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Diphosphinoazine rhodium(III) and iridium(III) octahedral complexes

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ABSTRACT

Rhodium(III) and iridium(III) octahedral complexes of general formula $[MCl_3\{R_2PCH_2C(Bu^t)=NN=C(Bu^t)CH_2PR_2\}]$ (M = Rh, Ir; R = Ph, c-C_6H_{11}, Pr^i, Bu^t; not all the combinations) were prepared either from the corresponding diphosphinoazines and $RhCl_3 \cdot 3H_2O$ or by the oxidation of previously reported bridging complexes $[\{MCl(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-}CH=CHCH_2CH_2CH=CHCH_2CH_2)\}_2\{\mu\text{-}R_2PCH_2C(Bu^t)=NN=C(Bu^t)CH_2PR_2\}]$ with chlorine-containing solvents. Depending on the steric properties of the ligands, complexes with facial or meridional configuration were obtained. Crystal and molecular structures of three facial and two meridional complexes were determined by X-ray diffraction. Hemilability of ligand in the complex *fac*-$[RhCl_3\{(C_6H_{11})_2PCH_2C(Bu^t)=NN=C(Bu^t)CH_2P(C_6H_{11})_2\}]$ consisting in reversible decoordination of the phosphine donor group in the six-membered ring was observed as the first step of isomerization between *fac* and *mer* isomers.

1. Introduction

Polydentate ligands continue to attract attention in modern coordination and organometallic chemistry [1]. Diphosphinoazines, a recent class of polydentate phosphorus–nitrogen ligands showing high variability of coordination numbers and ligand structures in the complexes with transition metals, were introduced by Shaw et al. [2]. Bis(diphenylphosphino)pinacolone azine (**1**) [2], which was the first and for some time the only known diphosphinoazine was shown to coordinate to transition metals of Groups 6 and 8–11 [2,3]. The synthesis of analogs of this ligand with various substituents on the phosphorus atoms (**2**–**5**) [4] opened the way for further tuning of the already broad coordination variability of the diphosphinoazine [5] and led to uncovering of the catalytic activity of the diphosphinoazine complexes in the organic reactions: the Heck reaction [6a], hydroamination [6b], and polymerization [6c].

Compared to data on Group 10 metal complexes, the knowledge of the chemistry of Group 9 metal complexes is rather limited, despite the fact that the ability of diphosphinoazines to reversibly transfer the hydrogen atom to a transition metal and to create a free coordination site at the metal was elegantly demonstrated in the latter group (Ir complexes) for the first time [3c]. Cobalt, iridium and especially rhodium at the same time belong to the transition metals most often used in catalysis. As far as we are aware, there is currently only one paper on diphosphinoazine rhodium complexes [7] describing a simple cleavage of the chloro bridge of chloro-(cycloocta-1,5-diene)-rhodium(I) dimer with diphosphinoazines. We now report the continuation of this work and isolation, characterization, and dynamic behavior of some mononuclear octahedral diphosphinoazine rhodium complexes.

2. Experimental

2.1. General

All the preparations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. Pentane and hexane were distilled from sodium, THF from sodium/benzophenone, dichloromethane from $CaCl_2$ and chloroform was purified by distillation from P_2O_5 and then from $CaCl_2$. Triethylamine was stored over KOH and rectified on the Fischer HMS 500 semi-microdistillation column prior to use.

^1H (299.9 MHz), ^{13}C (75.4 MHz) and ^{31}P (121.4 MHz) NMR spectra were recorded on Varian MercuryVX 300 spectrometer in CD_2Cl_2 or $CDCl_3$ solutions 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).

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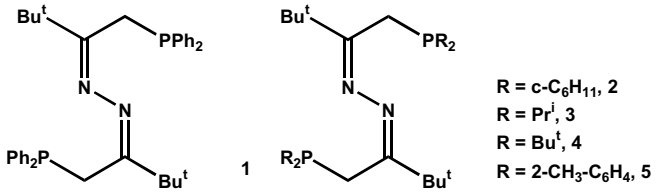
Assignments in complex NMR spectra were aided by gNMR V4.1.0. [8].

$RhCl_3 \cdot 3H_2O$ (Safina, Vestec) was used as received, diphosphinoazines $R_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PR_2$ (R = Ph, **1**, [2]; R = c-C_6H_{11}, **2**, [4]; R = Pr^i, **3**, [4]; R = Bu^t, **4**, [4]) were prepared as indicated.



Starting rhodium(I) and iridium(I) bridging complexes were synthesized by the reaction of $[RhCl(cod)]_2$ or $[IrCl(cod)]_2$ with two equivalents of an appropriate azine diphosphine ligand in chloroform at room temperature as described previously [7]. The following complexes were prepared.

[{RhCl(1,2-η:5,6-η-CH=$CHCH_2CH_2CH$=$CHCH_2CH_2$)}$_2${μ-Ph_2PCH_2-$C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2$] (**6**)

[{RhCl(1,2-η:5,6-η-CH=$CHCH_2CH_2CH$=$CHCH_2CH_2$)}$_2${μ-(c-C_6H_{11})$_2$-$PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P$(c-C_6H_{11})$_2$] (**7**).

[{RhCl(1, 2-η : 5, 6-η-CH=$CHCH_2CH_2CH$=$CHCH_2CH_2$)}$_2${μ-Pr^i_2-$PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPr^i_2$] (**8**).

[{IrCl(1,2-η:5,6-η-CH=$CHCH_2CH_2CH$=$CHCH_2CH_2$)}$_2${μ-Ph_2PCH_2 $C(Bu^t)$=NN=$C(Bu^t)$ CH_2PPh_2] (**9**).

[{IrCl(1,2-η:5,6-η-CH=$CHCH_2CH_2CH$=$CHCH_2CH_2$)}$_2${μ-(c-C_6H_{11})$_2$-$PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P$(c-C_6H_{11})$_2$] (**10**).

[{IrCl(1, 2-η : 5, 6-η-CH=$CHCH_2CH_2CH$=$CHCH_2CH_2$)}$_2${μ-Pr^i_2-$PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPr^i_2$] (**11**).

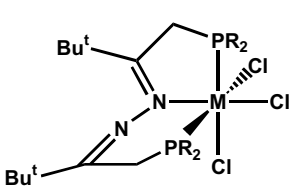
2.2. Synthesis of rhodium(III) complexes

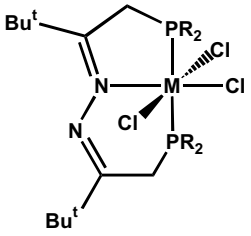
Two general procedures were used for the synthesis of octahedral Rh(III) complexes.

Method A: The reaction mixture of 0.0300 g (0.120 mmol) of $RhCl_3 \cdot 3H_2O$ and equimolar amount of azine diphosphine ligand was stirred under reflux in THF for a variable period of time. After cooling to ambient temperature, a small amount of precipitate (a side product, probably anhydrous rhodium trichloride, typically 5% of the starting material) was filtered off, the solvent was evaporated in vacuo and the product was dissolved in chloroform (1 ml). The product was isolated by crystallization via slow diffusion of hexane vapour to the chloroform solution at room temperature. Reaction times and yields are given in Table 1.

Method B: This method was used for the synthesis of both rhodium(III) and iridium(III) octahedral complexes. Suspensions of bridging complexes **7**–**11** in the chloroform were heated at 50–60 °C in ampoules sealed under vacuum for a variable period of time until all the starting complexes dissolved. Then the ampoule was opened and the solvent was partially evaporated in vacuo to about one quarter. The product was isolated by crystallization via slow diffusion of hexane vapour to the concentrated chloroform solution at room temperature. Complex **12** was prepared by standing of **6** in chloroform at room temperature for 15 days. The product was isolated after spontaneous crystallization. The yields for method B in Table 1 are referred to a ligand present in the starting complexes, not to the metal which is thus half-wasted but another crop of the product can be obtained after further addition of the ligand as discussed below for the reaction of complex **6**.

Complex **14** was prepared by the same way as complex **15**, except that the mixture of chloroform and oct-1-ene (1:1 v/v) was used.





2.2.1. *fac*-[$RhCl_3${$Ph_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2$}] (**12**)

Method A and method B, monocrystal suitable for the X-ray diffraction was obtained by the selection of a suitable crystal from the product obtained by method B.

^{31}P NMR: ($CDCl_3$): δ_{P1} = 39.6 dd ($^1J_{RhP}$ = 112.5 Hz, $^2J_{PP}$ = 13.4 Hz), δ_{P2} = 45.5 dd ($^1J_{RhP}$ = 123.5 Hz, $^2J_{PP}$ = 13.6 Hz).

^{1}H NMR ($CDCl_3$): 1.09 s (9H, *t*-Bu), 1.47 s (9H, *t*-Bu), 2.14 dd (1H, $^2J_{PH}$ = 12.4 Hz, $^2J_{HH}$ = 12.4 Hz, CH_2, PCH_2), 3.56 dd (1H, $^2J_{HH}$ = 14.8 Hz, $^2J_{PH}$ = 13.2 Hz, CH_2, PCH_2), 3.94 dd (1H, $^2J_{HH}$ = 18.0 Hz, $^2J_{PH}$ = 12.1 Hz, CH_2, PCH_2), 4.99 ddd (1H, $^2J_{HH}$ = 18.0 Hz, $^2J_{PH}$ = 9.8 Hz, J_{PH} = 1.4 Hz, CH_2, PCH_2), 6.65–6.71 m (2H, Ph), 6.89–6.94 m (4H, Ph), 7.07–7.24 m (6H, Ph), 7.36–7.42 m (2H, Ph), 7.47–7.51 m (2H, Ph), 8.14–8.21 m (4H, Ph).

^{13}C NMR ($CDCl_3$): 24.22 d ($^1J_{PC}$ = 22.61 Hz, CH_2, PCH_2), 27.35 s (CH_3, *t*-Bu), 28.41 s (CH_3, *t*-Bu), 39.93 d ($^3J_{PC}$ = 2.1 Hz, >C<, *t*-Bu), 41.19 d ($^3J_{PC}$ = 6.9 Hz, >C<, *t*-Bu), 46.17 d ($^1J_{PC}$ = 41.2, Hz, CH_2, PCH_2), 127.10 d (J_{PC} = 11.2 Hz, CH, Ph), 128.14 d (J_{PC} = 11.4 Hz, CH, Ph), 129.38–129.59 m (CH, Ph), 130.16 d (J_{PC} = 2.7 Hz, CH, Ph), 130.42 d (J_{PC} = 2.7 Hz, CH, Ph), 131.28 d (J_{PC} = 3.0 Hz, CH, Ph), 131.87 d (J_{PC} = 2.7 Hz, CH, Ph), 132.10 d ($^1J_{PC}$ = 2.2 Hz, >C<, Ph), 132.66 d ($^1J_{PC}$ = 2.1 Hz, >C<, Ph), 134.07 d ($^1J_{PC}$ = 2.9 Hz, >C<), 134.70 d ($^1J_{PC}$ = 2.8 Hz, >C<), 135.52–135.73 m (CH, Ph), 173.81 d ($^2J_{PC}$ = 1.9 Hz, >C<, >C=N), 184.13 d ($^2J_{PC}$ = 2.0 Hz, >C<, >C=N).

2.2.2. *fac*-[$RhCl_3${$(C_6H_{11})_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P(C_6H_{11})_2$}] (**13**)

Method A, monocrystal suitable for the X-ray diffraction was obtained by a slow diffusion of hexane vapour to a dichloromethane solution at room temperature.

Table 1
Preparation od Rh(III) diphosphinoazine complexes

Complex	Reaction time (h)	Temperature (°C)	Yield (%)
12[a]	1.5	66[c]	70
13[a]	1.5	66[c]	61
15[a]	3	66[c]	83
16[a]	4	66[c]	58
12[b]	360	25	58
14[b]	96	60	86[d]
15[b]	3	50	46
17[b]	72	50	64
18[b]	72	50	76
19[b]	72	50	48

[a] Method A.
[b] Method B.
[c] Reflux in THF.
[d] First crop (26 %) pure **14**, second crop (60%) mixture of **13** and **14**; chloroform/oct-1-ene (1:1, v/v) used as the solvent.

^{31}P NMR (CD_2Cl_2, −30 °C): δ_{P1} = 60.1 d ($^1J_{RhP}$ = 107.6 Hz), δ_{P2} = 65.7 d ($^1J_{RhP}$ = 120.1 Hz).

^{1}H NMR (CD_2Cl_2, −30 °C): 1.30 s (9H, *t*-Bu), 1.31 s (9H, *t*-Bu), 1.42–2.13 bm (CH_2, c-C_6H_{11}), 2.41–2.50 bm (CH_2, c-C_6H_{11}), 2.86–2.87 bm (CH_2, c-C_6H_{11}), 3.16–3.25 m (CH_2, c-C_6H_{11}), 3.23–3.41 m (CH, c-C_6H_{11}), 3.32–3.38 m (1H, CH_2, PCH_2), 3.55–3.72 m (CH, c-C_6H_{11}), 3.81–3.89 m (1H, CH_2, PCH_2), 4.11 dd (1H, $^2J_{HH}$ = 23.5 Hz, $^2J_{PH}$ = 11.7 Hz, CH_2, PCH_2), 4.74 dd (1H, $^2J_{HH}$ = 17.0 Hz, $^2J_{PH}$ = 10.2 Hz, CH_2, PCH_2).

^{13}C NMR (CD_2Cl_2, −30 °C): 22.20 d ($^1J_{PC}$ = 19.9 Hz, CH_2, PCH_2), 26.49–26.63 m (CH_2), 28.97–35.37 m (CH_2, c-C_6H_{11}), 30.93 s (CH_3, *t*-Bu), 31.48 s (CH_3, *t*-Bu), 37.54 d ($^1J_{PC}$ = 31.2 Hz, CH_2, PCH_2), 37.54 d ($^1J_{PC}$ = 31.2 Hz, CH, c-C_6H_{11}), 40.67 d ($^1J_{PC}$ = 14.1 Hz, CH, c-C_6H_{11}), 42.53 d ($^1J_{PC}$ = 25.2 Hz, CH, c-C_6H_{11}), 43.63 d ($^3J_{PC}$ = 2.2 Hz, >C<, *t*-Bu), 43.95 d ($^3J_{PC}$ = 6.4 Hz, >C<, *t*-Bu), 47.17–47.62 m (CH, c-C_6H_{11}), 176.22 s (>C<, >C=N), 188.16 s (>C<, >C=N).

^{31}P NMR spectra simulation [8] parameters describing the exchange **13**–**13a**–**14**.

−30 °C: Complex **13**, δ_{P1} = 60.1 ($^1J_{RhP}$ = 107.9 Hz), δ_{P2} = 65.7 ($^1J_{RhP}$ = 120.4 Hz), $^2J_{PP}$ = 4.6 Hz, relative concentration 1; complex **13a**, δ_{P1} = 62.8 ($^1J_{RhP}$ = 109.0 Hz), δ_{P2} = −4.7 ($^1J_{RhP}$ = 0 Hz), $^2J_{PP}$ = 0 Hz, relative concentration 0.0095; complex **14**, δ_{P1} = 41.5 ($^1J_{RhP}$ = 84.8 Hz), δ_{P2} = 40.8 ($^1J_{RhP}$ = 86.8 Hz), $^2J_{PP}$ = 545 Hz, relative concentration 0.11. Exchange rates, r_1 (**13**–**13a**) 135 s^{-1}, r_2 (**13a**–**14**) 2030 s^{-1}.

25 °C: Complex **13**, δ_{P1} = 57.0 ($^1J_{RhP}$ = 119.3 Hz), δ_{P2} = 62.9 ($^1J_{RhP}$ = 123.9 Hz), $^2J_{PP}$ = 4.5 Hz, relative concentration 1; complex **13a**, δ_{P1} = 70.0 ($^1J_{RhP}$ = 109.5 Hz), δ_{P2} = 0.7 ($^1J_{RhP}$ = 0 Hz), $^2J_{PP}$ = 0 Hz, relative concentration 0.023; complex **14**, δ_{P1} = 41.5 ($^1J_{RhP}$ = 84.8 Hz), δ_{P2} = 40.8 ($^1J_{RhP}$ = 86.8 Hz), $^2J_{PP}$ = 545 Hz, relative concentration 0.13. Exchange rates, r_1 (**13**–**13a**) 5900 s^{-1}, r_2 (**13a**–**14**) 3.02 × 10^{16} s^{-1}.

*2.2.3. mer-[RhCl$_3${(C$_6$H$_{11}$)$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$P(C$_6$H$_{11}$)$_2$}] (**14**)*

Complex was prepared by method B, in the manner described above. A monocrystal suitable for the X-ray diffraction was selected from the crystalline product obtained by method B.

^{31}P NMR ($CDCl_3$): ABX 40.8 ($^1J_{RhP}$ = 86.8 Hz), 41.5 ($^1J_{RhP}$ = 84.8 Hz) ($^2J_{PP}$ = 545.0 Hz).

^{1}H NMR ($CDCl_3$): 1.21 s (9H, CH_3, *t*-Bu), 1.24 s (9H, CH_3, *t*-Bu), 1.44–1.53 m (CH_2, c-C_6H_{11}), 1.70–1.88 m (CH_2, c-C_6H_{11}), 2.05–2.09 m (CH_2, c-C_6H_{11}), 2.46 d (2H, $^2J_{PH}$ = 5.8 Hz, CH_2, PCH_2), 2.52 broad s (CH_2, c-C_6H_{11}), 2.72–2.78 m (2H, CH, c-C_6H_{11}), 2.81–2.86 m (CH_2, c-C_6H_{11}), 2.97–3.04 m (2H, CH, c-C_6H_{11}), 3.67 d (2H, $^2J_{PH}$ = 4.0 Hz, CH_2, PCH_2).

^{13}C NMR ($CDCl_3$): 19.36 dd ($^1J_{PC}$ = 6.4 Hz, $^3J_{PC}$ = 4.0 Hz, CH_2, PCH_2), 26.60 s (CH_2, c-C_6H_{11}), 26.82 s (CH_2, c-C_6H_{11}), 27.50–28.19 m (CH_2, c-C_6H_{11}) 28.14 s (CH_3, *t*-Bu), 28.33 s (CH_3, *t*-Bu), 29.52 d (*J* = 2.5 Hz, CH_2, c-C_6H_{11}), 29.66 s (CH_2, c-C_6H_{11}), 30.40 d (*J* = 3.9 Hz, CH_2, c-C_6H_{11}), 30.50 s (CH_2, c-C_6H_{11}), 34.73 dd ($^1J_{PC}$ = 14.8 Hz, $^3J_{PC}$ = 7.1 Hz, CH_2, PCH_2), 35.86 dd ($^1J_{PC}$ = 10.1 Hz, $^3J_{PC}$ = 7.7 Hz, CH, c-C_6H_{11}), 36.11 dd ($^1J_{PC}$ = 11.2 Hz, $^3J_{PC}$ = 8.9 Hz, CH, c-C_6H_{11}), 41.32 s (>C<, *t*-Bu), 41.45 broad s (>C<, *t*-Bu), 173.13 s (>C<, >C=N), 189.17 dd ($^2J_{PC}$ = 4.1 Hz, $^4J_{PC}$ = 4.0 Hz, >C<, >C=N).

*2.2.4. fac-[RhCl$_3${Pr$^i_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPr$^i_2$}] (**15**)*

Complex was prepared both by method A and by method B. A monocrystal suitable for the X-ray analysis was obtained by a slow evaporation of the solvent at room temperature.

^{31}P NMR ($CDCl_3$): δ_{P1} = 64.1 dd ($^1J_{RhP}$ = 109.6 Hz, $^2J_{PP}$ = 11.5 Hz), δ_{P2} = 64.8 dd ($^1J_{RhP}$ = 118.5 Hz, $^2J_{PP}$ = 12.4 Hz).

^{1}H NMR ($CDCl_3$): 1.03 dd (3H, $^2J_{PH}$ = 14.1 Hz, $^3J_{HH}$ = 6.9 Hz, CH_3, *i*-Pr), 1.32 s (9H, *t*-Bu), 1.32 s (9H, *t*-Bu), 1.36–1.48 m (12 H, CH_3, *i*-Pr), 1.48 dd (3H, $^2J_{PH}$ = 17.8 Hz, $^3J_{HH}$ = 7.5 Hz, CH_3, *i*-Pr), 1.53–1.61 m (1H, CH_2, PCH_2), 1.65 dd (3H, $^2J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.2 Hz, CH_3, *i*-Pr), 1.66 dd (3H, $^2J_{PH}$ = 16.1 Hz, $^3J_{HH}$ = 7.3 Hz, CH_3, *i*-Pr), 2.38–2.56 m (2H, CH, *i*-Pr), 3.22 dd (1H, $^2J_{HH}$ = 16.0 Hz, $^2J_{PH}$ = 11.7 Hz, CH_2, PCH_2), 3.24 dd (1 H, $^2J_{HH}$ = 16.0 Hz, $^2J_{PH}$ = 11.7 Hz, CH_2), 3.64 d sep (2H, $^2J_{PH}$ = 14.4 Hz, $^3J_{HH}$ = 7.2 Hz, CH, *i*-Pr), 4.23 d sep (2H, $^2J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.5 Hz, CH, *i*-Pr), 4.57 dd (1H, $^2J_{HH}$ = 17.9 Hz, $^2J_{PH}$ = 9.3 Hz, CH_2).

^{13}C NMR ($CDCl_3$): 17.77 s (CH_3, *i*-Pr), 18.94 s (CH_3, *i*-Pr), 19.57d ($^2J_{PC}$ = 7.3 Hz, CH_3, *i*-Pr), 20.19–20.57 m (3× CH_3, *i*-Pr), 20.32 s (CH_3, *i*-Pr), 21.19 d ($^1J_{PC}$ = 19.8 Hz, CH_2, PCH_2), 21.63 s (CH_3, *i*-Pr), 26.57 d ($^1J_{PC}$ = 15.0 Hz, CH, *i*-Pr), 27.73 s (CH_3, *t*-Bu), 28.20 s (CH_3, *t*-Bu), 29.53 d ($^1J_{PC}$ = 27.9 Hz, CH, *i*-Pr), 31.20 d ($^1J_{PC}$ = 29.1 Hz, CH, *i*-Pr), 33.58 d ($^1J_{PC}$ = 20.4 Hz, CH, *i*-Pr), 34.69 d ($^1J_{PC}$ = 31.4 Hz, CH_2, PCH_2), 40.63 d ($^3J_{PC}$ = 2.3 Hz, >C<, *t*-Bu), 41.11 d ($^3J_{PC}$ = 6.6 Hz, >C<, *t*-Bu), 174.00 d ($^2J_{PC}$ = 2.0 Hz, >C<, >C=N), 185.62 s (>C<, >C=N).

*2.2.5. mer-[RhCl$_3${Bu$^t_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PBu$^t_2$}] (**16**)*

Complex was prepared by method A, monocrystal suitable for X-ray diffraction was obtained by slow diffusion of hexane vapour to a chloroform solution at room temperature.

^{31}P NMR ($CDCl_3$): ABX 10.8 ($^1J_{RhP}$ = 85.9 Hz), 57.4 ($^1J_{RhP}$ = 86.0 Hz) ($^2J_{PP}$ = 528.0 Hz).

^{1}H NMR ($CDCl_3$) (−30 °C): 1.31 s (9H, *t*-Bu), 1.35 s (9H, t-Bu), 1.45 s (9H, *t*-Bu), 1.49 s (9H, *t*-Bu), 1.65 d (9H, *J* = 14.3 Hz, *t*-Bu), 1.71 d (9H, *J* = 14.4 Hz, *t*-Bu), 2.48 ddd (1H, $^2J_{HH}$ = 18.0 Hz, $^2J_{PH}$ = 13.2 Hz, $^4J_{PH}$ = 7.5 Hz, CH_2, PCH_2), 3.37 ddd (1H, $^2J_{HH}$ = 18.5 Hz, $^2J_{PH}$ = 11.6 Hz, $^4J_{PH}$ = 7.7 Hz, CH_2, PCH_2), 3.51 dd (1H, $^2J_{HH}$ = 18.0 Hz, $^2J_{PH}$ = 9.0 Hz, CH_2), 4.28 dd (1H, $^2J_{HH}$ = 18.8 Hz, $^2J_{PH}$ = 5.2 Hz, CH_2, PCH_2).

^{13}C NMR ($CDCl_3$): 16.75 d ($^1J_{PC}$ = 16.4 Hz, CH_2, PCH_2), 29.32 s (CH_3, *t*-Bu), 29.48 s (CH_3, *t*-Bu), 31.58 broad s (CH_3, *t*-Bu), 31.76 broad s (CH_3, *t*-Bu), 37.45 dd ($^1J_{PC}$ = 19.1 Hz, $^3J_{PC}$ = 3.0 Hz, CH_2, PCH_2), 38.85–39.47 m (>C<, *t*-Bu), 41.38–41.78 m (>C<, *t*-Bu), 43.64 d ($^3J_{PC}$ = 4.7 Hz, >C<, *t*-Bu), 43.87 d ($^3J_{PC}$ = 4.8 Hz, >C<, *t*-Bu), 173.25 s (>C<, >C=N), 197.46 dd ($^2J_{PC}$ = 4.9 Hz, $^4J_{PC}$ = 1.5 Hz, >C<, >C=N).

*2.2.6. fac-[IrCl$_3${Ph$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPh$_2$}] (**17**)*

Complex was prepared by method B.

^{31}P NMR ($CDCl_3$): δ_{P1} = −8.3 d, δ_{P2} = 30.0 d ($^2J_{PP}$ = 21.3 Hz).

^{1}H NMR ($CDCl_3$): 0.99 s (9H, *t*-Bu), 1.45 s (9H, *t*-Bu), 4.23 d (1H, $^2J_{PH}$ = 9.5 Hz, CH_2, PCH_2), 4.30 d (1H, $^2J_{PH}$ = 9.3 Hz, CH_2, PCH_2), 4.39 d (1H, $^2J_{PH}$ = 5.7 Hz, CH_2, PCH_2), 4.48 d (1H, $^2J_{PH}$ = 6.0 Hz, CH_2, PCH_2), 6.74–6.80 m (2H, CH, Ph), 6.97–7.07 m (4H, CH, Ph), 7.16–7.21 m (2H, CH, Ph), 7.31–7.74 m (14H, CH, Ph).

^{13}C NMR ($CDCl_3$): 25.87 d ($^1J_{PC}$ = 17.1 Hz, CH_2, PCH_2), 27.83 s (CH_3, *t*-Bu), 28.81 s (CH_3, *t*-Bu), 39.98 d ($^3J_{PC}$ = 2.0 Hz, >C<, *t*-Bu), 40.62 d ($^3J_{PC}$ = 5.8 Hz, >C<, *t*-Bu), 45.21 dd ($^1J_{PC}$ = 32.3 Hz, $^3J_{PC}$ = 2.6 Hz, CH_2, PCH_2), 128.41–129.80 m (CH, Ph), 130.51–131.23 m (CH, Ph), 132.02 d ($^1J_{PC}$ = 4.9 Hz, >C<, Ph), 133.06 d ($^1J_{PC}$ = 6.0 Hz, >C<, Ph), 133.36–133.52 m (CH, Ph), 133.55 d ($^1J_{PC}$ = 9.6 Hz, >C<, Ph), 134.04 d ($^1J_{PC}$ = 4.9 Hz, >C<, Ph), 174.14 s (>C<, >C=N), 184.23 dd (*J* = 7.0 Hz, *J* = 2.7 Hz, >C<, >C=N).

*2.2.7. fac-[IrCl$_3${(C$_6$H$_{11}$)$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$P(C$_6$H$_{11}$)$_2$}] (**18**)*

Complex was prepared by method B.

^{31}P NMR ($CDCl_3$): δ_{P1} = 7.0 d, δ_{P2} = 18.9 d ($^2J_{PP}$ = 20.4 Hz).

^{1}H NMR ($CDCl_3$): 1.22 broad s (18H, *t*-Bu), 1.24–1.36 m (CH_2, c-C_6H_{11}), 1.61–2.14 m (CH_2, c-C_6H_{11}), 3.88 d (1H, $^2J_{PH}$ = 2.8 Hz, CH_2, PCH_2), 4.01 broad s (1H, CH_2, PCH_2), 4.84 broad s (1H, CH_2, PCH_2), 5.56 d (1H, $^2J_{PH}$ = 2.8 Hz, CH_2, PCH_2).

^{13}C NMR ($CDCl_3$): 22.55 d ($^1J_{PC}$ = 15.3 Hz, CH_2, PCH_2), 25.97–32.03 m (CH_2, c-C_6H_{11}), 28.05 s (CH_3, *t*-Bu), 31.20 s (CH_3, *t*-Bu), 33.90 d ($^1J_{PC}$ = 11.8 Hz, CH_2, PCH_2), 39.72 d ($^1J_{PC}$ = 2.0 Hz, CH, c-C_6H_{11}), 43.57 d ($^1J_{PC}$ = 1.8 Hz, CH, c-C_6H_{11}), 48.02 d ($^1J_{PC}$ = 1.9 Hz, CH, c-C_6H_{11}), 50.44 d ($^1J_{PC}$ = 1.2 Hz, CH, c-C_6H_{11}), 58.35 broad s (>C<, *t*-Bu), 58.90 broad s (>C<, *t*-Bu), 174.66 broad s (>C<, >C=N), 181.34 broad s (>C<, >C=N).

2.2.8. fac-[$IrCl_3\{Pr^i_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPr^i_2\}$] (**19**)

Complex was prepared by method B.

^{31}P NMR ($CDCl_3$): δ_{P1} = 12.2 d, δ_{P2} = 25.6 d ($^2J_{PP}$ = 23.3 Hz).

^1H NMR ($CDCl_3$): 1.06–1.70 m (24H, CH_3, *i*-Pr), 1.24 s (9H, *t*-Bu), 1.32 (9H, *t*-Bu), 2.55–2.67 m (2H, CH, *i*-Pr), 3.01–3.12 m (2H, CH, *i*-Pr), 3.25–3.35 m (2H, CH_2, PCH_2), 3.66–3.73 m (2H, CH_2, PCH_2).

^{13}C NMR ($CDCl_3$): 19.34 d (J = 1.6 Hz, CH_3, *i*-Pr), 19.39 s (CH_3, *i*-Pr), 20.20 d (J = 2.8 Hz, CH_3, *i*-Pr), 20.30 s (CH_3, *i*-Pr), 22.86 d ($^1J_{PC}$ = 10.2 Hz, CH_2, PCH_2), 23.18 d ($^1J_{PC}$ = 14.3 Hz, CH, *i*-Pr), 23.53 d ($^1J_{PC}$ = 15.3 Hz, CH, *i*-Pr), 27.96 s (CH_3, *t*-Bu), 28.57 s (CH_3, *t*-Bu), 39.61 d (J = 4.3 Hz, >C<, *t*-Bu), 39.77 d ($^3J_{PC}$ = 2.5 Hz, >C<, *t*-Bu), 42.93 d ($^1J_{PC}$ = 27.9 Hz, CH_2, PCH_2), 174.98 s (>C<, >C=N), 189.71 d ($^2J_{PC}$ = 3.3 Hz, >C<, >C=N).

2.2.9. Crystallographic data

Single crystals suitable for the X-ray diffraction were obtained as mentioned below. Data were collected at 150 K on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation. The structure was solved by direct methods [9].

*2.2.10. fac-[$RhCl_3\{Ph_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPh_2\}$] (**12**)*

X-ray: $C_{36}H_{42}Cl_3N_2P_2Rh \cdot 2CHCl_3$. M = 1012.65 g/mol, monoclinic, space group $P2_1/n$, a = 13.7068(2), b = 15.5865(2), c = 21.2606(3) Å, β = 101.4034(6)°, Z = 4, V = 4452.50(1) Å^3, D_{calc} = 1.51 g cm^{-3}, μ(Mo Kα) = 1.03 mm^{-1}, crystal dimension of 0.3 × 0.5 × 0.5 mm. The structure was refined by full matrix least-squares on F^2 values [10]. All the heavy atoms, with the exception of three Cl atoms in one disordered molecule of chloroform, were refined anisotropically. The disorder of both chloroform molecules was modeled. All the hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0347 and R_w = 0.0817 using 8645 independent reflections (θ_{max} = 27.51°).

*2.2.11. fac-[$RhCl_3\{(C_6H_{11})_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P(C_6H_{11})_2\}$] (**13**)*

X-ray: $C_{36}H_{66}Cl_3N_2P_2Rh \cdot 2CH_2Cl_2$. M = 968.01 g/mol, orthorhombic system, space group $P2_12_12_1$, a = 10.8560(1), b = 17.4580(1), c = 25.0920(2) Å, Z = 4, V = 4655.54(6) Å^3, D_{calc} = 1.35 g cm^{-3}, μ(Mo Kα) = 0.85 mm^{-1}, crystal dimensions of 0.2 × 0.3 × 0.3 mm. Approximately 11/2 disordered molecules of solvent were found in an asymmetric part. It was not possible to fit the disorder with a reasonable model thus the solvent molecules were removed and the structure was treated by the SQUEEZE procedure [11]. In the solvent accessible void of 1175 A^3 341 electrons were found; that nicely corresponds to two dichloromethane solvent molecules in the asymmetric part. The structure was refined by full matrix least-squares on F values [12]. All the heavy atoms were refined anisotropically. All the hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0254 and R_w = 0.0301 using 5637 independent reflections (θ_{max} = 27.48°). The Flack enantiomorph parameter (0.06 ± 0.02) was calculated from uncorrected data.

*2.2.12. mer-[$RhCl_3\{(C_6H_{11})_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2P(C_6H_{11})_2\}$] (**14**)*

X-ray: $C_{36}H_{66}Cl_3N_2P_2Rh \cdot CHCl_3$. M = 927.52 g/mol, monoclinic system, space group $P2_1/n$, a = 11.8350(1), b = 19.9620(3), c = 19.0040(3) Å, β = 101.099(1)°, Z = 4, V = 4405.7(1) Å^3, D_{calc} = 1.38 g cm^{-3}, μ(Mo Kα) = 0.85 mm^{-1}, crystal dimensions of 0.1 × 0.2 × 0.2 mm. The structure was refined by full matrix least-squares on F values [12]. All the heavy atoms were refined anisotropically. The disorder of one cyclohexyl group was modeled. All the hydrogen atoms were localized from the expected geometry and were not refined. This model converged to the final R = 0.0349 and R_w = 0.0158 using 7941 independent reflections (θ_{max} = 27.48°).

2.2.13. fac-[$RhCl_3\{Pr^i_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PPr^i_2\}$] (**15**)

X-ray: $C_{24}H_{50}Cl_3N_2P_2Rh \cdot CHCl_3$. M = 757.26 g/mol, monoclinic system, space group $P2_1/n$, a = 11.7100(2), b = 19.3300(3), c = 15.4240(2) Å, β = 97.510(1)°, Z = 4, V = 3461.34(9) Å^3, D_{calc} = 1.45 g cm^{-3}, μ(Mo Kα) = 1.07 mm^{-1}, crystal dimensions of 0.2 × 0.2 × 0.5 mm. The structure was refined by full matrix least-squares on F values [12]. All the heavy atoms were refined anisotropically. The hydrogen atoms were localized from the expected geometry and were refined isotropically. This model converged to the final R = 0.0317 and R_w = 0.0358 using 5952 independent reflections (θ_{max} = 27.49°).

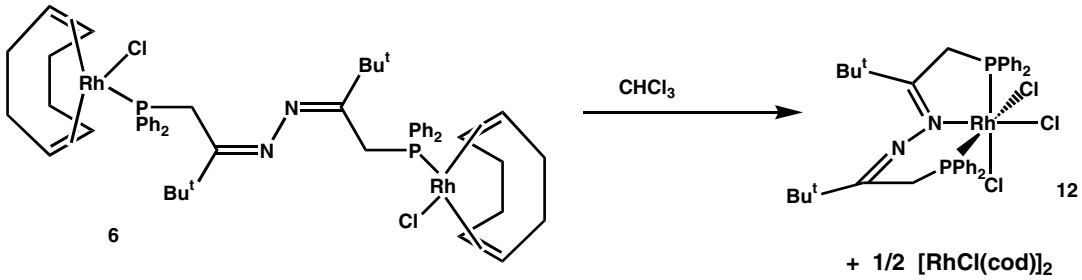
2.2.14. mer-[$RhCl_3\{Bu^t_2PCH_2C(Bu^t)$=NN=$C(Bu^t)CH_2PBu^t_2\}$] (**16**)

X-ray: $C_{28}H_{58}Cl_3N_2P_2Rh$, M = 693.99 g/mol, monoclinic system, space group $C2/c$, a = 22.5920(7), b = 10.7420(3), c = 15.98820(4) Å, β = 122.272(2)°, Z = 4, V = 3279.4(2) Å^3, D_{calc} = 1.41 g cm^{-3}, μ(Mo Kα) = 0.88 mm^{-1}, crystal dimensions of 0.2 × 0.2 × 0.3 mm. The structure shows pseudo inversion centre in the $C2/c$ space group. The asymmetric unit contains only half of the complex molecule that is possible to refine with the 25% disorder. The structure was refined by full matrix least-squares on F values [12]. All the heavy atoms were refined anisotropically. The hydrogen atoms were localized from the geometry and those with the full occupancy were refined isotropically. This model converged to the final R = 0.0395 and R_w = 0.0333 using 6936 independent reflections (θ_{max} = 27.59°).

3. Results and discussion

3.1. Synthesis and characterization of complexes

During the synthesis of complex **6** [7] we observed its spontaneous transformation to an octahedral complex of Rh(III), **12**, upon staying in the chloroform at room temperature for two weeks. Other chlorinated solvents (CH_2Cl_2, C_6H_5Cl and $C_6H_5CH_2Cl$) were equally effective in the oxidation of the Rh(I) complex to the Rh(III) product. The stoichiometry of the reaction (Scheme 1) required that only one of the two rhodium atoms of binuclear complex **6** was oxidized and complexed to the diphosphinoazine. The other rhodium atom remained complexed to cycloocta-1,5-diene in the



Scheme 1.

form of chloro(cycloocta-1,5-diene)rhodium(I) dimer as was confirmed by the addition of a half-molar amount of diphosphinoazine **1** to the reaction mixture. Ligand **1** then reacted with the dimer forming another portion of complex **6** as shown by ^{31}P NMR which afterwards slowly reacted with the solvent again. The analogous complexes **7**–**11** reacted in the same way as complex **6**, but heating of the solutions was necessary. Being heated in chlorinated solvents, all the bridging complexes of rhodium(I) and iridium(I) [7] formed facial octahedral complexes of Rh(III) **12**, **15** and Ir(III)**17**–**19** with *P*,*N*,*P*′-coordinated azine diphosphine ligand in (*E*, *Z*) configuration (Table 1).

The synthesis of octahedral complexes from binuclear dimers **6**–**11** was denoted method B. An alternative way of synthesis of the octahedral complexes was the reaction of an azine diphosphine ligand with an equimolar amount of $RhCl_3 \cdot 3H_2O$ (method A). All the facial complexes **12**, **13**, **15**, **17**–**19** could be prepared by this reaction.

It was possible to determine whether the configuration of the azine diphosphine ligand in Rh(III) and Ir(III) complexes is facial or meridional from the proton, carbon and phosphorus NMR spectra. The values of the interaction constants $^2J_{PP}$ in Rh(III) facial complexes with phosphine groups mutually *cis* were low, in range from 11.4 to 13.6 Hz. In the case of complex **13**, it was not possible to determine the value of this constant directly from the spectrum, due to the broadening of signals, even under −30 °C. The values of $^1J_{RhP}$ were different for phosphorus atoms P1 and P2 of the ligands and were in the range typical for such kind of interaction (P1: 107.6–112.5 Hz, P2: 118.5–123.5 Hz).

In the case of Ir(III) complexes the interaction constants $^2J_{PP}$ were higher, in range of 20.4–23.3 Hz, which nevertheless confirmed *cis* configuration of the two phosphorus atoms. ^{31}P NMR spectra of iridium(III) complex **18** did not exhibit any signal broadening similar to that found in complex **13**, suggesting that the reversible decoordination of the phosphine group observed in the rhodium complex (see below) did not take place. Proton (Table 2) and carbon NMR spectra of complexes **12**, **13**, **15**, **17**–**19** were very similar to each other as far as diphosphinoazine ligand frame is concerned, the differences were naturally stemming from different substituents on phosphoruses P1 and P2. Four different signals of methylene protons were observed for complexes **12**, **13**, **15**, **17**, **18**. Depending on the particular complex these signals were multiplets, doublets of doublets with very well resolved $^2J_{PH}$ and $^2J_{HH}$, or even doublets of doublets of doublets, where the signal was further split. The origin of this additional splitting, which was not maintained after broadband phosphorus decoupling and could not therefore be due to the coupling with rhodium, was ascribed either to the seven bond coupling $^7J_{PP}$ [13] or more likely to $^4J_{PH}$ coupling with the second phosphorus atom. In complex **19** signals of protons collapsed into two broad multiplets. Two different signals of methylene carbons confirmed the tridentate structure with one of the nitrogens coordinated by an electron pair. The NMR spectra of known similar iridium [3d] and tungsten or molybdenum [14] complexes with bis(diphenylphosphino)pinacoloneazine ligand exhibited the same features.

Heating of complex **7** in chloroform/hex-1-ene or chloroform/oct-1-ene mixture (1:1) led somewhat unexpectedly to a meridional complex **14**. We believe that the presence of the olefin in the reaction mixture was crucial because the azine diphosphine ligand was forced to be in the meridional configuration in the complex by the temporary coordination of the olefin.

Method A allowed also the synthesis of complex **16**, inaccessible by method B. We suppose that this complex had the ligand in the meridional configuration due to the bulkiness of phosphine *tert*-butyl groups. By contrast, it was not possible to synthesize analogous iridium(III) complex in this manner.

Interaction constants $^1J_{RhP}$ of both meridional complexes **14** and **16** were found to be lower than in analogous facial rhodium complexes but the values of the $^2J_{PP}$ interaction constant were high due to *trans* arrangement of the phosphorus atoms (545.0 Hz for **14** and 528.2 Hz for **16**). ^{31}P NMR spectra of meridional complexes **14** and **16** were assigned as ABX spin systems in both cases. Chemical shifts and interaction constants of both phosphorus atoms were determined by the computer simulation in gNMR [8] program. Measurement of the proton NMR spectra of meridional complexes at 25 °C showed that the methylene protons of the azine ligand backbone were equivalent in complex **14** and spectrum contained only one signal for each pair of CH_2 protons. However, the corresponding protons in complex **16** were mutually non-equivalent and therefore it was possible to observe signals of four different protons in ^{1}H NMR spectra. These signals were broad multiplets at 25 °C, it was possible to determine their multiplicity and interaction constants at −30 °C. As was found out by comparison of ^{1}H NMR spectra, in complex **14** methylene protons in each CH_2 groups were equivalent in full range of temperatures (from −30 to 80 °C). It means that even at low temperature change of conformation occurs. Complex **16** did not exhibit a similar behavior at

Table 2
^{1}H NMR spectra of facial diphosphinoazine complexes

Complex	**12**[b]	**13**[a]	**15**[b]	**17**[b]	**18**[b]	**19**[b]
t-Bu CH_3[c]	28.14 s	31.48 s	28.20 s	28.81 s	31.20 s	28.57 s
δ (ppm)/*J* (Hz)						
t-Bu CH_3[d]	27.35 s	30.93 s	27.73 s	27.83 s	28.05 s	27.96 s
δ (ppm)/*J* (Hz)						
t-Bu $\rangle C\langle$[c]	41.19 d	43.95 d	41.11 s	40.62 d	58.90 s	39.77 d
δ (ppm)/*J* (Hz)	(6.9)	(6.4)		(5.8)		(2.5)
t-Bu $\rangle C\langle$[d]	39.93 d	43.65 d	40.63 s	39.98 d	58.35 s	39.61 d
δ (ppm)/*J* (Hz)	(2.1)	(2.2)		(2.0)		(4.3)
CH_2[c]	46.17 d	37.54 d	34.69 d	45.21 dd	33.90 d	42.93 d
δ (ppm)/*J* (Hz)	(41.2)	(31.2)	(31.4)	(32.3; 2.6)	(11.8)	(27.9)
CH_2[d]	24.22 d	22.2 d	21.19 d	25.87 d	22.55 d	22.86 d
δ (ppm)/*J* (Hz)	(22.6)	(19.9)	(19.8)	(17.1)	(15.3)	(10.2)
$\rangle C{=}N$[c]	184.13 d	188.16 s	185.62 s	184.23 dd	181.34 bs	189.71 d
δ (ppm)/*J* (Hz)	(2.0)			(7.0; 2.7)		(3.3)
$\rangle C{=}N$[d]	173.81 d	176.22 s	174.00 d	174.14 s	174.66 bs	174.98 s
δ (ppm)/*J* (Hz)	(1.9)		(2.0)			

[a] Measured in CD_2Cl_2.
[b] Measured in $CDCl_3$.
[c] Five-membered ring.
[d] Six-membered ring.

25 °C, in this complex separate non-equivalent signals of each of the four protons were found. Partial coalescence of the proton signals was reached at 80 °C.

The existence of two or four different proton signals in complexes **14** and **16** at low and high temperature was an evidence that dynamic effects took part in these complexes. The origin of the mentioned effects was the inversion of the diphosphinoazine backbone. The different conformations of the six-membered rings of the azine diphosphinoazine ligand backbones in complexes **14** and **16** were found in X-ray structures. The analysis of the ring puckering parameters [15] revealed $B_{2,5}$ and $^{1}H_{6}$ conformation in **14** and **16**, respectively (calculated in PARST97 [16]). The value of the dihedral angle N1–Rh1–P2–C4 was −7.3° for complex **14** and 39.0° for complex **16**. Interconversion between both conformations occurred much easily in complex **14** than in complex **16** which was more rigid. The difference is apparent in the superposition of both ligand backbones found in the solid state (Fig. 1).

Facial configuration of the azine diphosphine ligand in three facial complexes **12**, **13**, **15** and meridional configuration in two meridional complexes **14** and **16** was confirmed by X-ray diffraction (Figs. 2–6). Compound **12** crystallized as a solvate with two molecules of chloroform, compound **13** with two molecules of dichloromethane, compounds **14** and **15** crystallized as solvates with one molecule of chloroform. The X-ray analysis confirmed that the azine diphosphine ligands were coordinated to the metal

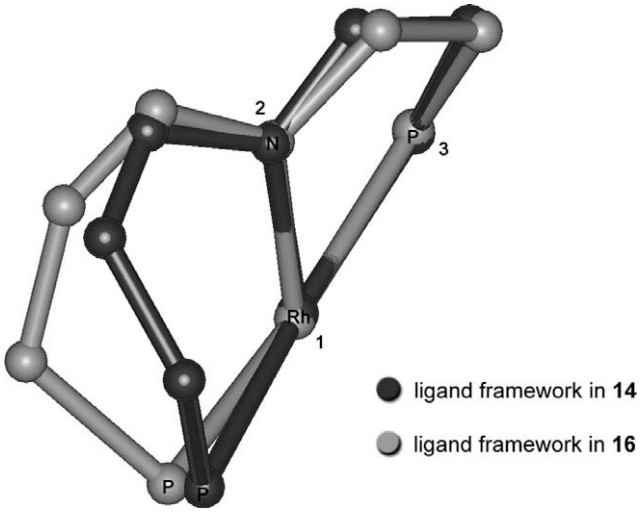


Fig. 1. Superposition of ligand backbones in complexes **14** and **16**.

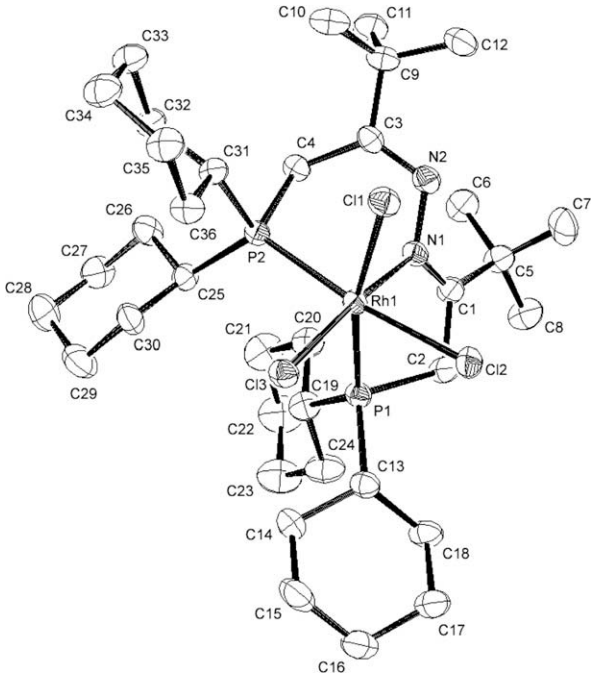


Fig. 3. ORTEP view of **13**. Hydrogen atoms are omitted for clarity.

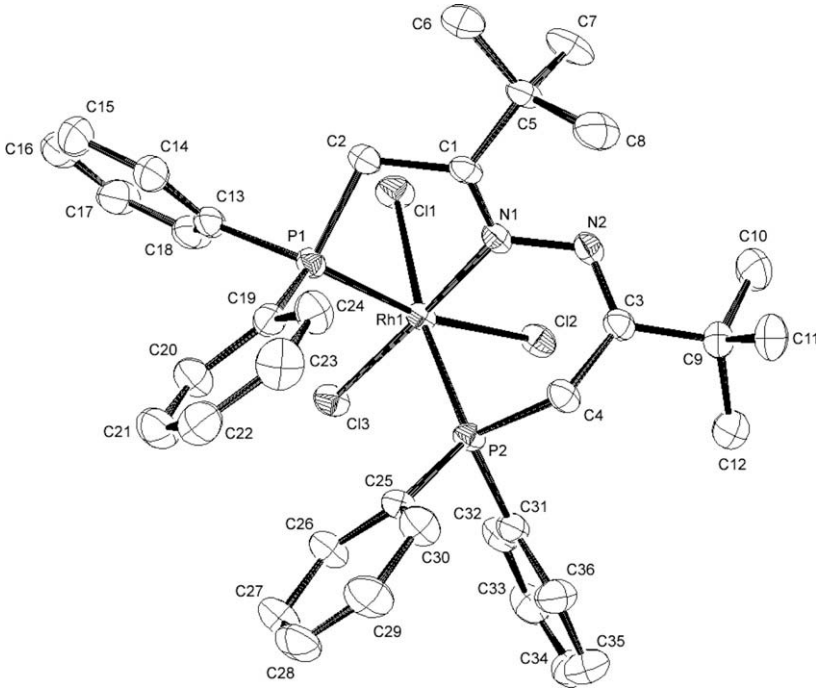


Fig. 2. ORTEP view of **12**. Hydrogen atoms are omitted for clarity.

center by both phosphorus atoms and also by the free electron pair on nitrogen. Three chlorine atoms were fully equivalent in meridional ligand arrangement with the average Rh–Cl distance 2.351 Å while in facial complexes these atoms showed three different Rh–Cl bond-distances in the range 2.34–2.45 Å. In contrast to that, the rest of Rh–X bond-distances showed stronger coordination of N and P atoms to Rh in facial complexes than in meridional complexes.

The determined molecular structure of **12** suggested, that phenyl groups in parallel orientation exhibited π–π interaction. The distance of interacting rings was in range 3.34–3.64 Å, what is the length typical for this type of interaction. Existence of such an interaction may be the reason why the meridional complex did not form. Considerable spatial demands can be well demonstrated on the structure of **15**. In this structure, methine protons of both "internal" isopropyl groups protruded towards each other

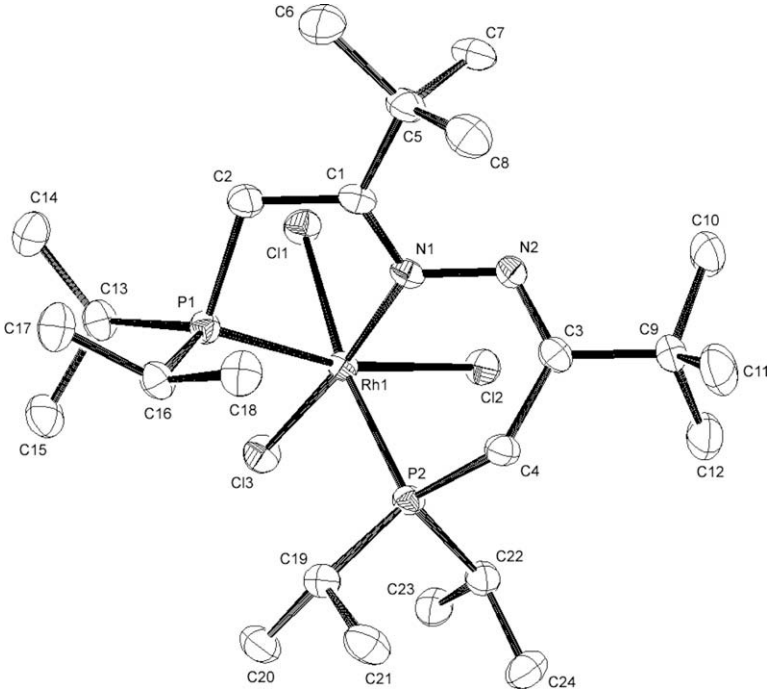


Fig. 4. ORTEP view of **15**. Hydrogen atoms are omitted for clarity.

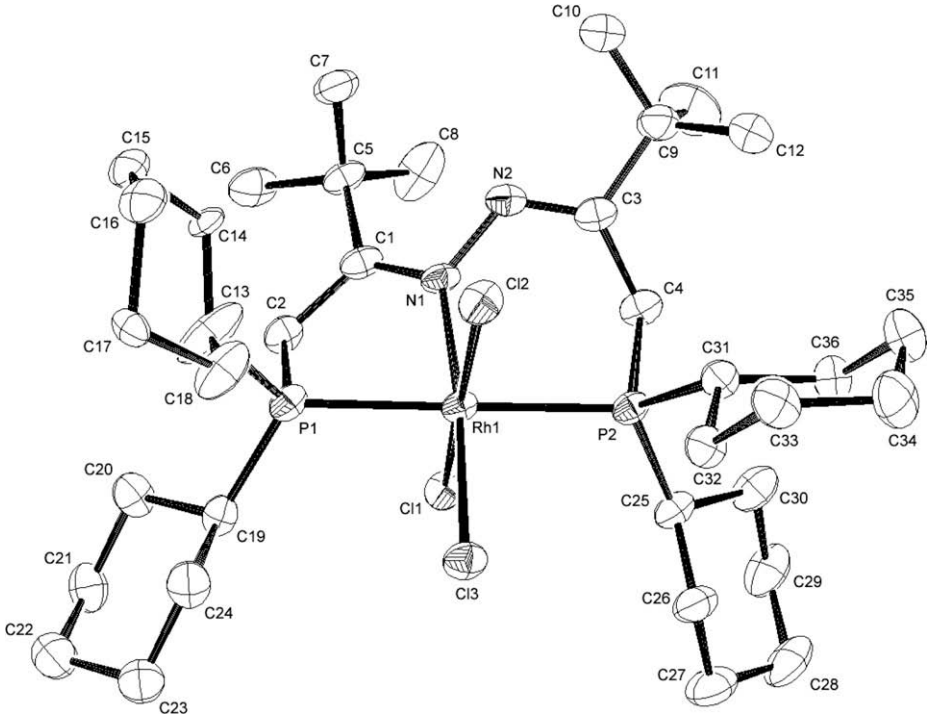


Fig. 5. ORTEP view of **14**. Hydrogen atoms are omitted for clarity.

and the distance between them was only 2.06 Å. This arrangement of ligand did not allow the formation of facial complexes with a ligand bearing sterically high demanding phosphine groups, for example ligand **4**.

3.2. Equilibrium between fac complex *13* and mer complex *14*

^{31}P NMR spectra of complex **13** measured in CD_2Cl_2 at 25 °C (Fig. 7) exhibited dynamic features consistent with reversible decoordination of the phosphine group of the longer arm of the azine backbone which formed a six-membered ring. Signal of this phosphorus atom measured at 25 °C was very broad (450 Hz), but it changed to a broad doublet on cooling down to −30 °C. We suggested an equilibrium between complex **13** and complex **13a** which had the P atom originally in the six-membered ring decoordinated. When simulated by gNMR V4.1.0. [8], however, it turned out that another species, namely the *mer* complex **14**, had to be included into the whole exchanging system. The full lineshape analysis of the equilibrium (Scheme 2), see also the synthesis of **13** in the experimental part) gave relative concentrations of **13**:**13a**:**14** about 1:0.023:0.13 and rates of exchange at laboratory temperature 5 900 s^{-1} for the decoordination step and 3.02×10^{16} s^{-1} for the fast recoordination to the *mer* complex. The interconversion of isomers **13** and **14** was further confirmed experimentally. Heating of $RhCl_3 \cdot 3H_2O$ with an appropriate amount of the ligand for 1 h provided a mixture of *fac* and *mer* isomers in 3:1 ratio. However, additional heating of the mixture for 12 h changed the ratio of isomers to 1:1, the ratio changed no longer with time. Heating of complex **7** in chlorinated solvents (50–70 °C, 12 h) also led to an approximately equimolar mixture of isomers which again did not change on further heating.

Isomerization between *fac* and *mer* isomers of diphosphinoazine complexes of Ir(III) has already been observed [3c]. Cationic facial dihydridocarbonyl and alkylhydridocarbonyl complexes with

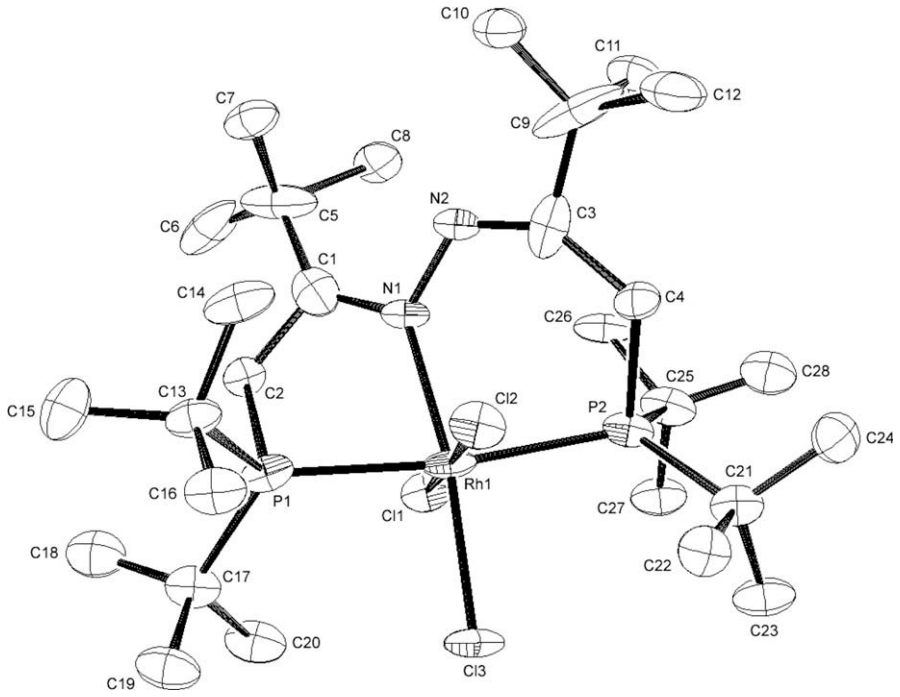


Fig. 6. ORTEP view of **16**. Hydrogen atoms are omitted for clarity.

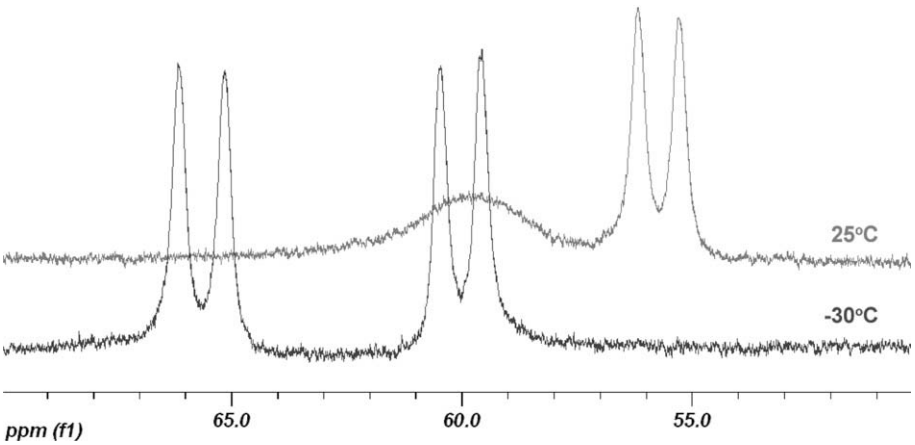
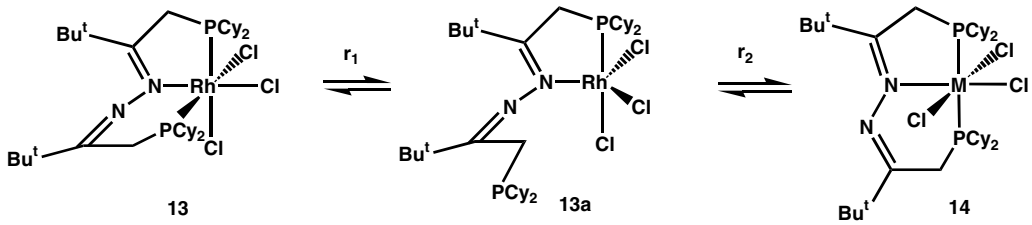


Fig. 7. ^{31}P NMR spectra of **13** at two temperatures in CD_2Cl_2.



Scheme 2.

ligand **1** isomerized essentially completely into their meridional isomers during several hours at 20 °C or on heating for 4 h at 75 °C, respectively. The mutual *cis* arrangement of hydride or alkyl/hydride ligands was retained during the isomerization. Although no explanation for this particular isomerization was suggested [3c] meridional isomers are usually preferred in $[MX_3L_3]$ complexes of both Ir(III) [17] and Rh(III) [18] owing to steric reasons.

4. Conclusions

New octahedral Rh(III) and Ir(III) complexes of diphosphinoazines were prepared by two independent methods and characterized by NMR and in several cases by the X-ray diffraction. Complexes with both facial and meridional configuration were isolated, the preference for the particular configuration being probably controlled by steric reasons. An equilibrium between *fac* and *mer* isomers of the complex with dicyclohexylphosphino groups mediated by hemilability of the diphosphinoazine ligand was experimentally observed by variable temperature NMR spectroscopy.

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Appendix A. Supplementary material

CCDC 653218, 649242, 649243, 649244 and 649245 contain the supplementary crystallographic data for this paper. 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.ica.2008.03.080.

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