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## Rhodium pincer complexes of 2,2'-bis(diphenylphosphino)diphenylamine

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Dedicated to Professor H. Werner on the occasion of his 70th birthday

### Abstract

The novel pincer ligand 2,2'-bis(diphenylphosphino)diphenylamine (**1**) has been synthesized by treatment of 2,2'-dibromodiphenylamine with *n*-butyl lithium and subsequent reaction with diphenylchlorophosphine. When ligand **1** is treated with RhCl<sub>3</sub> hydrate the dinuclear complex **1a** forms which can be converted into the square planar carbonyl complex **1c** upon reduction with Na/Hg in the presence of CO. Depending on the reaction conditions two different complexes were isolated when **1** reacts with [(COE)<sub>2</sub>RhCl]<sub>2</sub>. In THF the hydrochloro complex **1b** and with *n*-butyl lithium the COE complex **1d** is generated. Interestingly, the formation of **1b** represents a rare case of N–H oxidative addition to a late transition metal complex fragment. Compound **1c** is observed upon reaction of the COE complex **1d** with carbon monoxide. Quantum chemical calculations at different levels of theory are in good agreement with the experimental structure of **1c**.

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**Keywords:** PNP pincer ligand; Rhodium complexes; N–H oxidative addition; Quantum chemical calculations

### 1. Introduction

Tridentate pincer ligand complexes [1–8] are versatile reagents with promising applications in the areas of sensors [9], catalysis [10,11], and dendrimer synthesis [12]. Most of these compounds have a central anionic atom (N, C, Si [13]) or functional group and a variety of donor atoms (N, S, O, P) which coordinate the metal atom to the ligand backbone. In this paper we report on the synthesis of nitrogen based pincer complexes and the

X-ray structure of Rh(CO){N[(*o*-PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>} (**1c**). The experimental structural analysis was supplemented by the results of various density functional calculations. The hybrid amine phosphine tridentate ligand **1** was chosen to study the effect of an amide ligand on the chemistry of low valent late transition metals. The amine is positioned between two diphenylphosphine groups in order to take advantage of the strong metal binding properties of the phosphines. The chelate effect of the ligand prevents the dissociation of the highly electron rich amide from an electron rich low valent late transition metal. Furthermore, the ortho derivatized diphenyl amine does not contain β hydrogens which could transfer onto the metal and lead to decomposition of the amide.

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## 2. Experimental

### 2.1. General remarks, materials, and instrumentation

Reactions were performed under Ar using standard Schlenk techniques according to previously described procedures [14,15] unless otherwise specified.

Benzene, hexane and etheral solvents were distilled from benzophenone ketyl,  $\text{CH}_2\text{Cl}_2$  from  $\text{LiAlH}_4$ , MeOH, EtOH and toluene from sodium. Deuterated solvents were degassed and distilled from  $\text{LiAlD}_4$ .  $[(\text{COE})_2\text{RhCl}]_2$  was prepared according to the procedure of Van der Ent and Onderdelinden [16]. 2,2'-Dibromodiphenylamine was prepared according to the procedure described by Jones and Mann [17]. **Note!** We found that a temperature of 255–265 °C was necessary for the Chapman rearrangement to occur.

### 2.2. Synthesis of 2,2'-bis(diphenylphosphino)diphenylamine $\text{HN}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2$ (**1**)

Under a nitrogen atmosphere 58 ml (97.44 mmol) of *n*-butyl lithium (1.68 M in hexane) was added dropwise to 9.9 g (30.09 mmol) of 2,2'-dibromodiphenylamine in 50 ml  $\text{Et}_2\text{O}$  at 0 °C. The reaction mixture was allowed to stir for 1.5 h. 17.5 ml (97.48 mmol) diphenylchlorophosphine in 50 ml  $\text{Et}_2\text{O}$  were added dropwise at 0 °C and the solution was stirred at room temperature (r.t.) overnight. The reaction mixture was then hydrolyzed with 30 ml of concentrated hydrochloric acid, the solution washed with water, and the product precipitated with EtOH. The colorless 2,2'-bis(diphenylphosphino)diphenylamine (**1**) can be purified by recrystallization from  $\text{CH}_2\text{Cl}_2$  and EtOH. Yield: 7.8 g (48.3%). m.p. 200–201 °C. Anal. Calc. for  $\text{C}_{36}\text{H}_{29}\text{NP}_2$ : C, 80.44; H, 5.44; N, 2.61. Found: C, 80.29; H, 5.53; N, 2.62%.  $^1\text{H-NMR}$  (500.12 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.67 (dd,  $^2J_{\text{HH}} = 7.5$  Hz, 7.5 Hz, 2H,  $\text{H}_3$ ), 7.00 (m, 16H,  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_4$ ,  $\text{H}_6$ ), 7.31 (m, 11H, NH,  $\text{H}_5$ ,  $\text{H}_7$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (202.47 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -19.2 (s). IR (KBr pellet): 3340  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ ). MS (DCI):  $m/z$  538 ( $\text{M}^+$ ), Calc. 537.58.  $m/z$  532 [ $\text{M} - \text{PPh}_2^+$ ], Calc. 351.39.

### 2.3. Synthesis of $\text{Rh}_2\text{Cl}_4\{\text{HN}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}$ (**1a**)

A solution of 198 mg (0.83 mmol)  $\text{RhCl}_3$  hydrate (42.9% Rh) and 481 mg (0.89 mmol) 2,2'-bis(diphenylphosphino)diphenylamine (**1**) in 50 ml MeOH was refluxed under a nitrogen atmosphere for 18 h. A yellow precipitate forms which can be isolated by filtration, washing with hexane, and recrystallization from  $\text{CH}_2\text{Cl}_2$ –hexane. The crystals formed quickly turn to a powder when removed from the mother liquor. Yield: 316 mg (84.7%). Anal. Calc. for  $\text{C}_{36}\text{H}_{29}\text{Cl}_4\text{NP}_2\text{Rh}_2$ : C, 48.82; H, 3.30. Found: C, 48.83; H 3.23%.  $^1\text{H-NMR}$

(500.12 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  6.78 (m, 4H,  $\text{PPhPh}' \text{H}_6$ ), 7.01 (m, 4H,  $\text{PPhPh}' \text{H}_5$ ), 7.13 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H,  $\text{PPhPh}' \text{H}_7$ ), 7.36 (m, 4H,  $\text{PPhPh}' \text{H}_6$ ), 7.46 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2H,  $\text{PPhPh}' \text{H}_7$ ), 7.50 (m, 2H,  $\text{H}_3$ ), 7.58 (m, 2H,  $\text{H}_4$ ), 7.72 (m, 2H,  $\text{H}_2$ ), 7.93 (m, 4H,  $\text{PPhPh}' \text{H}_5$ ), 8.04 (m, 2H,  $\text{H}_1$ ), 8.30 (s, br, 1H, NH).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (121.4 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  37.1 (d,  $^1J_{\text{RHP}} = 115.8$  Hz). MS (DCI):  $m/z$  674 ( $\text{RhCl}\{\text{HN}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}^+$ ), Calc. 674.91;  $m/z$  639 ( $\text{Rh}\{\text{HN}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}^+$ ), Calc. 639.48. UV–vis ( $\text{CH}_2\text{Cl}_2$ ):  $\epsilon_{236} = 2.70 \times 10^4$ ,  $\epsilon_{270} = 2.51 \times 10^4$ ,  $\epsilon_{394} = 1530$ .

### 2.4. Synthesis of $\text{Rh}(\text{H})(\text{Cl})(\text{THF})\{\text{N}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}$ (**1b**)

A suspension of 86 mg (0.02 mmol)  $[(\text{COE})_2\text{RhCl}]_2$  and 138 mg (0.26 mmol) 2,2'-bis(diphenylphosphino)diphenylamine (**1**) in 25 ml THF was stirred at r.t. for 3.5 h and refluxed for 4 h. After vacuum removal of the solvent and dissolution in 3 ml toluene the product precipitates as a yellow solid. Yield: 44 mg (24.7%). Anal. Calc. for  $\text{C}_{40}\text{H}_{37}\text{ClINOP}_2\text{Rh}$ : C, 64.28; H, 4.99; N, 1.87. Found: C, 64.07; H, 5.10; N, 1.81%.  $^1\text{H-NMR}$  (500.12 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -21.77 (dt,  $^1J_{\text{RH}} = 29.5$  Hz,  $^2J_{\text{PH}} = 11.4$  Hz, 1H, Rh-H), 1.64 (m, br, 4H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.52 (m, br, 4H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 6.61 (m, 2H,  $\text{H}_3$ ), 7.06 (m, 2H,  $\text{H}_2$ ), 7.46 (m, 14H,  $\text{H}_4$ ,  $\text{H}_6$ ,  $\text{H}_7$ ), 7.64 (m, 4H,  $\text{H}_5$ ), 7.69 (m, 2H,  $\text{H}_1$ ), 7.94 (m, 4H,  $\text{H}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (121.4 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  35.1 (d,  $^1J_{\text{RHP}} = 108.8$  Hz).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.76 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  25.8 (s,  $\text{CH}_2\text{CH}_2\text{O}$ ), 68.4 (s,  $\text{CH}_2\text{CH}_2\text{O}$ ), 118.0 (m), 118.1 (s), 128.9 (m), 129.1 (m), 130.5 (s), 131.1 (s), 131.4 (s), 133.6 (m), 134.7 (m), 135.4 (s). MS (DCI):  $m/z$  674 [ $\text{M} - \{\text{H} + \text{THF}\}^+$ ], Calc. 674.89;  $m/z$  639 ( $\text{Rh}\{\text{N}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}^+$ ), Calc. 639.48.

### 2.5. Synthesis of $\text{Rh}(\text{CO})\{\text{N}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}$ (**1c**)

#### 2.5.1. Method A

40 mg (0.05 mmol) of  $\text{Rh}_2\text{Cl}_4\{\text{HN}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}$  (**1a**) were added to sodium amalgam prepared from 25  $\mu\text{l}$  (1.69 mmol) mercury and 5 mg (0.23 mmol) sodium. 20 ml of THF were added and the flask was flushed with carbon monoxide. The reaction mixture was stirred vigorously for 18 h at r.t. The solid was allowed to settle and the solution was filtered in air. The air stable yellow product is obtained by removal of the solvent in vacuo, and recrystallized from  $\text{CH}_2\text{Cl}_2$ –hexane. Yield: 18 mg (60%).

#### 2.5.2. Method B

25 mg (0.03 mmol)  $\text{Rh}(\text{COE})\{\text{N}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}$  (**1d**) were dissolved in 30 ml benzene and left under one atmosphere of carbon monoxide for several hours at r.t.  $\text{Rh}(\text{CO})\{\text{N}[(o\text{-PPh}_2)\text{C}_6\text{H}_4]_2\}$  (**1c**) precipitated as a yellow powder. Yield: 100% (based on  $^{31}\text{P}\{^1\text{H}\}$ -NMR).

Anal. Calc. for  $C_{37}H_{28}NOP_2Rh$ : C, 66.59; H, 4.23. Found: C, 66.30; H, 4.06%.  $^1H$ -NMR (500.12 MHz,  $C_6D_6$ ):  $\delta$  6.43 (m, 2H,  $H_3$ ), 6.96 (m, 14H,  $H_2$ ,  $H_6$ ,  $H_7$ ), 7.13 (m, 2H,  $H_4$ ), 7.76 (ddd,  $^3J_{PH} = 12.5$  Hz,  $^3J_{HH} = 6.5$  Hz,  $^4J_{RhH} = 1.5$  Hz, 8H,  $H_5$ ), 7.81 (m, 2H,  $H_1$ ).  $^{31}P\{^1H\}$ -NMR (121.4 MHz,  $C_6D_6$ ):  $\delta$  41.8 (d,  $^1J_{RhP} = 135.1$  Hz). MS (DCI):  $m/z$  667 [ $M^+$ ], Calc. 667.49;  $m/z$  639 ( $Rh\{N[(o-PPh_2)C_6H_4]_2\}^+$ ), Calc. 639.48. IR (KBr pellet):  $1960\text{ cm}^{-1}$  ( $\nu_{CO}$ ). UV-vis ( $CH_2Cl_2$ ):  $\epsilon_{240} = 3.96 \times 10^4$ ,  $\epsilon_{318} = 1.93 \times 10^4$ ,  $\epsilon_{345} = 1.67 \times 10^4$ ,  $\epsilon_{386} = 12.9 \times 10^4$ ,  $\epsilon_{580} = 184$ ,  $\epsilon_{654} = 126$ .

## 2.6. Synthesis of $Rh(COE)\{N[(o-PPh_2)C_6H_4]_2\}$ (**1d**)

A solution of 159 mg (0.29 mmol) lithium 2,2'-bis(diphenylphosphino)diphenylamide in 20 ml toluene was added dropwise to a solution of 102 mg (0.14 mmol)  $[(COE)_2RhCl]_2$  in 20 ml toluene at  $15^\circ C$ . The reaction mixture was stirred at r.t. for 90 min, the volatiles were removed in vacuo and the residue dissolved in 10 ml of toluene. The solution was concentrated to approximately 3 ml, filtered and the filtrate dried in vacuo. The product forms as a fine orange powder. Yield: 70 mg (32.9%).  $^1H$ -NMR (500.12 MHz,  $C_6D_6$ ): COE:  $\delta$  0.94 (m, 2H,  $CH_2$ ), 1.24 (m, 8H,  $CH_2$ ), 2.26 (m, 2H,  $CH_2$ ), 3.64 (m, br, 2H, =CH).  $N[(o-PPh_2)C_6H_4]_2$ :  $\delta$  6.43 (m, 2H,  $H_3$ ), 6.85 (m, 2H,  $H_2$ ), 7.04 (m, 12H,  $H_6$ ,  $H_7$ ), 7.23 (m, 2H,  $H_4$ ), 7.55 (m, 2H,  $H_1$ ), 7.97 (m, br, 8H,  $H_5$ ).  $^{31}P\{^1H\}$ -NMR (121.4 MHz,  $C_6D_6$ ):  $\delta$  38.8 (d,  $^1J_{RhP} = 148.3$  Hz).  $^{13}C\{^1H\}$ -NMR (125.76 MHz,  $C_6D_6$ ): COE:  $\delta$  26.6 (s,  $CH_2$ ), 31.8 (s,  $CH_2$ ), 32.0 (s,  $CH_2$ ), 68.5 (d,  $^1J_{RhC} = 11.3$  Hz, =CH),  $N[(o-PPh_2)C_6H_4]_2$ :  $\delta$  115.8 (m), 117.3 (m), 128.3 (s), 128.6 (m), 129.3 (s), 129.9 (s), 131.4 (s), 133.1 (s), 134.1 (m), 134.9 (m). MS (DCI):  $m/z$  749 [ $M^+$ ], Calc. 749.68;  $m/z$  639 ( $Rh\{N[(o-PPh_2)C_6H_4]_2\}^+$ ), Calc. 639.48.

## 2.7. X-ray structural analysis for $Rh(CO)\{N[(o-PPh_2)C_6H_4]_2\}$ (**1c**)

Crystal data:  $C_{37}H_{28}NOP_2Rh$ ,  $M = 667.45$ , orthorhombic, space group  $Fdd2$ ,  $a = 18.513(2)$ ,  $b = 32.643(4)$ ,  $c = 10.153(1)$ ,  $V = 6135.7(12)\text{ \AA}^3$ ,  $Z = 8$ ,  $T = 298\text{ K}$ ,  $\mu = 0.68\text{ mm}^{-1}$ , graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069\text{ \AA}$ ), yellow–orange skewed bipyramids with dimensions ca.  $0.47 \times 0.4 \times 0.3\text{ mm}$ , crystal mounted on a glass fiber with epoxy and transferred to a Blake Industries four-circle diffractometer,  $\theta$  range for data collection  $2\text{--}32.5^\circ$ , 2249 unique reflections with  $I > 3\sigma(I)$  of 3030 collected reflections and used for refinement of 199 parameters via least-squares method on  $|F|$ , final  $R(I > 3\sigma(I)) = 4.6$ ,  $R_w(I > 3\sigma(I)) = 5.5$ , GOF = 1.6. The structure was solved by a combination of direct and Patterson methods and Fourier syntheses using the crystallographic computing package by C.E. Strouse, Dep. of Chemistry, UCLA, Los Angeles, CA,

90024. Hydrogen atoms were located in the difference map and refined with fixed isotropic thermal parameters (see Section 5).

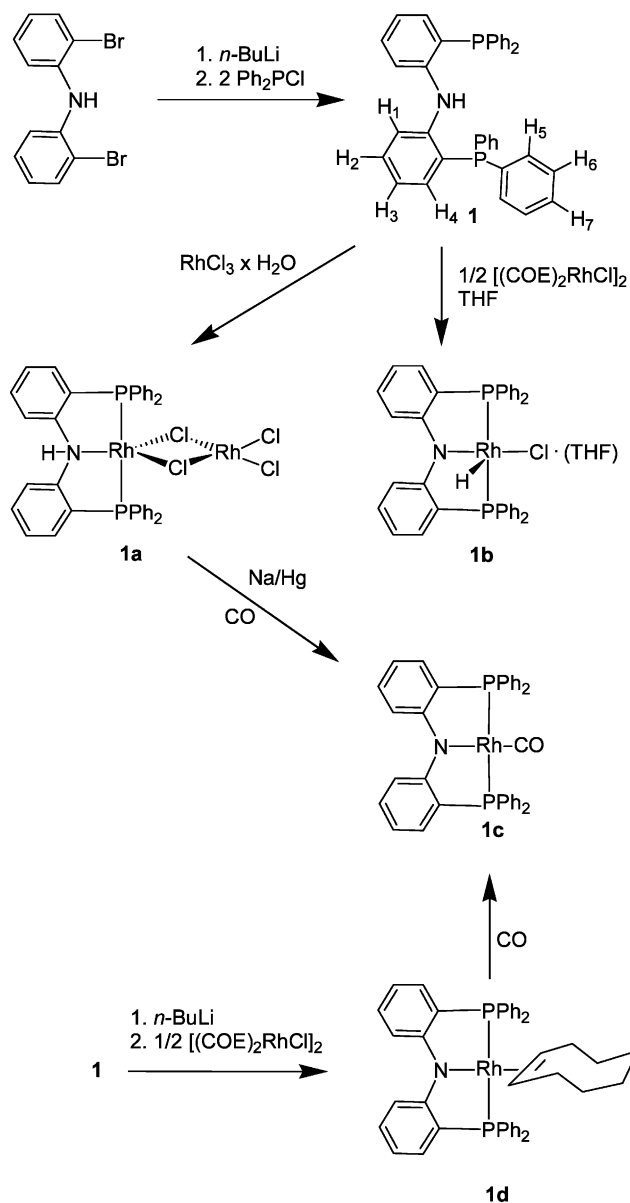
## 2.8. Quantum chemical calculations

Density functional (DFT) calculations for  $Rh(CO)\{N[(o-PPh_2)C_6H_4]_2\}$  (**1c**) were performed at various levels of theory using the program Jaguar 4.1 [18]. The geometric structure was optimized at the local density approximation (SVWN) [19,20] as well as with the gradient-corrected B3LYP [19–22] and B3GGA-II [19–24] functionals. For all calculations, the pseudo-potential LACVP\* basis set [25] was applied. In this basis, Rh is described by an effective core potential, whereas the outermost core orbitals are taken into account explicitly. For the other atoms in the compound considered here Pople's 6-31G\* basis set was used.

## 3. Results and discussion

The synthesis of  $HN[(o-PPh_2)C_6H_4]_2$  (**1**) was achieved by treatment of 2,2'-dibromodiphenylamine with *n*-butyl lithium to effect halogen metal exchange followed by the reaction of the lithio adduct with diphenylchlorophosphine (Scheme 1). Because the multiplets in the aromatic region of the  $^1H$ -NMR spectrum of the pincer ligand **1** appeared rather broad the NH proton could not be located. A singlet in the  $^{31}P\{^1H\}$ -NMR spectrum at  $-19.2$  ppm supports the formation of **1**. The highest molecular peak in the mass spectrum of **1** represents the ligand,  $HN[(o-PPh_2)C_6H_4]_2$ . This and the H, C, and N elemental analysis provide the positive information that two and not one of the diphenylphosphine groups are present in **1**.

Upon refluxing  $RhCl_3$  hydrate with **1** in methanol under an  $N_2$  atmosphere the air stable pale yellow dinuclear complex  $Rh_2Cl_4\{N[(o-PPh_2)C_6H_4]_2\}$  (**1a**) precipitated from the reaction mixture (Scheme 1). The NMR data are consistent with a plane of symmetry in **1a** which contains the NH unit, the two rhodium atoms, and the two bridging chlorides. Consequently the  $^1H$ -NMR spectrum of **1a** displays ten unique hydrogen multiplets which arise from the NH hydrogen, the four non-equivalent hydrogens on the aromatic rings of the ligand backbone, and the two pairs of non-equivalent phenyl groups of the diphenylphosphines. Also in agreement with this is the observation of only one doublet in the  $^{31}P\{^1H\}$ -NMR spectrum of **1a**. The phosphorus rhodium interaction of 116 Hz is very close to  $J_{RhP}$  of square pyramidal **1b**, a Rh(III) species, and is significantly smaller than  $J_{RhP}$  (135–148 Hz) for the square planar Rh(I) complexes **1c,d** prepared with ligand **1**. Although the highest molecular weight peak in the mass spectrum is generated by the  $RhCl\{N[(o-$



Scheme 1.

PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>)<sup>+</sup> fragment the elemental analysis confirms Rh<sub>2</sub>Cl<sub>4</sub>{N[(*o*-PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>} (**1a**).

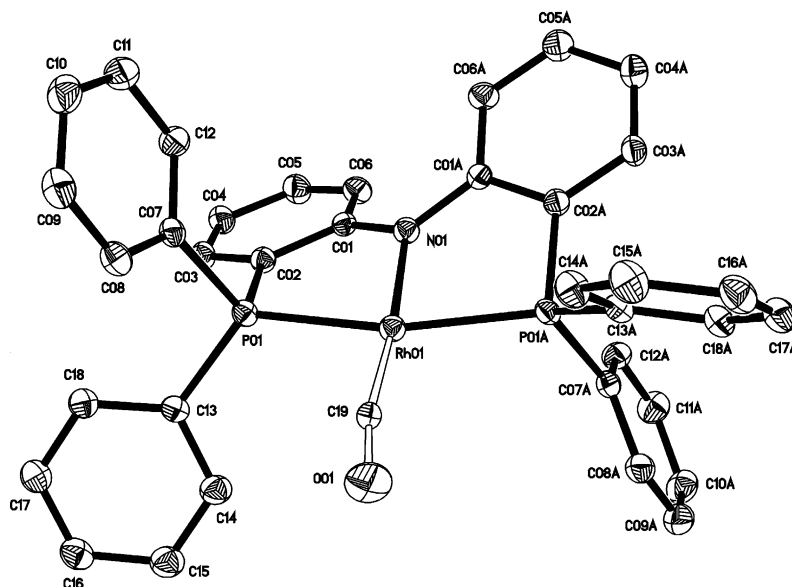
Reaction between the ligand **1** and [(COE)<sub>2</sub>RhCl]<sub>2</sub> in THF generates Rh(H)(Cl)(THF){N[(*o*-PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>} (**1b**) and requires a reaction time of 8 h for ideal product yield. By oxidative addition of the N–H bond to a rhodium complex fragment a square pyramidal complex is formed with the hydride located in the apical position. In addition one molecule of THF is weakly bound to the empty coordination site. The structure as shown in Scheme 1 is confirmed by <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}-, <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopy and mass spectrometry as well as by elemental analysis. A characteristic feature in the <sup>1</sup>H-NMR spectrum is the hydride resonance at δ –21.77 which is split into a doublet of triplets (<sup>1</sup>J<sub>RhH</sub> = 29.5 Hz,

<sup>2</sup>J<sub>PH</sub> = 11.4 Hz) by the interaction with rhodium and the two equivalent phosphine groups. Also one set of resonances due to one molecule of THF is observed in the <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra. Furthermore the <sup>1</sup>J<sub>RhP</sub> coupling constant of 108.8 Hz agrees well with a Rh(III) system. The formation of **1b** is a rare instance where chelate assisted oxidative addition of the N–H bond occurs with rhodium.

The yellow–orange pincer complex Rh(CO){N[(*o*-PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>} (**1c**) was synthesized by treating Rh<sub>2</sub>Cl<sub>4</sub>{N[(*o*-PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>} (**1a**) with Na/Hg in the presence of carbon monoxide in THF. A second method was direct treatment of Rh(COE){N[(*o*-PPh<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>} (**1d**) with CO. The yellow carbonyl product is stable in air as a solid and in solution. The carbonyl group cannot be removed with trimethylamine oxide or photolysis without decomposition of the complex. Addition of gaseous HCl decolorizes the yellow solution but removal of solvent under vacuum gives back the starting material.

The <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}- and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra are consistent with the structure represented in Scheme 1. The structural details supported by the NMR data were confirmed by an X-ray structural analysis illustrated in Fig. 1 and by quantum chemical calculations.

The coordination sphere of the rhodium atom is a slightly distorted square plane. The rhodium, nitrogen and phosphorus atoms lie in one plane with the phosphorus atoms pulled back toward the nitrogen atom thus forming a P–Rh–P angle of 163.8°. The carbonyl group is bent slightly away from the axis taking up one of the two possible positions related by the 180° rotation. The amide nitrogen atom is planar as required by symmetry. Some relevant structural parameters of **1c** as obtained by X-ray diffraction and density functional calculations (SVWN/LACVP\*, B3LYP/LACVP\*, B3GGA-II/LACVP\*) are compared in Table 1. The same distorted square-planar coordination geometry around rhodium as observed in the experiment is predicted by the computational procedures. The phosphorus atoms are bent away from the carbonyl group and an envelope configuration of the five-membered rings is obtained. The gas-phase calculations yield a C<sub>1</sub> molecular symmetry since free rotation of the phenyl groups is allowed, whereas in the crystal structure the phenyl groups arrange in a C<sub>2</sub> symmetry, according to the space group. However, due to the disorder of the CO ligand, the symmetry of an actual molecule is C<sub>1</sub>. In most cases, the bond lengths obtained using the B3GGA-II functional agree best with the X-ray diffraction values, whereas the B3LYP bond lengths are too long and the SVWN distances are too short. An exception is the C(19)–O(1) multiple bond, which is predicted by all calculations to be much longer than the experimentally observed value but within the relatively high error limits (3 sigma) for this disordered part. The

Fig. 1. ORTEP plot of  $\text{Rh}(\text{CO})\{\text{N}[(o\text{-PPh}_2)_2\text{C}_6\text{H}_4]_2\}$  (**1c**).

comparatively large deviation between experiment and theory observed for this distance is certainly due to the fact, that the lengths of multiple bonds in general are underestimated in X-ray structures. In any case, it is expected that geometrical parameters as obtained by ab initio calculations (which relate to the gas-phase equilibrium structure of a molecule at 0 K) would compare better to the results of a corresponding neutron diffraction or gas-phase electron diffraction analysis.

The bond angles for the more rigid part of the structure, as predicted by the SVWN and B3GGA-II functionals, are in good agreement with the experiment (within the experimental error limits). The overall agreement between the experimental crystal structure and the gas-phase structures as predicted by the theoretical procedures, especially by the B3GGA-II

functional, is satisfactory. The calculations, thus, confirm the experimental data.

The infrared stretching frequency of the CO ligand is  $1960\text{ cm}^{-1}$  which suggests significant  $\pi$ -bonding with the Rh atom. Although amide complexes of the early transition metals are well known [26], compounds with the late transition metals are not so common and thermally less stable [27]. Moreover,  $\pi$ -bonding of the filled metal orbitals with the filled  $2p_z$  nitrogen orbital is likely to be minimal. Single metal–nitrogen bond distances are expected to lie within  $1.95\text{--}2.15\text{ \AA}$ . The experimental Rh–N bond distance of  $2.074(9)\text{ \AA}$  as well as the theoretically calculated values for **1c** suggest that this bond is a single bond even though the planarity of the amide bond does not necessarily confirm whether  $\pi$ -bonding occurs between the rhodium and the nitrogen

Table 1

Relevant structural parameters of  $\text{Rh}(\text{CO})\{\text{N}[(o\text{-PPh}_2)_2\text{C}_6\text{H}_4]_2\}$  (**1c**) as obtained by X-ray diffraction and density functional calculations<sup>a</sup>

	X-ray	SVWN/LACVP*	B3LYP/LACVP*	B3GGA-II/LACVP*
Symmetry	$C_1$	$C_1$	$C_1$	$C_1$
<i>Bond lengths (Å)</i>				
Rh(1)–C(19)	1.855	1.818	1.863	1.845
Rh(1)–N(1)	2.074(9)	2.072	2.125	2.106
Rh(1)–P(1)	2.292(3)	2.256	2.333	2.307
Rh(1)–P(1A)		2.259	2.325	2.305
C(19)–O(1)	1.125(23)	1.168	1.163	1.162
<i>Bond angles (°)</i>				
P(1)–Rh(1)–P(1A)	163.8	165.7	162.5	162.7
C(19)–Rh(1)–N(1)	173.7	178.4	178.1	177.3
C(19)–Rh(1)–P(1)	95.0	97.2	98.0	98.5
C(19)–Rh(1)–P(1A)		96.9	98.0	97.8
C(1)–N(1)–C(1A)	122.5(7)	122.5	123.2	122.4
O(1)–C(19)–Rh(1)	167.0(40)	177.7	178.1	178.9

<sup>a</sup> For atom labeling see Fig. 1.

atom. Some  $\pi$ -bonding can occur in the complex  $\text{Cp}_2\text{Hf}(\text{H})(\text{NHMe})$  [28] which shows an amide unit planar with the Hf–N bond distance of 2.027 Å where the amide adopts a conformation favorable for  $\pi$ -bonding to the empty orbitals of the Hf atom.

Our calculations give no indications for an interaction between the  $\text{Np}_z$  orbital and the  $\text{d}_{yz}$  orbital of the Rh atom [29]. According to a Mulliken population analysis [30] (B3GGA-II) both nitrogen (–0.7 a.u.) and rhodium (–0.3 a.u.) carry a negative charge. This electron density distribution is consistent with the chemical reactivity of the complex, which shows heightened reactivity of the low valent rhodium atom toward oxidative addition reactions and the increased bond order of the rhodium carbonyl carbon bond where excess electron density can be channeled into the anti-bonding orbitals of the carbon atom.

Treatment of the lithium salt of **1** with  $[(\text{COE})_2\text{RhCl}]_2$  in toluene at r.t. gave the square planar complex **1d** (Scheme 1) as deduced from elemental analysis and spectroscopic data. The brownish orange complex **1d** is air sensitive and unstable in chlorocarbons but can be stored in solid form. CO readily displaces the cyclooctene ligand to give **1c** (see above).

#### 4. Conclusion

The special design of the new tridentate amine phosphine ligand (**1**) allows the synthesis of new pincer complexes. Interestingly, an oxidative addition of an N–H bond to a rhodium complex fragment has been observed. Obviously the chelate effect of the ligand is responsible for the formation of a stable low valent late transition metal amide complex.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 205266. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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