DIPHOSPHINOAZINE RHODIUM(I) AND IRIDIUM(I) COMPLEXES

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

The first rhodium complexes of diphosphinoazines [{RhCl(1,2-η:5,6-η-CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$)}$_2$ {μ-R$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PR$_2$] (R = Ph, Cy, Pr^i) were prepared by cleavage of the bridge in chloro(cycloocta-1,5-diene)rhodium(I) dimer, the analogous iridium(I) complexes were also prepared for the first time. The X-ray structures of isostructural rhodium and iridium complexes with bis(dicyclohexylphosphino)pinacoloneazine were determined. Diphosphinoazine ligands in the complexes remained in (*Z*,*Z*) configuration bridging two RhCl(C$_8$H$_{12}$) units.

Keywords: Diphosphinoazines; Rhodium complexes; Iridium complexes; Cycloocta-1,5-diene complexes; Polydentate phosphorus-nitrogen ligands; X-ray diffraction.

Polydentate phosphorus–nitrogen ligands continue to atract attention in modern coordination and organometallic chemistry[1]. Recently, diphosphinoazines were introduced[2,3] as a new class of polydentate ligands showing high variability of coordination numbers and ligand structures in complexation to transition metals. They can coordinate as monodentate[3], unsymmetric PP′ and C_2 symmetric PP didentate[2,4–9], PNP′ tridentate[2,5,8–12] or even C_2 symmetric PNNP tetradentate[13] ligands most often in square planar and octahedral but also in tetrahedral and trigonally bipyramidal environments. Such a coordination variability together with the ability of hydrogen transfer from the ligand backbone to a metal[11–13] forming amido complexes led recently to the discovery of catalytic properties of diphosphinoazine complexes in the Heck reaction[14], in hydroamination[15], and in nickel-catalyzed polymerization[16]. It is therefore surprising that although

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numerous diphosphinoazine complexes of Groups 6, 8 and 10 of transition metals are known, there are only limited examples from Group 9 metals, those being exclusively iridium complexes[11,12,17]. Complexes of rhodium, a transition metal of high relevance to catalysis, are virtually unknown.

The present work aims at filling this gap and brings first examples of rhodium complexes with diphosphinoazine ligands, new iridium analogs of the rhodium complexes are also reported.

EXPERIMENTAL

General

All the manipulations were carried out in an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Hexane was distilled from Na, THF from sodium benzophenone ketyl, chloroform (Lach–Ner s.r.o.) was purified by washing with aqueous $NaHCO_3$ solution followed by distillation in argon atmosphere, first with P_2O_5 then with $CaCl_2$. Dichloromethane (Lach–Ner s.r.o.) and $RhCl_3 \cdot xH_2O$ (Safina Vestec) were used as received. Starting chloro(cycloocta-1,5-diene)rhodium dimer[18], chloro(cycloocta-1,5-diene)iridium dimer[19], and the diphosphinoazines[2,3] were prepared according to literature methods. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$, spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 80.98 and 75.44 MHz, respectively, 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 H_3PO_4 (^{31}P), coupling constants (*J*) are given in Hz. Elementary analyses were carried out on a PE 2400 Series II CHNS/O Analyzer (Perkin–Elmer, USA). FAB mass spectra were measured on a ZAB-EQ spectrometer (Micromass, Manchester, UK) with Xe bombarding gas at 8 kV using bis(hydroxyethyl)disulfide or thioglycerol/glycerol (3:1) as matrices.

X-ray Structure Determination

The diffraction-quality crystals of complexes **2**·$4CH_2Cl_2$ and **5**·$4CHCl_3$ were grown as mentioned below. 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[20]. The structures were solved by direct, and refined by full-matrix least-squares techniques (SIR92 [21], SHELXL97 [22]). Scattering factors for neutral atoms used were included in the program SHELXL97. The hydrogen atoms were kept in theoretical positions (SHELXL97) in both structures. Final geometric calculations were carried out with SHELXL97 and recent version of the PLATON program[23]. Table I gives pertinent crystallographic data. CCDC 282714 (for **2**) and 282713 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

TABLE I
Experimental data for the X-ray difraction studies of complexes **2** and **5**

Parameter	**2**·4CH_2Cl_2	**5**·4$CHCl_3$
Formula	$C_{56}H_{98}Cl_{10}N_2P_2Rh_2$	$C_{56}H_{94}Cl_{14}N_2P_2Ir_2$
M	1421.62	1737.97
T, K	150(1)	150(1)
Crystal dimension, mm	0.2 × 0.15 × 0.15	0.2 × 0.15 × 0.1
Color	deep orange	deep red
Crystal system	triclinic	triclinic
Space group	*P*-1 (No. 2)	*P*-1 (No. 2)
a, Å	11.0110(3)	10.7300(4)
b, Å	11.4580(3)	11.1600(4)
c, Å	13.7260(4)	15.8900(4)
α, °	73.392(2)	85.541(2)
β, °	79.035(2)	85.346(2)
γ, °	77.090(1)	63.221(1)
U, $Å^3$; *Z*	1602.67(7); 2	1691.3(1); 2
D_{calcd}, g cm^{-3}	1.473	1.706
λ, Å	0.71073	0.71073
μ, mm^{-1}	1.02	4.57
F(000)	742	870
θ range of data collection, °	1.89–27.54	1.29–27.60
Index ranges	–14,14; –14,14; –17,17	–13,13; –14,14; –20,20
No. of measured reflections	13666	14513
R_σ	0.0486	0.0622
No. of observed reflections [$I > 2\sigma(I)$]	6048	6858
No. of independent reflections	7370	7741
R_{int}	0.0292	0.0551
Coefficients in weighting scheme[a]	0.0259; 1.9310	0.1113; 26.0663
Data, restraints, parameters	7370/0/342	7741/0/340
Goodness-of-fit on F^2	1.029	1.076
Final *R*, *R′* indices [$I \geq 2\sigma(I)$][b]	0.0362; 0.0808	0.0692; 0.1996
Maximum shift, e.s.d.	0.001	0.001
Largest difference peak and hole, e $Å^{-3}$	0.934; –0.870	5.770; –4.260

[a] $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL97 [21]); [b] $R = \Sigma|F_o - F_c|/\Sigma|F_c|$, $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (SHELXL97 [21]).

Rhodium(I) Complexes

[{RhCl(1,2-η:5,6-η-CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$)}$_2$(μ-Ph$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPh$_2$] (**1**)

Complex [RhCl(cod)]$_2$ (60 mg, 0.12 mmol) was dissolved in chloroform (0.5 ml) and solution of bis(diphenylphosphino)pinacoloneazine (62.5 mg, 0.12 mmol) in chloroform (0.4 ml) added. The resulting solution was well shaken and left standing for 1 h. The product (purity according to ^{31}P NMR was 96%) was obtained by evaporation of the solvent in vacuo. Yield: 98 mg (81%). For $C_{52}H_{66}Cl_2N_2P_2Rh_2$ (1057.8)·0.75$CHCl_3$ calculated: 55.22% C, 5.86% H, 2.44% N; found: 55.14% C, 6.29% H, 2.18% N. FAB MS, *m/z*: 807.2 ([M – Cl – 2 C_8H_{12} + 2 H]$^+$), 775.2 ([M – Rh – 2 Cl – C_8H_{12}]$^+$), 667.1 ([M – Rh – 2 Cl – 2 C_8H_{12}]$^+$). ^{31}P NMR ($CDCl_3$): 24.7 d, $^1J_{RhP}$ = 150.6. ^{1}H NMR ($CDCl_3$): 1.27 s, 18 H (*t*-Bu); 1.88 m, 8 H (CH_2, COD); 2.27 m, 8 H (CH_2, COD); 2.78 bs, 4 H (CH, COD); 4.05 d, $^2J_{PH}$ = 12.7, 4 H (PCH_2); 5.44 bs, 4 H (CH, COD); 7.26–7.83 m, 20 H (CH, Ph). ^{13}C NMR ($CDCl_3$): 26.37 d, $^1J_{PC}$ = 15.0 (PCH_2); 28.79 s (CH_2, COD); 29.77 s (CH_3, *t*-Bu); 32.70 s (CH_2, COD); 40.31 s (C *t*-Bu); 70.46 d, $^1J_{RhC}$ = 14.0 (CH *cis* to P); 103.01 dd, $^2J_{PC}$ and $^1J_{RhC}$ 12.4 and 7.2 (CH *trans* to P); 127.85 d, *J* = 9.7 (CH); 130.14 s (CH); 131.83 d, $^1J_{PC}$ = 41.5 (>C<, Ph); 134.26 bs (CH, Ph); 172.74 dd, $^5J_{PC}$ = 1.4, $^2J_{PC}$ = 6.7 (>C=N).

[{RhCl(1,2-η:5,6-η-CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$)}$_2$(μ-(C$_6$H$_{11}$)$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$P(C$_6$H$_{11}$)$_2$] (**2**)

To a solution of complex [RhCl(cod)]$_2$ (60 mg, 0.12 mmol) in chloroform (0.5 ml), solution of bis(dicyclohexylphosphino)pinacoloneazine (72 mg, 0.12 mmol) in chloroform (0.4 ml) was added. The mixture was stirred for 2 h, then left standing for 5 h. The resulting precipitate was filtered off, washed twice with chloroform (0.2 ml) and dried in air. Yield 95 mg (72%). Crystals suitable for X-ray analysis were obtained by diffusion of hexane vapor into chloroform solution of the compound at room temperature. For $C_{52}H_{90}Cl_2N_2P_2Rh_2$ (1082.0)·1.5$CHCl_3$ calculated: 50.96% C, 7.31% H, 2.22% N; found: 50.62% C, 7.66% H, 2.08% N. FAB MS, *m/z*: 1081.4 ([M + 1]$^+$, 1045.4 ([M – Cl]$^+$), 1009.5 ([M – 2 Cl – H]$^+$), 972.3 ([M – C_8H_{12}]$^+$), 937.3 ([M – Cl – C_8H_{12}]$^+$), 831.4 ([M – Cl – 2 C_8H_{12} + 2 H]$^+$), 799.4 ([M – Rh – 2 Cl – C_8H_{12}]$^+$), 726.3 ([M – Rh – Cl – 2 C_8H_{12}]$^+$), 689.3 ([M – Rh – 2 Cl – 2 C_8H_{12} – 2 H]$^+$). ^{31}P NMR (CD_2Cl_2): 29.5 d, $^1J_{RhP}$ = 141.2. ^{1}H NMR (CD_2Cl_2): 1.19–2.10 bm (CH_2, cyclohexyl + COD); 1.58 s, 18 H (*t*-Bu); 2.32 m, 4 H (PCH); 3.46 d, 4 H, $^2J_{PH}$ = 13.0 (PCH_2); 4.31 bs, 4 H (CH, COD); 5.15 bs, 4 H (CH, COD). ^{13}C NMR (CD_2Cl_2): 22.76 d, *J* = 12.3 (PCH_2); 26.73 s (CH_2); 27.68 d, *J* = 9.0 (CH_2); 28.06 d, *J* = 12.0 (CH_2); 28.56 s (CH_2); 29.58 bs (CH_2, COD); 30.49 s (CH_3); 31.3 b (CH_2); 33.55 bs (CH_2, COD); 38.46–39.13 bm (PCH); 41.04 s (>C<); 66.84 d, $^1J_{RhC}$ = 13.2 (CH *cis* to P); 99.33 dd, $^2J_{PC}$ and $^1J_{RhC}$ 12.1 and 8.1 (CH *trans* to P); 173.91 bs (>C=N).

[{RhCl(1,2-η:5,6-η-CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$)}$_2$(μ-Pr$^i_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPr$^i_2$] (**3**)

Method A: To a solution of complex [RhCl(cod)]$_2$ (120 mg, 0.24 mmol) in THF (15 ml) bis(diisopropylphosphino)pinacoloneazine (105 mg, 0.24 mmol) was added while stirring. The resulting solution was refluxed for 2 h and an excess of pentane added to the hot solution. The mixture was quickly cooled down to about –78 °C (dry ice/ethanol mixture).

Bright yellow microcrystalline precipitate formed after 30 min and was isolated by filtration. Yield 112 mg (50%).

Method B: Complex $[RhCl(cod)]_2$ (60 mg, 0.18 mmol) was dissolved in $CHCl_3$ (0.4 ml) and solution of bis(diisopropylphosphino)pinacoloneazine (47 mg, 0.18 mmol) in $CHCl_3$ (0.2 ml) added. The resulting solution was left standing for 3 h. The product purity according to ^{31}P NMR was 82%; it was not isolated.

For $C_{40}H_{74}Cl_2N_2P_2Rh_2$ (621.7)·0.25$CHCl_3$ calculated: 50.81% C, 7.86% H, 3.04% N; found: 50.22% C, 8.45% H, 2.64% N. FAB MS, *m/z*: 943.6 ($[M + Na]^+$, 885.3 ($[M - Cl]^+$), 849.3 ($[M - 2\ Cl - H]^+$), 669.2 ($[M - 2\ Cl - C_8H_{12}]^+$), 639.2 ($[M - Rh - 2\ Cl - C_8H_{12}]^+$), 566.1 ($[M - Rh - Cl - 2\ C_8H_{12}]^+$), 531.1 ($[M - Rh - 2\ Cl - 2\ C_8H_{12}]^+$). ^{31}P NMR ($CDCl_3$): 38.2 d, $^1J_{RhP}$ = 142.0. ^1H NMR ($CDCl_3$): 1.02–1.38 m (CH_3, *i*-Pr); 1.55 s (CH_3, *t*-Bu); 1.81–1.93 m (CH_2, COD); 2.22–2.31 m (CH_2, COD); 2.62 sep, *J* = 6.71 (CH, *i*-Pr); 3.47 d, $^2J_{PH}$ = 13.0 (CH_2); 4.31 bs (CH, COD); 5.22 bs (CH, COD). ^{13}C NMR ($CDCl_3$): 18.72 s (CH_3, *i*-Pr); 20.81 d, $^2J_{PC}$ = 4.6 (CH_3, *i*-Pr); 23.77 d, *J* = 12.4 (CH_2); 27.41–27.93 m (CH, *i*-Pr); 28.16 s (CH_2, COD); 30.06 s (CH_3, *t*-Bu); 33.23 d, $^2J_{RhC}$ = 2.1 (CH_2, COD); 40.65 s (>C<, *t*-Bu); 65.88 d, $^1J_{RhC}$ = 13.8 (CH *cis* to P, COD); 99.84 dd, $^2J_{PC}$ and $^1J_{RhC}$ 11.7 and 7.6 (CH *trans* to P, COD); 174.44 dd, $^2J_{PC}$ = 5.8, $^5J_{PC}$ = 1.1 (>C=N).

Iridium(I) Complexes

$[\{IrCl(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-}CH{=}CHCH_2CH_2CH{=}CHCH_2CH_2)\}_2\{\mu\text{-}Ph_2PCH_2C(Bu^t){=}NN{=}C(Bu^t)CH_2PPh_2\}]$ (**4**)

Complex $[IrCl(cod)]_2$ (30 mg, 0.041 mmol) was dissolved in chloroform (0.3 ml) and solution of bis(diphenylphosphino)pinacoloneazine (23.3 mg, 0.041 mmol) in chloroform (0.2 ml) added with stirring. The resulting solution was left standing for 3 h. The product was obtained after slow evaporation of one third of the solvent. The resulting yellow-orange microcrystalline precipitate was filtered off, washed with ether (0.2 ml) and dried in vacuo. Yield 28.2 mg (53%). For $C_{52}H_{66}Cl_2N_2P_2Ir_2$ (1236.4)·0.5$CHCl_3$ calculated: 48.65% C, 5.17% H, 2.16% N; found: 48.07% C, 5.36% H, 1.90% N. FAB MS, *m/z*: 985.2 ($[M - Cl - 2\ C_8H_{12}]^+$), 865.3 ($[M - Ir - 2\ Cl - C_8H_{12}]^+$), 755.2 ($[M - Ir - 2\ Cl - 2\ C_8H_{12} - 2\ H]^+$). ^{31}P NMR ($CDCl_3$): 13.6 s. ^1H NMR ($CDCl_3$): 1.14 s, 18 H (*t*-Bu); 1.75 m, 8 H (CH_2, COD); 2.10 m, 8 H (CH_2, COD); 2.36 bs, 4 H (CH, COD); 4.18 d, $^2J_{PH}$ = 13.2, 4 H (PCH_2); 5.06 bs, 4 H (CH, COD); 7.30–7.82 m, 20 H (CH, Ph). ^{13}C NMR ($CDCl_3$): 25.69 d, $^1J_{PC}$ = 21.3 (PCH_2); 29.41 s (CH_2, COD); 29.78 s (CH_3, *t*-Bu); 33.07 s (CH_2, COD); 40.22 s (>C<, *t*-Bu); 53.65 s (CH *cis* to P); 91.53 d, $^2J_{PC}$ = 14.3 (CH *trans* to P); 127.79 d, *J* = 10.0 (CH); 130.35 s (CH); 131.19–131.43 (>C<, Ph); 134.25–134.57 (CH, Ph); 172.32 dd, $^5J_{PC}$ = 1.4, $^2J_{PC}$ = 7.4 (>C=N).

$[\{IrCl(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-}CH{=}CHCH_2CH_2CH{=}CHCH_2CH_2)\}_2\{\mu\text{-}(C_6H_{11})_2PCH_2C(Bu^t){=}NN{=}C(Bu^t)CH_2P(C_6H_{11})_2\}]$ (**5**)

Complex $[IrCl(cod)]_2$ (30 mg, 0.041 mmol) was dissolved in chloroform (0.3 ml) and a solution of bis(dicyclohexylphosphino)pinacoloneazine (23.3 mg, 0.041 mmol) in chloroform (0.2 ml) added while stirring. The resulting orange solution was left standing at room temperature for 24 h. The yellow-orange microcrystalline precipitate formed, was filtered off, washed twice with ether (0.2 ml) and dried in vacuo. Yield 35.6 mg (66%). Crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution. For

$C_{52}H_{90}Cl_2N_2P_2Ir_2$ (1260.6)·$CHCl_3$ calculated: 46.13% C, 6.65% H, 2.03% N; found: 45.68% C, 6.73% H, 1.89% N. FAB MS, *m/z*: 1223.5 ($[M - Cl - 2 H]^+$), 1189.5 ($[M - 2 Cl - H]^+$), 1117.4 ($[M - Cl - C_8H_{12}]^+$), 889.4 ($[M - Ir - 2 Cl - C_8H_{12}]^+$), 814.4 ($[M - Ir - Cl - 2 C_8H_{12} - 2 H]^+$), 779.4 ($[M - Ir - 2 Cl - 2 C_8H_{12} - 2 H]^+$). ^{31}P NMR ($CD_2Cl_2$): 16.6 s. ^{1}H NMR ($CD_2Cl_2$): 1.17–2.19 bm ($CH_2$, cyclohexyl + COD); 1.47 s, 18 H (*t*-Bu); 2.47 m, 4 H (PCH); 3.64 d, 4 H, $^2J_{PH}$ = 13.4 (PCH_2); 3.80 bs, 4 H (CH, COD); 4.76 bs, 4 H (CH, COD). ^{13}C NMR (CD_2Cl_2): 22.64 d, *J* = 18.0 (PCH_2); 26.74 s (CH_2); 27.77 d, *J* = 10.2 (CH_2); 28.00 d, *J* = 11.5 (CH_2); 29.04 s (CH_2); 30.03 bs (CH_2, COD); 30.57 s (CH_3, *t*-Bu); 30.67 s (CH_2); 34.32 bs (CH_2, COD); 38.57–39.13 bm (PCH); 41.10 s (>C<); 50.96 s (CH *cis* to P); 87.43 d, $^2J_{PC}$ = 13.8 (CH *trans* to P); 173.95 bs (>C=N).

[{IrCl(1,2-η:5,6-η-CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$)}$_2$(μ-Pr$^i_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PPr$^i_2$] (**6**)

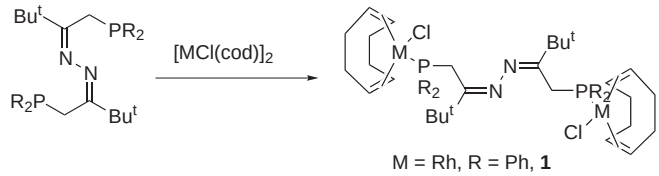
Complex $[IrCl(cod)]_2$ (15 mg, 0.020 mmol) was dissolved in $CDCl_3$ (0.3 ml) and solution of bis(diisopropylphosphino)pinacoloneazine (9 mg, 0.020 mmol) in $CDCl_3$ (0.3 ml) added with stirring. The resulting orange solution was left standing for 3 h and its NMR spectra were measured (purity 80%). The product was isolated by slow evaporation of the solvent. For $C_{40}H_{74}Cl_2N_2P_2Ir_2$ (1100.3)·2$CHCl_3$ calculated: 37.67% C, 5.72% H, 2.09% N; found: 37.58% C, 5.70% H, 1.86% N. ^{31}P NMR ($CDCl_3$): 25.3 s. ^{1}H NMR ($CDCl_3$): 1.06–1.38 m (CH_3, *i*-Pr); 1.48 s, 18 H (CH_3, *t*-Bu); 1.57–1.64 m, 8 H (CH_2, COD); 2.05–2.17 m, 8 H (CH_2, COD); 2.84 bm, 4 H (CH, *i*-Pr); 3.69 d, 4 H, $^2J_{PH}$ = 13.1 (CH_2); 3.86 m, 4 H (CH, COD); 4.88 m, 4 H (CH, COD). ^{13}C NMR ($CDCl_3$): 19.20 s (CH_3, *i*-Pr); 20.33 d, $^2J_{PC}$ = 2.9 (CH_3, *i*-Pr); 22.70 d, $^1J_{PC}$ = 18.2 (CH_2); 27.84 d, $^1J_{PC}$ = 23.3 (CH, *i*-Pr); 28.60 d, $^2J_{PC}$ = 1.5 (CH_2 *cis* to P, COD); 30.16 s (CH_3, *t*-Bu); 34.00 d, $^2J_{PC}$ = 3.2 (CH_2 *trans* to P, COD); 40.72 s (>C<, *t*-Bu); 49.99 s (CH *cis* to P, COD); 87.91 d, $^2J_{PC}$ = 13.7 (CH *trans* to P, COD); 174.57 dd, $^2J_{PC}$ = 6.5, $^5J_{PC}$ = 1.3 (>C=N).

RESULTS AND DISCUSSION

Cycloocta-1,5-diene (COD) complexes of transition metals are common starting materials in organometallic chemistry due to easy substitution of a diene ligand with other electron donors like e.g. phosphines. Since the cleavage of chlorine bridge in chloro(cycloocta-1,5-diene)rhodium dimer with phosphines should leave the COD ligand intact, we have chosen as the first target in rhodium and iridium chemistry of diphosphinoazines the cycloocta-1,5-diene complexes.

Reaction of $[MCl(cod)]_2$ (M = Rh, Ir) with 1 equivalent of a diphosphinoazine in a suitable solvent (mostly chloroform) gave complexes [{MCl(1,2-η:5,6-η-CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$)}$_2$(μ-R$_2$PCH$_2$C(Bu^t)=NN=C(Bu^t)CH$_2$PR$_2$] (M = Rh, R = Ph, Pr^i, Cy; M = Ir, R = Ph, Pr^i, Cy) (Scheme 1), identified in solution according to their ^{31}P NMR spectra represented by a singlet signal (Ir complexes) or a doublet with characteristic $^1J_{RhP}$ coupling constant of 141–151 Hz (Rh complexes). The equivalence of the two phos-

phorus atoms in the spectra points out to the (*Z*,*Z*) configuration of the free diphosphinoazine conserved in the complexes. This was further supported by X-ray diffraction studies of two of the complexes (see below). While bis(dicyclohexylphosphino)pinacoloneazine complexes spontaneously precipitated from chloroform solutions and had to be dissolved in CD_2Cl_2 for the NMR measurement, the other complexes were isolated after partial or total solvent evaporation and were soluble in $CDCl_3$. ^{1}H NMR spectra of the complexes further confirmed the symmetry of the ligands in (*Z*,*Z*) configuration. In all of the complexes there was only one signal of *tert*-butyl protons, and only one signal (doublet due to the coupling to ^{31}P, $^2J_{PH}$ = 12–13 Hz) of methylene protons on the carbon atom next to phosphorus. Chemical shifts of vinyl cycloocta-1,5-diene hydrogens differed depending on which double bond (coordinated *trans* to chlorine or *trans* to phosphine) they were.



M = Rh, R = Ph, **1**
M = Rh, R = Cy, **2**
M = Rh, R = Pr^i, **3**
M = Ir, R = Ph, **4**
M = Ir, R = Cy, **5**
M = Ir, R = Pr^i, **6**

SCHEME 1

Similar features were observed in ^{13}C NMR spectra. All the carbon signals of one half of the complex molecules were equivalent with signals of the other half. Typical $^1J_{PC}$ between the phosphorus and methylene carbon was 12–15 Hz, the signals of C=N carbons were broad in bis(dicyclohexylphosphino)pinacoloneazine complexes, other complexes showed multiplets that at the given resolution looked like doublets of doublets. The multiplets could be either true doublets of doublets with well resolved $^2J_{PC}$ and $^5J_{PC}$ coupling, as assigned, or they could be carbon parts of second order spectra of three-spin systems with the other two spins being the two phosphoruses coupled by a seven bond coupling[24]. No attempt was made to differentiate between those two alternatives since it would require measurement of carbon spectra of quarternary carbons with high signal-to-noise ratio and simulation. Cycloocta-1,5-diene carbons of the double bonds coordinated to rhodium were assigned according to the magnitude

of their coupling constant with ^{31}P: those with $^{2}J_{PC}$ about 12 Hz were assigned to the double-bonded carbons *trans* to phosphorus whereas the carbons *cis* to phosphorus were coupled to rhodium only.

The X-ray structures of the rhodium complex **2** and the iridium complex **5** are shown in Figs 1 and 2, respectively. It should be mentioned that although the structures of a free bis(diphenylphosphino)pinacoloneazine[2] and two diphosphinoazine dioxides[3,24], all in (*Z*,*Z*) configuration, are known, no X-ray structure of a complex with bridging (*Z*,*Z*)-diphosphinoazine has been published so far. Palladium η^3-2-methylallyl complexes of bridging (*Z*,*Z*)-diphosphinoazines were reported recently without X-ray structures[3].

The molecules of complexes **2** and **5** were centrosymmetric and isostructural. The coordination geometry around a metal was square planar, as expected, and cycloocta-1,5-diene was bonded in the usual manner. The azine moiety was strictly planar the torsional angles on N1–N1a bonds (see Figs 1 and 2) being 180° as follows from the symmetry of the complexes and the mean standard deviations from planarity in C1–C2–N1–N1a–C2a–C1a planes being 0.0151 and 0.0168 Å in complexes **2** and **5**, respectively. The bulky cyclohexyl groups on phosphorus were oriented towards cycloocta-1,5-diene ligand (torsional angles C1–P–M–Cl1 are 37 and 42° for **2** and **5**, respectively) (Table II).

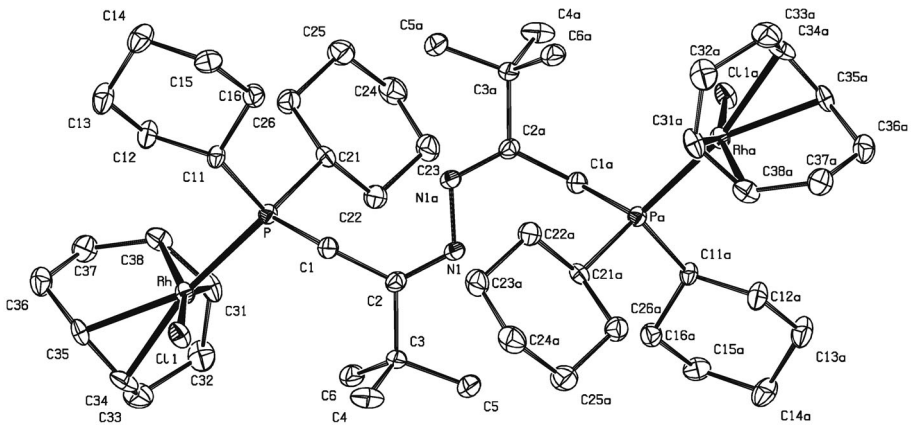


FIG. 1
ORTEP view of the molecular structure of complex **2**. Hydrogen atoms are omitted for clarity

TABLE II
Selected bond lengths (in Å) and angles (in °) with e.s.d.'s in parentheses for complexes **2** and **5**

Bond	**2**	**5**
M–P	2.3633(7)	2.349(2)
M–C31	2.111(3)	2.123(8)
M–C34	2.218(3)	2.167(9)
M–C35	2.198(3)	2.212(8)
M–C38	2.135(3)	2.109(9)
M–Cl1	2.3832(7)	2.370(2)
P–C1	1.868(3)	1.872(8)
C1–C2	1.412(3)	1.526(12)
C2–N1	1.289(3)	1.290(12)
N1–N1a	1.427(4)	1.414(14)
C1–P–M–Cl1	37.11(9)	41.7(3)
P–C1–C2–N1	99.5(5)	102.2(9)

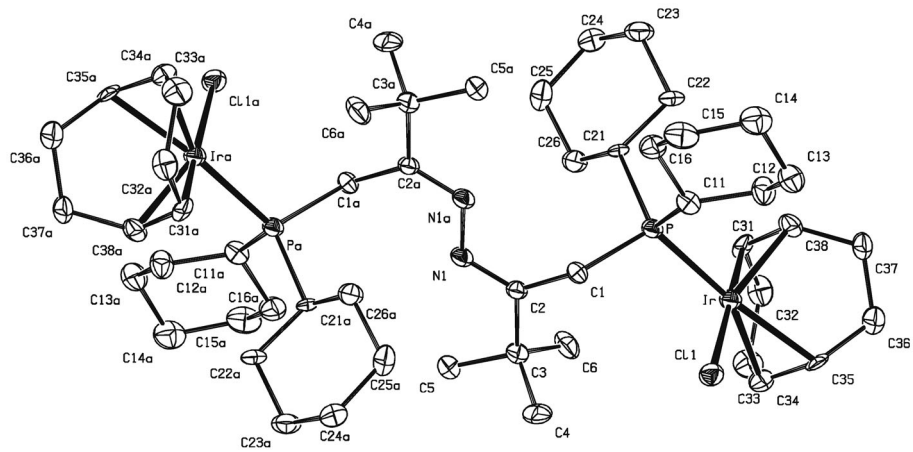


FIG. 2
ORTEP view of the molecular structure of complex **5**. Hydrogen atoms are omitted for clarity

In conclusion, the first rhodium and some new iridium complexes with diphosphinoazine ligands were prepared and characterized by NMR and X-ray diffraction of two of the complexes. The diphosphinoazine ligands in the complexes remained in (*Z*,*Z*) configuration bridging two square planar –MCl(cod) (M = Rh, Ir) units.

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