A New Class of Ruthenium Carbene Complexes: Synthesis and Structures of Highly Efficient Catalysts for Olefin Metathesis**

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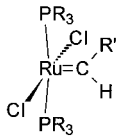
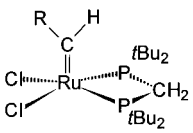
Dedicated to Professor Hans Hofmann on the occasion of his 70th birthday

Efficient, well-defined, single-component, single-site homogeneous catalysts for olefin metathesis have recently provided new, elegant tools for C–C bond formation in organic synthesis and polymer chemistry.[1a] Due to their stability, Grubbs-type square-pyramidal ruthenium(II) carbene complexes with *trans*-phosphane ligands (**1a–c**) have found wide application in ring opening metathesis polymerization (ROMP), in ring-closing metathesis (RCM), in acylic diene metathesis (ADMET), and in acyclic olefin metathesis reactions.[1–3] Attempts to improve their catalytic performance have focussed upon varying the carbene fragment,[3,4] the phosphane[3] or anionic ligand,[5] replacement of the phosphane and chloro ligand by chelating Schiff-bases,[6] on exchanging the two *trans*-phosphanes by Wanzlick–Arduengo-type carbenes,[7] and upon Lewis acid addition.[8a,b] Quite recently Grubbs et al. prepared neutral and cationic Ru^{II}(Tp) carbenes (Tp = tris(pyrazolyl)borate), which seem to be inactive.[9] Based on previous experience[10] with bis(di-*tert*-butylphosphanyl)methane (dtbpm) $tBu_2PCH_2PtBu_2$[11] as a ligand, we recently prepared the first Grubbs-type catalyst with a rigid *cis*-stereochemistry of phosphane ligands **2a**.[12]



1a: R = Cy, R' = Ph
1b: R = Cy, R' = CH=CPh$_2$
1c: R = Ph, R' = CH=CPh$_2$



2a: R = CH=CMe$_2$
2b: R = CH=⬡
2c: R = CH=CPh$_2$
2d: R = CHMe$_2$

Here we report the synthesis, structures, and properties of a novel class of cationic Ru^{II} carbene complexes[13] with high catalytic activity in ROMP reactions. They are easily obtained from **2a** and from its congeners **2b–d** by chloride abstraction with trimethylsilyl triflate.

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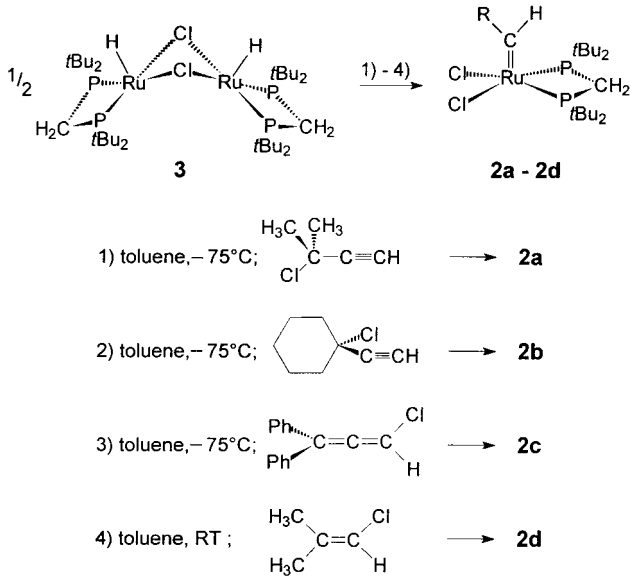
Reactions of ruthenium hydrides with propargyl or vinyl chlorides yielding Grubbs-type carbene complexes are well established.[14] The dinuclear dihydride **3**, accessible in a one-pot reaction from $[(cod)RuCl_2]_x$ (cod = 1,5-cyclooctadiene), has been shown to be an excellent precursor for **2a** (Scheme 1),[12] and the cyclohexylidene derivative **2b** can be



Scheme 1. Synthesis of complexes **2a–d** from **3** and propargyl, allenyl, and vinyl chlorides.

prepared from **3** and 1-chloro-1-ethynylcyclohexane[15] in an analogous way. In the synthesis of the diphenyl derivative **2c**, we discovered that 1-chloro-3,3-diphenyl-1,2-propadiene is a more suitable substrate than the corresponding isomeric propargyl compound 3-chloro-3,3-diphenyl-1-propyne.[16] Compound **2c** was obtained from **3** and the chloroallene in 74% yield. Chloroallenes thus are established as another convenient class of organic precursors for the synthesis of carbene complexes $[(\kappa^2\text{-dtbpm})Cl_2Ru{=}CH{-}CH{=}CR^1R^2]$ from **3**. When the vinyl chloride 1-chloro-2-methyl-1-propene was employed as a substrate, the saturated carbene complex **2d** could be isolated in 41% yield. The structures of all new carbene complexes **2b–d** have been confirmed by single-crystal X-ray diffraction.[17a] Their molecular geometries, represented in Figure 1 for **2d** as a typical case, display interesting subtle differences, which have been discussed on the basis of EH and DFT calculations elsewhere.[12] Similar to **2a**, complexes **2b–d** are active catalysts for ROMP reactions of norbornene.

The catalytic ROMP activity of the neutral complexes, both with unsaturated and saturated carbene ligands, can be dramatically enhanced, however, by treating them with trimethylsilyl triflate in CH_2Cl_2 at ambient temperature. The irreversible formation of Me_3SiCl by chloride abstraction from **2a** and **2d** leads to air-stable, dinuclear dications **4a** and **4d** as triflates, which can be isolated in 89–94% yield (Scheme 2). The cations **4b** and **4c** were synthesized analogously from **2b** and **2c**. The molecular structure of **4a**, which is very similar to that of **4d**, is displayed in Figure 2.[17b]

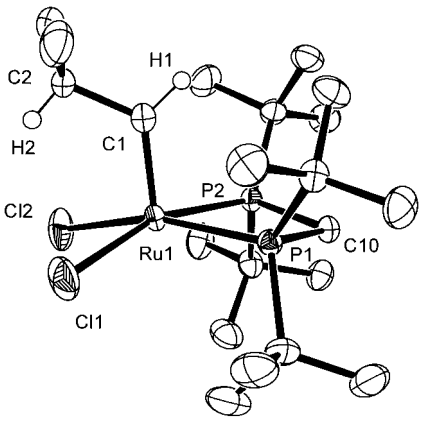
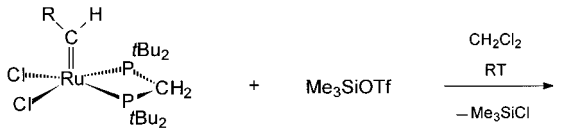
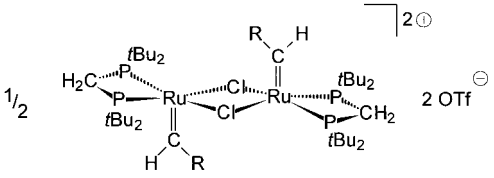


Figure 1. Molecular structure of the saturated carbene complex **2d** in the crystal (ORTEP, 50% probability, CH hydrogen atoms except H1 and H2 of the carbene moiety omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru1–P1 2.3328(5), Ru1–P2 2.3435(5), Ru1–Cl1 2.4099(6), Ru1–Cl2 2.4047(6), Ru1–C1 1.826(2), C1–C2 1.513(3); P1-Ru1-P2 73.485(17), Cl1-Ru1-Cl2 87.76(2), P1-Ru1-Cl1 95.82(2), P2-Ru1-Cl1 162.08(2), P1-Ru1-Cl2 160.46(3), P2-Ru1-Cl2 97.77(2), C1-Ru1-P1 97.62(7), C1-Ru1-P2 96.17(7), C1-Ru1-Cl1 99.53(8), C1-Ru1-Cl2 100.73(7).



2a: R = CH=CMe$_2$
2d: R = CHMe$_2$



4a: R = CH=CMe$_2$
4d: R = CHMe$_2$

Scheme 2. Preparation of **4a** and **4d** from **2a** and **2d** using Me_3SiOTf. $OTf = OSO_2CF_3$.

Each ruthenium center of **4a** and **4d** is in a square-pyramidal ligand environment with P atoms of κ^2-dtbpm and the μ-chloro ligands in the basal plane and the carbene moiety in an apical position, nearly bisecting the P-Ru-P angle. In the solid state, the two carbene fragments are *trans* to each other. The two triflate ions are not coordinated to the ruthenium centers. ^{13}C and ^{31}P NMR spectra of **4a** in solution show a complete double set of signals, indicating the presence of two stereoisomers. Variable-temperature NMR spectra in CD_2Cl_2 reveal a dynamic equilibrium between two dimeric species with *cis* and *trans* arrangement of the carbene moieties. At $-40\,^{\circ}C$ the ^1H NMR signals of the olefinic β protons of the two isomers are well resolved ($\delta = 9.18, 9.29$; $^3J(H_\beta,H_\alpha) = 11.1$ and 11.3 Hz, respectively, Figure 3).[18]

Equilibration between both structures occurs through mononuclear, solvent-stabilized, five-coordinate cationic carbene complexes $[(\kappa^2\text{-dtbpm})ClRu{=}CH{-}CH{=}CMe_2(Solv)]^+$.

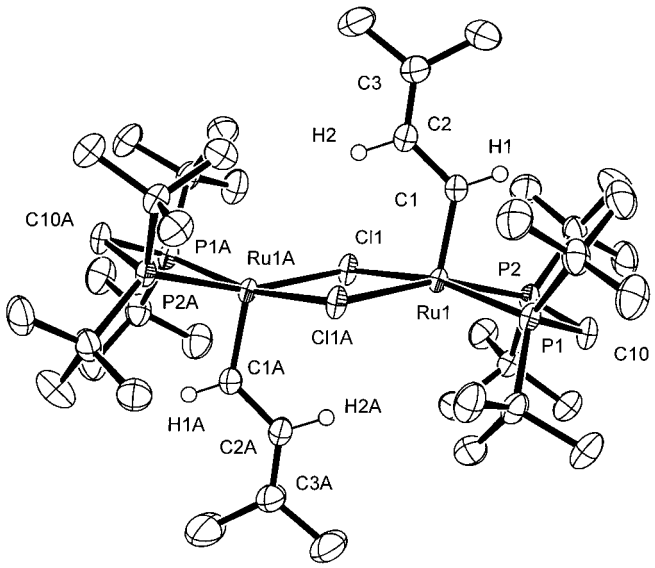


Figure 2. Molecular structure of dication **4a** in the crystal (ORTEP, 50% probability, CH hydrogen atoms except H1, H1A, H2, and H2A of the carbene moieties omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru1–P1 2.3253(9), Ru1–P2 2.336(1), Ru1–Cl1 2.4659(9), Ru1–Cl1A 2.5040(9), Ru1–C1 1.857(4), C1–C2 1.417(6), C2–C3 1.345(6); P1-Ru1-P2 73.63(3), Cl1-Ru1-Cl1A 80.95(3), P1-Ru1-Cl1 161.38(4), P2-Ru1-Cl1 100.01(3), P1-Ru1-Cl1A 101.23(3), P2-Ru1-Cl1A 166.63(4), C1-Ru1-P1 93.85(13), C1-Ru1-P2 95.08(13), C1-Ru1-Cl1 104.25(13), C1-Ru1-Cl1A 97.61(13), Ru1-Cl1-Ru1A 99.05(3).

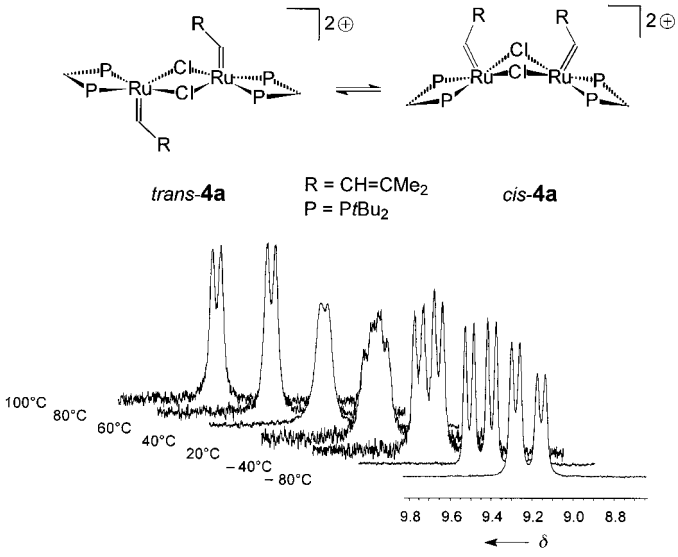
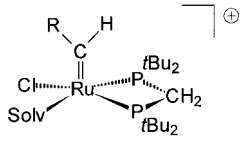


Figure 3. Variable-temperature ^1H NMR spectra of **4a** in CD_2Cl_2 (vinyl proton resonances), indicating *cis*–*trans* interconversion between the dinuclear carbene species *cis*-**4a** and *trans*-**4a**.[18]

We are able to observe such a monomeric species **6d** in ^1H and ^{31}P NMR spectra of **4d** in CD_2Cl_2. In a 1:1 mixture of **4a** and **4d** in the same solvent the signals of all dinuclear dicationic cross products (*cis* and *trans* isomers) can be detected and identified. The new cationic carbene complexes are very efficient catalysts for ROMP reactions. In con-



6a: R = CH=CMe$_2$, Solv = CD_2Cl_2
6d: R = CHMe$_2$, Solv = CD_2Cl_2

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trast to the cationic carbyne systems described by Werner et al.,[13b] they are thermally stable in solution (CD_2Cl_2), without signs of decomposition (NMR spectroscopy) for three days at ambient temperature under an argon atmosphere. The turnover frequency (TOF) for the polymerization of norbornene in CH_2Cl_2 rises from 60 h^{-1} for **2a** (71% *trans*) to 8400 h^{-1} for **4a** (80% *trans*); cyclopentene is also efficiently polymerized. To get a precise comparison with Grubbs' catalyst (**1a**) and Herrmann's *trans*-[L_2Cl_2Ru=CHPh] (**5**, L = *N*,*N*′-diisopropylimidazolin-2-ylidene),[7] which currently are the most active Ru^{II} carbene complexes, we have studied the polymerization of cyclooctene with **4a** as catalyst by ^1H NMR spectroscopy. The relative activity of Grubbs' catalyst **1a**, which is more active than **5**,[7] could be reproduced by our measurements conducted under identical conditions. The much higher reactivity of **4a** required an increase of the [cyclooctene]:[Ru] ratio by a factor of 50. The rates of formation of cyclooctenamer with **1** and **4a** under these conditions is compared in Figure 4.[19] To the best of our knowledge, **4a** and its derivatives represent the most active homogeneous Ru^{II} ROMP catalysts described so far.

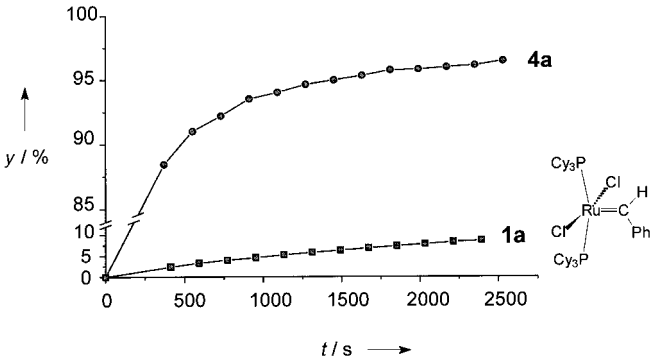

Figure 4. Kinetics of the ROMP reaction of cyclooctene. Comparison of polyoctenamer production using **4a** versus carbene complex **1a** as monitored by ^1H NMR spectroscopy. $T = 23\,^\circ C$; 0.5 mL CD_2Cl_2; [cyclooctene]/[Ru] = 12500:1.[19] *y* = yield.

Unlike the neutral compounds **2a**–**d**, dication **4a** also catalyzes the RCM of 1,7-octadiene to cyclohexene. In ^1H NMR experiments at temperatures between -80 to $0\,^\circ C$ (CD_2Cl_2, [diene]:[Ru] = 24:1), the reaction already starts at $-40\,^\circ C$, yielding cyclohexene (24%) along with octadiene isomers (26%).[20] While **4a** slowly disappears, a second, transient carbene species can be identified by a carbene hydrogen quartet at $\delta = 16.97$.

Although detailed investigations will be necessary to establish the role of dinuclear [(κ^2-dtbpm)(μ-Cl)Ru=CHR]$_2^{2+}$ species **4a**–**d**, we believe the observed mononuclear cations [(κ^2-dtbpm)ClRu=CHR(Solv)]$^+$ (**6**) (Solv = CD_2Cl_2) function as the active catalysts in ROMP and RCM reactions of **4a** and its congeners.

In summary, a facile, general two-step synthesis of neutral Ru^{II} carbenes [(κ^2-dtbpm)Cl_2Ru=CHR] from **3** and propargyl, vinyl, or allenyl chlorides, followed by chloride abstraction with trimethylsilyl triflate as a convenient and efficient reagent, has made accessible a new class of highly active, cationic Ru^{II} metathesis catalysts. Halide abstraction is facilitated by the chelating phosphane ligand dtbpm, which forces the P-Ru-Cl *trans* arrangement. It should be noted that in these cases, halide as opposed to phosphane dissociation, claimed to be the initiating step in metathesis reactions of Grubbs-type *trans* complexes,[5b, 21] leads to remarkably increased catalytic activity. Similar effects of halide abstraction have been observed by Osborn et al. for tungsten carbenes.[22] Efforts to tune the catalytic properties of systems **4** by modifying the ligand set, counterion, and carbene structure, along with polymer characterization, mechanistic, and computational studies are under way in order to establish the potential of these novel catalysts.

Experimental Section

All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. Abbreviations used for NMR data are: s = singlet, d = doublet, t = triplet, "d" = pseudodoublet, "t" = pseudotriplet, "q" = pseudoquartet, "quint." = pseudoquintet, "sept." = pseudoseptet, m = multiplet, Σ_H = sum of integrals in ^1H NMR spectra for specified resonances.

2c: A solution of 1-chloro-3,3-diphenyl-1,2-propadiene (85 mg, 0.376 mmol) in toluene (6 mL) was added under stirring to a solution of complex **3** (158 mg, 0.179 mmol) in toluene (6 mL) at $-75\,^\circ C$. The reaction mixture was allowed to warm to ambient temperature within 1 h, and then stirred for an additional 2 h at this temperature. The resulting microcrystalline green precipitate, which was separated from the brown supernatant solution by cannula filtration, was washed with toluene (2×1 mL) and hexane (3×2 mL). The remaining yellow-green solid was dried in vacuo (10^{-5} bar). Yield: 177 mg (74%). Elemental analysis (%): calcd: C 57.48, H 7.54, P 9.26; found: C 57.37, H 7.52, P 9.31. The molecular structure was confirmed by single-crystal X-ray diffraction. ^1H NMR (CD_2Cl_2, 300 MHz): $\delta = 1.05$ ("d", 18H, *t*Bu-H), 1.54 ("d", 18H, *t*Bu-H), 3.90 ("quint.", ABX_2 system, $^2J(H,H) = 16.7$ Hz, $^2J(H,P) = 9.1$ Hz, 1H, PCH*H*P), 4.04 ("quint.", ABX_2 system, $^2J(H,H) = 16.5$ Hz, $^2J(H,P) = 8.8$ Hz, 1H, PC*H*HP), 7.16–7.69 (m, 10H, Ar-H), 9.44 (d, $^3J(H,H) = 10.4$ Hz, 1H, CHC*H*=CPh_2), 15.74 ("q", $^3J(H,H) = 10.8$ Hz, $^3J(P,H) = 11.0$ Hz, 1H, Ru=CH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): $\delta = 25.2$ (s, *P*-CH_2-*P*); IR (KBr): $\tilde{\nu} = 1526$ cm^{-1} (C=C).

2d: 1-Chloro-2-methyl-1-propene (338 mg, 3.73 mmol) was added to a solution of **3** (200 mg, 0.226 mmol) in toluene (20 mL) at ambient temperature. After the mixture was left to stand for 72 h a red crystalline precipitate had formed. The solid was isolated from the supernatant deep red solution by cannula filtration and washed with toluene (5×2 mL) and hexane (3×4 mL). The remaining red solid was dried in vacuo (10^{-5} bar). Yield: 98 mg (41%). Elemental analysis (%): calcd: C 47.37, H 8.71, P 11.63, Cl 13.32; found: C 47.44, H 8.68, P 11.73, Cl 12.93; ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 1.19$ (d, 6H, $^3J(H,H) = 6.9$ Hz, CHCH(CH_3)$_2$), 1.30 ("d", 18H, *t*Bu-H), 1.56 ("d", 18H, *t*Bu-H), 4.01 ("sept.", $N = 61.0$ Hz, 2H, PCH_2P), 5.50 (m, $N = 40.8$ Hz, 1H, CHC*H*(CH_3)$_2$), 16.22 (dt, $^1J(H,H) = 7.9$ Hz, $^3J(H,P) = 11.8$ Hz, 1H, Ru=CH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): $\delta = 22.7$ (s, PCH_2P).

4a: $Me_3SiOSO_2CF_3$ (63 mg, 0.283 mmol) was added to a solution of **2a** (50 mg, 0.092 mmol) in CH_2Cl_2 (5 mL) at ambient temperature. The red-brown reaction solution was stirred for 1 h and then concentrated to 1 mL in vacuo. Upon addition of hexane (5 mL), a green solid precipitated that was separated from the mother liquid by cannula filtration. The solid was dissolved in CH_2Cl_2 (1 mL) and reprecipitated with hexane (3 mL). After this procedure had been repeated three times, the remaining green microcrystalline green solid was washed with hexane (3×3 mL) and dried in vacuo (10^{-5} bar). Yield: 57 mg (94%). Elemental analysis (%): calcd: C 41.97, H 7.04; found: C 41.46, H 7.02; ^1H NMR (CD_2Cl_2, 300 MHz, $-40\,^\circ C$): $\delta = 1.21$ (m, 72H, $N = 20.5$ Hz, *t*Bu-H), 1.56 ("d", 36H, *t*Bu-H), 1.64 ("d", 36H, *t*Bu-H), 1.70, 1.73, 1.80, 1.83 (each s, each 6H, CHCH=C(CH_3)$_2$), 4.27 ("t", $N = 18.2$ Hz, 8H, PCH_2P), 9.18 (d, $^3J(H,H) = 11.1$ Hz, 2H, CHC*H*=C(CH_3)$_2$), 9.29 (d, $^3J(H,H) = 11.3$ Hz, 2H, CHC*H*=C(CH_3)$_2$), 17.32 (m, $N = 43.0$ Hz, 4H, Ru=CH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz):

$\delta = 26.7$ (s, PCH_2P), 27.4 (s, PCH_2P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): $\delta =$ 22.0, 22.2, 28.8, 29.1 (each s, $CH{=}C(CH_3)_2$), 30.3, 30.4, 31.2, 31.3 (each s, $C(CH_3)_3$), 37.8 (m, PCH_2P), 38.6 (m, $N = 21.1$ Hz, $C(CH_3)_3$), 39.4 (m, $N =$ 16.5 Hz, $C(CH_3)_3$), 148.6, 148.8 (each s, $CH{=}C(CH_3)_2$), 149.8, 150.2 (each s, $CH{=}C(CH_3)_2$), 301.5 (not well resolved, Ru=CH); IR (KBr): $\tilde{\nu} = 1567\ cm^{-1}$ (C=C).

Cationic complexes **4b–d** can be prepared in an analogous manner.The structures of **4b** and **4d** were confirmed by single-crystal X-ray diffraction.

4d: Elemental analysis (%): calcd: C 40.90, H 7.18; found: C 40.69, H 7.25; ^1H NMR (CD_2Cl_2, 500 MHz, $-20\,^\circ C$): $\delta = 1.19-1.32$ (m, *t*Bu-H, $CH(CH_3)CH_3$), 1.43 (d, $^3J(H,H) = 7$ Hz, $CH(CH_3)CH_3$), 1.51–1.56 (m, *t*Bu-H), 1.68 ("d", *t*Bu-H) Σ_H (1.19–1.68) = 42 H, 4.00 ("quint.", $^2J(H,H) =$ 16.9 Hz, $^2J(H,P) = 9.4$ Hz, $[(tBu_2PCHHPtBu_2)ClRu{=}CHCH(CH_3)_2\text{-}(CD_2Cl_2)]^+$), 4.19 ("quint.", $^2J(H,H) = 16.9$ Hz, $^2J(H,P) = 9.5$ Hz, $[(tBu_2PCHHPtBu_2)ClRu{=}CHCH(CH_3)_2(CD_2Cl_2)]^+$), 4.49 (m, $N =$ 64.6 Hz, *cis*- and *trans*-$\{[(tBu_2PCH_2PtBu_2)ClRu{=}CHCH(CH_3)_2]_2\}^{2+}$) Σ_H (4.00, 4.19, 4.49) = 2 H, 5.28 (broad s, $[(\kappa^2\text{-dtbpm})ClRu{=}CHCH(CH_3)_2\text{-}(CD_2Cl_2)]^+$, 6.40 (m, $N = 34.5$ Hz, *cis*- and *trans*-$\{[(\kappa^2\text{-dtbpm})ClRu{=}CHCH(CH_3)_2]_2\}^{2+}$) Σ_H (5.28, 6.40) = 1 H, 16.61 ("q", $^3J(H,H) =$ 9.9 Hz, $^3J(H,P) = 9.9$ Hz, "0.41 H", $[(\kappa^2\text{-dtbpm})ClRu{=}CHCH(CH_3)_2\text{-}(CD_2Cl_2)]^+$), 17.49 ("d", not well resolved, $^3J(H,P) = 10.6$ Hz, "0.05 H", *cis*-$\{[(\kappa^2\text{-dtbpm})ClRu{=}CHCH(CH_3)_2]_2\}^{2+}$), 17.55 ("q", $^3J(H,H) = 10.6$ Hz, $^3J(H,P) = 10.6$ Hz, "0.54 H", *trans*-$\{[(\kappa^2\text{-dtbpm})ClRu{=}CHCH(CH_3)_2]_2\}^{2+}$) Σ_H (16.61, 17.49, 17.55) = 1 H; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, $-60\,^\circ C$): $\delta = 22.4$ (s, *trans*-**4d**), 25.2 (s, *cis*-**4d**), 26.1 (d, $^2J(P,P) = 40.5$ Hz, $[(tBu_2PCH_2PtBu_2)ClRu{=}CHCH(CH_3)_2(CD_2Cl_2)]^+$), 27.9 (d, $^2J(P,P') =$ 40.5 Hz, $[(tBu_2PCH_2PtBu_2)ClRu{=}CHCH(CH_3)_2(CD_2Cl_2)]^+$).

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[17] a) Crystals suitable for X-ray diffraction were obtained from slow evaporation of a saturated solution of **2d** in CH_2Cl_2. Crystal dimensions $0.28 \times 0.24 \times 0.23\ mm^3$, crystal system orthorhombic, space group $Pca2_1$, $Z = 4$, $a = 21.5872(2)$, $b = 8.2840(1)$, $c =$ 14.4771(2) Å, $V = 2588.92(5)$ Å^3, $\rho_{calcd} = 1.366\ g\,cm^{-3}$, $2\theta_{max} = 51.2^\circ$, radiation $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, 0.3° ω scans with CCD area detector, $T = 200$ K, 18290 reflections measured, 4498 unique, 4328 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using the SADABS program based on the Laue symmetry of the reciprocal space, $\mu = 0.94\ mm^{-1}$, $T_{min} = 0.78$, $T_{max} = 0.84$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package, 257 parameters refined, hydrogen atoms were treated by using the appropriate riding models except of H1 and H2, which were refined isotropically, final residual values $R(F) = 0.017$, $wR(F^2) = 0.042$ for observed reflections, residual electron density -0.32 to $0.29\ e\,Å^{-3}$.[17c] b) Crystals suitable for X-ray diffraction were obtained from slow diffusion of pentane into a saturated solution of **4a** in CH_2Cl_2. Crystal dimensions $0.36 \times 0.28 \times 0.17\ mm^3$, crystal system monoclinic, space group $P2_1/n$, $Z = 2$, $a = 15.2553(1)$, $b = 15.2411(2)$, $c = 17.2867(1)$ Å, $V = 3672.97(5)$ Å^3, $\rho_{calcd} = 1.497\ g\,cm^{-3}$, $2\theta_{max} = 51.1^\circ$, radiation $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, 0.3° ω scans with CCD area detector, $T = 200$ K, 26585 reflections measured, 6343 unique, 5444 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied by using the SADABS program based on the Laue symmetry of the reciprocal space, $\mu = 0.98\ mm^{-1}$, $T_{min} = 0.77$, $T_{max} = 0.91$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package, 396 parameters refined, 24 geometrical restraints (disordered solvent), hydrogen atoms were treated by using appropriate riding models except of H1 and H2, which were refined isotropically, final residual values $R(F) = 0.041$, $wR(F^2) = 0.110$ for observed reflections, residual electron density -0.82 to $1.34\ e\,Å^{-3}$. c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-112064 (**2d**) and CCDC-112065 (**4a**). 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).

[18] The high-temperature ^1H NMR spectra were measured in a sealed high-pressure NMR tube under a pressure of 10 bar Ar.

[19] a) In a glovebox **4a** (1.6 mg, 1.25 μmol) was dissolved in CD_2Cl_2 (2.5 mL). From this solution 50 μL (0.025 μmol **4a**) were immediately transferred into an NMR tube and diluted with CD_2Cl_2 (0.45 mL). After addition of degassed cyclooctene (81.4 μL, 625 μmol; > 99.5 % (GC); Fluka) the NMR tube was sealed and shaken. The NMR spectra were recorded at 23 °C on a Bruker DRX 500 spectrometer at 500 MHz. b) Polymerization of cyclooctene with **1a** (0.05 μmol; Strem Chemicals Inc.) as catalyst was carried out under identical reaction conditions.

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