Synthesis, Molecular Structure, and Reactivity toward Ethene of a Carbenerhodium(I) Complex Containing a Chelating Bisphosphine

Thomas Pechmann, Carsten D. Brandt, and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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*Summary: Reaction of trans-[RhCl(=CPh$_2$)(SbiPr$_3$)$_2$] (**2**) with 1,2-C$_2$H$_4$(PtBu$_2$)$_2$ (dtbpe) afforded the chelate complex [RhCl(=CPh$_2$)(κ^2-dtbpe)] (**3**), the structure of which was determined crystallographically. Treatment of **3** with ethene gave besides [Rh(dtbpe)(μ-Cl)]$_2$ a mixture of C$_3$H$_4$Ph$_2$ isomers with 1,1-diphenylcyclopropane as the dominating species.*

Introduction

In attempting to prepare the carbene complex *trans*-[RhCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (**1**) as the parent member of the series of rhodium(I) compounds with the general composition *trans*-[RhCl{=C(=C)$_n$Ph$_2$}(P*i*Pr$_3$)$_2$] (n = 1,[1] 2,[2] and 4[3]) we reacted the dimer [Rh(P*i*Pr$_3$)$_2$(μ-Cl)]$_2$ with Ph$_2$CN$_2$, but instead of **1** isolated the diazoalkane derivative *trans*-[RhCl(N$_2$CPh$_2$)(P*i*Pr$_3$)$_2$] in excellent yield.[4] The successful route to obtain compound **1** was to prepare in the initial step the bis(stibine) complex *trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (**2**) from *trans*-[RhCl(C$_2$H$_4$)(Sb*i*Pr$_3$)$_2$] and Ph$_2$CN$_2$ and then displace the two stibine for two phosphine ligands.[5]

The rich chemistry offered by both **1** and **2**, in particular the high reactivity toward nucleophiles,[5,6] tempted us to find out whether the stibine ligands of compound **2** can also be substituted by a chelating bis(phosphine) and, if so, whether the modified stereochemistry has an impact on the reactivity of the new complex, e.g., toward ethene. The present note provides an answer to these questions.

Results and Discussion

In the context of our studies on ruthenium carbenes and vinylidenes,[7] we recently reported that both [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] and [RuCl$_2$(=C=CHPh)(P*i*Pr$_3$)$_2$] react with 1,2-C$_2$H$_4$(PCy$_2$)$_2$ (dcpe) by displacement of the two monodentate phosphines by the bis(phosphine) and formation of the corresponding chelate complexes [RuCl$_2$(=CHPh)(dcpe)] and [RuCl$_2$(=C=CHPh)(dcpe)], respectively.[8] With this experience in mind, we treated the bis(stibine) derivative **2** in dichloromethane with an equimolar amount of dcpe at both 0 and 25 °C and obtained in either case a mixture of products, among which the starting material **2**, the dimer [Rh(dcpe)(μ-Cl)]$_2$,[9] the chelate complex [Rh(dcpe)$_2$]Cl,[10] and an unknown compound could be detected by NMR spectroscopy. Working at lower temperatures did not alter the result. If a 2-fold excess of dcpe was used, the starting material was completely consumed and a mixture consisting mainly of [Rh(dcpe)$_2$]Cl and the unknown compound was formed. Although the ^{31}P NMR data of the latter with two doublets-of-doublets (both broadened) at δ 77.1 [J(Rh,P) = 198.3, J(P,P) = 28.0 Hz] and δ 63.8 [J(Rh,P) = 81.4, J(P,P) = 28.0 Hz] indicated that the required complex [RhCl(=CPh$_2$)(dcpe)] could have been generated, the attempts to separate the products either by column chromatography or by fractional crystallization failed.

Taking these results and the observation that compound **2** reacts with 1,2-C$_2$H$_4$(PPh$_2$)$_2$ (dppe) to give only [Rh(dppe)$_2$]Cl[11] into consideration, we decided to employ a bis(phosphine) which is even more bulky than dcpe. The matter of choice was 1,2-C$_2$H$_4$(P*t*Bu)$_2$ (dtbpe), for

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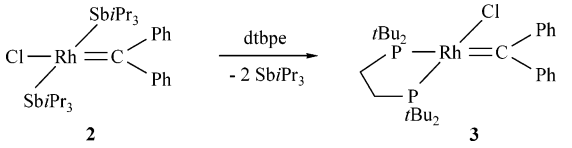
Scheme 1



2 3

which the cone angle according to Tolman is 184°.[12] There were some reports in the literature illustrating[13−16] that this bis(phosphine) represents an appropriate tool to stabilize ligand−metal fragments which with less bulky chelating ligands would smoothly decompose.

The reaction of **2** with a slight excess of dtbpe in benzene at room temperature is quite fast and affords, after removal of the solvent and recrystallization of the residue from toluene, the chelate complex **3** in 93% isolated yield (Scheme 1). The brown solid is moderately air-stable and readily soluble in benzene and dichloromethane. The most typical spectroscopic features are the ^{13}C NMR resonance for the carbene carbon atom at δ 355.1, being split into a doublet-of-doublets-of-doublets, and the two ^{31}P NMR signals at δ 96.5 and 72.6, showing a significantly different $^{103}Rh-^{31}P$ coupling. The ^{31}P NMR data of **3** are similar to those of [RhCl(CO)(κ^2-dcpe)][10] and [RhCl(CO)(κ^2-dppe)],[17] which is in agreement with the analogous stereochemistry.

The molecular structure of **3** is shown in Figure 1. Single crystals were grown from toluene and contain half a molecule of $C_6H_5CH_3$ in the unit cell. The coordination geometry around the rhodium center corresponds to a distorted square with bond angles along the P(1)−Rh−Cl and P(2)−Rh−C(1) axes of, respectively, 173.91(2)° and 171.70(8)°. The bond angle P(1)−Rh−C(1) deviates by ca. 9° from the 90° value, probably owing to the steric hindrance between the *tert*-butyl and the phenyl groups. The bite angle P(1)−Rh−P(2) is rather similar to that of other complexes with dtbpe as chelating ligand.[14a,15] The Rh−C(1) bond length of **3** is significantly longer (ca. 0.05 Å) than that of **1**,[5] which illustrates the strong *trans* influence of the *trans*-disposed P*t*Bu$_2$ unit. In contrast, the Rh−Cl distance of **3** is shorter than in **1**, being also a consequence of the different stereochemistry.

Similarly to **1**, also the chelate complex **3** reacts with ethene to form a mixture of 1:1 adducts of CPh_2 and C_2H_4. However, while the main product (ca. 90%) of the reaction of **1** with ethene is 1,1-diphenylpropene (formally built up by CPh_2 and $CHCH_3$, the isomer of ethene), the dominating species formed from **3** and C_2H_4 is the corresponding disubstituted cyclopropane (see

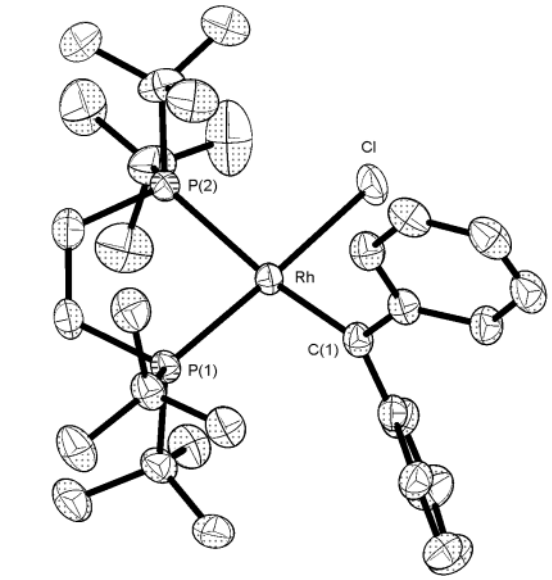
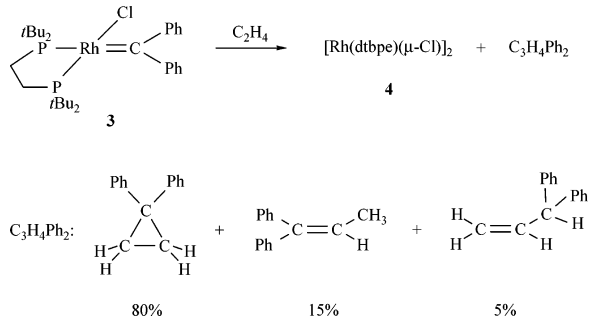


Figure 1. Perspective view of the molecular structure of **3** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh−Cl 2.4118(6), Rh−C(1) 1.925(2), Rh−P(1) 2.2829(6), Rh−P(2) 2.4306(6); P(1)−Rh−P(2) 86.54(2), P(1)−Rh−Cl 173.91(2), P(1)−Rh−C(1) 99.07(7), P(2)−Rh−Cl 89.63(2), P(2)−Rh−C(1) 171.70(8), C(1)−Rh−Cl 85.26(7).

Scheme 2



Scheme 2). The isomeric 1,1- and 3,3-diphenylpropenes are generated in smaller quantities. We note that in organic synthesis dinuclear rhodium(II) complexes such as [$Rh_2(\mu$-$O_2CCH_3)_4$] and derivatives thereof are used as excellent catalysts for the formation of cyclopropanes from olefins and diazoalkanes, other C−C coupling products being of minor importance.[18] Although in these reactions carbenerhodium compounds have generally been postulated as intermediates, evidence for their formation is still lacking.

In summarizing we confirmed that besides the numerous compounds of the general composition *trans*-[RhCl(=CRR′)(L)$_2$], with L mainly PR_3, also a four-coordinate carbenerhodium(I) complex with a *cis*-disposed RhCl(=CRR′) unit is accessible. The different stereochemistry between *trans*-[RhCl(=CPh_2)(P*i*Pr_3)$_2$] (**1**) and [RhCl(=CPh_2)(κ^2-dtbpe)] (**3**) is reflected not only in some of the NMR parameters but also in the reactivity of the two compounds toward ethene. As already

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mentioned, the catalytic activity of both **1** and **3** in olefin metathesis (e.g., in ROMP of cyclooctene) is poor, which is possibly due to the effective shielding of the metal centers by the bulky phosphine ligands and the stability of the Rh−P bonds.

Experimental Section

All operations were carried out under argon using standard Schlenk techniques. The starting material **2** was prepared as described in the literature.[5] NMR spectra were recorded on a Bruker AMX 400 instrument. Abbreviations used: s, singlet; d, doublet; m, multiplet. GC/MS measurements were carried out using a Hewlett-Packard GCD instrument. Melting point was determined by DTA.

Preparation of [RhCl(=CPh$_2$)(κ^2-dtbpe)] (3). A solution of **2** (84 mg, 0.11 mmol) in benzene (30 mL) was treated with dtbpe (53 mg, 0.17 mmol) and stirred for 30 min at room temperature. A rapid change of color from dark green to brown occurred. The solvent was evaporated in vacuo, and the residue was washed three times with pentane (5 mL each) and then dissolved in toluene (5 mL). After the solution was stored at −25 °C for 2 days, brown crystals precipitated, which were separated from the mother liquor, washed with pentane (3 mL), and dried: yield 61 mg (93%); mp 108 °C dec. Anal. Calcd for $C_{31}H_{50}ClP_2Rh\cdot 1/2C_7H_8$: C, 61.93; H, 8.13. Found: C, 62.16; H, 8.07. ^{1}H NMR (400 MHz, C_6D_6): δ 7.87 (m, 4H, *ortho*-H of C_6H_5), 7.25 (m, 2H, *para*-H of C_6H_5), 7.07 (m, 4H, *meta*-H of C_6H_5), 1.50 (d, 18H, J(P,H) = 11.7 Hz, PCCH_3), 1.42, 1.23 (both m, 4H, C_2H_4), 0.97 (d, 18H, J(P,H) = 12.6 Hz, PCCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 355.1 (ddd, J(P,C) = 95.3, J(Rh,C) = 31.8, J(P′,C) = 5.1 Hz, *C*Ph$_2$), 159.7 (d, J(P,C) = 1.9 Hz, *ipso*-C of C_6H_5), 129.4, 128.3, 127.9 (all s, C_6H_5), 37.3 (dd, J(P,C) = 16.5, J(Rh,C) = 2.6 Hz, P*C*CH$_3$), 35.9 (d, J(P,C) = 6.4 Hz, P*C*CH$_3$), 31.2 (d, J(P,C) = 4.8 Hz, PC*C*H$_3$), 30.3 (d, J(P,C) = 4.8 Hz, PC*C*H$_3$), 26.3, 20.4 (both m, P(CH$_2$)$_2$P). ^{31}P NMR (162.0 MHz, C_6D_6): δ 96.5 (dd, J(Rh,P) = 183.1, J(P,P) = 23.7 Hz), 72.6 (dd, J(Rh,P) = 81.4, J(P,P) = 23.7 Hz).

Reaction of 3 with Ethene. A slow stream of ethene was passed through a solution of **3** (19 mg, 0.03 mmol) in benzene (5 mL) for 1 min at room temperature. After the solution was warmed at 50 °C and stirred for 10 h, it was cooled to 20 °C, and then the solvent was removed. The ^{31}P NMR spectrum of the residue revealed that as the rhodium-containing product only the dimer [Rh(dtbpe)(μ-Cl)]$_2$ (**4**) was formed.[12] The residue was suspended in pentane (2 mL), and the suspension was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 10 cm). With pentane, an off-white fraction was eluted, which was shown by GC/MS to contain a mixture of 1,1-diphenylcyclopropane (ca. 80%), 1,1-diphenylpropene (ca. 15%), and 3,3-diphenylpropene (ca. 5%).

X-ray Structural Analysis of 3. Single crystals were grown from toluene at −25 °C; they contain one-half of a molecule of toluene in the unit cell. Crystal data (from 8180 reflections, 2.303° < θ < 28.759°): monoclinic, space group *C*2/*c* (No. 15), a = 28.5222(16) Å, b = 16.4719(9) Å, c = 16.7660(9) Å, β = 119.7420(10)°, V = 6839.3(6) Å^3, Z = 8, D_{calcd} = 1.300 g cm^{-3}, T = 173(2) K, μ(Mo Kα) = 0.692 mm^{-1}, crystal size 0.27 × 0.23 × 0.22 mm. Solution details: Stoe IPDS diffractometer using ω-scan mode ($2\theta_{max}$ = 52.74°); 54 547 reflections scanned, 7000 unique [R(int) = 0.0241], 6613 observed ($I > 2\sigma(I)$); intensity data corrected by Lorentz and polarization effects; direct methods (SHELXS-97);[19] atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms refined by full-matrix least squares on F^2 (SHELXL-97);[20] 362 parameters refined to give R_1 = 0.0351 and wR_2 = 0.0932 with a reflex/parameter ratio of 19.34 and a residual electron density +1.405/−509 e Å^{-3}.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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