Organometallics **2005,** *24,* 4065−4071 4065

Bidentate Ruthenium Vinylcarbene Catalysts Derived from Enyne Metathesis

Alois Fürstner,* Paul W. Davies, and Christian W. Lehmann

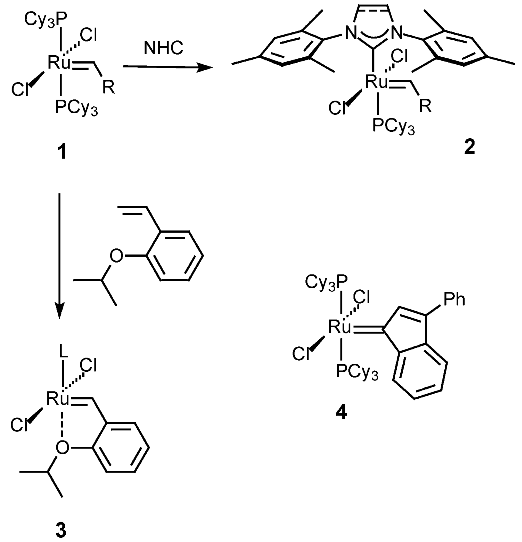
Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

Received April 20, 2005

The preparation, structure, and catalytic activity of a series of bidentate η^1-vinylcarbene ruthenium complexes derived from the standard metathesis catalysts **1**, **2**, or **4** by enyne metathesis with phenylacetylene derivatives bearing an isopropoxy substituent at their *ortho* position are described. Terminal as well as non-terminal phenylacetylene derivatives react with similar ease, thus providing ample opportunity for the preparation of catalysts with tailor-made properties. Use of the silyl propargyl ether derivative **13b** as the substrate results in the formation of complex **15**, in which the silyl ether moiety rather than the isopropoxy substituent ligates the metal center. The structures of the new chelate complexes **6**, **7**, **9**, **14**, and **15** in the solid state were determined by X-ray crystallography.

The development of well-defined, highly tolerant, and user-friendly catalysts for olefin metathesis has triggered an avalanche of interest in this transformation as witnessed by an explosive growth of applications in organic synthesis and polymer chemistry during the past decade.[1,2] The most successful catalyst design was pioneered by Grubbs, who introduced five-coordinate ruthenium carbene complexes of the general type **1** bearing two electron-rich phosphines as ancillary ligands.[3] Several modifications of this basic structural motif have been proposed later on, among which the heteroleptic complexes of type **2**[4] bearing an *N*-heterocyclic carbene (NHC) ligand as a substitute for one of the phosphines as well as ruthenium complexes with bidentate carbene moieties such as **3** (L = PCy_3, NHC) were most successful.[5−8] The latter are commonly prepared by ligand exchange of **1** with suitable styrenyl ether derivatives (Scheme 1) and turned out to be particularly useful for catalytic cross metathesis (CM) and ring-closing metathesis (RCM), as well as (asym-

Scheme 1. Standard Metathesis Catalysts 1−4[a]



[a] Established methods for the conversion of the parent Grubbs catalyst **1** into “second-generation” catalysts **2** and Hoveyda-type catalysts **3**, respectively.

---

* To whom correspondence should be addressed. Tel: +49 208 3062342. Fax: +49 208 3062994. E-mail: fuerstner@mpi-muelheim.mpg.de.

(1) (a) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vols. 1−3. (b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997. (c) *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, 1998.

(2) Selected reviews: (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (b) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043. (c) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592−4633. (d) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900−1923. (e) Deiters, A.; Martin, S. F. *Chem. Rev.* **2004**, *104*, 2199−2238. (f) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565−1604. (g) Fürstner, A. *Top. Catal.* **1997**, *4*, 285−299. (h) Castarlenas, R.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **2004**, *213*, 31−37.

(3) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(4) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (c) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787−4790. (d) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416−2419. (e) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956. (f) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204−2207.

(5) Review: Hoveyda, A. H.; Gillingham, D. G.; Van Veldhuizen, J. J.; Kataoka, O.; Garber, S. B.; Kingsbury, J. S.; Harrity, J. P. A. *Org. Biomol. Chem.* **2004**, *2*, 8−23.

(6) (a) Harrity, J. P. A.; La, D. S.; Cefalo, D. R.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 2343−2351. (b) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791−799. (c) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168−8179. (d) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502−12508.

(7) (a) Gessler, S.; Randl, S.; Blechert, S. *Tetrahedron Lett.* **2000**, *41*, 9973−9976. (b) Randl, S.; Connon, S. J.; Blechert, S. *Chem. Commun.* **2001**, 1796−1797. (c) Zaja, M.; Connon, S. J.; Dunne, A. M.; Rivard, M.; Buschmann, N.; Jiricek, J.; Blechert, S. *Tetrahedron* **2003**, *59*, 6545−6558. (d) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2403−2405.

(8) (a) Michrowska, A.; Bujok, R.; Harutyunyan, S.; Sashuk, V.; Dolgonos, G.; Grela, K. *J. Am. Chem. Soc.* **2004**, *126*, 9318−9325. (b) Grela, K.; Kim, M. *Eur. J. Org. Chem.* **2003**, 963−966.

10.1021/om050310w CCC: $30.25

metric) ring-opening metathesis (ROM) reactions. Outlined below is an alternative entry into this series based upon the formal insertion of an alkyne into the M=C bond of a metal alkylidene by what is proposed to be an elementary step of "enyne metathesis". Along those lines we explored the reactions between the parent compound **1**, its readily available indenylidene analogue **4**,[9,10] or a "second-generation" complex derived from **2** and variously substituted phenylacetylene derivatives.[11,12]

Results and Discussion

Exposure of terminal alkynes to suitable metal carbene complexes results in "living" polymerization with formation of polyacetylene derivatives by stepwise insertion of the monomer into the $M=CR_2$ moiety terminating the growing polymer chain.[13] We reasoned that it might be possible to interrupt this process after the first insertion step if the alkyne monomer carries a suitable substituent able to chelate the metal center. The stability of catalysts of type **3**[5−8] suggests that an isopropoxy group at the *ortho* position of a phenylacetylene substrate should serve this purpose well. In fact, treatment of the parent Grubbs catalyst **1** with 1 equiv of alkyne **5** resulted in the clean formation of the bidentate ruthenium vinylcarbene complex **6**, provided that the reaction is performed in CH_2Cl_2 at ambient temperature in the presence of AgCl as a sink for the released phosphine (Scheme 2).

Although small amounts of the *Z*-configured isomer are present in the crude product, crystallization from CH_2Cl_2/pentane affords pure samples of the major *E*-isomer. Likewise, the ruthenium indenylidene complex **4**, which is readily prepared on a large scale without recourse to hazardous diazo compounds,[9] provides the analogous complex **7** in similar yields. Access to the "second-generation" analogue **9** was gained by reaction of **5** with the bis-pyridine adduct **8**;[14] in this case, the addition of AgCl is not required.

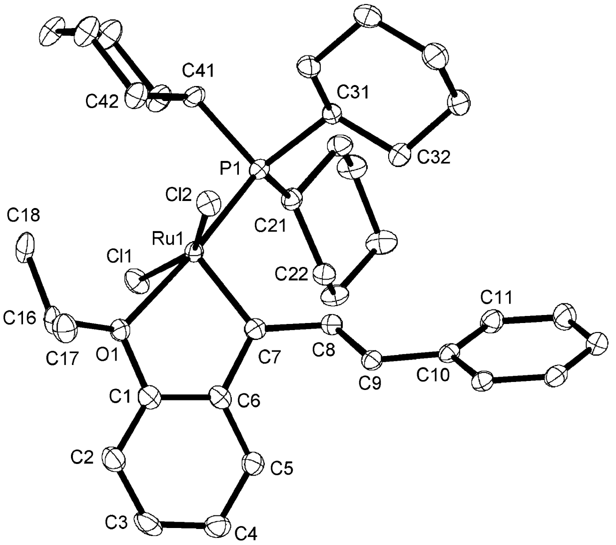
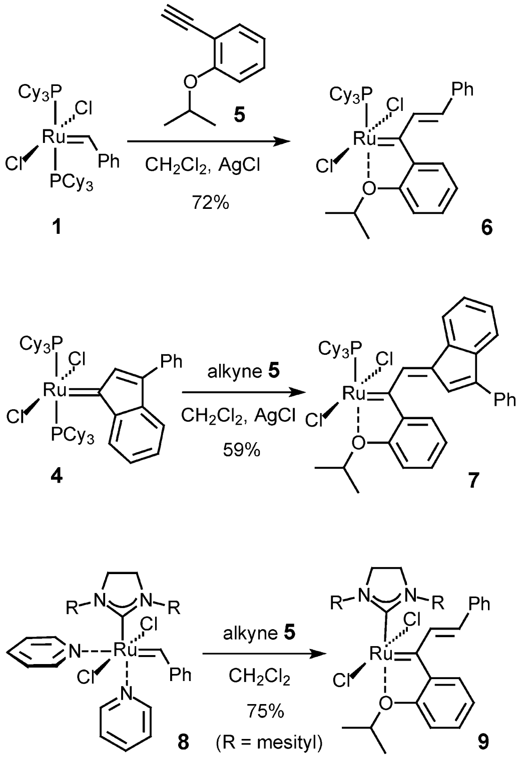


Figure 1. Molecular structure of complex **6** in the solid state. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(7)–Ru(1) 1.865(3), P(1)–Ru(1) 2.2904(9), O(1)–Ru(1) 2.243(2), Cl(1)–Ru(1) 2.3356(8), Cl(2)–Ru(1) 2.3483(8), C(7)–C(8) 1.449(4), C(8)–C(9) 1.345(4); Cl(1)–Ru(1)–Cl(2) 158.16(3), O(1)–Ru(1)–P(1) 173.34(6).

Scheme 2. Preparation of Bidentate Ruthenium Vinylcarbene Complexes by Enyne Metathesis.



The structures of the Hoveyda-type complexes **6** and **9** in the solid state are depicted in Figures 1 and 2, whereas the structure of complex **7** is found in the Supporting Information. Compound **9** shows considerable distortion of the NHC ligand, which nonetheless remains aligned to the ruthenium−alkylidene bond. Specifically, the bidentate vinylcarbene ligand is oriented parallel to the molecular axis C(1)−Ru(1)−O(1). Therefore the α-carbon atom C(4) is in close proximity to the mesityl group of the NHC. The resulting steric

---

(9) (a) Fürstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811−4820. (b) See also: Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 601−602.

(10) Applications: (a) Fürstner, A.; Thiel, O. R. *J. Org. Chem.* **2000**, *65*, 1738−1742. (b) Fürstner, A.; Grabowski, J.; Lehmann, C. W. *J. Org. Chem.* **1999**, *64*, 8275−8280. (c) Fürstner, A.; Radkowski, K. *Chem. Commun.* **2001**, 671−672. (d) Fürstner, A.; Jeanjean, F.; Razon, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2097−2101. (e) Fürstner, A.; Radkowski, K.; Wirtz, C.; Goddard, R.; Lehmann, C. W.; Mynott, R. *J. Am. Chem. Soc.* **2002**, *124*, 7061−7069. (f) Fürstner, A.; Leitner, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 308−311. (g) Fürstner, A.; Jeanjean, F.; Razon, P.; Wirtz, C.; Mynott, R. *Chem. Eur. J.* **2003**, *9*, 320−326. (h) Fürstner, A.; Schlede, M. *Adv. Synth. Catal.* **2002**, *344*, 657−665.

(11) Recent reviews on enyne metathesis: (a) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317−1382. (b) Mori, M. *Top. Organomet. Chem.* **1998**, *1*, 133−154. (c) Poulsen, C. S.; Madsen, R. *Synthesis* **2003**, 1−18.

(12) (a) For a related experiment see: Hansen, E. C.; Lee, D. *J. Am. Chem. Soc.* **2004**, *126*, 15074−15080. (b) For a recent study proposing differently ligated vinylcarbenes as the intermediates and resting states in enyne metathesis see: Galan, B. R.; Giessert, A. J.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005**, *127*, 5762−5763. (c) For an insightful mechanistic discussion see: Lippstreu, J. J.; Straub, B. F. *J. Am. Chem. Soc.* **2005**, *127*, 7444−7457. (d) For a conceptually different recent approach to ruthenium vinyl carbenes see: Castarlenas, R.; Eckert, M.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2576−2579.

(13) (a) Schrock, R. R. In *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser: Munich, 1993; pp 129−156. (b) Schrock, R. R. *Pure Appl. Chem.* **1994**, *66*, 1447−1454.

(14) (a) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035−4037. (b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314−5318.

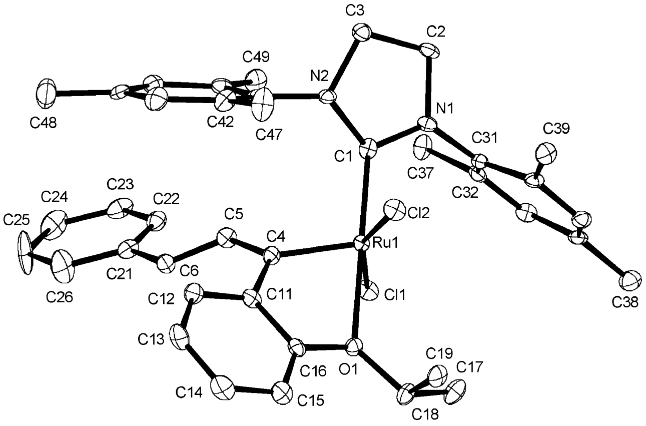
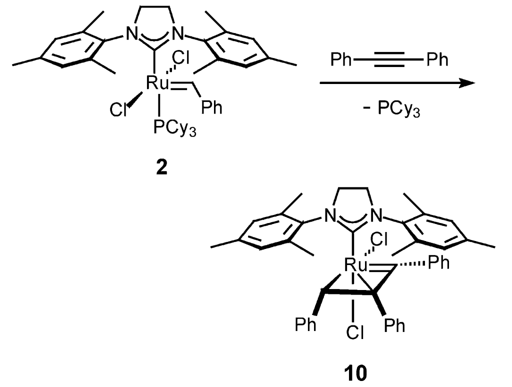


Figure 2. Molecular structure of complex **9** in the solid state. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–C(4) 1.858(4), Ru(1)–C(1) 1.984(4), Ru(1)–O(1) 2.301(3), Ru(1)–Cl(1) 2.3586(12), Ru(1)–Cl(2) 2.3430(13), C(4)–C(5) 1.443(6), C(5)–C(6) 1.363(6), C(1)–N(1) 1.349(6), C(1)–N(2) 1.367(5); Cl(1)–Ru(1)–Cl(2) 159.14(4), N(1)–C(1)–N(2) 107.3(4), C(1)–Ru(1)–O(1) 170.26(13), N(1)–C(1)–Ru(1) 119.2(3), N(2)–C(1)–Ru(1) 131.4(3).

hindrance is reduced by (i) distorting the five-membered metallacycle into an envelope conformation, (ii) a slight pyramidalization of carbon atom C(4), and (iii) tilting of the NHC ligand in combination with pyramidalization of the carbene center C(1). The N(1)–C(1)–N(2) angle is no longer bisected by the C(1)–Ru(1) bond, but asymmetric bond angles of 119.2° and 131.4° are observed. This is in agreement with the geometry reported for the original Hoveyda catalyst **3** (L = IMes), which exhibits an almost identical tilt of the carbene ligand with angles of 120.8° and 131.5°.[6c] The same trend is also observed in enhanced form for Hoveyda's chiral NHC complex.[15]

It was interesting to extend the concept to nonterminal alkynes as the substrates. Grubbs et al. have recently shown that reaction of diphenylacetylene with **2** affords compound **10** bearing a η^3- rather than η^1-coordinated vinyl carbene unit which is devoid of catalytic activity in standard RCM reactions (Scheme 3).[16] We were pleased to find that the presence of an *ortho*-isopropoxy group on the phenyl ring of the starting material ensures the regular η^1-coordination mode and therefore leads to catalytically competent materials. This aspect is illustrated by the reactions of alkyne **11** end-capped with a trimethylsilyl group and of the ester-bearing substrate **13a** (R = $C(O)CH_2CH_2COOMe$) (Scheme 4). The X-ray crystal structure analysis of the resulting complex **14** proved that the functionalized side chain is branching off the bidentate vinyl carbene moiety (cf. Supporting Information). It is surmised that this structural motif offers ample opportunity for immobilization of the catalyst on appropriate support materials as well as for tailoring its properties for applications in supercritical CO_2[17] or phase separation regimens,[18,19] e.g., by attachment of PEG-ylated or perfluorinated ponytails.

Scheme 3. Formation of η^3-Vinylcarbene Complex 10 with *cis*-Configured Chloride Ligands by Reaction of Complex 2 with Diphenylacetylene[a]



[a] cf. ref 16.

A particularly noteworthy and surprising result was obtained upon reaction of complex **1** with the propargyl silyl ether derivative **13b** (R = $SiMe_3$). Although one might assume that the *i*PrO group on the phenyl ring might be a better donor to the Lewis-acidic ruthenium center, the structure analysis of the resulting complex **15** shows that the silyl ether acts as the chelating moiety in the solid state (Figure 3). We assume that this structure is also preserved in solution as deduced from the characteristic shift of the $-OCH(Me)_2$ signal in the ^1H NMR spectrum of **15**, which resonates at $\delta = 4.38$ ppm, whereas the corresponding signal in all complexes engaging this moiety in chelation to the ruthenium atom appears at $\delta \approx 5.19$ ppm in the spectra. Because complex **16**, derived from **15** by treatment with HCl in CH_2Cl_2/MeOH, shows the same pattern signature in the ^1H NMR spectrum ($\delta = 4.40$ ppm), we assume that this complex features an interaction of the *free* –OH group and the metal center. Such an unusual coordination mode has recently been observed by our group in certain ruthenium carbene complexes bearing hydroxy alkyl side chains on their NHC ligands.[20]

Since the rather labile ligation of the $-OSiMe_3$ moiety in **15** should easily liberate the required vacant coordination site for an incoming substrate molecule, **15** might serve as a rapidly initiating and active metathesis catalyst. In line with this notion, this complex was found

---

(15) Van Veldhuizen, J. S.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954–4955.

(16) Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Organometallics* **2001**, *20*, 3845–3847.

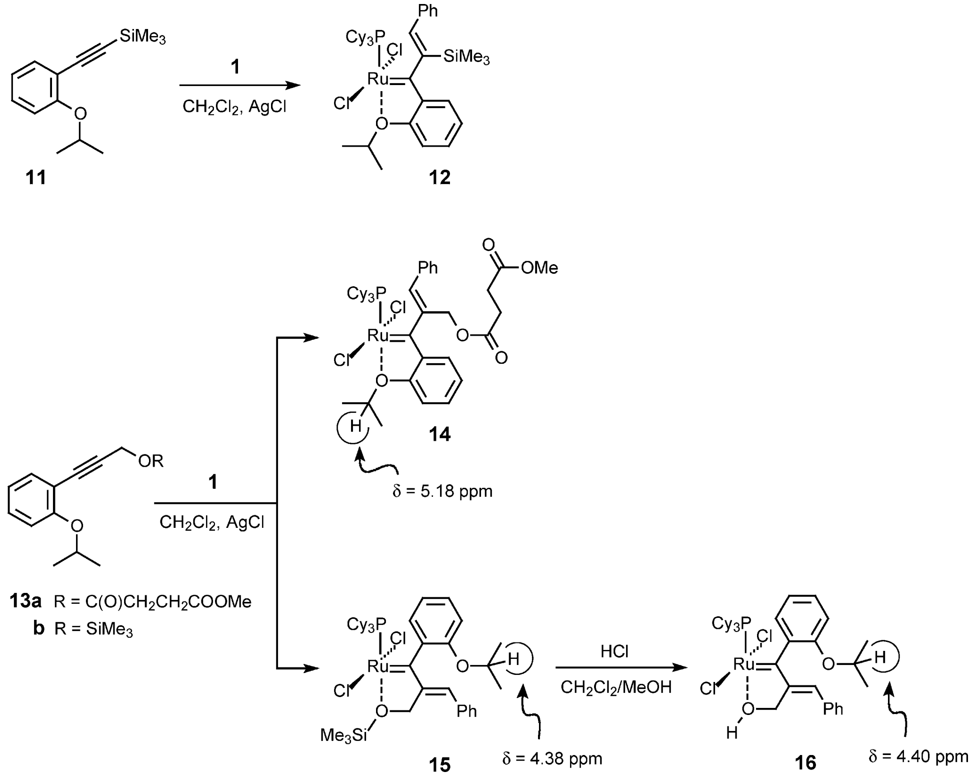
(17) (e) Fürstner, A.; Ackermann, L.; Beck, K.; Hori, H.; Koch, D.; Langemann, K.; Liebl, M.; Six, C.; Leitner, W. *J. Am. Chem. Soc.* **2001**, *123*, 9000–9006. (b) Fürstner, A.; Koch, D.; Langemann, K.; Leitner, W.; Six, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2466–2469.

(18) For leading references see: (a) Matsugi, M.; Curran, D. P. *J. Org. Chem.* **2005**, *70*, 1636–1642. (b) Clavier, H.; Audic, N.; Mauduit, M.; Guillemin, J.-C. *Chem. Commun.* **2004**, 2282–2283. (c) Zarka, M. T.; Nuyken, O.; Weberskirch, R. *Macromol. Rapid Commun.* **2004**, *25*, 858–862. (d) Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 777–784. (e) Yao, Q.; Zhang, Y. *J. Am. Chem. Soc.* **2004**, *126*, 74–75. (f) Yao, Q.; Zhang, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3395–3398. (g) Dowden, J.; Savovic, J. *Chem. Commun.* **2001**, 37–38. (h) Randl, S.; Buschmann, N.; Connon, S. J.; Blechert, S. *Synlett* **2001**, 1547–1550. (i) Connon, S. J.; Dunne, A. M.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, 41, 3835–3838. (j) Grela, K.; Tryznowski, M.; Bieniek, M. *Tetrahedron Lett.* **2002**, *43*, 9055–9059. (k) Varray, S.; Lazaro, R.; Martinez, J.; Lamaty, F. *Organometallics* **2003**, *22*, 2426–2435.

(19) (a) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236–3253. (b) Fürstner, A.; Krause, H.; Ackermann, L.; Lehmann, C. W. *Chem. Commun.* **2001**, 2240–2241. (c) Mayr, M.; Wang, D.; Kröll, R.; Schuler, N.; Prühs, S.; Fürstner, A.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2005**, *347*, 484–492.

(20) Prühs, S.; Lehmann, C. W.; Fürstner, A. *Organometallics* **2004**, *23*, 280–287.

Scheme 4. Formation of η^1-Vinylcarbene Complexes by Enyne Metathesis of Functionalized Nonterminal Alkynes with the Grubbs Catalyst 1



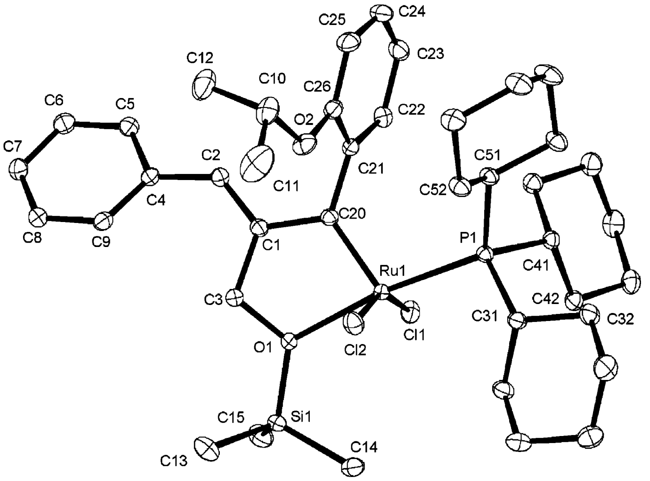
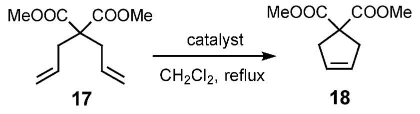


Figure 3. Molecular structure of complex **15** in the solid state. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–C(20) 1.8532(16), Ru(1)–O(1) 2.1973(12), Ru(1)–Cl(1) 2.3414(4), Ru(1)–Cl(2) 2.3439(4), Ru(1)–P(1) 2.3284(4), O(1)–C(3) 1.437(2), O(1)–Si(1) 1.6895(13); Cl(1)–Ru(1)–Cl(2) 154.459(17), O(1)–Ru(1)–P(1) 172.12(3).

Table 1. Comparison of the Catalytic Activity of η^1-Vinylcarbene Ruthenium Complexes in the Cyclization of Diene 17 to Product 18 (NMR yields, unless stated otherwise)[a]



entry	catalyst	time	yield (%)
1	**6**	2 h	98%[b]
2	**9**	5 min	>95%
3	**14**	8 h	32%
4	**15**	1 h	>95%

[a] The reactions were carried out in refluxing CH_2Cl_2 using 5 mol % of the catalyst. [b] Isolated yield

to be the most active species among all novel, PCy_3-bearing catalysts prepared in this study; as expected however, its activity is surpassed by that of the "second-generation" variant **9** bearing an NHC ligand (Table 1).

Finally, it should be noted that all novel bidentate ruthenium vinylcarbene complexes, while stable in the solid state for extended periods of time, decompose to baseline material upon attempted chromatography on silica gel.[21] Although—at first sight—this seems disappointing, decomposition to easily separable polar residues might actually be a significant bonus in preparative terms in view of the efforts that are usually necessary to obtain colorless and metal-free products as required for all compounds intended for later biological use when working with any of the established catalyst systems.[22]

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: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), DMF

---

[21] This property contrasts the known stability of the original Hoveyda catalysts towards silica gel, cf. refs 5–8.

[22] For procedures allowing the removal of metal impurities (other than using immobilized or phase-separated catalysts) see: (a) Maynard, H. D.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 4137–4140. (b) Paquette, L. A.; Schloss, J. D.; Efremov, I.; Fabris, F.; Gallou, F.; Méndez-Andino, J.; Yang, J. *Org. Lett.* **2000**, *2*, 1259–1261. (c) Cho, J. H.; Kim, B. M. *Org. Lett.* **2003**, *5*, 531–533. (d) Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411–1413.

(Desmodur), toluene (Na). Flash chromatography: Merck silica gel, type 9385, 230−400 mesh. NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. MS: Finnigan MAT 8200 (70 eV). ESI-MS: Hewlett-Packard HP 5989 B MS-Engine. HR-MS: Finnigan MAT 95. IR: Nicolet FT-7199 spectrometer. Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available reagents were used as received.

Iodo-2-isopropoxybenzene. K_2CO_3 (5.47 g, 39.6 mmol) and isopropyl iodide (2.00 g, 11.8 mmol) were added to a stirring solution of 2-iodophenol (1.99 g, 9.0 mmol) in DMF (18 mL), and the resulting suspension was stirred at 45 °C for 12 h. The mixture was then diluted with water (200 mL) and extracted three times with Et_2O (200 mL portions). The combined organic extracts were washed three times with water (150 mL portions) before being dried over Na_2SO_4, filtered, and evaporated under reduced pressure to afford the pure iodide as a colorless oil (2.30 g, 98%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.6, 1.6 Hz, 1H), 7.26 (m, 1H), 6.83 (dd, J = 8.4, 1.2 Hz, 1H), 6.68 (m, 1H), 4.56 (sept, J = 6.4 Hz, 1H), 1.40 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 139.6, 129.2, 122.5, 114.4, 88.6, 72.1, 22.1 (2C); IR (KAP) 3060, 2977, 2932, 1581, 1470, 1438, 1384, 1373, 1273, 1245, 1125, 1105, 1017, 952 cm^{-1}; MS (EI) m/z (%) 262 (22) $[M]^+$; HR-MS (EI) m/z calcd for $C_9H_{11}IO$ 261.9855, found 261.9854 $[M]^+$.

[(2-Isopropoxyphenyl)ethynyl](trimethyl)silane (11). $PdCl_2(PPh_3)_2$ (106 mg, 0.15 mmol) and CuI (29 mg, 0.15 mmol) were added to a solution of iodo-2-isopropoxybenzene (2.00 g, 7.6 mmol) and trimethylsilylacetylene (1.12 g, 11.4 mmol) in NEt_3 (50 mL), and the mixture was heated at 50 °C for 1 h. After cooling, the mixture was diluted with hexanes, the suspension was filtered, and the filtrate was evaporated. The residue was purified by flash chromatography, eluting in 3% MTBE/hexanes, to afford alkyne **11** as a colorless liquid (1.76 g, 100%): IR (neat) 2976, 2900, 2159, 1594, 1485, 1447, 1287, 1250, 1120 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.0, 1.6 Hz, 1H), 7.23 (ddd, J = 8.0, 8.0, 1.6 Hz, 1H), 6.88 (m, 2H), 4.57 (sept, J = 6.0 Hz, 1H), 1.36 (d, J = 6.0 Hz, 6H), 0.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 59.4, 133.7, 129.6, 120.8, 116.0, 114.7, 101.8, 98.2, 72.3, 22.2 (2C), 0.03 (3C); MS (EI) m/z (%) 232 (23) $[M]^+$, 190 (12), 175 (100); HR-MS (EI) m/z calcd for $C_{14}H_{20}OSi$ 232.1283, found 232.1280 $[M]^+$.

1-Ethynyl-2-isopropoxybenzene (5). Alkyne **11** (1.39 g, 6.00 mmol) and K_2CO_3 (143 mg, 1.05 mmol) were stirred together in MeOH (7.5 mL) at ambient temperature. When the reaction appeared complete by TLC, the mixture was diluted with hexanes and washed with water and aqueous saturated NH_4Cl (1:1 mix) before being dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure affording alkyne **5** as a colorless oil (0.89 g, 93%): IR (neat) 3285, 2979, 2934, 2107, 1594, 1573, 1486, 1446, 1384, 1374, 1280, 1250, 1119, 953, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.1, 1.9 Hz, 1H), 7.19 (m, 1H), 6.85 (m, 2H), 4.51 (sept, J = 6.1 Hz, 1H), 3.17 (s, 1H), 1.30 (d, J = 6.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 134.3, 130.0, 120.3, 114.8, 113.2, 80.8, 80.4, 71.8, 22.1 (2C); MS (EI) m/z (%) 160 (34) $[M]^+$, 118 (100); HR-MS (EI) m/z calcd for $C_{11}H_{12}O$ 160.0888, found 160.0889 $[M]^+$.

{[3-(2-Isopropoxyphenyl)-2-propynyl]oxy}(trimethyl)silane (13b). $PdCl_2(PPh_3)_2$ (162 mg, 0.23 mmol) and CuI (44 mg, 0.23 mmol) were added to a solution of iodo-2-isopropoxybenzene (3.00 g, 11.46 mmol) and 2-propynyl trimethylsilyl ether (2.19 g, 17.2 mmol) in NEt_3 (75 mL), and the mixture was heated at 50 °C overnight. After cooling, the mixture was diluted with hexanes, the suspension was filtered, and the filtrate was evaporated. The residue was purified by flash chromatography, eluting in 5% MTBE/hexanes, to afford alkyne **13b** as a colorless liquid (1.50 g, 50%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.6 Hz, 1H), 7.23 (m, 1H), 6.87 (m, 2H), 4.57 (sept, J = 6.2 Hz, 1H), 4.58 (s, 2H), 1.36 (d, J = 6.2 Hz, 6H), 0.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 133.8, 129.4, 120.6, 114.6, 113.8, 91.2, 81.8, 71.4, 51.9, 22.1 (2C), −0.1 (3C); MS (EI) m/z (%) 262 (30) $[M]^+$, 220 (100).

1-Methyl 4-(2-propynyl)succinate. To a solution of propargyl alcohol (0.68 g, 10 mmol) in CH_2Cl_2 (30 mL) was added DCC (2.48 g, 12 mmol) and DMAP (122 mg, 1 mmol) at 0 °C. The solution was then cooled to −20 °C and succinic acid monomethyl ester (1.32 g, 10 mmol) introduced after 5 min. The resulting solution was allowed to warm to room temperature slowly with stirring overnight. The precipitate was filtered off and the organic solution washed with aqueous saturated $NaHCO_3$ and brine before being dried over Na_2SO_4, filtered, and evaporated. The residue was purified by flash chromatography to afford the title compound as a colorless oil (1.19 g, 70%); IR (kap) 3286, 3000, 2955, 2129, 1739, 1439, 1369, 1351, 1318, 1270, 1214, 1158, 1026, 998, 847, 673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.67 (d, J = 2.4 Hz, 2H), 3.67 (s, 3H), 2.64 (m, 4H), 2.46 (t, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 171.4, 77.4, 74.9, 52.1, 51.8, 28.8, 28.7; MS (EI) m/z (%) 139 (15) $[M - OMe]^+$, 115 (100); HR-MS (ESI+) m/z calcd for $C_8H_{11}O_4$ 171.0657, found 171.0659 [M + H].

1-[3-(2-Isopropoxyphenyl)-2-propynyl]4-methyl Succinate (13a). Et_3N (10 mL) was added to a mix of iodo-2-isopropoxybenzene (0.24 g, 0.92 mmol) and 1-methyl 4-(2-propynyl) succinate (0.31 g, 1.83 mmol) before Ar was bubbled through the solution for 5 min. $Pd(PPh_3)_2Cl_2$ (13.0 mg, 0.018 mmol) and CuI (3.5 mg (0.018 mmol) were added, and the solution was placed in a preheated oil bath at 50 °C. GC analysis shows consumption of the alkyne to be faster than the aryl iodide, and after 4 h, a further portion of the alkyne (0.20 g, 1.2 mmol) was added and the solution stirred overnight. Hexane and methyl *tert*-butyl ether (MTBE) (1:1, 10 mL) were added to the solution at room temperature, the mixture was filtered, and the solvent was evaporated. The residue was purified by flash chromatography eluting in 20% MTBE/hexanes to afford alkyne **13a** as a pale yellow oil (271 mg, 97%): IR (kap) 3278, 2979, 2953, 2235, 1740, 1489, 1446, 1439, 1385, 1371, 1350, 1265, 1215, 1156, 1124, 1024, 997, 951, 847, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.9, 1.8 Hz, 1H), 7.25 (m, 1H), 6.88 (m, 2H), 4.97 (s, 2H), 4.56 (sept, J = 6.1 Hz, 1H), 3.70 (s, 3H), 2.69 (m, 4H), 1.36 (d, J = 6.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 171.6, 159.1, 133.9, 130.0, 120.6, 115.0, 113.2, 86.3, 83.4, 71.9, 53.4, 51.8, 29.0, 28.8, 22.1 (2C); MS (EI) m/z (%) 304 (18) $[M]^+$, 262 (17), 173 (16), 130 (100); HR-MS (ESI+) m/z calcd for $C_{17}H_{20}NaO_5$ 327.1208, found 327.1209 [M + Na].

Representative Procedure for the Preparation of the Vinylcarbene Ruthenium Complexes. AgCl (1 equiv) and complex **1** (1 equiv) were placed into a dry Schlenk flask and vacuum applied, backfilling with Ar. CH_2Cl_2 was added (10 mL) followed by the alkyne (1 equiv) before the Schlenk tube was sealed, and the solution was stirred at room temperature until no starting material remained. Roughly half the solvent was removed in vacuo, and pentane was added to the stirring solution (ca. 3−4 times volume of CH_2Cl_2). The off-white precipitate ($AgCl{\cdot}PCy_3$, the precipitation of which can be encouraged by the application of mild vacuum) was removed by filtering the solution through a plug of Celite, flushing with pentane. The solution was collected in a two-necked round-bottomed flask fitted with an argon inlet/vacuum tap and stir bar. The solvent was removed under reduced pressure, leading to the precipitation of the product, which can be isolated in pure form by filtration and washing with pentane unless otherwise mentioned. The spectroscopic and analytical data of the complexes prepared by this method are compiled below.

Complex 6: dark green microcrystalline solid (400 mg, 72%, *E*-isomer). A second crop was obtained as a light brown microcrystalline mixture of *E*/*Z* isomers (40 mg, 7%): mp = 191−192 °C (dec); IR (kap) 3072, 2925, 2848, 1592, 1573, 1472, 1446, 1385, 1286, 1273, 1221, 1103 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.8, 1.5 Hz, 1H), 7.64 (m,1H), 7.54 (m, 2H), 7.34 (m, 3H), 7.24 (d, $J = 16.5$ Hz, 1H), 7.06 (d, $J = 8.3$ Hz, 1H), 6.94 (dd, $J = 7.3, 7.3$ Hz, 1H), 6.64 (d, $J = 16.5$ Hz, 1H), 5.19 (sept, $J = 6.1$ Hz, 1H), 2.35−1.10 (33H), 1.69 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$, [signals of rotamer]) δ 282.8, 155.8, 147.9 (d, $J = 2.7$ Hz), 144.9, 138.1, 130.6, 130.1 (2C), 128.7, 127.8 (2C), 122.8, 119.9, 119.6, 114.2, 147.9, 76.6, 36.9 (d, $J = 22.6$ Hz), [32.1], 31.2 (brd), 28.5 (d, $J = 10.6$ Hz), [27.9 (d, $J = 12.1$ Hz)], 27.1 (brd), [26.7], 22.8 (2C); ^{31}P NMR (122 MHz, CDCl$_3$) δ 46.6; MS (EI) *m/z* (%) 702 (45) [M]$^+$, 624 (45), 315 (67), 279 (67), 198 (100); HR-MS (ESI+) *m/z* calcd for $C_{36}H_{51}ClOPRu$ 667.2403, found 667.2422 [M − Cl]$^+$. Anal. Calcd for $C_{36}H_{51}RuCl_2PO$: C, 61.53; H, 7.31. Found: C, 61.39; H, 7.29. Yellow monoclinic crystals suitable for X-ray crystal structure analysis were grown by layering a concentrated CH$_2$Cl$_2$ solution of the complex with pentane.

Complex 7: brown crystalline solid (249 mg, 59%); mp = 207−208 °C (dec); IR (kap) 3072, 2925, 2848, 1592, 1573, 1472, 1446, 1385, 1286, 1273, 1221, 1103 cm^{-1}; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, only signals related to major complex are given, major: minor isomer = 14.3:1) δ 7.86 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.66 (m, 2H), 7.49 (m, 1H), 7.42 (m, 2H), 7.32−7.24 (m, 5H), 7.06 (d, J 8.3 Hz, 1H), 6.88 (dd, $J = 7.6, 7.6$ Hz, 1H), 6.82 (s, 1H), 5.94 (s, 1H), 5.19 (m, 1H), 2.50−0.20 (brd, 33H), 1.71 (d, $J = 5.8$ Hz, 6H); ^{31}P NMR (122 MHz, CD$_2$Cl$_2$) δ 41.5 (major), 47.7 (minor); MS (EI) *m/z* (%) 802 [M]$^+$; HR-MS (ESI+) *m/z* calcd for $C_{44}H_{55}ClOPRu$ 767.2734, found 767.2737 [M − Cl]$^+$. Anal. Calcd for $C_{44}H_{55}Cl_2OPRu$: C, 65.82; H, 6.90. Found: C, 65.68; H, 6.88. Brown monoclinic crystals suitable for X-ray crystal structure analysis were grown by layering a concentrated CH$_2$Cl$_2$ solution of the complex with pentane.

Complex 12: brown solid (127 mg, 36%), which can be further purified by dissolving in the minimum CH$_2$Cl$_2$, layering with pentane, and cooling to −78 °C to afford a brown crystalline material (101 mg, 29%): mp = 162−163 °C (dec); IR (neat) 3057, 2977, 2927, 2850, 1591, 1573, 1471, 1446, 1384, 1282, 1246, 1226, 1106, 933, 849, 750 cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.71 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.56 (ddd, $J = 8.6, 7.6, 1.6$ Hz, 1H), 7.44 (m, 2H), 7.35 (m, 2H), 7.29 (m, 1H), 7.02 (d, $J = 8.3$ Hz, 1H), 6.93 (s, 1H), 6.90 (ddd, $J = 7.7, 7.7, 0.7$ Hz, 1H), 5.19 (sept, $J = 6.0$ Hz, 1H), 2.70−0.50 (brd, 33H), 1.81 (d, $J = 6.0$ Hz, 3H), 1.33 (d, $J = 6.0$ Hz, 3H), 0.26 (s, 9H); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$) δ 36.5; MS (ESI+) *m/z* (%) 780.45 (14) [M]$^+$, 739.37 (100); HR-MS (ESI+) *m/z* calcd for $C_{39}H_{59}ClOPRuSi$ 739.2814, found 739.2805 [M − Cl]$^+$. Anal. Calcd for $C_{39}H_{59}Cl_2OPRuSi$: C, 60.45; H, 7.67. Found: C, 60.51; H, 7.59.

Complex 14. Crystallization of the crude product from Et$_2$O affords complex **14** as a brown crystalline solid: mp = 117.5−119 °C; IR (neat) 2928, 2843, 1727, 1590, 1573, 1445, 1407, 1380, 1362, 1269, 1227, 1208, 1157, 1097, 1001, 982, 926, 850, 752 cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.89 (d, $J = 7.9$ Hz, 1H), 7.63 (m, 1H), 7.40 (s, 2H), 7.39 (s, 2H), 7.31 (m, 1H), 7.04 (d, $J = 8.7$ Hz, 1H), 6.92 (dd, $J = 7.6$ Hz, 1H), 6.50 (s, 1H), 5.18 (sept, $J = 6.2$ Hz, 1H), 4.90 (2H, s), 3.51 (s, 3H), 2.50−1.00 (brd multiplets, 43H); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$) δ 34.4; HR-MS (ESI+) *m/z* calcd for $C_{42}H_{59}ClO_5PRu$ 811.2844, found 811.2850 [M − Cl$^+$]. Anal. Calcd for $C_{42}H_{59}Cl_2O_5Pru$: C, 59.57; H, 7.02. Found: C, 59.46; H, 6.85.

Complex 15: yellow brown solid (119 mg, 25%), mp = 128−129 °C (dec); IR (neat) 2923, 2855, 1739, 1588, 1476, 1442, 1249, 1232, 1116, 1035, 846,754 cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.34 (m, 1H), 7.24 (m, 5H), 7.04 (dd, $J = 7.2, 1.6$ Hz 1H), 6.93 (s, 1H), 6.83 (dd, $J = 7.4$ Hz, 1H), 6.72 (d, $J = 8.3$ Hz, 1H), 5.27 (d, $J = 11.5$ Hz, 1H), 4.88 (d, $J = 11.5$ Hz, 1H), 4.38 (sept, $J = 6.0$ Hz, 1H), 2.10−0.90 (39H), 0.29 (s, 9H); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$) δ 30.8; MS (EI) *m/z* (%) 804 (25) [M]$^+$, 315 (100); HR-MS (ESI$^+$) *m/z* calcd for $C_{40}H_{61}ClO_2PRuSi$ 769.2920, found 769.2919 [M − Cl]$^+$. Crystals suitable for X-ray crystal structure analysis were grown from a CH$_2$Cl$_2$/pentane mixture that was cooled slowly to −60 °C.

Complex 16. HCl (2 M in Et$_2$O, 50 μL) was added to a solution of alkylidene **15** (90 mg, 0.112 mmol) in CH$_2$Cl$_2$ (5 mL) and MeOH (5 mL) and the solution stirred for 10 min at room temperature before the solvent was evaporated. The residue was dissolved in the minimum CH$_2$Cl$_2$ and carefully layered with pentane to afford complex **16** as an orange-red solid (52 mg, 63%): mp = 162−163 °C (dec); IR (neat) 3058, 2928, 2846, 1737, 1588, 1552, 1474, 1442, 1382, 1370, 1284, 1230, 1119, 1105, 1011, 956, 917, 846, 751, 693 cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.36 (m, 1H), 7.24 (m, 5H), 6.99 (s, 1H), 6.98 (dd, $J = 7.4, 1.7$ Hz, 1H), 6.84 (ddd, $J = 8.1, 7.4, 0.7$ Hz, 1H), 6.74 (d, $J = 8.3$ Hz, 1H), 5.33 (brd, 1H), 5.19 (brd, 1H), 4.40 (sept, $J = 6.0$ Hz, 1H), 3.07 (td, $J = 6.8, 1.9$ Hz, 1H), 2.10−0.80 (brd m, 39H); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$) δ 32.9; MS (ESI+) *m/z* (%) 739.37 (100) [M]$^+$; HR-MS (ESI+) *m/z* calcd for $C_{37}H_{53}ClO_2PRu$ 697.2524, found 697.2534 [M − Cl]$^+$.

Complex 9. 1-Ethynyl-2-isopropoxybenzene **5** (24 mg, 0.15 mmol) was added to a solution of bispyridine catalyst **8** (100 mg, 0.137 mmol) in CH$_2$Cl$_2$ (2 mL), and the mixture was stirred at room temperature for 30 min. Vacuum was applied until ~0.5 mL of CH$_2$Cl$_2$ remains, pentane was added with stirring, and the mixture was cooled to −10 °C. Filtration and washing with pentane affords complex **9** as a pale green solid (75 mg, 75%), which can be further refined by dissolving in the minimum CH$_2$Cl$_2$ and layering with pentane to afford a green crystalline material (55 mg): mp = 198−199 °C (dec); IR (kap) 2916, 1484, 1444, 1258, 1109, 964, 937, 853, 749 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 (m, 5H), 7.20 (m, 2H), 6.90 (m, 4H), 6.71 (m, 2H), 4.71 (sept, $J = 6.1$ Hz, 1H), 3.95 (brd, 4H), 2.60−1.80 (brd, 18H), 0.89 (d, $J = 6.1$ Hz, 6H); HR-MS (ESI+) *m/z* calcd for $C_{39}H_{44}ClN_2ORu$ 693.2195, found 693.2206 [M − Cl$^+$]. Anal. Calcd for $C_{39}H_{44}Cl_2N_2ORu$: C, 64.28; H, 6.09. Found: C, 64.24; H, 5.91.

Crystal Data for Complex 6: $C_{36}H_{51}Cl_2OPRu$, M_w = 702.71, yellow blocks, crystal size 0.05 × 0.02 × 0.02 mm, monoclinic, $P2_1/c$ [No. 14], $a = 12.3362(5)$ Å, $b = 14.3118(6)$ Å, $c = 19.2817(8)$ Å, $\beta = 98.826(2)°$, $V = 3363.9(2)$ Å^3, $T = 100$ K, $Z = 4$, $D_x = 1.388$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.700 mm^{-1}, Nonius KappaCCD diffractometer, $3.04° < \theta < 31.01°$, semiempirical absorption correction from equivalents, 42 508 measured, 10 700 independent reflections, 7075 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.054$ [$I > 2\sigma(I)$], $wR_2 = 0.117$, 372 parameters, H atoms riding, $S = 1.083$, $\Delta/\sigma = 0.001$, residual electron density +0.9/−0.6 e Å^{-3}; CCDC 266243.

Crystal Data for Complex 7. The structure is depicted in the Supporting Information. $C_{44}H_{55}Cl_2OPRu$, M_w = 802.82, brown plates, crystal size 0.36 × 0.30 × 0.08 mm, monoclinic, $P2_1/c$ [No. 14], $a = 15.66000(10)$ Å, $b = 16.27930(10)$ Å, $c = 16.81110(10)$ Å, $\beta = 114.20°$, $V = 3909.03(4)$ Å^3, $T = 100$ K, $Z = 4$, $D_x = 1.364$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.612 mm^{-1}, Nonius KappaCCD diffractometer, $5.13° < \theta < 31.00°$, semiempirical absorption correction from equivalents, 103 391measured, 12 363 independent reflections, 11 581 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.026$ [$I > 2\sigma(I)$], $wR_2 = 0.067$, 444 parameters, H atoms riding, $S = 1.023$, $\Delta/\sigma = 0.001$, residual electron density +1.6/−0.8 e Å^{-3}; CCDC 266246.

Crystal Data for Complex 9: $C_{39}H_{44}Cl_2N_2ORu$, M_w = 728.73, green blocks, crystal size 0.06 × 0.03 × 0.02 mm, monoclinic, $P2_1/c$ [No. 14], $a = 20.7180(6)$ Å, $b = 11.514(5)$ Å, $c = 14.3789(7)$ Å, $\beta = 99.93(2)°$, $V = 3378.7(14)$ Å^3, $T = 100$ K, $Z = 4$, $D_x = 1.433$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.656 mm^{-1}, Nonius KappaCCD diffractometer, $6.62° < \theta < 32.46°$, 43 542 measured and independent reflections, 22 979 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.103$ [$I > 2\sigma(I)$], $wR_2 = 0.284$, 415 parameters, H atoms riding, $S = 1.019$, $\Delta/\sigma = 0.001$, residual electron density +2.3/−2.2 e Å^{-3}.

The crystal is twinned, twin lattice orthorhombic C, $a' = 11.514$, $b' = 14.3789$, $c' = 81.720$ Å; CCDC 266244.

Crystal Data for Complex 14. The structure is depicted in the Supporting Information. $C_{42}H_{59}Cl_2O_5PRu \cdot 0.25C_4H_{10}O$, $M_w = 865.36$, dark red blocks, crystal size 0.08 × 0.07 × 0.05 mm, triclinic, $P\bar{1}$ [No. 2], $a = 9.95470(10)$ Å, $b = 11.37650(10)$ Å, $c = 20.5889(3)$ Å, $\alpha = 104.0860(10)°$, $\beta = 102.1350(10)°$, $\gamma = 91.3140(10)°$, $V = 2204.28(4)$ Å^3, $T = 100$ K, $Z = 2$, $D_x = 1.304$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.554 mm^{-1}, Nonius KappaCCD diffractometer, $2.98° < \theta < 33.11°$, Gaussian absorption correction ($T_{max} = 0.98$, $T_{min} = 0.96$), 62675 measured, 16 707 independent reflections, 14 665 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.033$ [$I > 2\sigma(I)$], $wR_2 = 0.093$, 478 parameters, H atoms riding, $S = 1.061$, $\Delta/\sigma = 0.001$, residual electron density +1.9/−0.7 e Å^{-3}; CCDC 266245.

X-ray Crystal Structure Analysis of Complex 15: $C_{40}H_{58}Cl_2O_2PRuSi$, $M_w = 801.89$, yellow plates, crystal size 0.07 × 0.04 × 0.01 mm, triclinic, $P\bar{1}$ [No. 2], $a = 11.4345(2)$ Å, $b = 11.8682(3)$ Å, $c = 16.0928(4)$ Å, $\alpha = 85.0330(10)°$, $\beta = 83.2670(10)°$, $\gamma = 87.6350(10)°$, $V = 2159.63(9)$ Å^3, $T = 100$ K, $Z = 2$, $D_x = 1.233$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.581 mm^{-1}, Nonius KappaCCD diffractometer, $2.92° < \theta < 31.00°$, Gaussian absorption correction ($T_{max} = 0.99$, $T_{min} = 0.97$), 45455 measured, 13 764 independent reflections, 11 668 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.033$ [$I > 2\sigma(I)$], $wR_2 = 0.087$, 429 parameters, H atoms riding, $S = 1.034$, $\Delta/\sigma = 0.001$, residual electron density +1.1/−0.5 e Å^{-3}. Difference Fourier maps revealed the presence of additional electron density associated with cocrystallized solvent. Despite various attempts, no chemically reasonable model could be fitted to the electron density. Using the method described by Spek [van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194−201] observed structure factors were corrected for the disordered solvent region and structure refinement continued. Although a high-quality structural model for **15** was obtained, no fractional coordinates are given, since only part of the crystal structure could be determined.

Acknowledgment. Generous financial support by the Max-Planck-Society and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Structures of complexes **7** and **14** in the solid state, as well as a complete list of atom coordinates and anisotropic displacement parameters and tables containing all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050310W