Synthesis and Molecular Structure of trans-[RhCl₂(tBu₂PPh)₂]: a Rare Example of a Mononuclear Rhodium(II) Complex

Hans-Christian Böttcher,*[a] Peter Klüfers,[a] Thomas Mies,[a] and Peter Mayer[a]

Dedicated to Professor Peter Comba on the Occasion of His 65th Birthday

Abstract. During the reaction of [[Rh(μ-Cl)(coe)₂]₂] (I) (coe = cis-cyclooctene) with the tertiary phosphane tBu₂PPh in a nitrogen atmosphere the square planar rhodium(II) complex trans-[RhCl₂(tBu₂PPh)₂] (2) was identified as a side product in moderate yield. 2 was synthesized in a defined manner in higher yields using a known procedure starting from [[Rh(μ-Cl)(coe)₂]₂], tBu₂PPh (molar ratio Rh:P of 1:2), and Na-chlorosuccinimide as the oxidizing agent in THF at room temperature. The molecular structure of 2 was determined by X-ray crystallography. Additionally, to further confirm the molecular structure of trans-[RhCl₂(tBu₂PPh)₂], extensive DFT calculations were undertaken, which gave further evidence for its molecular structure. In contrast to the remarkable stability of 2 in the solid state, the investigation of solutions of this compound afforded hints at a dynamic equilibrium, which renders more difficult the collection of adequate NMR spectroscopic data for the title complex.

Introduction

Recently we reported investigations on the reaction of [[Rh(μ-Cl)(coe)₂]₂] (I) (coe = cis-cyclooctene) with the secondary phosphane tBu₂PH in different solvents using various molar ratios of reactants.[1] Operating in heptane (molar ratio Rh:P of 1:2) afforded [[Rh(μ-Cl)(tBu₂PH)₂]₂] in nearly quantitative yield and the molecular structure of the latter in the solid was confirmed by X-ray diffraction.

In this context we were interested in the analogous reaction using the tertiary phosphane tBu₂PPh to obtain the related complex [[Rh(μ-Cl)(tBu₂PPh)₂]₂] by the same way. Unfortunately, till now, we were unable to grow suitable crystals of the latter for an X-ray diffraction study to confirm its molecular structure. During the chosen synthetic procedure and by subsequent crystallization attempts we obtained by accident a side structure. During the chosen synthetic procedure and by subsequent crystallization attempts we obtained by accident a side structure. In contrast to the remarkable stability of 2 in the solid state, the investigation of solutions of this compound afforded hints at a dynamic equilibrium, which renders more difficult the collection of adequate NMR spectroscopic data for the title complex.

Thus, the crystal and molecular structure of trans-[RhCl₂(tBu₂PPh)₂] was reported.[6] This species was discussed earlier as a paramagnetic impurity during the synthesis of Wilkinson’s catalyst [RhCl(PPh₃)₃]. Unfortunately, the latter structure analysis was not correct and other authors examined some times later the structure analysis in detail. They recognized this...
species as \( \text{trans-}[\text{RhCl(CO)(PPh}_3]_2 \) crystallizing orthorhombically as yellow crystals exhibiting disordered carbonyl and chlorido ligands.\(^{[7]}\) 

Furthermore, the synthesis and the molecular structure of \( \text{trans-}[\text{RhCl}_2(\text{PPr}_3)_2] \) was described independently by two other groups.\(^{[8,9]}\) Harlow and co-workers obtained this complex as a by-product during the reaction of 1 with \( \text{PPr}_3 \) in a nitrogen atmosphere. This \( \text{Rh}^{II} \) complex was finally obtained by the authors in a defined manner by the reaction of complex 1 with the phosphine in a nitrogen atmosphere using \( N \)-chlorosuccinimide (NCS) as the oxidizing agent. A second method started from \( \text{trans-}[\text{RhCl}(\text{N}_2)(\text{PPr}_3)_2] \) using the same oxidizing agent.\(^{[8]}\) Werner et al. obtained \( \text{trans-}[\text{RhCl}_2(\text{PPr}_3)_2] \) during the reaction of \( [{\text{Rh}(\mu-\text{Cl})(\text{PPr}_3)_2}]_2 \) with carbon tetracloride.\(^{[9]}\) In contrast to the former report,\(^{[8]}\) in which the authors described this rhodium(II) species as dark red crystals, Werner and co-workers reported this complex as deep blue crystals.

Presumably, there is a possible explanation, why the latter discrepancies concerning the colors of the same compound were reported. In this context Bennett and Longstaff described, already in 1969, that \( \text{trans-}[\text{RhCl}_3(\text{P}(\text{o-tolyl})_1)_2] \) crystallized as a solid in two modifications.\(^{[10]}\) They reported a blue-green paramagnetic modification from ethanol at room temperature and a purple paramagnetic modification, which was obtained at 273 K from dichloromethane. Moreover, they described a possible transformation of both modifications into each other. For example, by dissolving the purple solid in acetone at room temperature they obtained the blue-green modification. Unfortunately, no X-ray crystal structure data of both these modifications have been reported to date.

Results and Discussion

To obtain compound 2 by a more defined method in higher yields we checked the above-mentioned procedure.\(^{[8]}\) Thus we reacted 1 with \( \text{tBu}_2\text{PPh} \) (molar ratio \( \text{Rh}:\text{P} = 1:2 \)) in THF at room temperature using \( N \)-chlorosuccinimide as the oxidizing agent. During 2 h a dark red-brown solution resulted, which precipitated as greenish-blue powder. The solid was washed with diethyl ether and dried in vacuo. Crystallization from hot THF resulted in the well-resolved NMR signal. Thus 2 crystallized from THF as crystals belonging to the orthorhombic space group \( \text{Pbca} \) with very similar unit-cell parameters, confirming that crystals of 2 and the palladium species are isomorphous.

The collection of NMR spectroscopic data of 2 in solution was complicated by the following reasons. Although 2 was stable as solid, even under air conditions for months (!), this could not be confirmed during dissolution of the solid in organic solvents. Here the deep red crystals showed the peculiar tendency to afford no corresponding red solutions. Contrary these solutions appeared immediately rather orange or yellow. The \(^1\text{H} \) NMR (400 MHz) spectrum of 2 in CD$_2$Cl$_2$ showed two very broad signals at \( \delta = 9.06 \) and 6.42 ppm that were obviously caused by the expected paramagnetism of the title compound 2. However, beside the latter ones, well-resolved signals could also be observed. A doublet at \( \delta = 1.20 \) ppm (J$_{\text{HH}}$ = 11.6 Hz) and two multiplets at 7.70 and 7.36 ppm could be assigned to the free ligand \( \text{tBu}_2\text{PPh} \). This assumption was unambiguously further confirmed by the \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum (CD$_2$Cl$_2$) showing a singlet at \( \delta = 39.9 \) ppm indicating the free \( \text{tBu}_2\text{PPh} \).

In contrast to the \(^1\text{H} \) NMR spectrum, the \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of 2 exhibited only sharp signals not hinting at a paramagnetic component in the solution. Here two main species were detected at 39.9 (s) and 62.6 ppm (d, J$_{\text{HH}}$ = 99.4 Hz). The singlet was assigned to the free ligand \( \text{tBu}_2\text{PPh} \) as mentioned before. The observed doublet indicated a species containing a direct Rh–P bond caused by the coupling with the rhodium nucleus. Interpreting these observations we assumed in solution an equilibrium between complex 2, a dinuclear Rh$^{II}$ species, \([\text{Rh}(\mu-\text{Cl})(\text{tBu}_2\text{PPh})_2]_2 \) (3), and the free ligand \( \text{tBu}_2\text{PPh} \). The hypothetical compound 3 may contain a Rh–Rh bond, therefore the paramagnetism should be compensated resulting in the well-resolved NMR signal.
The lack of a signal in the $^{31}$P($^1$H) NMR spectrum indicating the paramagnetic species 2 seemed unclear. It could be reasonable that the signal corresponding to the mononuclear title complex disappeared in the background of the spectrum because of shortened relaxation processes. Many attempts to separate the three discussed species from the solution equilibrium to obtain 3 as crystals for an X-ray diffraction study failed till now. Our assumption that the equilibrium scenario should be realistic was manifested mainly by the fact that, on cooling, these solutions afforded red crystals of 2 again by crystallization. That means that a reaction behavior in light of disproportionation processes, which has been often discussed for such systems in the literature,\cite{2} could be ruled out with certainty. The solid-state $^{31}$P NMR spectrum (202 MHz) of 2 showed only one broad signal centered at $\delta = 54.4$ ppm and indicated, not so clearly, the paramagnetism of this species. However, the paramagnetism of 2 was unambiguously confirmed by ESR spectroscopic measurements. The ESR powder spectrum of 2 at room temperature and at 77 K, respectively, showed various signals and provided evidence for the oxidation state +II ($d^7$, one unpaired electron) in the title complex (see Figure S1, Supporting Information). The shapes of the spectra were in good accordance with the reported ones for the closely related compounds $[\text{RhCl}_2(\text{PR}_3)_2]$ ($R = \text{cyclohexyl}, \text{o-toly})$.\cite{12} The spectra were temperature dependent. Unfortunately, no crystal data of the latter species for comparison purposes were available to date.

Figure 2 shows the UV/Vis spectrum of 2 in a diffuse-reflection set up. The same spectra were obtained for a blue powder of 2 as well as ground red crystals from recrystallization batches. The ordinate is assigned to the Kubelka–Munk function $K/S$ vs. the wave number for a solid sample of 2, diluted with barium sulfate. Positions of the maxima: $\tilde{\nu} = 28943, 24935, 23105, 21591, 17968, 17205, 16599$ cm$^{-1}$; $\lambda$ in the same order: 346, 401, 463, 557, 581, 602 nm.

![Figure 2. The Kubelka–Munk function $K/S$ vs. the wave number for a solid sample of 2, diluted with barium sulfate. Positions of the maxima: $\tilde{\nu} = 28943, 24935, 23105, 21591, 17968, 17205, 16599$ cm$^{-1}$; $\lambda$ in the same order: 346, 401, 463, 557, 581, 602 nm.](image)

Table 1. The positions of the four most intense, LMCT-type maxima of 2.

<table>
<thead>
<tr>
<th>$\tilde{\nu}$/cm$^{-1}$</th>
<th>TDDFT</th>
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<tr>
<td>17205</td>
<td>15630</td>
</tr>
<tr>
<td>21591</td>
<td>21053</td>
</tr>
<tr>
<td>24935</td>
<td>23759</td>
</tr>
<tr>
<td>28943</td>
<td>26542</td>
</tr>
</tbody>
</table>

The distinct absorption around 580 nm is responsible for the blue color. The entire spectrum in the visible range should result in a purple color.

### Computational Analysis of the Ground and Excites States of 2

Calculations within the framework of density-functional theory as well as preliminary calculations with wave-function methods are dominated by a small energetic difference of the molecular orbitals with Rh-d(z$^2$) and Rh-d(xy) contribution (axes: $z$ normal to the RhP$_2$Cl$_2$ plane, $x$ close to the Rh–Cl axis). All four ligands combine with d(z$^2$) to a $\sigma$-antibonding MO, whereas the chlorido ligands form $\pi$-antibonds with d(xy). Already in 1977, van Gaal et al. formulated a mixed d(z$^2$)/d(xy) occupation in their attempts to model ESR experiments on the blue compound $[\text{RhCl}_2(\text{PCy}_3)_2]$.\cite{13} In a later work, Harlow et al. stressed the partial occupancy, instead of a full electron pair of the Rh-d(z$^2$)Cl-p($z$) antibonds, as the origin of an unexpectedly short Rh–Cl bond (2.298 Å, compare 2.366 Å for Rh–P) in the related compound $[\text{RhCl}_2(\text{PPr}_3)_2]$\cite{8}.

A routine DFT approach on the BP86/def2-TZVP level of theory, including Grimme’s D3 van der Waals correction, confirmed the X-ray analysis within generally acceptable deviations of atomic distances and bond angles (Table 2). At this level, the singly occupied MO (SOMO) was the d(z$^2$) and Rh-d(xy) configuration as the first excited state ($\text{root } 1$), about 4000 cm$^{-1}$ above the ground state. Geometry optimization (BP86/def2-TZVP, D3) of the excited-state configuration showed, in agreement with Harlow’s considerations,\cite{8} a longer Rh–Cl bond together with an almost unaltered Rh–P distance (Table 2).

### Table 2. Distances /Å and angles /° for 2. DFT calculations on the BP86/def2-TZVP level of theory. GS: ground state; root 1: first excited state in a TDDFT approach; 5000 K: temperature used for Fermi smearing in a finite-temperature DFT calculation.

<table>
<thead>
<tr>
<th></th>
<th>Rh–Cl</th>
<th>Rh–P</th>
<th>P–Rh–Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>2.3094(7)</td>
<td>2.4074(7)</td>
<td>92.35(1)</td>
</tr>
<tr>
<td>DFT (GS)</td>
<td>2.295</td>
<td>2.384</td>
<td>92.15</td>
</tr>
<tr>
<td>DFT (root 1)</td>
<td>2.339</td>
<td>2.382</td>
<td>92.90</td>
</tr>
<tr>
<td>DFT (GS, 5000 K)</td>
<td>2.323</td>
<td>2.450</td>
<td>92.32</td>
</tr>
</tbody>
</table>

(1) A TDDFT calculation on the TPSSh/def2-TZVP level revealed the d(z$^2$)d(xy)$^2$ configuration as the first excited state (“root 1”), about 4000 cm$^{-1}$ above the ground state. Geometry optimization (BP86/def2-TZVP, D3) of the excited-state configuration showed, in agreement with Harlow’s considerations,\cite{8} a longer Rh–Cl bond together with an almost unaltered Rh–P distance (Table 2).

(2) As an entry to a correlated treatment, Grimme’s fractional-occupation-number-weighted density (FOD) was calcu-
labeled.[13] As a result, the molecular orbitals with Rh-d contributions showed marked static correlation in terms of their FOD values. Specifically, FODs decreased in the order d(\(xz\)) > d(\(z^2\)) > d(\(xy\)) on the TPSS/def2-TZVP level, and d(\(z^2\)) > d(\(xz\)) > d(\(xy\)) on the BHLYP/def2-TZVP level (both methods were employed using the recommended smearing temperatures, 5000 K and 15000 K, respectively). In addition to the calculation of FODs with the BP86/def2-TZVP-ground-state geometry, the structural parameters were optimized in a finite-temperature approach on the TPSS/def2-TZVP level of theory (Table 2).

(3) Attempts to use the CASSCF method next were impeded by both the size of the entity in question and rotations of metal orbitals to pure ligand MOs in the course of preliminary calculations. Since multideterminantal methods appear as adequate in terms of the FOD analysis, we thus switched to a truncated hypothetical model compound with two trimethylphosphane ligands instead of the bis(tert-butyl)phenyldiphosphane ligands of 2 at this point (MOs of this model complex see Figure S2, Supporting Information, and cartesian coordinates from a BP86/def2-TZVP optimization see Tables, Supporting Information).

(4) The truncation of the bulky phosphane ligands in 2 to trimethylphosphane appears to be a rather conservative step in terms of the Rh–Cl distance (2.296 Å) and the P–Rh–Cl angles (92.5° for the obtuse angle) on the BP86/def2-TZVP(+D3) level. The distance from the central rhodium atom to the phosphorus atom of the smaller phosphane model decreased to 2.317 Å. The single spin resides in a d(\(z^2\))/d(\(xz\)) linear combination. Starting from this structure, single-point CASSCF calculations converged in a small (7,5) active space (7 electrons in 5 orbitals). The extension to a second shell for rhodium converged as well CASSCF(7,10). Inclusion of dynamic correlation in a subsequent NEVPT2 step succeeded. However, the search for excitations results in only few low-lying excited states, which mirrored the multiconfigurational character of the system, and excitations to the far UV. In other words, the substance appeared to be colorless at this point. This situation changed after inclusion of the next occupied molecular orbital to a (9,11) active space. The additional MO was a Rh–P σ-bond with largely ligand and minor Rh-p, character. Attempts to further enlarging the active space failed due to convergence problems with the practically inactive additional orbitals. The multiconfigurational character of the species is mirrored in the d orbital population. Thus, Löwdin reduced active MOs are populated by 1.95, 1.59, 1.57, 1.55, 0.76 electrons in the order: Rh–P σ-bond, Rh-d-\(yz\), xy, \(z^2\), \(xz\), \(x^2\)-\(y^2\). These values result in Mulliken spin densities of the MOs with mainly Rh character to the \(z^2\)-bond to the d subshell to fill the \(xz\)/\(z^2\) hole. With this assignment, the interpretation of a TDDFT calculation was straightforward. At the TPSSh/def2-TZVP level of theory, the Rh–P-σ-bond-to-\(xz\)/\(z^2\) transition appeared at 17078 cm\(^{-1}\) (586 nm).

(5) For 2, the same transition was found at lower energy (first entry in Table 1). With this fixed point, other TDDFT transitions were assigned with the result that all of these resemble excitations from low-lying MOs with mainly ligand character to the \(β\)-LUMO. Hence, the color of 2 is a result of LMCT processes instead of d–d transitions within the open d subshell. It should be noted eventually, that the ESR analysis by van Gaal et al.[12] of a mixed d(\(xy\))/d(\(z^2\)) occupation with three electrons was fully substantiated in the course of the various calculations.

Conclusions

A new representative of the rare class of mononuclear paramagnetic rhodium(II) complexes, trans-[RhCl(\(t\)Bu\(_2\)PPh)]\(_2\) (2), was synthesized and characterized in a combined experimental and computational approach. The structure was determined by means of single-crystal X-ray diffractometry. Despite the fact that an unpaired electron resides on the central rhodium atom, no Rh–Rh bonds were found. Instead, mononuclear, low-spin-d\(^7\) doublet central rhodium atoms were coordinated square-planarly by two \(t\)rans-chlorido and two phosphane ligands. Distances and angles were reproduced at an appropriate level of accuracy in a DFT calculation.

In addition, a wave-function-theory-based (WFT) treatment on a correlated level was performed on a truncated model complex. As a result, the ground state of 2, as has been recognized decades ago in the course of EPR measurements, is multiconfigurational and, thus, is adequately described by a CASSCF(9,11) calculation with a subsequent NEVPT2 approach. The introduction of dynamic correlation in the latter step revealed necessary for the assignment of a typical electronic excitation in the visible region. Based on the WFT analysis, more transitions in a TDDFT calculation were assigned. In fact, all the transitions were of the LMCT type. They all start in ligand-based MOs and end in the complex’s \(β\)-LUMO, the Rh-d(\(xz\))/d(\(z^2\)) orbital. In solutions of 2, the NMR spectroscopic results indicated a dynamic equilibrium between 2, a hypothetical dinuclear Rh\(^{II}\) species \([\{\text{Rh}(\mu-\text{Cl})\text{-Cl}\text{(tBu}_2\text{PPh)}\}_2]\), and the free ligand /Bu\(_2\)PPh. Attempts to isolate the tentative dinuclear species from the solution were unsuccessful so far. Efforts in this direction will be the subject of our future work.

Experimental Section

General: All preparative work was carried out in a dry nitrogen atmosphere using standard Schlenk techniques. Chemicals were purchased from Sigma/Aldrich and used as received. \([\{\text{Rh}(\mu-\text{Cl})\text{(co}e)_2\}\] was prepared according to the literature procedure.[14] NMR spectra were recorded with a Jeol Eclipse 400 instrument operating at 400 MHz (\(^1\)H) and at 162 MHz (\(^31\)P). Chemical shifts are given in ppm relative to TMS (\(^1\)H) and 85 % H\(_3\)PO\(_4\) (\(^31\)P). \(^{31}\)P NMR MAS spectra were prepared according to the literature procedure.[14]
recorded with a Bruker Avance-III 500 spectrometer using a Larmor frequency of $v_{LH}(^{31}P) = 202.5$ MHz. For the measurements a commercial 2.5 mm MAS probe was used. UV/Vis spectra were recorded with a Varian Cary 50 spectrometer. The ESR spectra were acquired with a Bruker EMX-Nano X-band EPR instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

Orca4 was used for all computations. The methods as well as the basis set def2TZVP were used as integrated in Orca. In the DFT part, Grimme’s D3 van der Waals correction was applied, but no solvent model was used.

### Synthesis of trans-[RhCl₂(tBu₂PPh)₂] (2): To a solution of 1 (180 mg, 0.25 mmol) in THF (5 mL) tBu₂PPh (0.24 mL, 1 mmol) was added at room temperature with stirring. After 10 min N-chlorosuccinimide (70 mg, 0.5 mmol) was added and the solution stirred at room temperature for 2 h. During this time the color of the solution changed from orange to dark-red and a green-blue powder precipitated. The powder was filtered off and washed twice with diethyl ether (10 mL) and dried in vacuo. The product was recrystallized from 10 mL of hot THF. Standing overnight at room temperature afforded well-shaped dark red crystals suitable for X-ray diffraction. Yield: 120 mg (39 %). C₂₈H₄₆Cl₂P₂Rh (618.43): C 54.15 (calcd. 54.38); H 7.35 (7.50); Cl 11.19 (11.47) %.

### Crystal Structure Determination and Refinement:

Crystals of C₂₈H₄₆Cl₂P₂Rh (0.24 mL, 1 mmol) were dissolved in 10 mL and dried in vacuo. The product was recrystallized from orange to dark red-brown and a green-blue powder precipitated. The powder was filtered off and washed twice with diethyl ether (10 mL) and dried in vacuo. The product was recrystallized from 10 mL of hot THF. Standing overnight at room temperature afforded well-shaped dark red crystals suitable for X-ray diffraction. Yield: 120 mg (39 %). C₂₈H₄₆Cl₂P₂Rh (618.43): C 54.15 (calcd. 54.38); H 7.35 (7.50); Cl 11.19 (11.47) %.

UV/Vis (CD₂Cl₂): 571 nm.

### Acknowledgements

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### Supporting Information

ESR spectra and details of computational analysis.

### Keywords:
Crystal structure; DFT calculations; Phosphane complexes; Rhodium

### References


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