Unsaturated Ruthenium Hydrides as Reactive Intermediates: An Experimental Investigation and Theoretical Model Study of (dtbpm-κ^2P)Ru(H)Cl, (dtbpe-κ^2P)Ru(H)Cl and Their Dinuclear Dynamic Precursor Complexes

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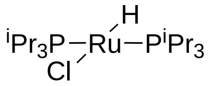
Dedicated to the memory of Professor *Luigi M. Venanzi*, a gentleman, great scientist, and friend

A detailed spectroscopic and quantum-chemical structure investigation of the dinuclear, 16-valence-electron complexes $[(^t\mathrm{Bu}_2\mathrm{P}(\mathrm{CH}_2)_n\mathrm{P}^t\mathrm{Bu}_2\text{-}\kappa^2P)\mathrm{RuH}]_2(\mu_2\text{-Cl})_2$ ($n = 1, 2$), stabilized by the bulky, electron-rich chelating ligands bis[di(*t*-butyl)phosphano]methane ($^t\mathrm{Bu}_2\mathrm{PCH}_2\mathrm{P}^t\mathrm{Bu}_2$, dtbpm) and 1,2-bis[di(*t*-butyl)phosphano]ethane ($^t\mathrm{Bu}_2\mathrm{PCH}_2\mathrm{CH}_2\mathrm{P}^t\mathrm{Bu}_2$, dtbpe) is reported. VT-NMR Spectroscopy of $[(\mathrm{dtbpm}\text{-}\kappa^2P)\mathrm{RuH}]_2(\mu_2\text{-Cl})_2$, an important precursor of olefin metathesis catalysts, and of its homologue $[(\mathrm{dtbpe}\text{-}\kappa^2P)\mathrm{RuH}]_2(\mu_2\text{-Cl})_2$ reveals facile interconversion of dinuclear *cis*- and *trans*-dihydride isomers for both systems. Crossover experiments provide evidence for the existence of short-lived, mononuclear intermediates (dtbpm-κ^2P)Ru(H)Cl and (dtbpe-κ^2P)Ru(H)Cl in solution. Mechanistic features of the *cis-trans* isomerization process as well as structural and electronic properties of model systems for the dinuclear complexes and mononuclear intermediates were treated theoretically by DFT calculations.

Introduction. – The characterization of coordinatively and electronically unsaturated, highly reactive and therefore short-lived transition metal complexes is a matter of general interest due to the central importance of such compounds as key intermediates in various homogeneous catalytic processes [1]. Among these transient species, hydride complexes, which can catalyze hydrogenation, hydrosilylation, and hydroboration as well as CH-bond activation of organic substrates, are of particular significance. Furthermore, transition metal hydride complexes often are useful precursors in organometallic syntheses [2] and illustrate basic principles of metal–ligand bonding.

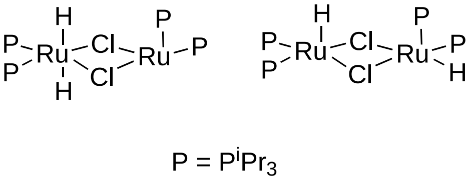
Recently, there has been some experimental and theoretical controversy regarding the existence and structure of 14-electron bisphosphane Ru-hydride complexes of the type $(\mathrm{PR}_3)_2\mathrm{Ru(H)Cl}$. An X-ray structure determination of the Ru-complex $(\mathrm{P}^i\mathrm{Pr}_3)_2\mathrm{Ru(H)Cl}$ (**1a**) by *Van der Schaaf et al.*, describing this compound as a square-planar complex with a *trans*-phosphane arrangement in the solid state, had to be revised and turned out to be a pentacoordinate N_2-adduct [3], which had, in fact, been previously disclosed by *Caulton* and co-workers in an independent study [4c,e]. It still remains unclear whether the formation of the N_2-adduct proceeds *via* the mononuclear hydride as an intermediate.



$$^i\mathrm{Pr}_3\mathrm{P{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{Ru}}}\mathrm{{-}P}^i\mathrm{Pr}_3$$

1a

In a series of papers, *Caulton* and co-workers identified $(PR_3)_2Ru(H)Cl$ ($R = {}^iPr$), as μ-Cl-bridged dimers ($[(P^iPr_3)_2RuH]_2(\mu_2\text{-}Cl)_2$) (**1b**) in the solid state, with the monodentate phosphanes in a *cis* arrangement on the metal centers [4] (*cf.* also previously assumed monomeric structure in solution [4d]). However, as in many X-ray-crystallographic studies, the hydride ligands could not be located unambiguously.

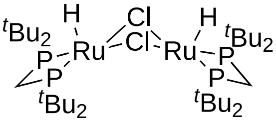


1b

Although mononuclear derivatives $(L)(P^iPr_3)_2Ru(H)Cl$ ($L = N_2$ or pyridine) of these dimers can be obtained by reacting **1b** with appropriate ligands L [4c], to date, no experimental evidence of the existence of monomeric, 14-electron hydrides $(PR_3)_2Ru(H)Cl$ generated by dissociation of, *e.g.*, **1b** has been provided.

In contrast to the systems of *Caulton* and co-workers, which have monodentate phosphane ligands, we have recently prepared and studied the dinuclear Ru-dihydride complex $[(\text{dtbpm-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$, (${}^tBu_2PCH_2P{}^tBu_2$, dtbpm) [5]. Its homologue $[(\text{dtbpe-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$, bearing the bulky 1,2-bis[di(*t*-butyl)phosphano]ethane ligand (${}^tBu_2PCH_2CH_2P{}^tBu_2$, dtbpe) is presented in this report. Variable temperature (VT)-NMR studies of both systems and crossover experiments reveal evidence for *cis-trans* isomerization processes of the dinuclear complexes *via* two different pathways, one of them being a dissociation into the unsaturated hydride intermediates (dtbpm-κ^2P)Ru(H)Cl and (dtbpe-κ^2P)Ru(H)Cl.

Results and Discussion. – *The Dinuclear Dihydride Complex* $[({}^tBu_2PCH_2P{}^tBu_2\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$. We have previously reported that $[({}^tBu_2PCH_2P{}^tBu_2\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$ (**2**) is a convenient precursor for the syntheses of Ru-carbene complexes with bis[di(*t*-butyl)phosphano]methane (${}^tBu_2PCH_2P{}^tBu_2$, dtbpm) as a chelating ligand [5][6]. From the X-ray structure of **2**, and from NMR and IR data, the Cl-bridged dinuclear structure with terminal hydride ligands was deduced in the solid state as well as in solution and is further substantiated in this work by crossover experiments [5]. Since the hydride locations could not be assigned from the single-crystal X-ray diffraction data, *Orpen*'s method [7] was applied to deduce their positions in the solid state [5].



2

As reported, complex **2** in (D_8)THF displays a *triplet* for the hydrides at -25.67 ppm (${}^2J(H,P) = 30.3$ Hz) in the ${}^1H$-NMR spectrum at 298 K. In the ${}^{31}P\{{}^1H\}$-NMR spectrum, a *singlet* at 57.7 ppm is detected. Upon cooling a sample of compound **2** in (D_8)THF, the hydride signal in the ^{1}H-NMR spectrum broadens and is split into two *triplets* at -24.0 ppm (^2J(H,P) = 25 Hz) and -27.3 ppm (^2J(H,P) = 30 Hz) at 159 K, with the two species in the ratio 1:3.5 (*Fig. 1*). The ^{31}P{^{1}H}-NMR spectrum at 159 K exhibits two *singlets* at 52.1 and 55.1 ppm.

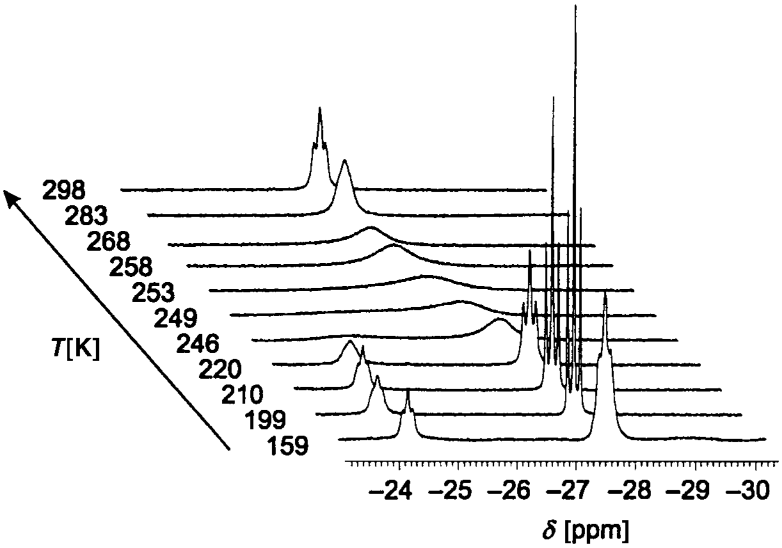


Fig. 1. *Hydride region of the* ^{1}*H-VT-NMR spectrum of* **2** *in* (D_8)*THF*

For the related dinuclear dicationic Ru^{II}-carbene complexes [(dtbpm-κ^2P)ClRu=CHR]$_2^{2+}$, we have established the existence of *cis-trans* isomers in solution [5] and in the solid state [5][8] (*Fig. 2*). For the dinuclear dihydride **2**, the NMR observations outlined above can be explained by an analogous equilibrium process between the species *cis*-**2** and *trans*-**2** (*Scheme 1*). The ratio of the two species (1:3.5 at 159 K) indicates that they must be very similar in energy ($\Delta G_{159K} \approx 0.4$ kcal mol^{-1}). It

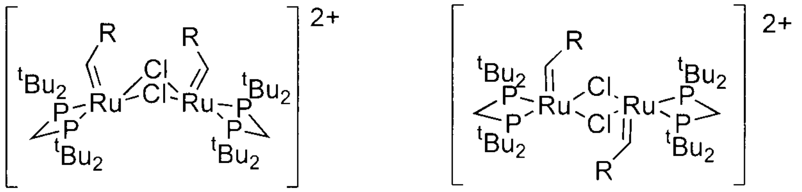
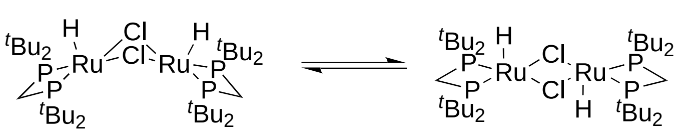


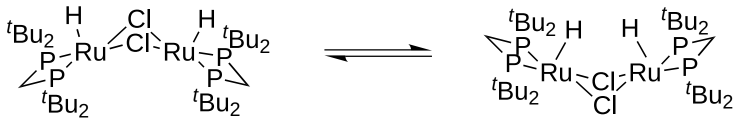
Fig. 2. cis- *and* trans-*isomers of similar dinuclear dicationic Ru^{II}-carbene complexes* ([(dtbpm-κ^2P)ClRu=CHR]$_2^{2+}$)

Scheme 1



cis-**2** *trans*-**2**

Scheme 2

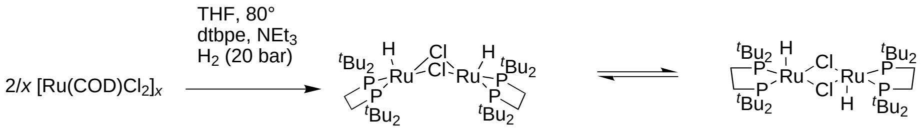


cis-exo-**2** *cis-endo*-**2**

should be noted that, from the NMR data alone, the presence of isomer *cis-endo*-**2** cannot be excluded (*Scheme 2*). However, for steric reasons, the *cis-exo* arrangement [5] is considered to be more likely, which is in agreement with results from application of *Orpen*'s hydride-location method [7]. The observed dynamic process is postulated to be the *cis-trans* (*Scheme 1*) rather than a *cis-endo-exo* (*Scheme 2*) isomerism. Therefore, in the following, we will only use the term *cis* without specifying whether this infers the presence of only *cis-exo* or also involves *cis-endo*.

Synthesis and Properties of $[(^tBu_2PCH_2CH_2P^tBu_2\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$. Complex $[(^t\mathrm{Bu_2PCH_2CH_2P}^t\mathrm{Bu_2}\text{-}\kappa^2P)\mathrm{RuH}]_2(\mu_2\text{-Cl})_2$ (**3**) was synthesized in a fashion similar to its dtbpm analogue **2** in 92% yield as a yellow-beige powder (*Scheme 3*). Complex **3** decays rapidly in the presence of air in solution as well as in the solid state. Decomposition to unidentified products is observed in chlorinated solvents such as $\mathrm{CH_2Cl_2}$ at ambient temperature. Overall, **3** turns out to be much more sensitive and reactive than **2**. The characteristic Ru–H vibration, which is detected at 2103 $\mathrm{cm^{-1}}$, clearly shows the hydrides to be terminal and not bridging ligands, and is very similar to that of $[(\mathrm{dtbpm}\text{-}\kappa^2P)\mathrm{RuH}]_2(\mu_2\text{-Cl})_2$ (**2**) at 2099 $\mathrm{cm^{-1}}$ [5].

Scheme 3



cis-**3** *trans*-**3**

In the ^{1}H-NMR spectrum of **3** at 298 K in ($\mathrm{D_8}$)THF, a sharp *triplet* for the hydride resonance is observed at –30.04 ppm (^2J(H,P) = 34.2 Hz). In the ^{31}P{^{1}H}-NMR spectrum of **3**, a *singlet* at remarkably low field (125.9 ppm) is detected. Upon cooling the sample to 173 K, the hydride signal in the ^{1}H-NMR spectrum broadens and is split into two *triplets* at –29.74 ppm (^2J(H,P) = 34 Hz) and –30.96 ppm (^2J(H,P) = 34.2 Hz). As expected, the ^{31}P{^{1}H}-NMR spectrum at 173 K exhibits two *singlets* (119.9 and 122.9 ppm).

The NMR data for compound **3** indicate an analogous *cis-trans* equilibrium as proposed for complex **2**. In the case of compound **3**, the ratio of the two species is 1 : 8.3, indicating that both isomers have very similar energies ($\Delta G_{173\mathrm{K}} \approx 0.7$ kcal mol^{-1}), as in the case of **2**.

Crossover Experiment. To gain more mechanistic insight into the isomerization processes of **2** and **3** outlined above, a crossover experiment was carried out. The objective was to determine whether a *cis-trans* isomerization process in solution occurs

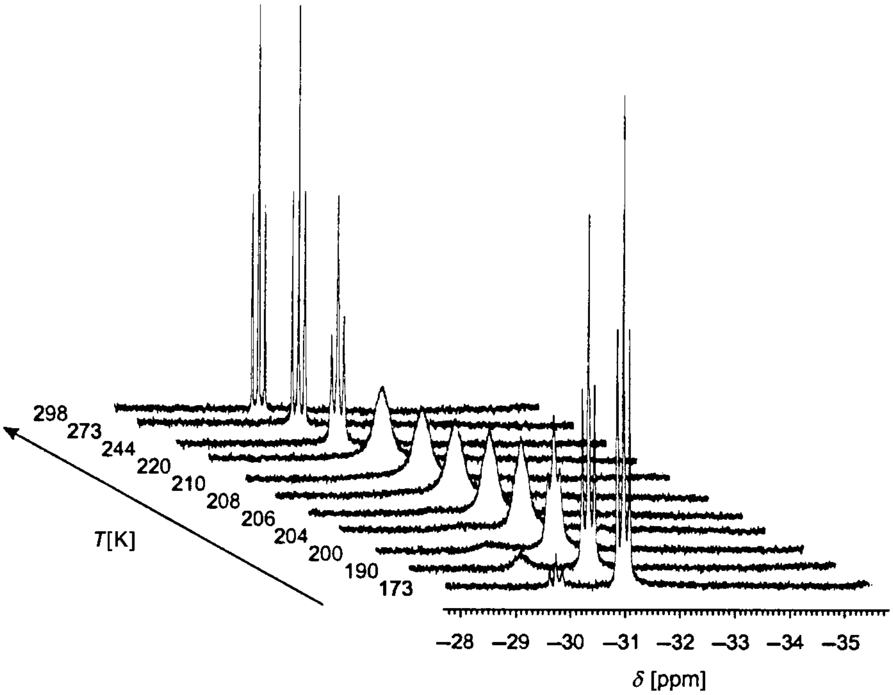


Fig. 3. *Hydride region of the ^{1}H-VT-NMR spectrum of* **3** *in* (D_8)*THF*

via mononuclear species (dtbpm-κ^2P)Ru(H)Cl and (dtbpe-κ^2P)Ru(H)Cl. Solutions of compounds **2** and **3** at a ratio of *ca.* 1:1 were mixed in (D_8)THF at ambient temperature.

The ^{1}H-NMR spectrum of this mixture after storing the sample for 6 h at ambient temperature was measured at 313 K. It displays the *triplets* for **2** and **3** and two additional *triplets* at -24.40 ppm (^2J(H,P) = 32 Hz) and -30.50 ppm (^2J(H,P) = 23.4 Hz)1)). Four *singlets* at 56.6, 60.0, 122.1, and 124.0 ppm are observed in the $^{31}P\{^1H\}$-NMR spectrum at the same temperature (*Fig. 4*). These NMR data point conclusively to the formation of the mixed complex {[(dtbpm-κ^2P)RuH][(dtbpe-κ^2P)RuH]}(μ_2-Cl)$_2$ (**4**, *Scheme 4*), which is present in solution as two stereoisomers with *cis*- and *trans*-arrangements of the hydrides, just as found for the homodimers **2** and **3**. At 313 K, all possible *cis-trans* isomerization processes for **2**, **3**, and **4** are fast on the NMR time scale.

Thus, in the ^{1}H-NMR spectrum, only two hydride *triplets* at -24.40 and -30.50 ppm and, in the $^{31}P\{^1H\}$-NMR, two *singlets* for the phosphane ligands at 60.0 and 122.1 ppm are detected for the mixed dimer **4**. The four hydride *triplets* of the mixture remain well resolved up to 373 K2)). Stepwise cooling of the sample to 180 K reveals a total of eight hydride signals as expected (two for *cis-trans*-**2**, two for *cis-trans*-**3**, and four for *cis-trans*-**4**).

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1) At 298 K, the signal at 24.40 ppm is already slightly broadened in the ^{1}H-NMR spectrum; a sharp *t* for each species was obtained at 313 K.

2) The HT-NMR experiment up to 373 K in (D_8)THF was carried out in an NMR pressure tube under 10 bar Ar.

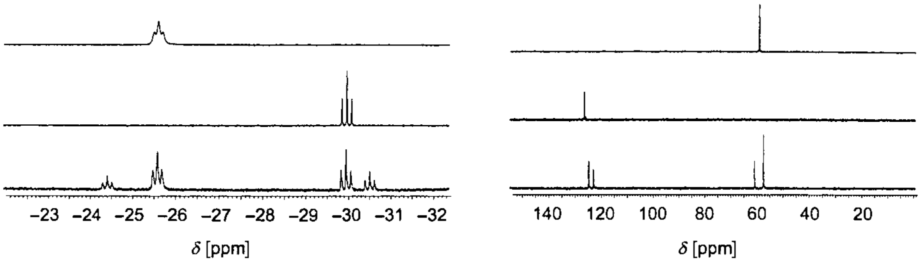
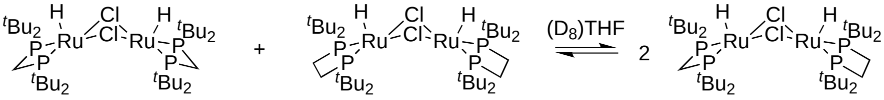


Fig. 4. *Left panel: ¹H-NMR spectrum* (hydride region) *at 313 K* (top: **2**, center: **3**, bottom: crossover experiment showing **2**, **3**, and **4**). *Right panel: ³¹P-NMR spectrum at 313 K* (top: **2**, center: **3**, bottom: crossover experiment showing **2**, **3**, and **4**).

Scheme 4



2 **3** **4**

The crossover experiment confirms that these complexes are dinuclear in solution under the given conditions, because, if **2** and **3** were present only as their mononuclear fragments, a new species would not be detected upon mixing **2** and **3**.

Furthermore, the exchange process must proceed through a dissociation of the dinuclear compounds into mononuclear fragments, which, in a donor solvent such as THF, presumably are solvent coordinated and may be written as (dtbpm-κ^2P)Ru(H)Cl · ((D$_8$)THF) and (dtbpe-κ^2P)Ru(H)Cl · ((D$_8$)THF). The subsequent recombination of these short-lived intermediates to the dimers is accompanied by loss of the solvent. Whether such a recombination takes place by an attack of the Cl of a second mononuclear Ru fragment with simultaneous loss of the donor solvent and reclosure of the Cl bridge *via* an '18-electron transition state' to form the dimer or *via* a '16-electron transition state', in which the solvent is lost prior to reassociation, may not be conclusively derived from the experimental data. However, for the following reasons, we consider the latter case to be more likely. The extremely electron-rich and bulky *t*-butyl-substituted phosphanes supply a high electron density to the metal and effectively shield the coordination sphere of the complex. These two factors provide access to a wide range of pentacoordinate 16-valence-electron complexes, which are isoelectronic to (dtbpm-κ^2P)Ru(H) · (D$_8$)THF and (dtbpe-κ^2P)Ru(H) · (D$_8$)THF and are not susceptible to coordination of a sixth ligand leading to 18-valence-electron complexes. For example, in the much more electrophilic cationic complex [(dtbpm-κ^2P)Cl(MeCN-κN)Ru=CH–CH=C(Me)$_2$]$^+$, the coordination of a second MeCN, which is sterically less demanding than THF, is not observed [6b]. Along these lines, it seems likely that the loss of the solvent in the hydride complexes (dtbpm-κ^2P)Ru(H) · (D$_8$)THF and (dtbpe-κ^2P)Ru(H) · (D$_8$)THF takes place prior to recombination, and that the tetracoordinate hydride complexes (dtbpm-κ^2P)Ru(H)Cl and (dtbpe-κ^2P)Ru(H)Cl are, in fact, intermediates in solution.

The use of a chelating bisphosphane ligand instead of bulky monodentate phosphanes for the crossover is essential, since scrambling by phosphane dissociation/association processes can be excluded from experiments with the tightly bound chelating ligands. However, our findings are also of relevance for the isoelectronic phosphane Ru-hydride complexes with monodentate spectator ligands, implying that similar unsaturated systems $(PR_3)_2Ru(H)Cl$ are true transient species in the chemistry of $[(PR_3)_2RuH]_2(\mu_2\text{-}Cl)_2$ as has been proposed previously [4].

Further information may be gleaned from the failure to detect coalescence of the four hydride signals in the crossover experiment up to 373 K. Only two hydride *triplets* were to be expected, if the fragments (dtbpm-$\kappa^2 P$)Ru(H)Cl and (dtbpe-$\kappa^2 P$)Ru(H)Cl of all dinuclear species were to undergo exchange that is fast on the NMR time scale. This is not the case. However, the *cis-trans* isomerization of all dinuclear species is already fast on the NMR time scale at a much lower temperature (313 K) in the crossover experiment. This implies that, for the *cis-trans* stereomutation of **2**, **3**, and **4**, there has to be at least one other mechanistic pathway lower in energy than the monomerization process. This problem of an additional stereomutation path has been addressed by quantum-chemical model calculations for relevant species.

Model Calculations. – The simplest model for the mononuclear phosphane-coordinated species discussed in this report is *trans*-$(PH_3)_2Ru(H)Cl$ (**5**). This system has been treated theoretically by *Eisenstein* and *Caulton* and co-workers by density-functional-theory (DFT) calculations [9] in the context of insertion reactions with alkenes and alkynes. As expected from simple MO arguments, **5** was predicted to exhibit a sawhorse geometry [9]. It is worth noting in this context that experimental work (compare isoelectronic structures) [10][11] as well as various theoretical analyses [12] suggest this type of sawhorse geometry even for the simpler, isoelectronic d^6-anion $[RuH_4]^{2-}$, which can be regarded as the parent structure of all d^6-ML_4 species discussed here. It may thus serve also as a model for our systems with *cis* chelating diphosphane ligands. Before describing in detail the results of the DFT calculations for models of the dtbpm and dtbpe complexes, a short discussion of the basic electronic structure characteristics as found by an extended *Hückel* (EH)-MO analysis for the parent $[RuH_4]^{2-}$ anion is presented.

MO Description of $[RuH_4]^{2-}$. In *Fig. 5*, an interaction diagram is displayed that constructs the valence MOs of D_{4h} $[RuH_4]^{2-}$ from the valence AO levels of four H^- donor ligands and a Ru^{2+} center from EH calculations [13][14][3]).

The HOMO-LUMO gap of only 0.26 eV (6.0 kcal mol^{-1}) implies that a square-planar $[RuH_4]^{2-}$ will not represent a stable closed-shell geometry for this system. Rather, a second-order *Jahn-Teller*-type distortion [13] predicts a change of the geometry of $[RuH_4]^{2-}$ from square-planar D_{4h} ($\alpha = 180°$) to a sawhorse arrangement with C_{2v} symmetry ($\alpha = 90°$). This is depicted in the *Walsh* diagram (displaying only the relevant MOs $1b_{1g}$ to $2a_{1g}$) in *Fig. 6*.

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[3]) Off-diagonal elements H_{ij} were calculated by the weighted H_{ij} formula [14c], the programs used were FORTICON8 [14d] and CACAO [14e]. Atomic parameters for C, H, P, and Cl were standard values. The Ru H_{ii} values (wave-function parameters) used were: H_{ii} Ru(4d) = – 12.2 eV ($\xi_1 = 5.378$, $\xi_2 = 2.303$, $c_1 = 0.5573$, $c_2 = 0.6642$); H_{ii} Ru(5s) = – 9.26 eV ($\xi = 2.078$); H_{ii} Ru(5p) = – 5.47 eV ($\xi = 2.043$).

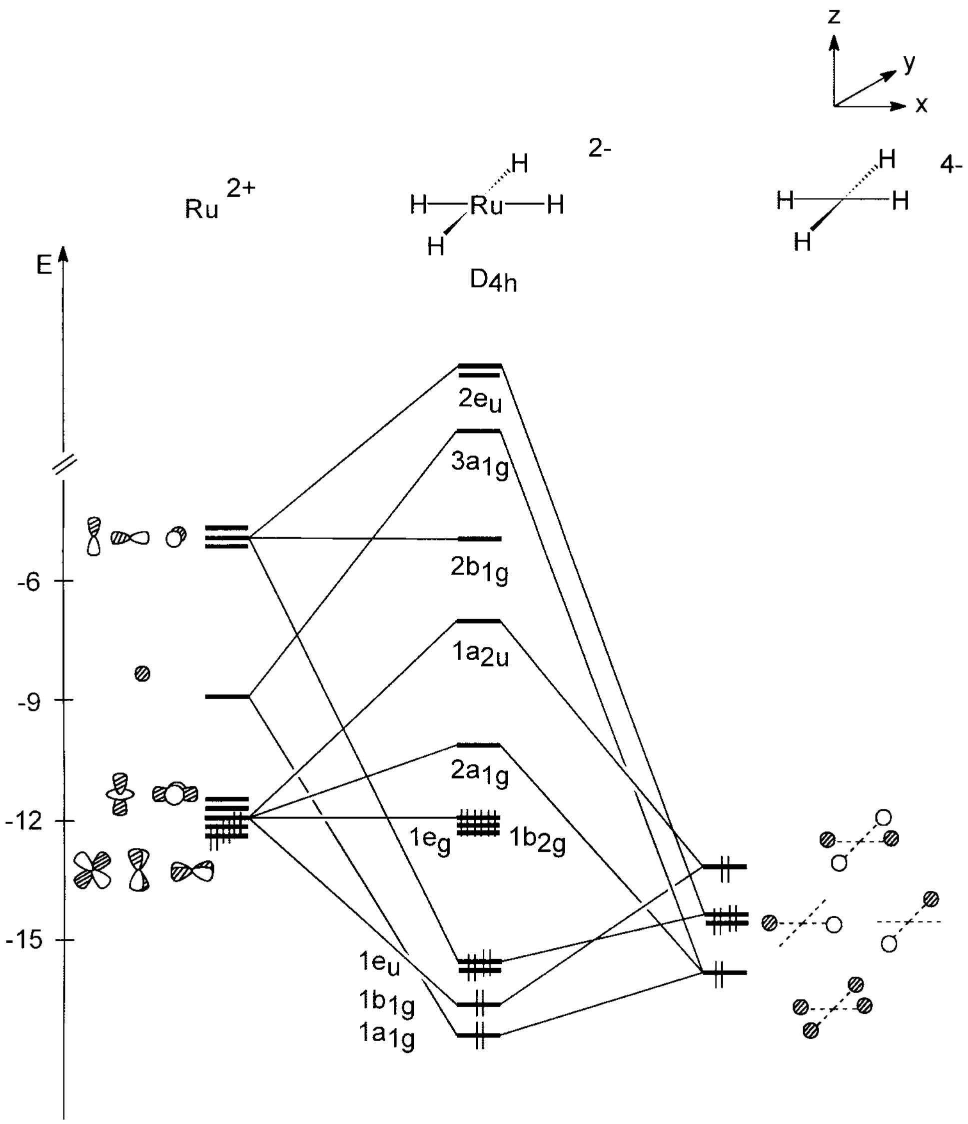


Fig. 5. *Valence MO interaction diagram for* D_{4h} *$[RuH_4]^{2-}$ from EH calculations*

In the simple EH model, the total energy is 0.61 eV (14.1 kcal mol^{-1}) lower for the sawhorse minimum ($\alpha = 90°$) than for the square-planar ($\alpha = 180°$) structure. This stabilization is caused mainly by mixing the d_{yz} AO of Ru in a bonding fashion into the p_y-based RuH bonding level. This leads to a better overlap of the hydride ligand sphere with the metal. The HOMO-LUMO gap is increased to 1.76 eV (40.6 kcal mol^{-1}), which can be attributed mainly to the strong destabilization of the d_{yz} orbital by antibonding interaction with the symmetry-adapted 1s combination of the hydride ligands (*Fig. 6*). The same qualitative picture is obtained from EH calculations for the

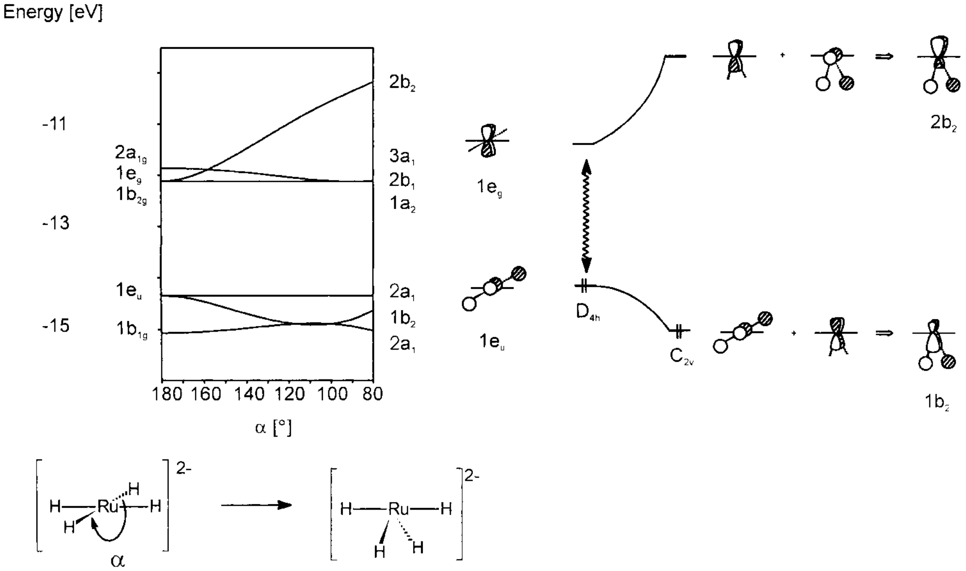


Fig. 6. *EH*-Walsh *diagram for distorting* $[RuH_4]^{2-}$ *from square-planar* (D_{4h}) *to sawhorse* (C_{2v}) *geometry.* Levels below $2a_{1g}/2b_2$ are filled.

more realistic model system *trans*-$(PH_3)_2Ru(H)Cl$, for which the total energy is lowered by 0.30 eV (6.9 kcal mol^{-1}), and the HOMO-LUMO gap is enlarged from 0.01 eV (0.2 kcal mol^{-1}) to 0.95 eV (21.9 kcal mol^{-1}) by distorting from the square-planar to the sawhorse structure. These results clearly suggest a nonplanar structure for the complex $(PR_3)_2Ru(H)Cl$ that may be present upon dissociation of the dinuclear species **1b** reported by *Caulton* and co-workers [4] and also indicate that our 14-valence-electron intermediates with chelating phosphanes should be nonplanar.

DFT Calculations for $(PH_3)_2Ru(H)Cl$, *(dhpm-κ²P)Ru(H)Cl*, *[(dhpm-κ²P)RuH]₂-(μ₂-Cl)₂*. Investigations at a higher theoretical level were carried out to quantify the results derived from simple MO arguments. As mentioned above, DFT calculations predicted a sawhorse geometry for $(PH_3)_2Ru(H)Cl$ [9]. To obtain a more detailed picture of the potential-energy surface for this model system, we examined different isomers of $(PH_3)_2Ru(H)Cl$. Special focus was put to square-planar structures as initially reported by *Van der Schaaf et al.* [3] to determine whether these complexes are unstable intermediates or transition states. Full geometry optimizations for all structures were carried out with Gaussian 98 (Rev. A5) at the B3LYP level [15]. For Ru, the LANL2DZ basis was employed, while, for the other atoms, the 6-31G** basis set was used; a diffuse function (6-31++G**) was added to the hydride ligand basis set. The nature of the optimized structures was assigned by frequency calculations. In *Fig. 7*, the relative energies of the different isomers are shown.

We were able to locate three minima on the potential-energy surface for this system, considering a *cis*- as well as a *trans*-phosphane ligand arrangement. It is noteworthy that the square-planar structure *trans*-**5b** was unambiguously identified as a transition state (NIMAG = 1; hydride moving up and down through the PRuP-plane), which is 26.9 kcal mol^{-1} less stable than the sawhorse geometry *trans*-**5a**. This underlines the

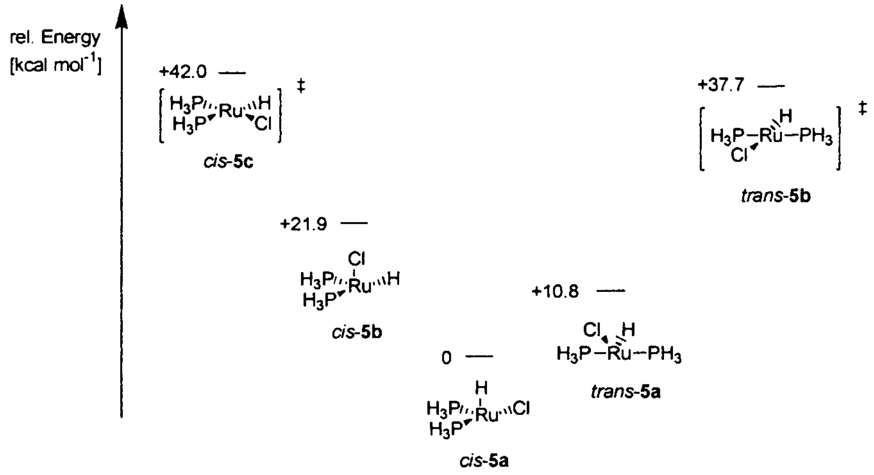


Fig. 7. *Relative energies* (in kcal mol^{-1}) *of various fully geometry-optimized structures of (PH$_3$)$_2$Ru(H)Cl* (**5**). Transition states marked by $^+$.

results obtained from simple MO arguments. In spite of the steric repulsion of bulky monodentate phosphanes in real systems, a *cis* arrangement of the PH$_3$ ligands is also considered here, since *Caulton* and co-workers have reported the crystal structure of [(P^{i}Pr$_3$)$_2$Ru(H)Cl]$_2$ [4], in which a *cis*-phosphane arrangement is found. Furthermore, *cis*-**5a** and *cis*-**5b** are instructive for systems involving bidentate chelating ligands. The sawhorse structure *cis*-**5a** with the Cl *trans* to PH$_3$ turns out to be the most stable isomer, while *cis*-**5b**, with the hydride *trans* to PH$_3$, is destabilized by 21.9 kcal mol^{-1}. This may easily be rationalized by the unfavorable *trans* arrangement of the two strong σ-donors H and PH$_3$. Interconversion of the model species *cis*-**5a** to its enantiomer *via* square-planar transition state *cis*-**5c**, which is 42.0 kcal mol^{-1} higher in energy than *cis*-**5a**, is very unfavorable. These results are of relevance for the different possible isomerization processes for the dinuclear systems with chelating phosphanes described below.

As outlined above, the dinuclear complexes **2** and **3** undergo facile *cis-trans* isomerization in solution. The crossover experiment between **2** and **3** revealed that one possible mechanistic pathway for this process is the dissociation into monomeric species and subsequent reassociation to the dimers (*cis* or *trans*). However, as *cis-trans* isomerization occurs at a much lower temperature than the crossover, another pathway must exist. In order to find out about other possible *cis-trans* isomerization mechanisms, model calculations on the dinculear structures [(dhpm-κ^2P)RuH]$_2$(μ_2-Cl)$_2$ (**6**) as well as the mononuclear chelate system (dhpm-κ^2P)Ru(H)Cl (**7**) were performed. The results for the fully geometry-optimized structures are shown in *Fig. 8*. Dinuclear species with different hydride arrangements are almost isoenergetic, with the model *trans*-**6** being most stable. Although the calculated complex *cis-endo*-**6** is slightly more stable than *cis-exo*-**6**, in the real system with sterically demanding ^{t}Bu groups, the *exo*-hydride arrangement is expected to be energetically favored [5]. Dissociation into two mononuclear species **7a** (*Fig. 8*) requires 39.8 kcal mol^{-1}. Its computed structure has the expected sawhorse geometry as shown in *Fig. 9*.

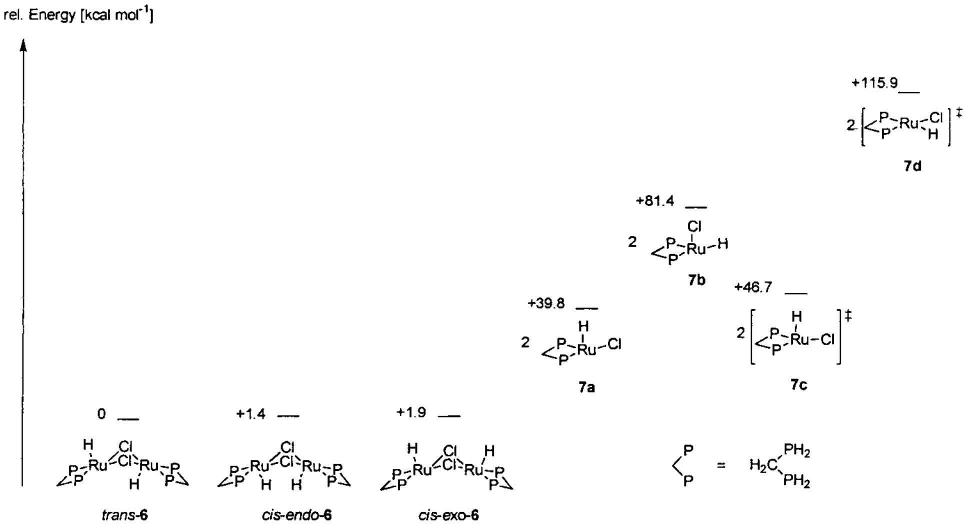


Fig. 8. *Relative energies* (in kcal mol^{-1}) *of fully geometry-optimized structures of* $[(dhpm\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$ (**6**) *and* $(dhpm\text{-}\kappa^2P)Ru(H)Cl$ (**7**)

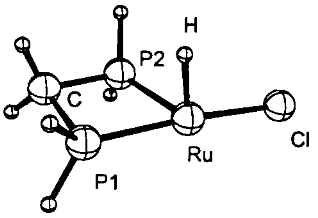
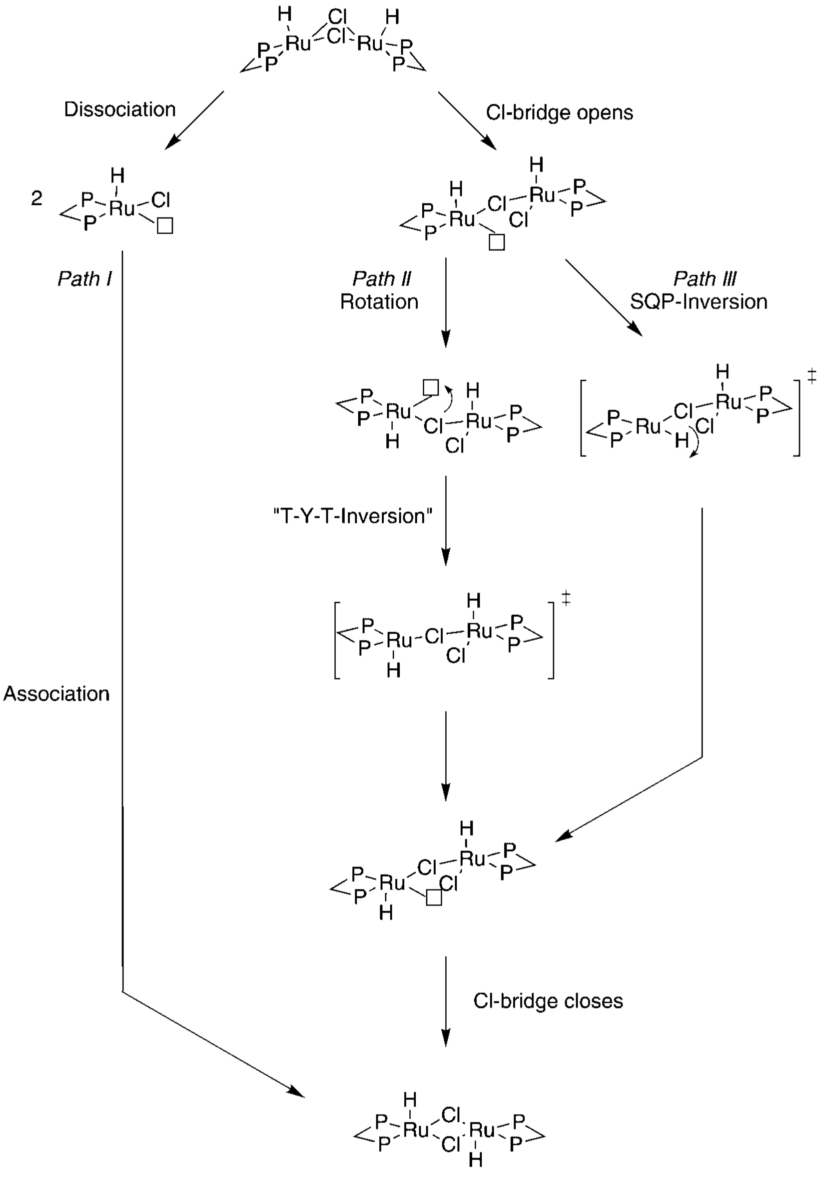


Fig. 9. *Geometry-optimized structure of* $(dhpm\text{-}\kappa^2P)Ru(H)Cl$ (**7a**). Selected bond lengths [Å] and angles [°]: Ru–P(1): 2.32, Ru–P(2): 2.21, Ru–H: 1.56, Ru–Cl: 2.34, P(1)–Ru–P(2): 73.6

As found for the systems with PH_3, the most stable monomeric structure **7a** also has Cl *trans* to P. The isomer **7b** with the hydride *trans* to one P atom is 20.8 kcal mol^{-1} higher in energy than **7a**. Interconversion of the two enantiomers of **7a** *via* transition state **7c**, in which the Cl swings back and forth within the PRuP plane ('T–Y–T-Inversion') is extremely facile, with a barrier of only 3.5 kcal mol^{-1}. As explained for the systems with PH_3 ligands, the interconversion of the two enantiomers of **7a** *via* the high-energy square-planar transition state **7d**, is not competitive.

On the basis of all experimental as well as computational data, the different possible mechanisms for the *cis-trans* isomerization of the dinuclear species are depicted in *Scheme 5*. As shown by the crossover experiment, dissociation into two mononuclear species followed by association (*Path I*) does occur and is in accord with the energies from DFT calculations. A second possible scenario (*Path II*) is an opening of one of the Cl-bridges followed by rotation of one Ru fragment, subsequent 'T–Y–T-Inversion' and closure of the Cl-bridge in the last step. *Path II* is even more facile than *Path I* for the following reasons. The complete dissociation of the dinuclear model *trans*-**6** to the monomers **7a**, breaking two Cl-bridges, requires 39.8 kcal mol^{-1}. Opening only one Cl-bridge, therefore, requires only *ca.* 20 kcal mol^{-1}, since one of the Ru centers retains its 16 VE configuration as in the dinuclear structures **6**. The subsequent rotation of one Ru fragment around the Ru–Cl single bond is expected to have a very low barrier as well, because neither in the model nor in the real system do sterics or electronics impose a barrier upon this process. The 'T–Y–T-Inversion', with a barrier of approximately 3.5 kcal mol^{-1} (*cf. Fig. 8*, **7c**), should also proceed easily, altogether favoring this path. A third process that may be envisioned (*Path III*, *Scheme 5*), in which opening of one Cl-bridge is followed by an inversion of the configuration at one Ru center *via* a square-

Scheme 5. *Different Isomerization Pathways for* cis-trans *Interconversion of Dinuclear Dihydrides*



planar transition state, and reclosure of the Cl-bridge may be excluded. The inversion process is blocked by a high barrier, which is calculated to be 38.1 kcal mol^{-1} for the analogous monomeric model system (*cf. Fig. 8*, **7d**).

From our calculations, we propose that the *cis-trans* isomerization process of the dinuclear complexes takes places *via Paths I* and *II*, the latter being more favorable. This interpretation is also in accord with all experimental data, which indicate that the dissociation of the dinuclear complexes **2** and **3** requires higher temperatures than their *cis-trans* isomerization.

Conclusions. – Employing the bulky, electron-rich ligands dtbpm and dtbpe, we have carried out a detailed investigation of the fluxional complexes $[(^tBu_2PCH_2P^tBu_2\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$ and $[(^tBu_2PCH_2CH_2P^tBu_2\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$. The *cis-trans* interconversion of the dinuclear dihydrides in solution was studied by VT-NMR. A crossover experiment for the first time provides evidence for the presence of the mononuclear species (dtbpm-κ^2P)Ru(H)Cl and (dtbpe-κ^2P)Ru(H)Cl in solution. These results are also relevant for the proposed general type of intermediates $(PR_3)_2Ru(H)Cl$ in the chemistry of dinuclear $[(PR_3)_2RuH]_2(\mu_2\text{-}Cl)_2$ systems with monodentate phosphanes PR_3. Theoretical treatment of the model complexes $(PH_3)_2Ru(H)Cl$, [(dhpm-κ^2P)RuH]$_2$(μ_2-Cl)$_2$ and (dhpm-κ^2P)Ru(H)Cl reveals their electronic structure and the relative stability of various isomers and gives mechanistic insight into the interconversion process of *cis*- and *trans*-dinuclear dihydrides that proceeds not only *via* monomers, but predominantly by stereomutation of dimers bridged by only one Cl.

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Experimental Part

General. All reactions were carried out under dry Ar with standard *Schlenk*-tube techniques. Solvents were dried according to standard procedures and saturated with Ar prior to use. [(dtbpm-κ^2P)RuH]$_2$(μ_2-Cl)$_2$ [5] and 1,2-bis[di-(*t*-butyl)phosphano]ethane [16] ($^tBu_2PCH_2CH_2P^tBu_2$, dtbpe) were synthesized according to the published procedures. IR: ν in cm^{-1}. NMR Spectra: *Bruker DRX-300* spectrometer; δ in ppm, J in Hz; ^{31}P-NMR spectra were calibrated to an external standard (85% H_3PO_4).

*Di-μ_2-chlorobis{[1,2-ethanediylbis{di(*tert*-butyl)phosphano}-κ^2*P*](hydrido)ruthenium(IV)} ([($^tBu_2PCH_2$-$CH_2P^tBu_2$-κ^2*P*)RuH]$_2$(μ_2-Cl)$_2$*; **3**). A 75 ml steel autoclave with a *Teflon* liner was charged with [{$RuCl_2$(η^4-COD)}$_x$] (259 mg, 0.95 mmol [Ru]), dtbpe (303 mg, 0.95 mmol), and Et_3N (133 µl, 0.95 mmol) in THF (18 ml). The autoclave was pressurized with H_2 (20 bar) and the mixture was stirred at 80° for 65 h. After cooling to r.t. and depressurizing, the orange-brown mother liquor containing the product was separated from the precipitated $HNEt_3^+Cl^-$ by cannula filtration. The precipitate $HNEt_3^+Cl^-$ was extracted 2 × with THF (5 ml) and the combined THF layers were taken to dryness *in vacuo*. The resulting yellow-brown solid was washed with hexane (3 × 3 ml) and then dried *in vacuo*. Yield: 388 mg (92%). IR (KBr): 2103*w* (Ru–H). ^{1}H-NMR (300 MHz, (D_8)THF)): –30.04 (*t*, ^2J(H,P) = 34.2, 2 H, Ru–H); 1.24 (*d*, ^3J(H,P) = 11.4, 36 H, ^{t}Bu); 1.40 (*d*, ^3J(H,P) = 11.4, 44 H, ^{t}Bu, $P(CH_2)_2P$). $^{13}C\{^1H\}$-NMR (75 MHz, (D_8)THF)): 23.6 ('*t*', J = 16, $(CH_2)_2$); 30.2 (*s*, C*Me*$_3$); 31.3 (*s*, C*Me*$_3$); 36.9 ('*t*', ^1J(C,P) = 6, *C*Me$_3$); 37.3 ('*t*', ^1J(C,P) = 9, *C*Me$_3$). $^{31}P\{^1H\}$-NMR (121 MHz, (D_8)THF)): 125.9 (*s*, *P*(CH$_2$)$_2$*P*). Anal. calc. for C 47.41, H 9.06, P 13.59; found: C 47.12, H 9.04, P 13.87.

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