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Square planar diphosphinoazine rhodium(I) amido carbonyl complexes with an unsymmetrical PNP′ pincer-type coordination

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ABSTRACT

A series of novel diphosphinoazine rhodium amido carbonyl complexes [{$R_2PCH{=}C(Bu^t)$–NN=$C(Bu^t)CH_2PR_2$}Rh(CO)] (R = Ph, Pr^i, c-C_6H_{11}, Bu^t) was prepared by deprotonation of cationic diphosphinoazine rhodium amino carbonyl complexes. The complexes were characterized by NMR as were also their precursors. The crystal structures of two cationic and one neutral deprotonated complex were determined by X-ray diffraction showing the complexes to be essentially planar with mutual *trans* arrangement of phosphine groups and nitrogens *trans* to carbonyl ligands. Measurement of valence vibration frequencies of carbonyl groups in the complexes allowed to estimate the electron density on the rhodium centre. The ene-hydrazone ligand backbone (nitrogen covalently bonded) is more electron donating than the azine backbone (nitrogen bonded by electron pair donation) as expected. In the neutral series of complexes electron donation increases with phosphine substitution in the order Ph < Pr^i = c-C_6H_{11} < Bu^t with the corresponding decrease of carbonyl valence vibration frequency. The *tert*-butyl cationic complex undergoes in a low yield an unusual diphosphinoazine bond cleavage with simultaneous oxidation of the metal resulting in a binuclear bis(iminophosphine)dirhodium complex [{$(Bu^t)_2PCH_2C(Bu^t){=}NH$}-$Rh(Cl)_2(\mu\text{-}Cl)]_2$ the structure of which was also determined by X-ray diffraction.

1. Introduction

Pincer ligands and pincer complexes are now well established in organometallic and coordination chemistry [1]. Tridentate bonding scheme (two-electron donor–covalently bonded atom–two-electron donor) usually creates a bicyclic complex with a metal belonging to both rings of the same size. However, unsymmetrical pincer complexes are now also common [2], the first reported being arguably (see below) those of Eberhard et al. [3].

The central covalently bonded monoanionic atom is usually carbon, but there are other possibilities. Among those, probably the most important one is nitrogen bonded as an amide [4]. Square planar Ni, Pd and Pt complexes with a rigid [donor–amide nitrogen–donor] framework are believed to show an unusual reactivity due to the presence of a strongly electron-donating amide *trans* to the potential reaction site [5].

Rhodium PNP symmetrical pincer complexes were studied by Ozerov et al. [4c, p. 287], but the first rhodium amido carbonyl pincer complex was reported by Mayer and Kaska [6] only recently.

We published synthesis of palladium(II) diphosphinoazine amido complexes with an unsymmetrical PNP′ pincer-type coordination [7] and later reported their catalytic activity in the Heck reaction [8]. Previously, palladium [9a], platinum [9a], and iridium [9b,9c] complexes of this type were reported but only with the diphosphinoazine bearing phenyl groups on phosphorus atoms. Rhodium diphosphinoazine amido complexes and in particular amido carbonyl complexes are unknown. At the same time, rhodium pincer complexes with PCP frame were thoroughly studied mainly by Milstein's group and used in further stoichiometric and catalytic transformations [10]. Here we report the first synthesis and characterization including X-ray diffraction of diphosphinoazine rhodium(I) amido carbonyl complexes with an unsymmetrical PNP′ pincer-type coordination.

2. Experimental

2.1. General

All preparations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. Pentane, hexane and methanol were distilled from sodium, tetrahydrofuran was distilled from sodium/benzophenone, dichloromethane was distilled from $CaCl_2$ and chloroform was purified by distillation from P_2O_5 and then from $CaCl_2$.

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Triethylamine was stored over KOH and distilled on the Fischer distillation column prior to use.

Complex $[Rh(CO)_2Cl]_2$ [11] and the starting diphosphinoazines $Ph_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2$ (**1**) [12], $(C_6H_{11})_2PCH_2C(Bu^t)$=N–N=C–$(Bu^t)CH_2P(C_6H_{11})_2$ (**2**) [13], $Pr^i{}_2PCH_2C(Bu^t)$=NN=$C(Bu^t)$-$CH_2PPr^i{}_2$ (**3**) [13], and $Bu^t{}_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2$ $PBu^t{}_2$ (**4**) [13] were prepared according to published procedures, as indicated.

^1H (299.9 MHz), ^{13}C (75.4 MHz) and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian MercuryVX 300 spectrometer in $CDCl_3$ solution unless stated otherwise. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to hexamethyldisilane or the solvent peak (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P). Assignments in NMR spectra were aided by gNMR V4.1.0 [14].

IR spectra were obtained on Nicolet Impact 400 by the specular reflection method in range 400–4000 cm^{-1} with resolution 2 cm^{-1}.

3. Syntheses of the complexes

3.1. Cationic complexes

All cationic square planar diphosphinoazine complexes of Rh(I) of the general formula [Rh(CO)L]Cl (L = **1**–**4**) were prepared by a general procedure as follows. Rhodium precursor $[Rh(CO)_2Cl]_2$ (0.0500 g, 0.108 mmol) was dissolved in 5 ml of $CHCl_3$ and an appropriate amount of ligands **1** (0.121 g, 0.216 mmol), **2** (0.126 g, 0.216 mmol), **3** (0.093 g, 0.216 mmol), **4** (0.104 g, 0.216 mmol), in 5 ml of $CHCl_3$ was added. Solution was stirred at room temperature for 5 h. Solvent was partially removed by evaporation *in vacuo* to ca. 2 ml and product was obtained by precipitation after addition of 15 ml of methanol. Mother liquor was filtered off by cannula and the residue was washed twice with methanol and dried *in vacuo*. By this method 0.122 g (78%) of yellow complex **5**, 0.136 g (81%) of pale yellow complex **6**, 0.078 g (61%) of yellow complex **7** and 0.079 g (61%) of yellow–orange complex **8** was obtained.

3.1.1. [{$Ph_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2$}Rh(CO)]Cl (**5**)

Anal. Calc. for $C_{37}H_{42}ClN_2OP_2Rh$: C, 60.79; H, 5.79; N, 3.83. Found: C, 60.45; H, 5.72; N, 3.77%. ^{31}P NMR ($CDCl_3$): ABX 54.5 ($^1J_{RhP}$ = 123.0 Hz), 63.6 ($^1J_{RhP}$ = 139.6 Hz) ($^2J_{PP}$ = 310.0 Hz) ^1H NMR ($CDCl_3$): 0.77 s (9H, *t*-Bu), 1.24 s (9H, *t*-Bu), 3.66 dd (2H, $^2J_{PH}$ = 12.3 Hz, $^4J_{PH}$ = 2.3 Hz, PCH_2), 4.50 dd (2H, $^2J_{PH}$ = 10.0 Hz, $^4J_{PH}$ = 4.5 Hz, PCH_2), 7.48–7.54 m (12H, CH, meta and para protons Ph), 7.73–7.80 m (4H, CH, ortho protons Ph), 7.84–7.91 m (4H, CH, ortho protons Ph).

^{13}C NMR ($CDCl_3$): 25.29 d ($^1J_{PC}$ = 15.6 Hz, PCH_2), 26.80 s (CH_3, *t*-Bu), 27.95 s (CH_3, *t*-Bu), 39.94 d (J = 1.7 Hz, >C<, *t*-Bu), 40.36 d (J = 5.5 Hz, >C<, *t*-Bu), 41.22 d ($^1J_{PC}$ = 24.2 Hz, PCH_2), 129.36 d ($^4J_{PC}$ = 10.9 Hz, CH, Ph), 129.15 d ($^4J_{PC}$ = 10.8 Hz, CH, Ph), 129.58 dd ($^1J_{PC}$ = 4.0 Hz, $^3J_{RhC}$ = 2.0 Hz, >C<, Ph), 130.15 dd ($^1J_{PC}$ = 4.0 Hz, $^3J_{RhC}$ = 2.0 Hz, >C<, Ph), 131.57 d ($^5J_{PC}$ = 1.9 Hz, CH, Ph), 132.86 d ($^3J_{PC}$ = 12.8 Hz, CH, Ph), 133.65 d ($^3J_{PC}$ = 12.87 Hz, CH, Ph), 171.25 s (>C<, >C=N), 187.26 dd ($^2J_{PC}$ = 5.8 Hz, $^5J_{PC}$ = 2.6 Hz, >C<, >C=N),190.52 broad m (>C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1972.

3.1.2. [{$(C_6H_{11})_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P(C_6H_{11})_2$}Rh(CO)]Cl (**6**)

Anal. Calc. for $C_{37}H_{66}ClN_2OP_2Rh$: C, 58.84; H, 8.81; N, 3.71. Found: C, 58.72; H, 8.71; N, 3.63%. ^{31}P NMR: ($CDCl_3$) ABX 70.6 ($^1J_{RhP}$ = 115.6 Hz), 78.8 ($^1J_{RhP}$ = 128.5 Hz) ($^2J_{PP}$ = 265.9 Hz) ^1H NMR: ($CDCl_3$) 1.12–1.41 m (24H, CH_2, c-C_6H_{11}), 1.24 s (9H, *t*-Bu), 1.35 s (9H, *t*-Bu), 1.66–2.10 m (20H, CH + CH_2, c-C_6H_{11}), 2.56 d (2H, $^2J_{PH}$ = 9.6 Hz, PCH_2), 3.61 dd (2H, $^2J_{PH}$ = 8.3 Hz, $^4J_{PH}$ = 4.1 Hz, PCH_2).

^{13}C NMR: ($CDCl_3$) 16.65 d ($^1J_{PC}$ = 10.4 Hz, PCH_2), 25.68 d (J = 3.7 Hz, CH_2, c-C_6H_{11}), 26.24–26.74 m (CH_2, c-C_6H_{11}), 27.58 s (CH_3, *t*-Bu), 28.43 s (CH_2, c-C_6H_{11}), 28.50 s (CH_2, c-C_6H_{11}), 28.62 s (CH_3, *t*-Bu), 29.33 d ($^2J_{PC}$ = 2.5 Hz, CH_2), 30.49 s (CH_2, c-C_6H_{11}), 33.29 d ($^1J_{PC}$ = 19.2 Hz, PCH_2), 34.17 d ($^1J_{PC}$ = 22.2 Hz, CH, c-C_6H_{11}), 35.84 d ($^1J_{PC}$ = 20.4 Hz, CH, c-C_6H_{11}), 40.86 d ($^3J_{PC}$ = 5.6 Hz, >C<, *t*-Bu), 40.87 d ($^3J_{PC}$ = 1.7 Hz, >C<, *t*-Bu),172,57 s (>C<, >C=N), 190.37 dd ($^2J_{PC}$ = 4.7 Hz, $^5J_{PC}$ = 2.7 Hz, >C<, >C=N), 194.64 m (>C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1950.

Single crystal suitable for X-ray analysis was grown by slow diffusion of hexane vapour to the chloroform solution at room temperature. Structure of the complex was determined as [{$(C_6H_{11})_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P(C_6H_{11})_2$}Rh(CO)][$(CO)_2RhCl_2$] (**6a**).

3.1.3. [{$Pr^i{}_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPr^i{}_2$}Rh(CO)]Cl (**7**)

^{31}P NMR: ($CDCl_3$): ABX 78. 9 ($^1J_{RhP}$ = 115.9 Hz), 86.7 ($^1J_{RhP}$ = 128.6 Hz) ($^2J_{PP}$ = 265.7 Hz). ^1H NMR ($CDCl_3$): 1.28–1.38 m (24H, CH_3, *i*-Pr), 1.29 s (9H, *t*-Bu), 1.40 s (9H, *t*-Bu), 2.29 d sep. (2H, $^2J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 7.1 Hz, CH, *i*-Pr), 2.35 d sep. (2H, $^2J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 7.1 Hz, CH, *i*-Pr), 2.61 dd (2H, $^2J_{PH}$ = 10.9 Hz, $^4J_{PH}$ = 2.7 Hz, PCH_2), 3.65 dd (2H, $^2J_{PH}$ = 8.3 Hz, $^4J_{PH}$ = 4.1 Hz, PCH_2).

^{13}C NMR ($CDCl_3$): 16.59 d ($^1J_{PC}$ = 9.9 Hz, PCH_2), 19.15 d ($^2J_{PC}$ = 4.3 Hz, CH_3, *i*-Pr), 20.0 d ($^2J_{PC}$ = 2.7 Hz, CH_3, *i*-Pr), 24.86 ddd ($^1J_{PC}$ = 21.9 Hz, $^2J_{RhC}$ = 1.7 Hz, $^3J_{PC}$ = 1.8 Hz, CH, *i*-Pr), 25.98 ddd ($^1J_{PC}$ = 20.9 Hz, $^2J_{RhC}$ = 2.0 Hz, $^3J_{PC}$ = 2.4 Hz, CH, *i*-Pr), 27.50 s (CH_3, *t*-Bu), 28.50 s (CH_3, *t*-Bu), 33.18 d ($^1J_{PC}$ = 19.0 Hz, PCH_2), 40.83 d ($^3J_{PC}$ = 1.7 Hz, >C<, *t*-Bu), 40.92 d ($^3J_{PC}$ = 5.6 Hz, >C<, *t*-Bu), 172.29s (>C<, >C=N), 190.61 ddd ($^2J_{PC}$ = 6.4 Hz, $^5J_{PC}$ = 2.7 Hz, $^2J_{RhC}$ = 1.5 Hz, >C<, >C=N), 192.12–192.93 m (>C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1952.

3.1.4. [{$Bu^t{}_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PBt^t{}_2$}Rh(CO)]Cl (**8**)

Anal. Calc. for $C_{37}H_{42}ClN_2OP_2Rh$: C, 53.50; H, 8.98; N, 4.30. Found: C, 52.47; H, 7.77; N, 4.13%. ^{31}P NMR ($CDCl_3$): ABX 93.0 ($^1J_{RhP}$ = 116.1 Hz), 97.8 ($^1J_{RhP}$ = 129.7 Hz) ($^2J_{PP}$ = 256.2 Hz). ^1H NMR ($CDCl_3$): 1.35 s (9H, *t*-Bu), 1.41 d (18H, $^3J_{PH}$ = 6.8 Hz, *t*-Bu), 1.42 s (9H, *t*-Bu), 1.5 d (18H, $^3J_{PH}$ = 7.0 Hz, *t*-Bu), 2.52 dd (2H, $^2J_{PH}$ = 10.0 Hz, $^4J_{PH}$ = 2.2 Hz, PCH_2), 3.67 dd (2H, $^2J_{PH}$ = 6.9 Hz, $^4J_{PH}$ = 4.0 Hz, PCH_2).

^{13}C NMR ($CDCl_3$): 14.30 d ($^1J_{PC}$ = 5.5 Hz, CH_2, PCH_2), 28.47 s (CH_3, *t*-Bu), 28.99 s (CH_3, *t*-Bu), 29.38 d ($^2J_{PC}$ = 4.3 Hz, CH_3, *t*-Bu), 29.53 d ($^2J_{PC}$ = 4.9 Hz, CH_3, *t*-Bu), 33.77 d ($^1J_{PC}$ = 15.5 Hz, CH_2, PCH_2), 35.86 d ($^1J_{PC}$ = 18.1 Hz, >C<, *t*-Bu), 37.15 d ($^1J_{PC}$ = 14.7 Hz, >C<, *t*-Bu), 41.07 d ($^3J_{PC}$ = 4.9 Hz, >C<, *t*-Bu), 41.94 d ($^3J_{PC}$ = 2.0 Hz, >C<, *t*-Bu), 173.60 d ($^2J_{PC}$ = 1.2 Hz >C<, >C=N), 191.33 ddd ($^2J_{PC}$ = 6.4 Hz, $^5J_{PC}$ = 3.3 Hz, $^2J_{RhC}$ = 1.81 Hz, >C<, >C=N), 194.34 ddd ($^1J_{RhC}$ = 71.40 Hz, $^2J_{PC}$ = 14.5 Hz, $^2J_{PC}$ = 14.5 Hz, >C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1972.

Single crystal suitable for X-ray analysis was grown by slow diffusion of hexane vapour to the chloroform solution at room temperature.

3.2. Ene-hydrazone complexes

3.2.1. {Ph_2PCH=$C(Bu^t)$–NN=$C(Bu^t)CH_2PPh_2$}Rh(CO)] (**9**)

Solution of $[Rh(CO)_2Cl]_2$ (0.0300 g, 0.065 mmol), ligand (**1**) 0.0726 g (0.130 mmol) and 0.6 g (11 mmol) of sodium methoxide in 5 ml of THF was sealed under vacuum in a glass ampoule and the reaction mixture was sonicated for 1 h. Then the reaction mixture was left standing for 15 days. Dark red solution was filtered and the product was obtained by evaporation of solvent *in vacuo*.

Single crystal suitable for X-ray analysis was grown by slow evaporation of chloroform solvent at room temperature.

^{31}P NMR (CD_2Cl_2): ABX 37.1 ($^1J_{RhP}$ = 126.8 Hz), 63.6 ($^1J_{RhP}$ = 144.9 Hz) ($^2J_{PP}$ = 296.1 Hz). ^{1}H NMR (CD_2Cl_2): 0.74 s (9H, *t*-Bu), 1.34 s (9H, *t*-Bu), 3.01 dd (2H, $^2J_{PH}$ = 11.4 Hz, $^4J_{PH}$ = 1.8 Hz, PCH_2), 4.53 dd (1H, $^2J_{PH}$ = 2.7 Hz, $^4J_{PH}$ = 2.1 Hz, PCH), 7.32–7.35 m (6 H, CH, Ph), 7.38–7.43 m (6H,CH, Ph), 7.66–7.73 m (8H, CH, Ph).

^{13}C NMR (CD_2Cl_2): 21.86 d ($^1J_{PC}$ = 17.3 Hz, CH_2, PCH_2), 28.61 s (CH_3, *t*-Bu), 31.10 s (CH_3, *t*-Bu), 39.07 d ($^3J_{PC}$ = 2.3 Hz, >C<, *t*-Bu), 39.49 d ($^3J_{PC}$ = 15.4 Hz, >C<, *t*-Bu), 75.40 d ($^1J_{PC}$ = 53.3 Hz, CH, PCH), 128.77 d (J_{PC} = 20.7 Hz, CH, Ph), 128.90 d (J_{PC} = 20.4 Hz, CH, Ph), 129.80 d (J_{PC} = 2.1 Hz, CH, Ph), 131.00 d (J_{PC} = 1.8 Hz, CH, Ph), 132.54 d (J_{PC} = 12.1 Hz, CH, Ph), 133.78 d (J_{PC} = 12.7 Hz, CH, Ph), 134.08 d ($^1J_{PC}$ = 45.3 Hz, >C<, Ph), 137.29 d ($^1J_{PC}$ = 49.2 Hz, >C<, Ph), 150.37 s (>C<, ≥C–N), 190.11 dd ($^2J_{PC}$ = 25.3 Hz, $^5J_{PC}$ = 2.67 Hz, >C<, >C=N), 194.85–197.28 m (>C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1957.

3.2.2. [{$(C_6H_{11})_2PCH{=}C(Bu^t)$–NN=$C(Bu^t)CH_2P(C_6H_{11})_2$}Rh(CO)] (**10**)

Solution of $[Rh(CO)_2Cl]_2$ (0.0250 g, 0.055 mmol), ligand (**2**) 0.0605 g (0.110 mmol) and 0.6 g (11 mmol) of sodium methoxide in 5 ml of THF was sealed under vacuum in glass ampoule and reaction mixture was sonicated for 1 h. Then the reaction mixture was kept at room temperature for 15 days. Dark red solution was filtered and the product was obtained by evaporation of solvent *in vacuo*.

^{31}P NMR: (CD_2Cl_2) ABX 51.3 ($^1J_{RhP}$ = 120.9 Hz), 67.0 ($^1J_{RhP}$ = 130.0 Hz) ($^2J_{PP}$ = 268.3 Hz). ^{1}H NMR: ($CDCl_3$): 1.14 s (9H, *t*-Bu), 1.26 s (9H, *t*-Bu), 1.19–1.44 m (24H, CH_2, c-C_6H_{11}), 1.70–2.06 m (20H, CH + CH_2, c-C_6H_{11}), 2.24 dd (2H, $^2J_{PH}$ = 10.7 Hz, $^4J_{PH}$ = 1.7 Hz, PCH_2), 3.80 dd (1H, $^2J_{PH}$ = 3.6 Hz, $^4J_{PH}$ = 1.8 Hz, PCH).

^{13}C NMR ($CDCl_3$): 13.38 d ($^1J_{PC}$ = 14.1 Hz, CH_2, PCH_2), 26.63 s (CH_2, c-C_6H_{11}), 26.85 s (CH_2, c-C_6H_{11}), 27.22–27.56 m (CH_2, c-C_6H_{11}), 28.65 s (CH_2, c-C_6H_{11}), 29.01 s (CH_2, c-C_6H_{11}), 29.19 s (CH_3, *t*-Bu), 30.22 d (J = 14.2 Hz, CH_2, c-C_6H_{11}), 30.25 d (J = 10.2 Hz, CH_2, c-C_6H_{11}), 31.50 s (CH_3, *t*-Bu), 35.55 d ($^1J_{PC}$ = 18.7 Hz, CH, c-C_6H_{11}), 35.63 d ($^1J_{PC}$ = 29.9 Hz, CH, c-C_6H_{11}), 38.99 d ($^3J_{PC}$ = 14.7 Hz, >C<, *t*-Bu), 39.88 d ($^3J_{PC}$ = 2.2 Hz, >C<, *t*-Bu), 71.03 d ($^1J_{PC}$ = 43.9 Hz, CH, PCH), 145.85 s (>C<, ≥C–N), 189.31 dd ($^2J_{PC}$ = 22.2 Hz, $^5J_{PC}$ = 2.7 Hz, >C<, >C=N), 197.05–197.41 m (>C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1944.

3.2.3. [{$Pr^i_2PCH{=}C(Bu^t)$–NN=$C(Bu^t)CH_2PPr^i_2$}Rh(CO)] (**11**)

Solution of $[Rh(CO)_2Cl]_2$ 0.0300 g (0.065 mmol), ligand (**3**) 0.0660 g (0.130 mmol) and 0.6 g (11 mmol) of sodium methoxide in 5 ml of THF was sealed under vacuum in glass ampoule and reaction mixture was sonicated for 1 h. Then the reaction mixture was left standing for 15 days. Dark red solution was filtered and the product was obtained by evaporation of solvent *in vacuo*.

^{31}P NMR (CD_2Cl_2): ABX 60.0 ($^1J_{RhP}$ = 120.6 Hz), 76.6 ($^1J_{RhP}$ = 132.6 Hz) ($^2J_{PP}$ = 268.2 Hz). ^{1}H NMR (CD_2Cl_2): 1.05–1.30 bm (24H, CH_3, *i*-Pr), 1.17 s (9H, CH_3, *t*-Bu), 1.28 s (9 H, CH_3, *t*-Bu), 2.08–2.21 bm (4H, CH, *i*-Pr), 2.26 dd (2H, $^2J_{PH}$ = 10.7 Hz, $^4J_{PH}$ = 2.2 Hz, CH_2, PCH_2), 3.86 dd (1H, $^2J_{PH}$ = 3.9 Hz, $^4J_{PH}$ = 2.2 Hz, CH, PCH).

^{13}C (CD_2Cl_2): 12.81 d ($^1J_{PC}$ = 13.8 Hz, CH_2, PCH_2), 18.39 s (CH_3, *i*-Pr), 18.97 s (CH_3, *i*-Pr), 19.64 d ($^2J_{PC}$ = 2.2 Hz, CH_3, *i*-Pr), 19.74 d ($^2J_{PC}$ = 5.4 Hz, CH_3, *i*-Pr), 25.54 d ($^1J_{PC}$ = 20.8 Hz, CH, *i*-Pr), 26.03 d ($^1J_{PC}$ = 29.2 Hz, CH, *i*-Pr), 29.30 s (CH_3, *t*-Bu), 31.59 s (CH_3, *t*-Bu), 39.13 d ($^2J_{PC}$ = 14.6 Hz, >C<, *t*-Bu), 39.98 d ($^2J_{PC}$ = 1.9 Hz, >C<, *t*-Bu), 70.44 d ($^1J_{PC}$ = 44.2 Hz, CH, PCH), 145.24 s (>C<, ≥C–N), 190.01 dd ($^2J_{PC}$ = 21.7 Hz, $^5J_{PC}$ = 2.5 Hz, >C<, >C=N), 197.47 ddd ($^1J_{RhC}$ = 64.2 Hz, $^2J_{PC}$ = 15.5 Hz, $^2J_{PC}$ = 15.5 Hz, >C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1943.

3.2.4. [{$Bu^t_2PCH{=}C(Bu^t)$–NN=$C(Bu^t)CH_2PBu^t_2$}Rh(CO)] (**12**)

Rhodium(I) precursor $[Rh(CO)_2Cl]_2$ (0.0300 g, 0.065 mmol) and ligand (**4**) 0.0750 g (0.130 mmol) were dissolved in chloroform and 0.1 ml (0.720 mmol) of triethylamine was added. Reaction mixture was stirred for 24 h. Dark red solution was filtered off from a small amount of precipitate and the product was obtained by drying *in vacuo*.

^{31}P NMR ($CDCl_3$): ABX 73.8 ($^1J_{RhP}$ = 123.2 Hz), 91.3 ($^1J_{RhP}$ = 133.9 Hz) ($^2J_{PP}$ = 267.7 Hz). ^{1}H NMR ($CDCl_3$): 1.22 s (9H, *t*-Bu), 1.27 s (9H, *t*-Bu), 1.32 d (18H, $^3J_{PH}$ = 5.6 Hz, *t*-Bu), 1.36 d (18H, $^3J_{PH}$ = 5.2 Hz, *t*-Bu), 2.20 dd (2H, $^2J_{PH}$ = 10.5 Hz, $^4J_{PH}$ = 2.5 Hz, CH_2, PCH_2), 4.19 dd (1H, $^2J_{PH}$ = 3.5 Hz, $^4J_{PH}$ = 2.3 Hz, CH, PCH).

^{13}C NMR ($CDCl_3$): 10.16 d ($^1J_{PC}$ = 9.5 Hz, CH_2, PCH_2), 28.70 d ($^2J_{PC}$ = 5.0 Hz, CH_3, *t*-Bu), 29.18 d ($^2J_{PC}$ = 4.9 Hz, CH_3, *t*-Bu), 29.80 s (CH_3, *t*-Bu), 30.89 s (CH_3, *t*-Bu), 35.15 d ($^1J_{PC}$ = 21.31 Hz, >C<, (P–$C(CH_3)_3$)), 35.56 d ($^1J_{PC}$ = 12.8 Hz, >C<, (P–$C(CH_3)_3$)), 38.30 d ($^3J_{PC}$ = 14.1 Hz, >C<, *t*-Bu), 39.74 d ($^3J_{PC}$ = 3.4 Hz, >C<, *t*-Bu), 73.66 d ($^1J_{PC}$ = 42.9 Hz, CH, PCH), 143.06 s (>C<, ≥C–N), 187.76 dd ($^2J_{PC}$ = 21.3 Hz, $^5J_{PC}$ = 2.8 Hz, >C<, >C=N), 198.48 ddd ($^1J_{RhC}$ = 65.1 Hz, $^2J_{PC}$ = 15.5 Hz, $^2J_{PC}$ = 15.5 Hz, >C<, CO).

IR (ν_{CO}, $CHCl_3$, cm^{-1}) 1938.

3.2.5. [{$(Bu^t)_2PCH_2C(Bu^t){=}NH$}$Rh(Cl)_2(\mu$-Cl)]$_2$ (**13**)

Complex [($Bu^t_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PBu^t_2$)Rh(CO)] (**8**) (0.1000 g, 0.154 mmol) was dissolved in 1 ml of chloroform and 0.2 ml of 35% aqueous HCl was added. Reaction mixture was left at room temperature for 2 months with occasional stirring. The red product which precipitated was dried in vacuo, then dissolved in 0.5 ml of chloroform and isolated by crystallization via slow diffusion of hexane vapour to the chloroform solution at room temperature. Yield 0.011 g (8%).

Crystal suitable for X-ray analysis was grown by slow diffusion of hexane vapour to the chloroform solution at room temperature.

^{31}P NMR (CD_2Cl_2): 96.7 d ($^1J_{RhP}$ = 121.4 Hz). ^{1}H NMR (CD_2Cl_2): 1.38 s (18H, *t*-Bu), 1.57 bs (36H, *t*-Bu), 3.15 dd (2H, $^2J_{PH}$ = 17.0 Hz, $^2J_{HH}$ = 10.5 Hz, CH_2), 3.45 dd (2H, $^2J_{PH}$ = 16.2 Hz, $^2J_{HH}$ = 9.1 Hz, CH_2), 10.48 bs (2H, NH).

3.3. Crystallographic data

The diffraction-quality crystals of complexes were grown as mentioned above. The crystals were selected in mother liquor and quickly transferred into Fluorolube oil, then mounted on glass fibres in random orientation and cooled to 150(1) K. Diffraction data were collected using Nonius Kappa CCD diffractometer (Enraf-Nonius) at 150(1) K (Cryostream Cooler Oxford Cryosystem) and analyzed using the HKL program package [15]. The structures were solved by direct methods and refined by full matrix least-squares techniques (SIR92 [16], SHELXL97 [17] or CRYSTALS [18]). Final geometric calculations were carried out with the recent version of the PLATON program [19].

3.3.1. [{$(C_6H_{11})_2PCH_2C(Bu^t){=}NN{=}C(Bu^t)CH_2P(C_6H_{11})_2$}Rh(CO)]-[$(CO)_2RhCl_2$] (**6**)

X-ray: $C_{39}H_{66}Cl_2N_2O_3P_2Rh_2$, M = 949.63 g/mol, triclinic, space group: $P\bar{1}$, a = 11.7725(2) Å, b = 17.6971(3) Å, c = 22.4909(6) Å, α = 93.954(1), β = 97.510(1), γ = 109.284(1)°, Z = 4, V = 4353.3(2) Å^3, D_{calc} = 1.45 g cm^{-3}, μ(Mo Kα) = 0.99 mm^{-1}, crystal dimensions of 0.1 × 0.1 × 0.2 mm. The independent part is created by two complex molecules. The structure was refined by full matrix least-squares on F values [18]. All heavy atoms were refined anisotropically. All hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0443 and R_w = 0.0509 using 10879 independent reflections (θ_{max} = 27.52°).

3.3.2. [{$Bu^t_2PCH_2C(Bu^t){=}NN{=}C(Bu^t)CH_2PBu^t_2$}Rh(CO)]Cl (**8**) · 2$CHCl_3$

X-ray: $C_{29}H_{58}ClN_2OP_2Rh \cdot 2CHCl_3(C_{31}H_{60}Cl_7N_2OP_2Rh)$. M = 889.81 g/mol, monoclinic, space group: $P2_1/n$, a = 11.0678(1) Å,

b = 24.404(2) Å, c = 15.3403(2) Å, β = 100.3023(6)°, Z = 4, V = 4243.03(8) Å^3, D_{calc} = 1.393 g cm^{-3}, μ(Mo Kα) = 0.945 mm^{-1}, crystal dimension of 0.35 × 0.4 × 0.45 mm. The structure was refined by full matrix least-squares on F values [17]. All heavy atoms were refined anisotropically. All hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0299 and R_w = 0.0660 using 8240 independent reflections ($F_o > 4\sigma(F_o)$; θ_{max} = 27.50°).

*3.3.3. 2 [{$Ph_2PCH{=}C(Bu^t)$–NN=$C(Bu^t)CH_2PPh_2$}Rh(CO)] (**9**) · CH_2Cl_2*

X-ray: $C_{74}H_{84}N_2O_2P_4Rh_2$. CH_2Cl_2 ($C_{75}H_{86}Cl_2N_2O_2P_4Rh_2$), M = 1476.13 g/mol, monoclinic, space group: Pc, a = 10.1220(2) AA, b = 24.9990(4) AA, c = 18.1989(2) Å, β = 129.521(1)°, Z = 4, V = 3552.3(1) Å^3, D_{calc} = 1.37 g cm^{-3}, μ(Mo Kα) = 0.68 mm^{-1}, crystal dimensions of 0.2 × 0.2 × 0.4 mm. The independent part is created by two complex molecules and one disordered solvent molecule. The structure was refined by full matrix least-squares on F values [18]. All heavy atoms were refined anisotropically. All hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0357 and R_w = 0.0372 using 10558 independent reflections (θ_{max} = 26.06°).

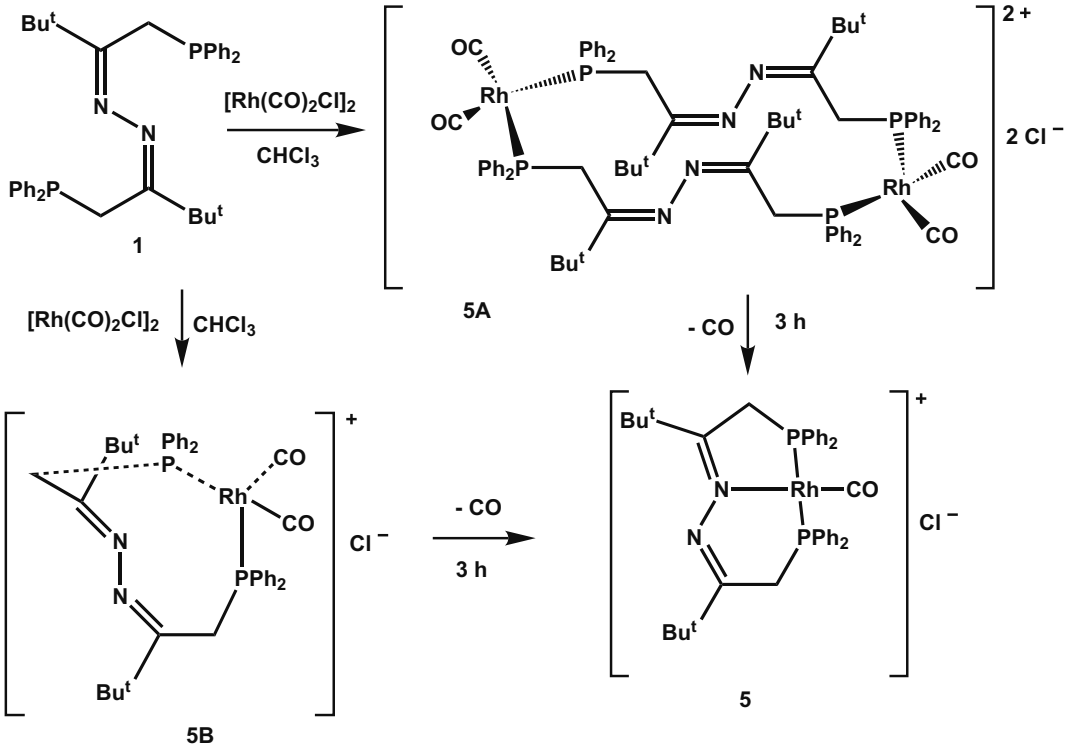
*3.3.4. [{$(Bu^t)_2PCH_2C(Bu^t)$=NH}Rh(Cl)$_2$(μ-Cl)]$_2$ (**13**) · 2$CHCl_3$*

X-ray: $C_{14}H_{30}Cl_3NPRh \cdot 2$ $CHCl_3$ ($C_{15}H_{31}Cl_6NPRh$; dimer). M = 571.99 g/mol, monoclinic, space group $P2_1/c$, a = 10.6868(2) Å, b = *17.7065(4)* Å, c = 12.9903(3) Å, β = *106.118(1)*°, Z = 4, V = 2361.48(9) Å^3, D_{calc} = 1.609 g cm^{-3}, μ(Mo Kα) = 1.470 mm^{-1}, crystal dimension of 0.15 × 0.25 × 0.25 mm. The structure was refined by full matrix least-squares on F values [17]. All heavy atoms were refined anisotropically. All hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0530 and R_w = 0.1313 using 4614 independent reflections ($F_o > 4\sigma(F_o)$; θ_{max} = 27.49°).

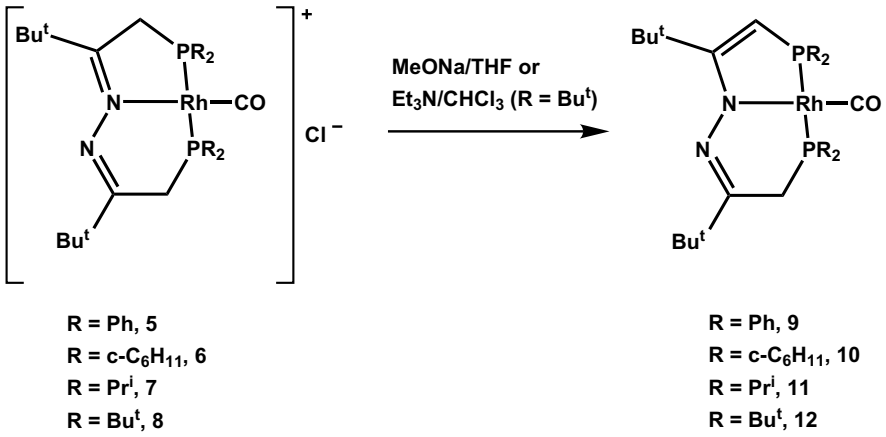
4. Results and discussion

Diphosphinoazine square planar cationic complexes of Rh(I) which are precursors to the amido carbonyl complexes were synthesized by cleavage of the chloride bridges of $[Rh(CO)_2Cl]_2$ and liberating one mole of carbon monoxide per rhodium atom. Complexes containing all four ligands with variable steric demands could be prepared. The formation of cationic complexes is very rapid, complete within several minutes, except the formation of complex **5**, whereby an intermediate was observed by NMR spectroscopy. Two possible structures **5A** and **5B** were proposed for this intermediate from the set of ^{31}P and ^{1}H NMR spectra (Scheme 1). Two diphosphinoazine ligands can act either as bridging ligands in a binuclear complex with 18–membered ring (**5A**), analogous to a known platinum complex [9a], or the intermediate is mononuclear with the chelating ligand (**5B**). It was not possible to decide between the two proposed structures from NMR spectra because ligand **1** is in (*Z,Z*) configuration in both structures and groups crucial for assignment are thus equivalent in both cases. In ^{31}P NMR spectra a characteristic doublet with an interaction constant 125 Hz was found which was attributed to two equivalent phosphorus nuclei that interact with rhodium. Proton spectra are consistent with phosphorus spectra and with both proposed intermediates since signals of the protons of the groups from both halves of the diphosphinoazine moiety are equivalent as well.

Ene-hydrazone amido carbonyl complexes of Rh(I) were prepared from the corresponding cationic complexes **5**–**8** *via* their deprotonation by a base. Ene-hydrazone complexes **9**–**11** containing less sterically demanding ligands **1**–**3** were synthesized by treating complexes **5**–**7**, generated *in situ* in anhydrous tetrahydrofuran from the starting materials, with an excess of sodium methoxide. Complex **12** with the bulkiest ligand **4** was prepared similarly from complex **8**, but triethylamine was used as the base and chloroform as the solvent (Scheme 2).



Scheme 1.



R = Ph, 5
R = c-C_6H_{11}, 6
R = Pr^i, 7
R = Bu^t, 8

R = Ph, 9
R = c-C_6H_{11}, 10
R = Pr^i, 11
R = Bu^t, 12

Scheme 2.

^{31}P NMR spectra of complexes **5**–**12** were assigned as ABX spin systems. The exact chemical shifts and interaction constants of both phosphorus atoms were determined by computer simulation in the gNMR [14] program. The phosphorus atoms are in *trans* arrangement in diphosphinoazine square planar complexes of Rh(I), but they are not equivalent due to coordination of one nitrogen atom to rhodium, which leads to the formation of two metallacycles of different sizes. The value of the interaction constant $^1J_{RhP}$ was different for phosphorus atoms P1 and P2 of the ligand in the square planar complexes **5**–**8** and was in the range typical for such interaction (P1: 115.6–123.0 Hz, P2: 128.5–139.6 Hz). Values of interaction constants $^1J_{RhP}$ in these complexes were very similar to the starting cationic complexes and were in the range from 120.6 to 126.8 Hz for P1 and from 130.0 to 144.9 Hz for P2. All ^{31}P NMR shifts and interaction constants are summarized in Tab. 1. From the ^{31}P NMR spectra it is evident that the chemical shift of phosphorus atoms increases with increasing value of the Tolman angle [20] of the phosphine groups, as the bulkiness increases and the *s*-character of the free electron pair decreases (Ph < c-C_6H_{11} < *i*-Pr < *t*-Bu). Since phosphorus atoms are *trans* their interaction constant $^2J_{PP}$ is relatively high, in the range of 256–310 Hz. Diphosphinoazine complexes of Ir(I) [9b] exhibit very similar $^2J_{PP}$ interaction constant (ca 308 Hz) as the discussed rhodium complexes. Similar value of phosphorus–phosphorus interaction constant (354–396 Hz) can be also found in rhodium(I) P,C,P pincer complexes [10d,21] similar to complexes **5**–**12**.

^{1}H and ^{13}C NMR spectra of diphosphinoazine cationic complexes and deprotonated ene-hydrazone complexes are similar to each other as far as diphosphinoazine or en-hydrazone ligand frame is concerned. Differences were naturally stemming from different substituents on phosphorus P1 and P2. Ligands are in (*E*,*Z*) configuration in all the cases as was confirmed from ^{1}H and ^{13}C NMR spectra and in three cases also by X-ray diffraction. Due to the P,N,P′ ligand coordination, five- and six-membered metallacycles have formed. Therefore two different signals of methylene protons were observed for complexes **5**–**8** and in complexes **9**–**12** only one signal of the methylene protons and one signal of methine proton was observed. Depending on the particular complex these signals were doublets (**6**) or doublets of doublets (**5**, **7**, **8**) with very well resolved $^2J_{PH}$ and $^4J_{PH}$; signal of methine proton in complexes **9**–**12** was doublet of doublets in all the cases.

All signals of the protonated carbons were identified from DEPT and qHSQC experiments, signals of quaternary carbon atoms were assigned from gHMBC experiment. Signals of methylene carbon atoms in complexes **5**–**8**, which are in the proximity of phosphorus atoms are split to doublets with interaction constants $^1J_{PC}$ in range of 5.5–15.5 Hz and 15.5–24.2 Hz for carbons belonging to the 6-membered ring and carbons belonging to the 5-membered ring, respectively. Values of $^1J_{PC}$ increase with increasing bulkiness of the phosphine groups of the ligand in the series Ph < Pr^i < c-C_6H_{11} < Bu^t.

Methylene and methine carbons in deprotonated complexes **9**–**12** exhibit analogous interactions with phosphorus atoms as do their cationic precursors and the signals of appropriate methylene carbons are split into doublets with $^1J_{PC}$ from 9.5 to 17.3 Hz. The signals of methine carbon are also split into doublets. In this case the value of the interaction constant $^1J_{PC}$ is somewhat higher, in the range of 42.9–53.3 Hz.

Differences in electrondonor properties of ligands with variable substitution were studied by infrared spectroscopy by means of the differences in the values of valence vibration of the carbonyl group which is known to be indirectly influenced by π-donation from the ligand to the metal atom. For this vibration a strong band in the range of 1950–1972 cm^{-1} for cationic complexes **5**–**8** and 1938–1957 cm^{-1} for deprotonated complexes **9**–**12** was found. The amide nitrogen of the ene-hydrazone ligand is a weaker π-acceptor, therefore due to the increasing electron density on the metal a reduction of the value of carbonyl valence vibration from 6 to 34 cm^{-1} was observed between pairs of corresponding complexes **5** and **9**, **6** and **10**, etc. The value of 1957 cm^{-1} for complex **9** is close to the value of 1960 cm^{-1} found by Mayer and Kaska [6] for the only rhodium PNP pincer amido carbonyl complex known

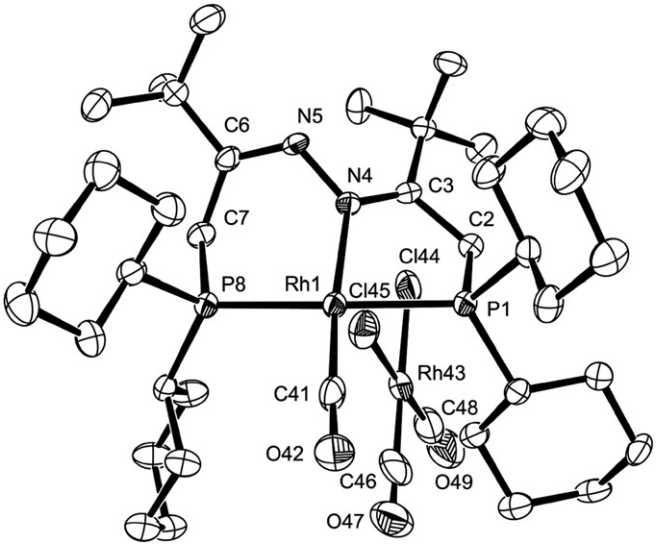


Fig. 1. ORTEP view of **6**. Hydrogen atoms are omitted for clarity.

so far. Significant further increase of electron density on rhodium was achieved by substituting phenyl groups on phosphorus atoms by more electron-donating groups, the value of carbonyl valence vibration for the *tert*-butyl substituted complex being 1938 cm^{-1}.

We have succeeded in growing the single crystals of cationic complexes **6** and **8** (Figs. 1 and 2) and of the amido complex **9**(Fig. 3). Single crystals of **6** and **8** were obtained by a slow diffusion of hexane vapour to chloroform solutions. A single crystal of **9** was obtained by a slow evaporation of dichloromethane solvent at room temperature. The structures of **6**, **8** and **9** showed that complexes were square planar with ligand P,N,P′ coordinated in the expected (*E*, *Z*) configuration in all the cases. Single crystal of the cationic complex **6** contains unexpected $[Rh(CO)_2Cl_2]^-$ anion while in complex **8** the counterion is a chloride anion. We explain the unusual counteranion by very long (1 month) crystallization of complex **6** whereby the chloride anion was substituted by the $[Rh(CO)_2Cl_2]^-$ anion, which most probably resulted from the partial decomposition of the complex in solution. All the structures exhibited only small deviations from planarity as far as atoms taking part in square planar coordination polyhedron are concerned. However, since one of the metallarings in the complexes is a six-membered ring, its puckering allowed pyramidal arrangement of bonds on an amide nitrogen in compound **9**. This alleviation of strain was not possible in case of two five membered rings of an analogous rhodium amido carbonyl complex [6]. Other important structural features are in accordance with the analogous data for this complex (in brackets). Nitrogen–rhodium distance 2.101 Å (2.074 Å) confirms single bond character, P–Rh–P′ angle 168.17° (163.8°) is a bit wider, again probably owing to less strained ligand backbone of our complex. Rhodium–carbonyl carbon distance 1.837 Å (1.855 Å) and carbonyl bond length 1.151 Å (1.125 Å) are similar and supporting slightly more electron-donating character of our ligand found by IR spectroscopy.

It was found, that complex **8** in chloroform in the presence of HCl undergoes splitting of the azine N–N bond and a complex of Rh(III) (**13**) is formed upon oxidation in a very small yield (Scheme 3). The X-ray structure of the complex (Fig. 4) shows that it is a dimer with two chloride bridges connecting two metal centres. Diphosphinoazine ligand $Bu^t_2PCH{=}C(Bu^t){-}NN{=}C(Bu^t)CH_2PBu^t_2$ is cleaved into two symmetric parts $(Bu^t)_2PCH_2C(Bu^t){=}NH$ coordinated to two rhodiums by the phosphorus and nitrogen atoms via their free electron

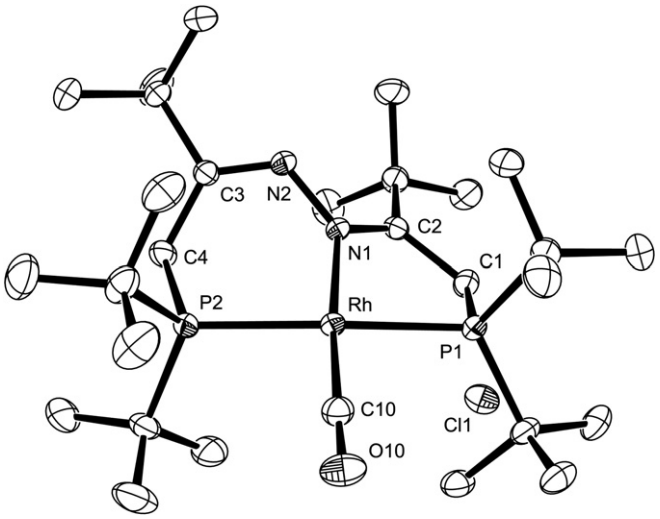


Fig. 2. ORTEP view of **8**. Hydrogen atoms are omitted for clarity.

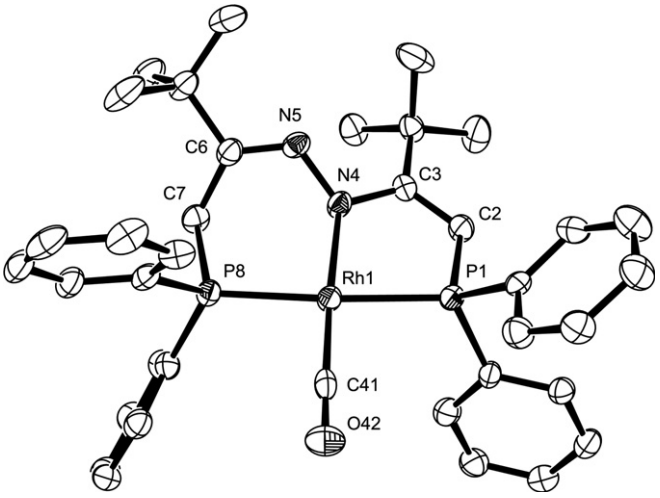


Fig. 3. ORTEP view of **9**. Hydrogen atoms are omitted for clarity.

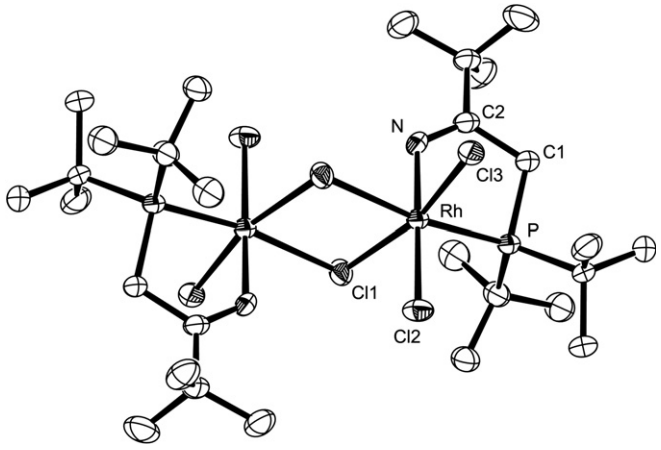
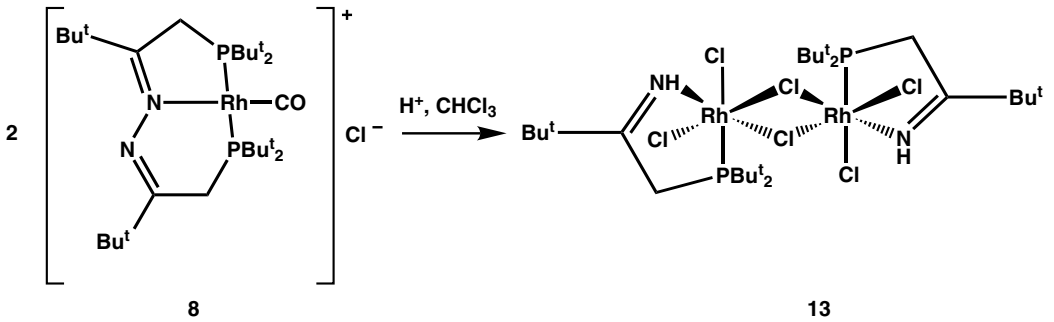


Fig. 4. ORTEP view of **13**. Hydrogen atoms are omitted for clarity.



8 13

Scheme 3.

pairs. Structure of this complex in solution was also confirmed by ^{1}H and ^{31}P NMR spectroscopy. Measurement of ^{13}C NMR spectra was not possible, because crystals of complex **13** are poorly soluble in common solvents used for NMR spectroscopy.

Cleavage of the N–N bond of the diphosphinoazine ligand is unique and has not been published, cleavage of an azine moiety was reported in several cases, however. Ketazines are cleaved giving ketiminato mononuclear [22a], binuclear homometallic [22b] or heterometallic [22c] complexes. Interestingly, substituted titanocene fragments cleave acetoneazine depending on the number of methyls on titanocene rings, giving either mononuclear monoketiminato complex or mononuclear bis(amido) complex with double C–H activation [22d]. Milstein et al. [22e] reported that aldazines are cleaved by rhodium PCP and PCN complexes in a sort of dismutation reaction resulting in an aldimine complex (or a free unstable aldimine) and a nitrile complex, ketimines were unreactive. On the basis of calculations, the reaction is believed to avoid direct oxidative addition of N–N bond to rhodium. We believe that in our case the oxidation of metal is caused by the presence of chloroform, similarly to the oxidation of Rh(I) observed in cycloocta-1,5-diene complexes [23], azine moiety being at the same time cleaved into two didentate phosphine–imine ligands. The source of hydrogen for iminato to imine transformation is unclear. It could be either HCl present in chloroform upon long standing or added purposefully or the hydrogen may come from another diphosphinoazine ligand which loses a rhodium atom entering a new complex. Owing to a low yield of the product we were unable to identify the fate of this free diphosphinoazine or its decomposition products.

5. Conclusions

The synthesis of a series of unsymmetrical pincer-like rhodium amido carbonyl complexes with four electronically and sterically different diphosphinoazine ligands considerably extends the available information about *trans* amido carbonyl arrangement on rhodium including data from X-ray diffraction. The comparison with the only known *trans* amido rhodium carbonyl symmetrical pincer complex shows that our complexes have basically the same structural features as the symmetrical complex. However, the ease of their preparation and specific features of the diphosphinoazine ligand backbone make them suitable candidates for future stoichiometric and possibly catalytic transformations on an electron-rich pincer-supported rhodium centre.

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Appendix A. Supplementary material

CCDC 671356, 665063, 671355 and 665064 contain the supplementary crystallographic data for compounds **6**, **8**, **9** and **13**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.02.029.

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