The First Grubbs-Type Metathesis Catalyst with *cis* Stereochemistry: Synthesis of [(η^2-dtbpm)$Cl_2Ru{=}CH{-}CH{=}CMe_2$] from a Novel, Coordinatively Unsaturated Dinuclear Ruthenium Dihydride

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 80th birthday

Abstract: The first ruthenium olefin metathesis catalyst with rigid *cis* stereochemistry of two phosphane ligands- in a square-pyramidal structure, [(η^2-dtbpm)$Cl_2Ru{=}CH{-}CH{=}CMe_2$] (**2**), was synthesized by using bis(di-*tert*-butylphosphanyl)methane $tBu_2PCH_2PtBu_2$ (dtbpm) as a chelating ligand. The ground state geometries, electronic structures and relative energies of *trans*-[$(PH_3)_2Cl_2Ru{=}CH_2$] (**3**), a model of Grubbs-type catalysts *trans*-[$(PR_3)_2Cl_2Ru{=}CR^1R^2$], and of its stereoisomer *cis*-[$(PH_3)_2Cl_2Ru{=}CH_2$] (**4**) were investigated by extended Hückel (EH) and density functional theory (DFT) calculations and compared to the chelate model [(η^2-$H_2PCH_2PH_2$)$Cl_2Ru{=}CH_2$] (**5**) of **2** and its isomer [(η^1-$H_2PCH_2PH_2$)$Cl_2Ru{=}CH_2$], formed by dissociation of one Ru−P bond. The prototype Grubbs complex [$(PPh_3)_2Cl_2Ru{=}CHPh$] reacts with $tBu_2PCH_2PtBu_2$ by phosphane attack at the carbene carbon atom. The dinuclear complex [{($tBu_2PCH_2PtBu_2CHPh$)Ru}$_2$(μ_2-Cl)$_3$]Cl (**7**) with ylidic, five-membered RuCPCP rings and agostic CH_3−Ru interactions is formed, which was characterized by X-ray diffraction. The mechanistic implications of this finding are discussed. An electronically unsaturated dihydride dimer [{(η^2-dtbpm)Ru(H)}$_2$(μ_2-Cl)$_2$] (**8**), accessible by treating [{$RuCl_2$(cod)}$_x$] (cod = 1,5-cyclooctadiene) in THF with dtbpm and H_2 in the presence of triethylamine, is a suitable precursor for **2**, which is formed by treating **8** with $HC{\equiv}CC(CH_3)_2Cl$. Both **8** and **2** were characterized by X-ray diffraction. Compound **2** catalyzes the ring opening metathesis polymerization (ROMP) of norbornene and cyclopentene. Our results may open interesting mechanistic perspectives for olefin metathesis with ruthenium carbene complexes.

Keywords: ab initio calculations · carbene complexes · hydrido complexes · metathesis · ruthenium

Introduction

Following the discovery by Grubbs et al. in 1992 of the 16-electron carbene complex *trans*-[$(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$] as a well-defined, mononuclear, single-component olefin metathesis catalyst,[1] various phosphane derivatives of this compound have been reported.[2] The accessibility of Grubbs-type catalysts *trans*-[$(PR_3)_2Cl_2Ru{=}CR^1R^2$] has been continuously improved, and the range of possible carbene ligand precursors extended from cyclopropenes[1] to diazoalkanes,[3] vinyl and propargyl chlorides,[4] 1,1-dihaloalkanes,[5] and finally to 1-alkynes.[6] Recently, ruthenium carbene complexes with bidentate Schiff base[7] and Wanzlick–Arduengo-type carbene ligands,[8] as well as Ru vinylidene systems with Cp, hydridotris(pyrazolyl)borate, Cp*,[9] and η^6-arene[10] ligands have extended the range of ruthenium-based metathesis catalysts. Within a few years, Grubbs-type *trans*-[$(PR_3)_2Cl_2Ru{=}CR^1R^2$] complexes have found wide application in polymer chemistry and organic synthesis.[11] Their catalytic efficiency in ring opening metathesis polymerization (ROMP), ring-opening metathesis (ROM), ring-closing metathesis (RCM), acyclic diene metathesis (ADMET), and intermolecular olefin cross metathesis, combined with an exceptional stability and functional group tolerance, has made them indispensable and elegant synthetic tools for C−C bond formation.

As shown by spectroscopy and X-ray diffraction, all known and catalytically active Grubbs-type Ru carbene complexes [$(PR_3)_2Cl_2Ru{=}CR^1R^2$] (**1**) have square-pyramidal (rather than trigonal-bipyramidal) ground-state geometries, in which the carbene ligands occupy the apical position opposite to the open coordination site of a distorted octahedral fragment, as expected for closed-shell 16-electron d^6 ML_5 systems. The phosphane ligands in the basal plane always occupy *trans*

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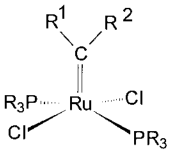
positions, consistent with the steric requirements of, for example, PPh_3, PCy_3, or $P(iPr)_3$. The P-Ru-P angles range from around 160 to 170°,[1, 3, 6a, 12, 16] and the *trans*-Cl-Ru-Cl angles lie in the range of 150–175°. Consequently, all mechanistic scenarios of olefin metathesis with $[(PR_3)_2Cl_2Ru{=}CR^1R^2]$ complexes are based on a *trans* arrangement of monodentate phosphanes in the active catalyst or catalyst precursor.



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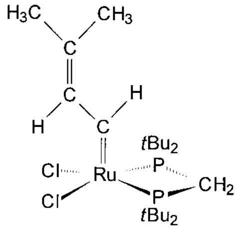

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Here we report the synthesis and full characterization of $[(\eta^2\text{-dtbpm})Cl_2Ru{=}CH{-}CH{=}CMe_2]$ (**2**), the first ruthenium metathesis catalyst with *cis* stereochemistry due to a chelating bis(di-*tert*-butylphosphanyl)methane (dtbpm) ligand. Our findings add a new facet to the chemistry of these systems and may bear relevance to the understanding of reaction mechanisms and structure–activity relationships in Ru-catalyzed olefin metathesis.

Abstract in German: *Der erste katalytisch metatheseaktive Ru-Carbenkomplex, $[(\eta^2\text{-dtbpm})Cl_2Ru{=}CH{-}CH{=}CMe_2]$ (**2**) mit zwei Phosphanliganden in cis-Anordnung bei insgesamt quadratisch-pyramidaler Geometrie wurde mit Bis(di-t-butylphosphino)methan, $tBu_2PCH_2PtBu_2$ (dtbpm), als Chelatligand synthetisiert. Grundzustandsgeometrien, Elektronenstrukturen und relative Energien von trans-$[(PH_3)_2Cl_2Ru{=}CH_2]$ (**3**), als Modell für Grubbs-Katalysatoren trans-$[(PR_3)_2Cl_2Ru{=}CR^1R^2]$, und von cis-$[(PH_3)_2Cl_2Ru{=}CH_2]$ (**4**) als Modell für analoge cis-Komplexe wurden mittels EH- and DFT-Berechnungen untersucht und mit dem Chelatkomplex $[(\eta^2\text{-}H_2PCH_2PH_2)Cl_2Ru{=}CH_2]$ (**5**) sowie mit dessen Stereoisomer $[(\eta^1\text{-}H_2PCH_2PH_2)Cl_2Ru{=}CH_2]$ (**5a**) verglichen, das durch Dissiozation einer Ru-P-Bindung entsteht. Der von Grubbs beschriebene Metathese-Katalysator $[(PPh_3)_2Cl_2Ru{=}CHPh$ reagiert mit $tBu_2PCH_2PtBu_2$ über einen Angriff des Phosphins am Carben, wobei der dinukleare Komplex $[\{(tBu_2PCH_2PtBu_2CHPh)Ru\}_2(\mu_2\text{-}Cl)_3]Cl$ (**7**) mit ylidisch gebundenen, fünfgliedrigen RuCPCP-Ringen und agostischen $CH_3{-}Ru$ Wechselwirkungen gebildet wird. Komplex **7** konnte durch Röntgenstrukturanalyse charakterisiert werden. Die mögliche Bedeutung dieses Befundes für den Mechanismus der Olefin-Metathese wird diskutiert. Mit dem elektronisch und koordinativ ungesättigten, dimeren Dihydrid $[\{(\eta^2\text{-dtbpm})Ru(H)\}_2(\mu_2\text{-}Cl)_2]$ (**8**), zugänglich über die Reaktion von $[\{RuCl_2(COD)\}_x]$ in THF mit dtbpm and H_2 in Gegenwart von Triethylamin, wird ein geeigneter Vorläufer für **2** synthetisiert, welches durch Umsetzung von **8** mit $HC{\equiv}C{-}C(CH_3)_2Cl$ einfach zugänglich ist. Die Strukturen von **8** und **2** wurden durch Einkristall-Röntgenbeugung gesichert. Der Carbenkomplex **2** katalysiert die ringöffnende Metathese-Polymerisation (ROMP) von Norbornen und Cyclopenten. Die Ergebnisse eröffnen interessante, mechanistische Perspektiven für die Olefin-Metathese mit Carbenkomplexen des Rutheniums.*

Results and Discussion

To date, there are only two detailed experimental studies[13] and one recent theoretical paper[14] on the reaction mechanism and catalyst activity in typical Grubbs systems. Two competing processes were postulated for Ru-catalyzed olefin metathesis: an associative pathway with direct olefin attack and metallacycle formation at the five-coordinate *trans*-$[(PR_3)_2Cl_2Ru{=}CR^1R^2]$ catalyst, and a parallel, dominant dissociative path, in which loss of one of the *trans*-phosphane ligands is followed by olefin coordination and metallacycle formation at a four-coordinate 14-electron fragment $[(PR_3)Cl_2Ru{=}CR^1R^2]$. The dissociative pathway was derived experimentally from kinetic data by Grubbs et al.[13a] It is supported by a recently isolated ruthenium chelate carbene–olefin complex,[15] in which an olefin side arm of the carbene moiety is intramolecularly coordinated to the Ru center and replaces one monodentate phosphane in the *trans* position. The only theoretical study available, a quantum molecular dynamics calculation by Meier et al.[14] also seems to support the mechanistic proposals of Grubbs et al.

Our interest in *cis* stereoisomers of $[(PR_3)_2Cl_2Ru{=}CR^1R^2]$ complexes was initially raised by a striking observation of Grubbs et al. in 1993.[16] According to NMR evidence, complexes *trans*-$[(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2]$ (R = Cy, *i*Pr) that were obtained from the corresponding PPh_3 complexes by phosphane exchange contained around 16–20% of the *cis* stereoisomers, both in solution and in the isolated product. It remained unclear whether the isomers are in equilibrium (either by intramolecular rearrangement, as expected given the well-known nonrigidity of ML_5 complexes,[17] or by phosphane dissociation[13c]) or exist as stable, noninterconverting species. Nevertheless, it was surprising that sterically demanding phosphanes with large cone angles such as PCy_3 and $PiPr_3$ would allow formation of *cis* complexes in observable quantities.

Apart from the above-mentioned mechanistic quantum MD study by Meier et al.,[14] there are only two other quantum chemical studies of Grubbs-type complexes in the literature. One of them employed restricted Hartree–Fock (HF) calculations with imposition of C_{2v} symmetry,[18] and the other reports a density functional theory (DFT) calculation on *trans*-$[(PH_3)_2Cl_2Ru{=}CHCH_3]$ at the B3LYP level.[19a] All three theoretical studies, however, were restricted to *trans* geometries; no theoretical investigations of structures with *cis*-phosphane ligands are available.

Electronic structures of ruthenium carbene complexes with *cis*- and *trans*-phosphane ligands: quantum chemistry model calculations: When we performed Extended Hückel (EH)[20] calculations on the simplified model complexes $[(PH_3)_2Cl_2Ru{=}CH_2]$, in which steric preferences should not overshadow electronic effects, the expected distorted square-pyramidal minimum-energy geometry was found for *trans*-[$(PH_3)_2Cl_2Ru{=}CH_2$], in good agreement with X-ray diffraction data and HF[18] and B3LYP[19a] calculations. However, we also found a square-pyramidal structure of similar energy with *cis* PH_3 and Cl ligands in the basal plane. Both structures have a significant HOMO–LUMO gap (ca. 1.7 eV in EHT), in accord with a stable 16-electron system, which is caused mainly by the π-donor chlorine ligands.[21] This result was corroborated by DFT calculations (B3LYP/LANL2DZ).[22] The DFT-optimized geometries **3** and **4** for *trans*- and *cis*-[$(PH_3)_2Cl_2Ru{=}CH_2$], which represent true minima on the energy surface,[23] are shown in Figure 1. Their energy difference is only 10 kcal mol^{-1} in favor of the *trans* isomer at the B3LYP/LANL2DZ level, and this decreases to 7 kcal mol^{-1} with a larger basis set.[24]

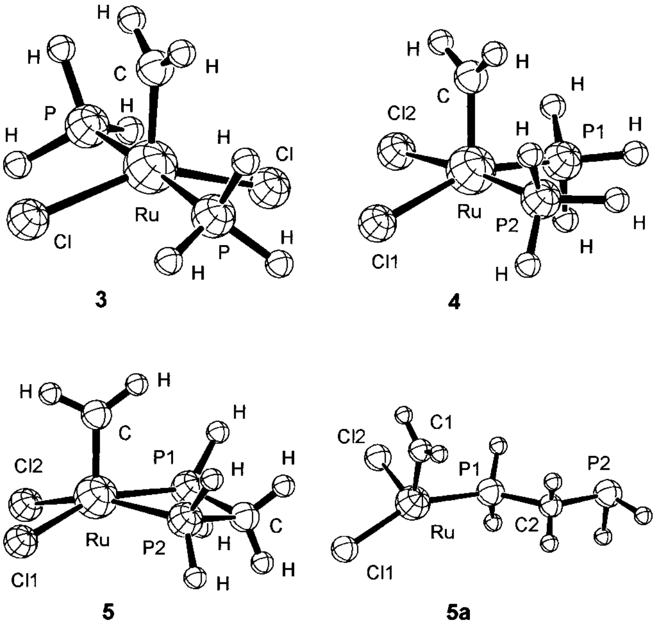


Figure 1. Geometry-optimized structures of **3**, **4**, **5**, and **5a** (B3LYP/LANL2DZ). Selected distances [Å] and angles [°]: **3** (C_{2v}): Ru–P 2.436, Ru–Cl 2.423, Ru–C 1.840, P-Ru-P 176.24, Cl-Ru-Cl 146.87, H-C-H 114.64; **4** (*C*1): Ru–P1 2.436, Ru–P2 2.430, Ru–Cl1 2.409, Ru–Cl2 2.453, Ru–C 2.839, P-Ru-P 100.90, Cl-Ru-Cl 92.66, P1-Ru-Cl1 157.13, P2-Ru-Cl2 175.03, H-C-H 116.32; **5** (C_s): Ru–P1 2.443, Ru–P2 2.442, Ru–Cl1 2.412, Ru–Cl2 1.411, Ru–C 1.842, P1-Ru-P2 73.15, Cl1-Ru-Cl2 92.60, P1-Ru-Cl1 159.07, P2-Ru-Cl2 158.64, H-C-H 115.79; **5a** (C_1): Ru–Cl1 2.361, Ru–Cl2 2.389, Ru–C1 1.827, Ru–P1 2.433, Cl1-Ru-Cl2 102.15, Cl1-Ru-P1 153.42, Cl2-Ru-P1 84.93, Cl1-Ru-C1 108.75, Cl2-Ru-C1 95.50, Cl2-Ru-P1-C2 166.33, Ru-P1-C2 120.26, P1-C2-P2 113.66.

The orientation of the carbene moiety allows for optimal backbonding from the metal fragment to the carbene acceptor orbital in both structures,[25] but the $Ru{=}CH_2$ rotation barriers are very small (< 9 kcal mol^{-1}).[26] In **4**, the P1-Ru-Cl1 unit that interacts with the π-acceptor orbital of the methylene carbon atom is more strongly bent (157.13°) than P2-Ru-Cl2 (175.03°). The LUMOs of both **3** and **4** are predominantly localized on the methylene ligand both at the EH and DFT level of theory. In the *trans* stereoisomer **3** it is practically degenerate with the LUMO – 1, an empty metal orbital (the equivalent of an empty d^2sp^3 hybrid) that points towards the open coordination site opposite to the carbene ligand, while in the *cis* structure **4** it lies at distinctly lower energy (DFT: 0.5 eV) than the metal acceptor level. This feature would predict a frontier orbital controlled attack of nucleophiles to occur at the carbene carbon atom (vide infra).

Given the fluxionality of d^6 ML_5 systems, the small calculated energy difference between **3** and **4** also implies only a marginal energy barrier for a *cis–trans* isomerization of [$(PR_3)_2Cl_2Ru{=}CR^1R^2$] complexes with monodentate phosphanes, with a small preference for the *trans* geometry. Therefore, *cis* complexes of the Grubbs type, although electronically nearly as stable as their well-known *trans* analogues, are expected to be isolable only if a *cis* to *trans* rearrangement is blocked by chelating biphosphane ligands with small bite angles, such as diphosphanylmethanes. The DFT (B3LYP/LANL2DZ) minimum-energy structure of the model system [$(\eta^2\text{-}H_2PCH_2PH_2)Cl_2Ru{=}CH_2$] (**5**) is shown in Figure 1. Complex **5** is electronically identical to **4**, except that in the geometry optimized structure of lowest energy the carbene plane now bisects the P-Ru-P and Cl-Ru-Cl angles both in EH and DFT calculations (overall C_s symmetry). The orbital structure of **5** closely resembles that of **4**, again with a carbene-centered (60%) p orbital as the LUMO and a predominantly d-type (70%) metal acceptor level *trans* to the methylene unit; the latter is around 0.7 eV (DFT) higher in energy than the LUMO. Molecular orbital contour plots (from EH; the DFT orbitals are analogous) for these two lowest lying empty levels LUMO and LUMO – 1 of structure **5** are displayed in Figure 2.

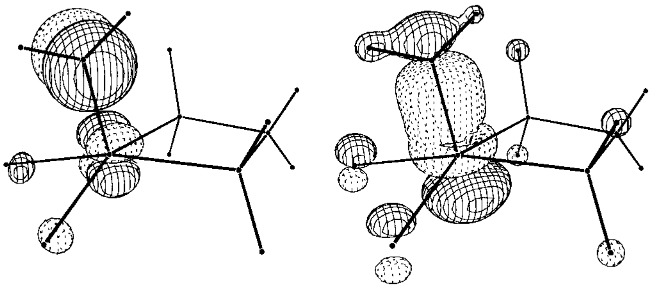


Figure 2. Three-dimensional MO contour plots (EH MOs, CACAO plots[20]) of the LUMO (left) and the LUMO-1 (right) of **5**.

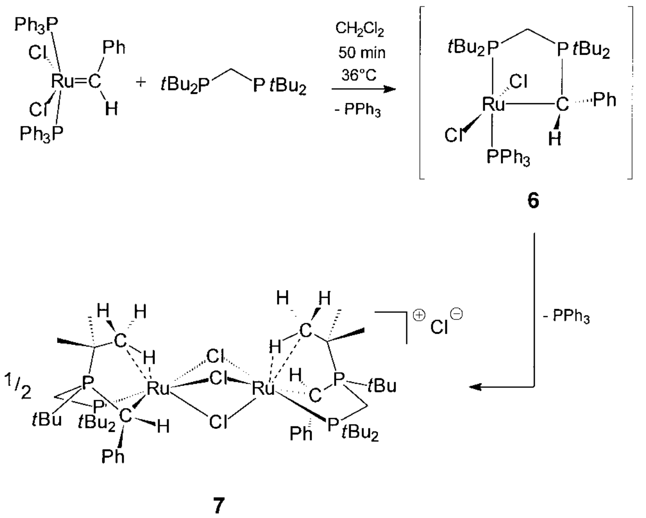
In chelate diphosphanylmethane complexes [$(\eta^2\text{-}R_2PCH_2PR_2)Cl_2Ru{=}CR^1R^2$], a phosphane dissociation equilibrium with a four-coordinate d^6 ML_4 14-electron species should be less favorable than for *trans* complexes [$(PR_3)_2Cl_2Ru{=}CR^1R^2$] (**1**). Geometry optimization (DFT; B3LYP/LANL2DZ) of [$(\eta^1\text{-}H_2PCH_2PH_2)Cl_2Ru{=}CH_2$], the four-coordinate isomer of our simplified model **5**, resulted in the pseudotetrahedral structure **5a** with one pending phosphane arm (Figure 1). This isomer lies 9 kcal mol^{-1} higher in energy than **5**. It is a true minimum on the energy surface and is calculated to have a closed-shell ground-state structure. Structures **5a** should be increasingly energetically disfavored with increasing steric demanding (*gem*-diakyl or Thorpe–Ingold effect) and electron-donating character of the substituents in ligands $R_2PCH_2PR_2$. Thus, complexes with appropriate chelating bisphosphane ligands should allow experimental investigation of the significance of phosphane dissociation in olefin metathesis. Moreover, nondissociating chelating bisphosphanes could in principle lead to chiral catalysts and enantioselective metathesis reactions, similar to the recently reported Mo catalysts of the Schrock type.[11f]

Our theoretical results prompted us to determine whether Grubbs-type ruthenium carbene complexes with *cis* stereochemistry can be made and whether they exhibit catalytic activity in olefin metathesis.

Phosphorus ylide formation by phosphane attack at the carbene carbon: mechanistic implications:

From earlier experience,[27] bis(di-*tert*-butylphosphanyl)methane ($tBu_2PCH_2PtBu_2$, dtbpm) seemed ideal for the preparation of a complex like **5** due to its preference for chelation rather than metal–metal bridging. Moreover, steric bulk and high donor strength of the phosphane favor metathesis activity in the *trans* complexes. A chelating dtbpm ligand should be electronically equivalent to two strongly donating $PtBu_2Me$ ligands in *cis* positions with an enforced, very small P-Ru-P angle.

We attempted to replace the two monodentate phosphane ligands of *trans*-$[(PPh_3)_2Cl_2Ru{=}CHPh]$ by the chelate ligand dtbpm, in analogy to the phosphane-exchange reactions with PCy_3 or $PiPr_3$ reported by Grubbs et al. However, the reaction of *trans*-$[(PPh_3)_2Cl_2Ru{=}CHPh]$ with dtbpm took a completely different course, which has implications for the mechanism of olefin metathesis with *trans*-$[(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2]$ as reported by Grubbs et al.[13a] The triply chloro-bridged, cationic, dimeric ruthenium complex **7** was obtained (Scheme 1), in which the phenylcarbene units are incorporated into five-membered RuPCPC rings.



Scheme 1. Synthesis of **7**.

As revealed by ^1H NMR spectroscopy (doublet at $\delta = -4.43$, $J_{P,H} = 11$ Hz, 6H) and by CH and PH COSY experiments, one methyl group of a *t*Bu substituent in each dtbpm unit binds in an agostic manner to ruthenium and thus completes the octahedral coordination sphere at both metal centers. Interestingly, even in solution the agostic CH_3 group does not exchange with the other two CH_3 groups, which give two separate doublets ($J_{P,H} = 12.8$ and 13.7 Hz). The molecular structure of **7** was confirmed by single-crystal X-ray diffraction (Figure 3).[31c]

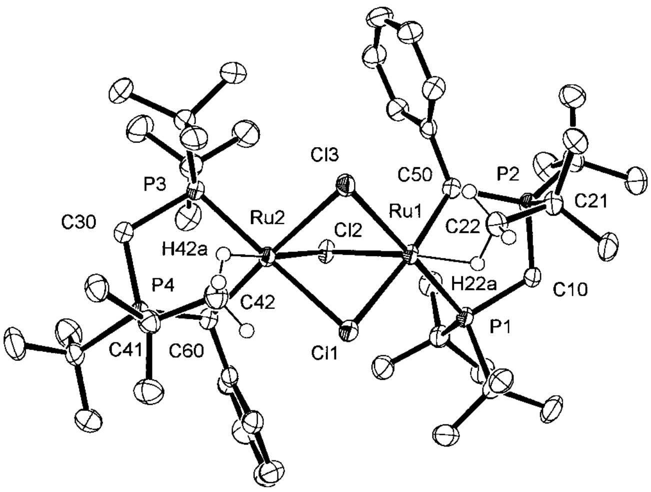


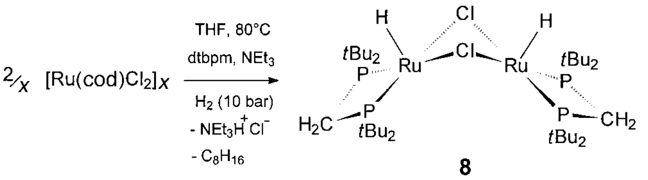
Figure 3. Molecular structure of the dinuclear cation of **7** in the crystal (ORTEP, 50% probability; CH hydrogen atoms, except for those of the agostic CH_3 groups, omitted for clarity). Selected distances [Å] and angles [°]: Ru1–Ru2 3.269(1), Ru1–P1 2.2707(9), Ru1–C50 2.156(3), Ru1–Cl1 2.4912(8), Ru1–Cl2 2.3789(8), Ru1–Cl3 2.5251(8), Ru1–C22 2.511(4), Ru2–P3 2.2611(8), Ru2–C60 2.146(3), Ru2–Cl1 2.5222(8), Ru2–Cl2 2.3848(8), Ru1–Cl3 2.4878(8), Ru2–C42 2.565(3), Ru1-Cl1-Ru2 81.41(2), Ru1-Cl2-Ru2 86.68(3), Ru1-Cl3-Ru2 81.41(2), Cl2-Ru1-C22 161.54(9), Cl2-Ru2-C42 161.84(9), P2-C21-C22 105.6(2), P4-C41-C42 105.3(2), Ru1-P1-C10 103.12(10), P1-Ru1-C50 84.69(9), P1-C10-P2 110.2(2), C10-P2-C50 101.1(2), P2-C50-Ru1 101.95(15).

The carbon atoms (C22 and C42) and even the hydrogen atoms (H22a, H42a) of the two agostic methyl groups were localized and refined. The sterically enforced proximity of the respective C–H bonds to the Ru centers *trans* to Cl2, as reflected in Ru–C distances of 2.51 (Ru1–C22) and 2.57 Å (Ru2–C42), leads to a strong CH–Ru interaction and represents another example for the importance of substituent bulk in agostic interactions.[29] The molecular structure of **7** also displays a distinct distortion around P2 and P4, which bear the agostically bound *t*Bu group. As is evident from the large bond angles *t*Bu-P2-*t*Bu and *t*Bu-P4-*t*Bu (112.4 and 114.5°, as opposed to 107.5 and 106.9° for tBu_2P1 and tBu_2P3) and the smaller P2-C21-C22 (105.6°) and P4-C41-C42 angles (105.3°), the agostic CH_3–Ru interactions cause the *t*BuP2 and *t*BuP4 units to lean over towards the empty coordination sites of the metal centers. Both five-membered RuPCPC chelate rings are nonplanar, and the former carbene carbon atom is the out-of-plane atom in an envelope geometry. There is also a significant difference between the two Ru–Cl distances *trans* to the agostic CH_3 groups (Ru1–Cl2, Ru2–Cl2 2.38 Å) and the four other Ru–Cl bond lengths (av 2.51 Å). There is no Ru–Ru bonding (Ru1–Ru2 3.269(1) Å).

Undoubtedly, **7** is formed by attack of a dtbpm phosphorus center at the carbene carbon atom, most probably via the intermediate **6**, which then dimerizes to **7**. The question remains whether substitution of PPh_3 by one tBu_2P group of dtbpm is followed by attack of the other on the carbene, or if carbene attack precedes PPh_3 displacement. In any case, the formation of **7** clearly shows that Grubbs-type complexes $[(PR_3)_2Cl_2Ru{=}CR^1R^2]$ react with electron-rich phosphanes at the carbene moiety, in accordance with the above-mentioned characteristics of the lowest unoccupied orbital manifold. In their kinetic and mechanistic studies of olefin metathesis, Grubbs et al.[13] apparently did not consider this possiblity. Their conclusions with respect to the importance of phosphane dissociation for olefin metathesis with *trans*-$[(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2]$, however, rely strongly upon experiments in which the presence of additional phosphane (e.g., PCy_3) slows down the reaction. If a pathway with phosphane attack at the carbene carbon atom and formation of ylidic intermediates also operates in these cases, the reaction would be slowed down as well.[30] The isolation of **7** at least points to such an alternative.

Synthesis of a *cis*-carbene complex precursor: The use of mononuclear metal hydrido complexes with monodentate phosphane ligands for the synthesis of transition metal carbene complexes is well established.[4] Hence, an analogous route starting from appropriate hydrido complexes with diphosphanylmethane ligands seemed attractive.

A suitable precursor complex for Ru carbene complexes of type **5** was prepared by treating $[\{RuCl_2(cod)\}_x]$ with dtbpm and H_2 (10 bar) in THF in the presence of triethylamine at 80 °C to give the novel, electronically unsaturated dihydride dimer **8** in 92% yield (Scheme 2). The presence of the base is essential, as in the absence of NEt_3 the same reaction conditions lead to the formation of the triply chloro-bridged dinuclear mixed hydrido–dihydrogen complex $[(\eta^2\text{-dtbpm})Ru(H)](\mu_2\text{-Cl})_3[Ru(\eta^2\text{-}H_2)(\eta^2\text{-dtbpm})]$.[28] Complex **8** is a dark red, extremely air-sensitive, highly reactive compound. Its molecular structure was determined by X-ray diffraction (Figure 4).[31a] As in similar compounds with dtbpm ligands, the methyl substituents of the *t*Bu groups refine with large vibrational amplitudes, but this does not affect the precision of the overall structure determination.



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Scheme 2. Synthesis of **8**.

Apart from the two hydrido ligands, the geometry of **8** is practically identical to those of the isoelectronic Rh[27a] and Ir[32] dimers $[\{(\eta^2\text{-dtbpm})M\}_2(\mu_2\text{-Cl})_2]$ (M = Rh, Ir). The presence of two hydrido ligands is apparent from the ^1H NMR spectrum of **8**, which displays a broad triplet at $\delta = -25.7$ (2H) with a $^2J_{H,P}$ coupling constant of 30.3 Hz.

There is no metal–metal bond (Ru–Ru 3.239(1) Å) and a 16 valence electron count is obtained for each ruthenium center, with two empty coordination sites presumably *trans* to the hydrido groups, to which we tentatively assign the positions indicated in Scheme 2 and Figure 4. The IR spectrum ($\tilde{\nu}_{Ru,H} = 2099\ cm^{-1}$) clearly shows that the two hydrido ligands are in terminal positions. Furthermore, the NMR spectra and the X-ray structure show that **8** is a symmetrical compound with a noncrystallographic mirror plane, and this excludes the possibility of two hydrido ligands at one of Ru centers. The ^1H NMR coupling pattern of the CH_2 groups of the four-membered (dtbpm)Ru chelate rings (doublets of triplets), as well as the temperature-independent appearance of two different *t*Bu signals, reveals that, unlike the hydride-free, isoelectronic complexes[27a, 32] $[\{(\eta^2\text{-dtbpm})M\}_2(\mu_2\text{-Cl})_2]$ (M = Rh, Ir; one triplet for CH_2, one *t*Bu signal), which dissociate in solution at the μ_2-Cl bridges,[32] **8** is not subject to any chemical exchange processes between the two types of *t*Bu groups or CH_2 protons. We interpret these findings in terms of a permanent and identical up-down asymmetry of each (dtbpm)Ru moiety. However, this still leaves more than one option for locating two terminal hydrido ligands in **8**. To obtain further information on the positions of the hydrido ligands of **8** without a neutron diffraction structure, we used a computational procedure for indirectly locating hydrido ligands in transition metal clusters.[33] This technique starts from the experimental heavy-atom positions without hydrides and locates the most probable holes for hydrido ligands by an energy-minimization procedure. For **8**, the program predicts only terminal locations for the hydrido ligands (H1–H4 in Figure 5).

This rather crude approach does not allow us to safely discern between *cis-exo* (H1, H2) or *cis-endo* (H3, H4) hydrido ligands in a molecule with a rigid folded $Ru_2(\mu\text{-Cl})_2$ core, or a structure with one *exo* and one *endo* hydride (H1, H4 or H2, H3) and a rapidly inverting heavy-atom framework. All three options are consistent with the spectroscopic properties of **8**, and their relative energies, as determined by Orpen's method[33] are identical within 0.7 kcal. In addition we cannot rule out at this point fluxional processes that exchange the hydride positions in solution or a statistical occupation of all four possible terminal hydride positions in the solid state. However, we consider a structure with two *exo* hydrido ligands (Figure 4) and two empty coordination sites at

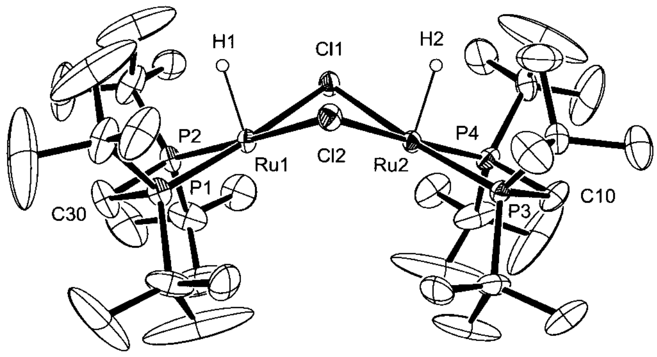


Figure 4. Molecular structure of **8** in the crystal (ORTEP, 30% probability; CH hydrogen atoms omitted for clarity; hydrido ligands shown in calculated positions). Selected distances [Å] and angles [°]: Ru1–Ru2 3.239(1), Ru1–P1 2.232(2), Ru1–P2 2.231(2), Ru1–Cl1 2.468(2), Ru1–Cl2 2.461(2), Ru2–P3 2.233(2), Ru2–P4 2.221(2), Ru2–Cl1 2.471(2), Ru2–Cl2 2.458(2), P1-Ru1-P2 75.38(6), P2-Ru1-Cl2 173.73(6), P1-Ru1-Cl2 99.60(6), P2-Ru1-Cl1 100.32(6), P1-Ru1-Cl1 174.34(6), Cl2-Ru1-Cl1 84.43(6), Ru1-Cl1-Ru2 81.96(5), Ru2-Cl2-Ru1 82.37(5).

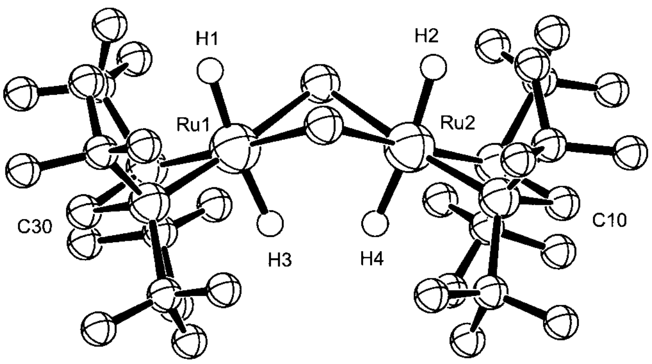
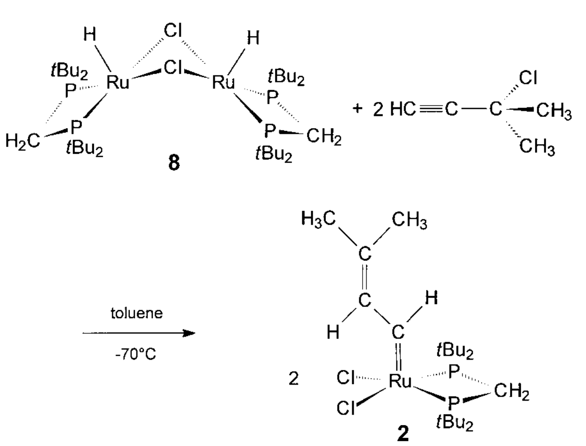


Figure 5. Schakal plot of **8** with experimental heavy-atom positions and calculated[33] positions H1 – H4 for hydrido ligands. The hydrogen atoms of the *t*Bu and CH_2 groups have been omitted for clarity.

each metal center on the *endo* face as the most likely option. The *t*Bu substituents on the concave side of the 16-electron dimer probably cause appreciable steric shielding of the two empty sites and make **8** an isolable compound. For the chemistry of Ru carbenes discussed in the following section, the precise locations of the hydrido ligands are not important.

Synthesis of a *cis* ruthenium carbene complex: Formally, the unsaturated dihydride **8** is the dimer of an even less saturated, four-coordinate $[(\eta^2$-dtbpm)Ru(H)(Cl)] unit with Ru^{II} and 14 valence electrons, which can be regarded as requiring the insertion of a CR moiety into the Ru–H bond and a second Cl ligand at the metal center to be transformed to the desired complex $[(\eta^2$-dtbpm)$Cl_2Ru{=}CHR]$. We therefore hoped that propargyl or vinyl chlorides[4] would be appropriate substrates for **8**. At –70 °C in toluene, **8** reacted smoothly with 3-chloro-3-methyl-1-butyne, and the green vinylcarbene complex $[(\eta^2$-dtbpm)$Cl_2Ru{=}CH{-}CH{=}CMe_2]$ (**2**) was isolated in 62 % yield (Scheme 3). The carbene complex **2** forms air-stable crystals and is highly soluble in dichloromethane, but less so in THF or diethyl ether. It exhibits the expected spectroscopic properties with a singlet for the two P nuclei at $\delta = 25$ and a ^1H NMR signal at $\delta = 16.25$ (doublet of triplets, appearing as a pseudo-quartet, $^3J_{H,H} = 10.7$, $^3J_{H,P} = 10.7$ Hz, 1 H) for the Ru=C*H* proton. The carbene carbon atom gives rise to a triplet at $\delta = 269$ ($^1J_{C,P} = 13.2$ Hz) in the ^{13}C NMR spectrum.



Scheme 3. Synthesis of **2**.

The molecular geometry of **2** in the crystal, as determined by single-crystal X-ray diffraction,[31b] is shown in Figure 6. Complex **2** has a square-pyramidal structure that corresponds well with the calculated structures of **4** and **5**. The carbene moiety occupies an apical position, the P-Ru-P angle in the chelate ring is 73.8°, and the Ru–C distance of 1.858(2) Å is nearly identical to that of *trans*-$[(PCy_3)_2Cl_2$-$Ru{=}CH{-}CH{=}CPh_2]$ (1.851(21) Å). The orientation of the carbene moiety in the crystal minimizes steric interactions with the *t*Bu groups of the dtbpm ligand. The carbene plane does not bisect the P1-Ru-P2 and Cl1-Ru-Cl2 angles, in contrast to the simplified chelate model **5** (see Figure 1), but is orthogonal to the P1-Ru-Cl1 axis. As a consequence, the acceptor orbital of the carbene carbon atom is parallel to P1-Ru-Cl1, and this lowers the angle P1-Ru-Cl1 to only 154.9°, with one chlorine atom (Cl1) bent out of the basal plane. This is precisely the structural feature which was calculated for *cis*-$[(PH_3)_2Cl_2Ru{=}CH_2]$ (**4**) (vide supra), in which the minimum energy orientation of the CH_2 plane is identical to that observed for the solid-state conformation of **2**.

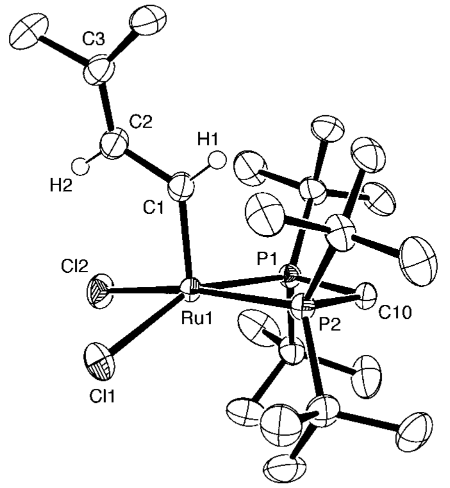


Figure 6. Molecular structure of **2** in the crystal (ORTEP, 50 % probability; CH hydrogen atoms, except for H1 and H2 of the vinylidene group, omitted for clarity). Selected distances [Å] and angles [°]: Ru1–P1 2.3176(5), Ru1–P2 2.3372(5), Ru1–Cl1 2.3896(6), Ru1–Cl2 2.4450(5), Ru1–C1 1.858(2), C1–C2 1.431(3), C2–C3 1.358(3), P1-Ru1-P2 73.78(2), Cl1-Ru1-Cl2 88.64(2), P1-Ru1-Cl1 154.90(2), P2-Ru1-Cl1 97.70(2), P1-Ru1-Cl2 94.93(2), P2-Ru1-Cl2 165.26(2), C1-Ru1-P1 96.39(7), C1-Ru1-P2 93.46(7), C1-Ru1-Cl1 107.82(7), C1-Ru1-Cl2 97.27(7).

Olefin metathesis experiments: Under standardized conditions as described in detail by Grubbs et al.[2] (see Experimental Section), **2** catalyzes the ring opening metathesis polymerization (ROMP) of norbornene. In contrast to the results of Grubbs et al., however, the viscous mixture became gel-like and could not be stirred further after only 30 min at ambient temperature. Attempts to dilute the mixture after 1 h with additional CH_2Cl_2 failed, so that filtration through a silica gel column was not possible. When the mixture was poured into methanol, the polymer was obtained as a yellowish material (42 % yield). When we tried to perform kinetic measurements by ^1H NMR spectroscopy in CD_2Cl_2, in

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analogy to those reported in the literature,[2] the reaction mixture in the NMR tube became so viscous after a few minutes that spectroscopic observation was hampered. At this point, 46 % of the monomer had polymerized, and 7.4 % of **2** had been converted into a propagating species, which gave rise to a new carbene signal at $\delta = 16.25$, adjacent to the signal at $\delta = 16.42$ for complex **2** (Figure 7). The new signal is too weak to obtain information about its exact coupling constants, but it can be assigned confidently to a propagating species on the basis of its general features. From integrated peak intensities in the course of the polymerization process, we also note that chain propagation is apparently much faster than chain initiation. This also is reflected in the large M_w/M_n value of the polymer (vide infra). We were also able to detect the product of the first metathesis step **9** (Scheme 4) by mass spectrometry. The calculated isotopic pattern matches the observed intensities well (Figure 7).

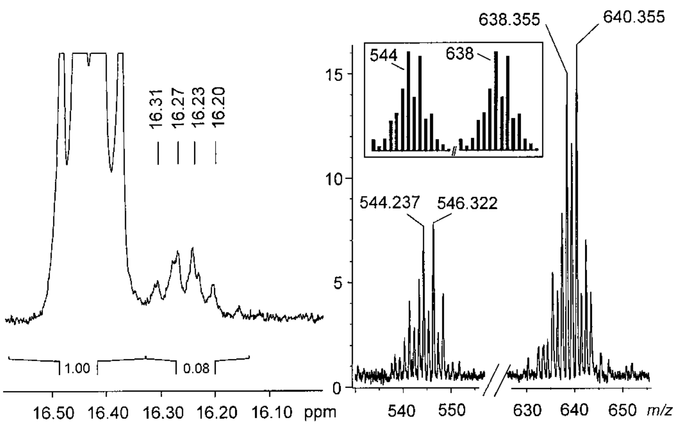
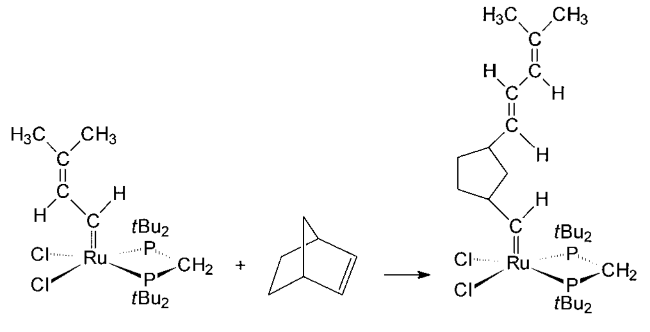


Figure 7. ^{1}H NMR (CD_2Cl_2) and mass spectra recorded during a ROMP experiment of norbornene with complex **2** as catalyst. The propagating species is detected by means of its carbene signal in the ^{1}H NMR spectrum (left), and the composition of carbene complex **9**, which is formed in the first metathesis step (**2**: $m/z = 544$; **9**: $m/z = 638$), can be assigned by mass spectrometry (FD$^+$, right).



2

9

Scheme 4. Synthesis of **9**.

In view of these results, polymerization of norbornene was conducted in a sixfold excess of solvent. The polymer yield increased to 55 % and the *trans*/*cis* ratio (by ^{1}H NMR spectroscopy) was 71/29, which is comparable to the ratio of 80/20 found by Grubbs et al. The value of 2.75 for M_w/M_n (determined by GPC) is much larger than that of the *trans* complexes and reflects slower initiation than propagation. Carbene complex **2** also catalyzes the polymerization of cyclopentene, but with very low activity. With a large excess of cyclopentene at 35 °C and a reaction time of 92 h the polymer was obtained in 1.42 % yield and was characterized by ^{1}H and ^{13}C NMR spectroscopy. The *trans*/*cis* ratio was 86/14, and M_w/M_n was 7.14. As expected from the ROMP reactivity profile of **2**, no ring-closing metathesis of 1,7-octadiene to cyclohexene was observed. Thus complex **2** is clearly a less active metathesis catalyst than other ruthenium(II) complexes, but is more active than the recently reported Cp, Cp*, and hydridotris(pyrazolyl)borate ROMP systems of Ozawa et al.[9] However, under the conditions used so far, only a small portion of the catalyst is active, while the larger part of **2** remains unaffected (see also Figure 7). We did not try to optimize our reaction conditions.

Conclusions

Complex **2** is the first Grubbs-type metathesis catalyst with a fixed *cis* stereochemistry of two phosphane ligands whose steric demand and electronic properties resemble those of the well-known catalytically active *trans* complexes. The catalytic metathesis activity of **2**, although not as high as that of other complexes, is of particular interest because the utilization of dtbpm as a chelating, electron-rich, bulky, strong donor ligand makes phosphane dissociation improbable, although an intermediate ring opening to a four-coordinate species analogous to **5a** cannot be rigorously excluded at this point. Further synthetic, mechanistic, and quantum chemical studies are underway to gain deeper insight into the details of metathesis reactions with **2** and its congeners. Of particular interest are mechanistic questions regarding olefin coordination in the initiation step of olefin metathesis (e.g., with other, non-vinyl-substituted carbene ligands), the dissociation of phosphane or chloro ligands, and similarities and differences between *cis* and *trans* complexes in catalytic metathesis reactions.

With respect to the crucial question of phosphane dissociation, our observation of attack on the carbene group by the electron-rich phosphane dtbpm in [*trans*-$(PPh_3)_2Cl_2$-Ru=CHPh] to give the ylide complex **7** has revealed a mechanistic facet of Ru-catalyzed olefin metathesis which certainly deserves further consideration.

The readily accessible unsaturated dihydride dimer **8** should not only allow other derivatives of this new class of Ru carbenes to be prepared from various organic carbene precursors, but will also be a valuable starting material for organometallic (dtbpm)Ru chemistry in general.

Experimental Section

All reactions were carried out under dry argon by standard Schlenk techniques. [$\{RuCl_2(cod)_x\}$][34] and *trans*-[$RuCl_2(PPh_3)_2$=CHPh][2] were prepared as described in the literature. Norbornene and cyclopentene were dried and degassed prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at room temperature on Bruker AMX300 or AMX500 instruments. ^{1}H NMR chemical shifts are relative to residual undeuterated solvent in [D$_8$]THF ($\delta =$ 1.74 and 3.58), $CDCl_3$ ($\delta = 7.24$), and CD_2Cl_2 ($\delta =$ 5.32), the ^{13}C NMR shifts relate to the solvents [D$_8$]THF ($\delta =$ 25.5 and 67.7), $CDCl_3$ ($\delta =$ 77.0) and CD_2Cl_2 ($\delta =$ 53.5), and the ^{31}P NMR shifts are relative 85% H_3PO_4 ($\delta = 0$). Mass spectra were recorded on a JEOL JMS700, IR spectra on a Bruker Equinox 55 FT-IR spectrometer and UV spectra on a Hewlett Packard 8453. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography with linear polyethylene as standard.

Synthesis of 2: Compound **8** (170 mg, 0.19 mmol) was dissolved in dry, oxygen-free toluene (6.5 mL). After cooling to −70 °C, a solution of 3-chloro-3-methyl-1-butyne (39.5 mg, 0.39 mmol) in toluene (1.5 mL) was added with stirring. After 10 min at −70 °C, the reaction mixture was allowed to warm to room temperature. After 1 h, **2** had precipitated as green microcrystals, which were isolated by filtering off the brown supernatant solution. The green solid was washed several times with small portions of cold toluene until the washings remained colorless. The compound was dried at 10^{-5} bar for 10 h. Yield of **2**: 130 mg (62%). Elemental analysis: calcd: C 48.53, H 8.51, P 11.38; found: C 48.32, H 8.34, P 11.20. ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 1.32$ (pseudo-d, 18 H, *t*Bu-*H*), 1.46 (s, 3 H, $\mathrm{CCH_3(}\mathit{CH}_3\mathrm{))}$), 1.55 (s, 3 H, $\mathrm{C}\mathit{CH}_3\mathrm{(CH_3))}$), 1.57 (pseudo-d, 18 H, *t*Bu-*H*), 4.12 (pseudo-quintet, ABX_2 system, ^{2}J(H,H) = 16.8, ^{2}J(H,P) = 9.2 Hz, 1 H, PCH*H*P), 4.28 (pseudo-quintet, ABX_2 system, ^{2}J(H,H) = 16.8, ^{2}J(H,P) = 8.4 Hz, 1 H, PC*H*HP), 8.68 (d, ^{3}J(H,H) = 10.7 Hz, 1 H, C=C*H*), 16.25 (pseudo-q: doublet of triplets, appearing as a pseudoquartet, ^{3}J(H,H) = 10.7, ^{3}J(H,P) = 10.7 Hz, 1 H, Ru=C*H*); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta = 20.9$ (s, $\mathrm{C}\mathit{C}\mathrm{H_3(CH_3))}$), 28.2 (s, $\mathrm{CCH_3(}\mathit{C}\mathrm{H_3))}$), 30.7 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 31.1 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 37.3 (pseudo-t, *J* = 23.4 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 37.8 (pseudo-t, *J* = 8.8 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 38.9 (t, ^{1}J(C,P) = 7.9 Hz, P*C*H_2P), 138.8 (s, C=*C*Me$_2$), 148.7 (s, *C*=CMe$_2$), 296.2 (t, ^{1}J(C,P) = 13.2 Hz, Ru=*C*); ^{31}P NMR (202 MHz, [D$_8$]THF): $\delta = 25.6$ (s, *P*CH$_2$*P*); IR (KBr): $\tilde{\nu} = 3008$ (m), 2957 (m), 2921 (m), 2902 (m), 2877 (m), 1572 (s), 1470 (m), 1457 (m), 1446 (m), 1435 (m), 1396 (m), 1370 (m), 1259 (w), 1179 (m), 1157 (m), 1092 (m), 1037 (m), 1024 (m) 937 (w), 797 (m), 726 (m), 686 (m), 674 (m), 586 (w), 520 (w), 488 cm^{-1} (w); UV/Vis (THF): λ_{max} (ε) = 358 (4047), 281 nm (4197).

Synthesis of 8: A 75 mL steel autoclave was charged with [{$RuCl_2$(cod)}$_x$] (450 mg, 1.61 mmol Ru), dtbpm (580 mg, 1.91 mmol) and NEt_3 (230 mL) in dry, oxygen-free THF (15 mL). The vessel was pressurized with H_2 (10 bar) and the reaction mixture was stirred at 80 °C for 70 h, after which the hydrogen pressure had dropped to about 7 bar. After cooling to ambient temperature and depressurising, precipitated $NEt_3H^+Cl^-$ was removed by filtration and the dark red solution is taken to dryness in vacuo. The resulting dark red solid was washed several times with small portions of cold methanol and finally dried at 10^{-5} bar for 10h. Yield of **8**: 656 mg (92%). Elemental analysis: calcd: C 46.20, H 8.89, Cl 8.02, P 14.02; found: C 46.10, H 8.91, Cl 7.96, P 14.01; ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta =$ −25.67 (t, ^{2}J(H,P) = 30.3 Hz, 2 H, Ru-*H*), 1.33 (pseudo-t, 36 H, *t*Bu-*H*), 1.51 (pseudo-t, 36 H, *t*Bu-*H*), 3.36 (pseudo-quintet, ABX_2 system, ^{2}J(H,H) = 16.2, ^{2}J(H,P) = 8.6 Hz, 2 H, P-CH*H*-P), 3.78 (pseudo-quintet, ABX_2 system, ^{2}J(H,H) = 16.2, ^{2}J(H,P) = 8.1 Hz, 2 H, P-C*H*H-P); ^{13}C NMR (75 MHz, [D$_8$]THF): $\delta =$ 31.7 (s, *t*Bu-*C*), 32.7 (s, *t*Bu-*C*), 37.7 (pseudo-t, *J* = 7.6 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 38.4 (pseudo-t, *J* = 12.4 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 45.0 (t, ^{2}J(C,P) = 8.0 Hz, P-*C*-P); ^{31}P NMR (121 MHz, [D$_8$]THF): $\delta =$ 57.7 (s, *P*-CH$_2$-*P*); IR (KBr): $\tilde{\nu} = 2948$ (s), 2897 (s), 2868 (s), 2099 (w, br, terminal RuH), 1473 (s), 1390 (s), 1366 (s), 1176 (s), 1104 (w), 1071 (m), 1019 (m), 935 (w), 812 (s), 719 (s), 648 (w), 593 (w), 519 (w), 489 cm^{-1}(m); λ_{max} (ε) = 358 (4047), 281 nm (4197).

Synthesis of 7: *trans*-[$Cl_2(PPh_3)_2Ru{=}CHPh$] (235 mg, 0.30 mmol) and dtbpm (1.0 g, 3.3 mmol) were dissolved in CH_2Cl_2 (20 mL) and stirred for 50 min under reflux. The solvent was reduced to a volume of 2 mL; addition of pentane (15 mL) precipitated brown microcrystals, which were redissolved in CH_2Cl_2 (2 mL) and again precipitated with pentane (15 mL). This procedure was repeated three times. The residue was then washed three times with 4 mL portions of pentane and dried at 10^{-5} bar for 10h. Yield of **7**: 130 mg (73%). Elemental analysis: calcd: C 50.87, H 7.83; found: C 47.80, H 7.68. This material allowed the full characterization of **7** by X-ray crystallography, ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy (including CH and PH COSY), and high-resolution mass spectrometry, although we have been unable so far to obtain a correct C,H elemental analysis. The carbon value was always too low, probably due to impurities, which also are visible as small additional peaks in the ^{1}H and ^{13}C NMR spectra but not in the ^{31}P NMR spectrum. No attempts were made to purify **7** further after the structure had been verified by X-ray crystallography. ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta =$ −4.43 (d, ^{3}J(H,P) = 11.0 Hz, 3 H, $\mathrm{C(CH_3)(CH_3)C}\mathit{H}_3$ (agostic)), 1.10 (d, ^{3}J(H,P) = 13.0 Hz, 9 H, *t*Bu-*H*), 1.11 (d, ^{3}J(H,P) = 13.5 Hz, 9 H, *t*Bu-*H*), 1.40 (d, ^{3}J(H,P) = 12.8 Hz, 3 H, $\mathrm{C(C}\mathit{H}_3\mathrm{)(CH_3)CH_3}$ (agostic)), 1.51 (d, ^{3}J(H,P) = 13.0 Hz, 9 H, *t*Bu-*H*), 1.59 (d, ^{3}J(H,P) = 13.7 Hz, 3 H, $\mathrm{C(CH_3)(C}\mathit{H}_3\mathrm{)CH_3}$; (agostic)), 2.39 (m, *J* = 33.7 Hz, 1 H, P-CH*H*-P), 2.71 (pseudo-quintet, ^{2}J(H,H) = 16.7 Hz, ^{2}J(H,P) = 8.5 Hz, 1 H, P-C*H*H-P), 4.37 (d, ^{2}J(H,P) = 16.3 Hz, 1 H, C*H*Ph), 7.11 (s, 5 H, CHPh-*H*); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta =$ −7.0 (d, ^{2}J(C,P) = 4.2 Hz, $\mathrm{C(CH_3)_2(}\mathit{C}\mathrm{H_3)}$ (agostic)), 8.0 (dd, ^{1}J(C,P) = 17.8 Hz, ^{2}J(C,P) = 5.1 Hz, Ru-*C*HPh-P), 18.1 (s, P-*C*H$_2$-P), 27.4 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 29.4 (d, ^{2}J(C,P) = 2.5 Hz, $\mathrm{C(}\mathit{C}\mathrm{H_3)(CH_3)(CH_3)}$ (agostic)), 29.5 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 30.0 (d, ^{2}J(C,P) = 2.3 Hz, $\mathrm{C(CH_3)(}\mathit{C}\mathrm{H_3)(CH_3)}$ (agostic)), 31.9 (br s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 38.7 (dd, ^{1}J(C,P) = 15.4, ^{3}J(C,P) = 3.4 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 39.5 (dd, ^{1}J(C,P) = 17.5z, ^{3}J(C,P) = 1.1 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 40.5 (dd, ^{1}J(C,P) = 12.7, ^{3}J(C,P) = 2.3 Hz, $\mathit{C}\mathrm{(CH_3)_3}$), 124.5 (d, ^{3}J(C,P) = 3.4 Hz, *o*-phenyl-*C*), 127.9 (m, *m*-phenyl-*C*, *p*-phenyl-*C*), 142.7 (dd, ^{2}J(C,P) = 3.5 Hz, ^{3}J(C,P) = 1.4 Hz, *ipso*-phenyl-*C*), the peak for $\mathit{C}\mathrm{(CH_3)_2(CH_3)}$(agostic) cannot be assigned; ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta =$ 71.1 (d, ^{2}J(P,P) = 42 Hz, *P*-CH$_2$-P), 88.5 (d, ^{2}J(P,P) = 42 Hz, P-CH$_2$-*P*); IR (KBr): $\tilde{\nu} = 3053$ (w), 3001 (m), 2951 (m), 2904 (m), 2871 (m), 2105 (w), 1593 (w), 1479 (m), 1448 (w), 1435 (m), 1403 (m), 1394 (m), 1373 (m), 1261 (w), 1176 (m), 1113 (m), 1091 (m), 1077 (m), 939 (w), 809 (m), 773 (m), 748 (m), 725 (m), 699 (s), 589 (w), 503 (m), 442 cm^{-1} (w); HR-MS (FAB$^+$): calcd for $[C_{48}H_{88}Cl_3P_4Ru_2]^+$ *m*/*z* = 1097.2989; found *m*/*z* = 1097.3033 ($\Delta =$ +4.0 ppm); isotopic pattern for $[C_{48}H_{88}Cl_3P_4Ru_2]^+$: *m*/*z* (calcd intensity, found intensity): 1087 (1, 2), 1088 (3, 4), 1089 (5, 6), 1090 (10, 11), 1091 (19, 21), 1092 (23, 26), 1093 (41, 44), 1094 (54, 59), 1095 (69, 75), 1096 (90, 95), 1097 (99, 100), 1098 (94, 97), 1099 (100, 99), 1100 (66, 71), 1101 (64, 67), 1102 (32, 34), 1103 (25, 25), 1104 (11, 12), 1105 (6, 7), 1106 (2, 3).

ROMP of norbornene: (conditions analogous to standardized ROMP procedure of Grubbs et al.,[2] except for the amount of solvent): Compound **2** (3.0 mg, 5.5 μmol) was added to a solution of norbornene (60 mg, 0.64 mmol) in CH_2Cl_2 (6 mL), and the green-brown solution was stirred at room temperature. Within 5 min the solution became viscous and the color changed slowly to yellow. After 1 h ethyl vinyl ether (0.1 mL) and CH_2Cl_2 (2 mL, containing 0.1% 2,6-di-*tert*-butyl-4-methylphenol (BHT)) were added, and the mixture was stirred for an additional 20 min. The resulting solution was filtered through a silica gel column (60 × 15 mm), and the polymer was eluted with CH_2Cl_2 (containing 0.1% BHT) directly into vigourously stirred methanol (100 mL, 0.1% BHT). The precipitated polymer was collected by filtration, washed several times with methanol, and dried in vacuo. Yield: 33 mg (55%); 71% *trans* (^{1}H NMR);[35] $M_w = 5.2 \times 10^5$; $M_w/M_n = 2.75$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.02 (s), 1.33 (br s), 1.53 (s), 1.75 (br s), 1.84 (br pseudo-t), 2.41 (br s), 2.76 (br s), 5.18 (br pseudo-d), 5.32 (s); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 32.2$ (s), 32.4 (s), 32.9 (s), 33.1 (s), 38.4 (s), 38.7 (s), 41.4 (s), 42.1 (s), 43.1 (s), 43.4(s), 132.9 (s), 133.0 (s), 133.1 (s), 133.9 (s).

ROMP of cyclopentene: (prolonged reaction time, higher temperature, and a larger excess of cycloalkene used than above): Compound **2** (3.4 mg, 6.2 μmol) was added to a solution of cyclopentene (1.0 mL, 11.35 mmol) in $ClCH_2CH_2Cl$ (1 mL), and the green brown solution was stirred at 35 °C. Within 24 h the solution became viscous. After 92 h ethyl vinyl ether (0.1 mL) was added, and the mixture was stirred for an additional 20 min. The resulting solution was filtered through a silica gel column (20 × 5 mm) and the polymer was eluted with CH_2Cl_2 (containing 0.1% BHT) directly into vigorously stirred methanol (20 mL, 0.1% BHT). The polymer was collected by filtration, washed several times with methanol and dried in vacuo. Yield: 11 mg (1.4%); 86% *trans* (^{1}H NMR); $M_w = 1.0 \times 10^4$; $M_w/M_n = 7.14$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.23 (s), 1.37 (m), 1.53 (s), 1.96 (m), 5.33 (br pseudo-t), 5.36 (br pseudo-t); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta =$ 130.4 (s), 130.3 (s), 129.8 (s), 32.2 (s), 32.1 (s), 29.9 (s), 29.7 (s), 29.5 (s), 26.9 (s), 26.7 (s).

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[24] In these calculations a large 6-311 + G(2d,2p) basis set was used for the main group atoms. The ruthenium basis for the Hay and Wadt ECP was expanded by uncontracting one s, one p, and one d function and by adding a diffuse d function and two f functions contracted from three primitive f functions.

[25] The π-acceptor orbital of the CH_2 group is parallel to the Cl-Ru-Cl axis in **3** and interacts with the metal d orbital which is most strongly destabilized by the π-donor Cl ligands. In **4** it is parallel to the more strongly bent P1-Ru-Cl1 axis.

[26] Similar small barriers were found in the Hartree–Fock calculations of Benson and Cundari for a series of *trans*-$[(PR_3)_2X_2Ru{=}CH_2]$ complexes.[18] For *trans*-$[(PH_3)_2Cl_2Ru{=}CHCH_3]$ the computed rotational barrier for the alkylidene group (DFT) is only 4.6 kcal mol^{-1}.[19a] Accordingly, different orientations are observed in crystal structures for a variety of *trans* complexes. Such low rotational barriers render questionable all mechanistic arguments in olefin metathesis that are based upon specific carbene orientations.

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[30] As one referee pointed out, the entire mechanistic picture elaborated by Grubbs et al. might need revision in this case.

[31] a) Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated THF solution of **8**. Crystal dimensions 0.34 × 0.18 × 0.10 mm, crystal system orthorhombic, space group $P2_12_12_1$, Z = 4, $a = 13.1756(1)$, $b = 16.7444(3)$, $c = 19.7378(3)$ Å, $V = 4354.5(1)$ Å^3, $\rho_{calcd} = 1.348$ g cm^{-3}, $2\theta_{max} = 51.2°$, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, 0.3° ω scans with CCD area detector, $T = 200$ K, 32003 reflections measured, 7572 unique reflections, 6359 observed reflections ($I > 2\sigma(I)$), intensities were corrected for Lorentzian and polarization effects, an empirical absorption correction was applied by using the SADABS program based on the Laue symmetry, $\mu = 0.98$ mm^{-1}, $T_{min} = 0.79$, $T_{max} = 0.90$. The structure was solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm with the SHELXTL-PLUS (5.03) software package; 379 parameters refined, 48 geometrical restraints, alkyl hydrogen atoms were treated with appropriate riding models, hydride hydrogen atoms were not found, final residual values $R(F) = 0.042$, $wR(F^2) = 0.093$ for observed reflections, max./min. residual electron density −0.60/0.85 e Å^{-3}. The two hydrido ligands of **8** are terminal, and we tentatively assign them to the two *exo* positions indicated in Scheme 2, although other static or dynamic disorder cannot be excluded with certainty at this point (see text). b) Crystals of **2** suitable for X-ray diffraction were obtained from the reaction of **8** (10 mg) with 3-chloro-3-methyl-1-butyne (2.15 μL) in toluene in a sealed NMR tube at −60° C followed by warming to room temperature. Crystal dimensions 0.23 × 0.22 × 0.14 mm, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.2056(3)$, $b = 16.0891(5)$, $c = 16.0150(5)$ Å, $\beta = 95.576(1)°$, $V = 2617.2(1)$ Å^3, $\rho_{calcd} = 1.382$ g cm^{-3}, $2\theta_{max} = 51.2°$, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, 0.3° ω scans with CCD area detector, $T = 200$ K, 19156 reflections measured, 4548 unique, 3883 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentzian and polarization effects, an empirical absorption correction was applied with the SADABS program based on the Laue symmetry, $\mu = 0.93$ mm^{-1}, $T_{min} = 0.82$, $T_{max} = 0.88$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm by using the SHELXTL-PLUS (5.03) software package, 266 parameters refined, hydrogen atoms were treated using appropriate riding models except of H1 and H2, which were refined isotropically, final residual values $R(F) = 0.022$, $wR(F^2) = 0.053$ for observed reflections, max./min. residual electron density −0.39/0.34 e Å^{-3}; c) Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **7** in CH_2Cl_2. Crystal dimensions 0.16 × 0.18 × 0.55 mm, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.857(1)$, $b = 17.479(1)$, $c = 30.954(2)$ Å, $V = 5857(1)$ Å^3, $\rho_{calcd} = 1.475$ g cm^{-3}, $2\theta_{max} = 51.2°$, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, 0.3° ω scans with CCD area detector, $T = 200$ K, 26823 reflections measured, 9989 unique reflections, 8540 observed reflections ($I > 2\sigma(I)$), intensities were corrected for Lorentzian and polarization effects, an empirical absorption correction was applied with the SADABS program based on the Laue symmetry of the reciprocal space, $\mu = 1.02$ mm^{-1}, $T_{min} = 0.73$, $T_{max} = 0.86$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm by using the SHELXTL-PLUS (5.03) software package, 671 parameters refined, 7 geometrical restraints (disordered solvent), hydrogen atoms were treated withg appropriate riding models, except for the three hydrogen atoms of the agostic methyl group and the hydrogen atoms of the former carbene moiety, which were refined isotropically; final residual values $R(F) = 0.033$, $wR(F^2) = 0.073$ for observed reflections, max./min. residual electron density −0.70/1.0 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 publications no. CCDC-101932 (**8**), CCDC-101931 (**2**), and CCDC-103028 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[32] [{(η^2-dtbpm)Ir}$_2$(μ_2-Cl)$_2$]: P. Hofmann, O. Steck, C. Meier, F. Rominger, V. Sporys, unpublished results; both this Ir complex and its Rh analogue[27a] dissociatiate in solution according to molecular weight determinations (Signer method).

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