21.8. ^{31}P NMR (CD_2Cl_2 , 81 MHz): 47.8. IR (KBr): 3058, 3024, 2927, 2846, 1712, 1650, 1585, 1562, 1468, 1446, 1372, 1363, 1337, 1319, 1296, 1236, 1206, 1173, 1154, 1101, 1089, 1051, 1028, 1002, 917, 887, 872, 851, 827, 786, 752, 732, 685, 515 cm^{-1} . MS (ESI): m/z 593.4 [$\text{M}^+ - \text{Cl}$]. Anal. Calcd for $\text{C}_{29}\text{H}_{45}\text{Cl}_2\text{O}_2\text{PRu}$ (628.62): C, 55.40; H, 7.21. Found: C, 55.32; H, 7.30.

Complex 5. To a solution of ester **3** (95 mg, 0.50 mmol) and complex **2** (423 mg, 0.50 mmol) in toluene (20 mL) was added CuCl (50 mg, 0.50 mmol), and the resulting mixture was stirred for 2.5 h at ambient temperature. Insoluble residues were filtered off, the filtrate was evaporated, and the crude product was purified by flash chromatography (pentane/ Et_2O , 1:2) to afford product **5** as a pale green solid (103 mg, 32%). Mp: 154–156 °C. ^1H NMR (CD_2Cl_2 , 200 MHz): δ 18.82 (1H, s), 8.13 (1H, dd, $J = 7.4, 1.5$ Hz), 7.70 (1H, ddd, $J = 7.4, 7.4, 1.5$ Hz), 7.62 (1H, ddd, $J = 7.4, 7.4, 1.5$ Hz), 7.15 (2H, s), 7.14 (2H, s), 7.09 (2H, s), 6.92 (1H, dd, $J = 7.4, 1.5$ Hz), 5.23 (1H, sept, $J = 6.2$ Hz), 2.49 (6H, s), 2.26 (12H, s), 1.33 (6H, d, $J = 6.3$ Hz). ^{13}C NMR (CD_2Cl_2 , 50.3 MHz): δ 298.1, 182.9, 173.8, 148.7, 139.9, 138.1, 136.9, 136.2, 132.4, 129.6, 129.5, 127.9, 125.6, 124.7, 72.5, 21.8, 21.3, 19.0. IR (KBr): 3169, 3133, 3084, 3046, 3018, 2977, 2920, 2853, 2744, 1715, 1652, 1607, 1584, 1560, 1480, 1446, 1393, 1374, 1366, 1303, 1260, 1234, 1179, 1164, 1152, 1106, 1082, 1036, 1017, 971, 936, 918, 894, 854, 826, 795, 731, 694, 686, 644, 592, 579 cm^{-1} . MS (EI): m/z 652 ($[\text{M}^+]$, 72), 581 (5), 494 (22), 440 (62), 404 (68), 305 (48), 178 (14), 136 (30), 118 (47), 91 (34), 65 (20), 43 (100); HR-MS (EI): m/z calcd for $\text{C}_{32}\text{H}_{36}\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$ 652.1191, found 652.1189. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$ (652.63): C, 58.89; H, 5.56; N, 4.29. Found: C, 59.06; H, 5.60; N, 4.22.

Crystal Data for Complex 4: $\text{C}_{29}\text{H}_{45}\text{Cl}_2\text{O}_2\text{PRu}$, $M_r = 628.59$, red-brown, crystal dimensions $0.68 \times 0.62 \times 0.50$ mm, triclinic, $P\bar{1}$ (No. 2), 100 K, $a = 9.9365(8)$ Å, $b = 11.0649(9)$ Å, $c = 13.9829(12)$ Å, $\alpha = 79.225(3)^\circ$, $\beta = 86.603(3)^\circ$, $\gamma = 70.517(3)^\circ$, $V = 1423.8(2)$ Å³, $Z = 2$, $\rho = 1.466$ Mg m⁻³, $\mu = 0.819$ mm⁻¹, $\lambda = 0.71073$ Å. X-ray diffraction data were collected using a Siemens SMART diffractometer employing ω -scans to cover reciprocal space up to 33.18° with 85.5% completeness; integration of raw data yielded a total of 15 535 reflections, merged into 9328 unique reflections with $R_{\text{int}} = 0.019$ after applying Lorentz, polarization, and absorption corrections. The structure was solved by direct methods using SHELXS-97;

atomic positions and displacement parameters (anisotropic for all non-hydrogen atoms) were refined using full-matrix least squares based on F^2 using SHELXL-97.¹⁹ Refinement of 318 parameters using all reflections converged at $R = 0.026$ and $R_w = 0.063$, the highest residual electron density peak being 0.6 Å³. Hydrogen atoms were constrained to idealized positions.

Crystal Data for Complex 5: $\text{C}_{36}\text{H}_{46}\text{Cl}_2\text{N}_2\text{O}_3\text{Ru}$, $M_r = 726.72$, yellow, crystal dimensions $0.25 \times 0.18 \times 0.10$ mm, triclinic, $P\bar{1}$ (No. 2), 100 K, $a = 9.3202(4)$ Å, $b = 14.5387(5)$ Å, $c = 14.7273(4)$ Å, $\alpha = 117.306(2)^\circ$, $\beta = 91.779(2)^\circ$, $\gamma = 92.9500(10)^\circ$, $V = 1767.52(11)$ Å³, $Z = 2$, $\rho = 1.365$ Mg m⁻³, $\mu = 0.631$ mm⁻¹, $\lambda = 0.71073$ Å. X-ray diffraction data were collected using a Nonius KappaCCD diffractometer employing ω -scans to cover reciprocal space up to 31.10° with 90.8% completeness, yielding a total of 15 244 reflections, merged into 10 323 unique reflections with $R_{\text{int}} = 0.081$. The structure was solved by direct methods using SHELXS-97, followed by full-matrix least-squares refinement based on F^2 using SHELXL-97.¹⁹ Refinement of 407 parameters using all reflections converged at $R = 0.061$ and $R_w = 0.181$, the highest residual electron density peak being 1.7 Å³. Hydrogen atoms were constrained to idealized positions. Complete lists of atom coordinates and anisotropic displacement parameters as well as tables of bond lengths and bond angles are available as Supporting Information.

Acknowledgment. Generous financial support by the Deutsche Forschungsgemeinschaft (Leibniz award to A.F.) and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Complete lists of atom coordinates and anisotropic displacement parameters as well as tables containing all bond lengths and bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0108503

(19) Sheldrick, G. M. SHELXS-97 and SHELXL-97 Programs for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 1997.