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Synthesis, structures, and characterization of benzildiimine complexes of rhodium(III) and iridium(I)

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Dedicated to Dr. Klaus Römer on the occasion of his 70th birthday.

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A B S T R A C T

The reactions of *trans*-[$(PPh_3)_2M(CO)Cl$] (M = Rh and Ir) with benzildiimine (H_2BDI = **2**) derived from benzil-bis(trimethylsilyl)diimine (Si_2BDI) (**1**) in a 1:2 and 1:1 molar ratio afforded the cationic bis-benzildiiminato complexes [$Rh(PPh_3)_2(HBDI)_2$]Cl (**3**) and the *mono*-benzildiimine complex [$Ir(PPh_3)_2(CO)$-(H_2BDI)]Cl (**4**), respectively. Both complexes are fully characterized using IR, FAB-MS, NMR spectroscopy and elemental analysis. The single crystal X-ray structure analysis reveals a distorted octahedral coordination geometry for the Rh(III) in **3** and a highly distorted square pyramidal geometry for Ir(I) in **4**. In addition, the solid-state structure of Si_2BDI is reported here for the first time showing the substituents highly twisted because of steric reasons.

1. Introduction

During the past quarter of last century, 1,4-diazabutadienes (α-diimines) have attracted considerable attention as useful reagents in organometallic chemistry due to (i) their different types of coordination modes and reactivity of their coordination complexes; (ii) the applications of such complexes in organic synthesis and catalysis; (iii) the utilization of such complexes as luminescence labels for detection and photochemical cleavage of DNA [1–3]. Benzil-bis(trimethylsilyl)diimine or 1,2-bis(trimethylsilylimino)-diphenylethane (**1** = Si_2BDI, Fig. 1) is an interesting model from the view point of the formation of heterocycles because it possesses two imino groups in 1,4-relationship and two very labile Me_3Si substitutents in the same molecule. A wide variety of heterocycles such as B,N heterocycles, diazaheteroles, imidazoles, oxazolines and also several coordination complexes were synthesized using **1** [4–7]. Si_2BDI was prepared and characterized by means of IR, NMR and elemental analysis, but no crystal structure of this compound was reported [8,9]. Often it was observed that during the reactions with metal complexes the two $SiMe_3$ groups of **1** are easily cleaved off as the N–$SiMe_3$ group is very reactive and sensitive to moisture, and sometimes also to chlorinated solvents. After cleavage, the two $SiMe_3$ groups are replaced by two H atoms and then H_2BDI (**2** = trimethylsilyl substituted benzildiimine, Fig. 1) resembles a typical 1,2-diimine ligand with unsubstituted imino groups. In the present study, we have chosen the benzildiimines **1** and **2** as the principal ligands, not only because they carry the diimine chromophore but also for their different coordination modes. However, only a few metal complexes of **1** are known where the two trimethylsilyl ($SiMe_3$) groups stay attached with the ligand. Some complexes with the general formula $Mo(CO)_4L$ (where L = **1** or similar phenylimine ligands) were prepared by thermal substitution reaction of $Mo(CO)_6$ with the respective ligands in refluxing C_6H_6 [10]. Only the magnetical and few spectrochemical properties of these complexes were investigated, the molecular structures however were not reported. In our prepared complexes (**3** and **4**), **1** as starting ligand changed into the diimine form **2** which is in good agreement with the complexes synthesized from **1**, but where the diimine form resulted as final ligand in bis- and tris-chelate complexes [11]. The complexes are of general formula of [$M(HL)_n$] $(ClO_4)_2$ [HL = benzildiimine, phenanthrenequinonediimine (phi); $n = 2$, M = Cu; $n = 3$, M = Fe, Ni] and [$CoL(HL)_2$]$(ClO_4)_2$ were prepared from the corresponding metal salts and alcoholic HL or alcoholic solution of the corresponding 1,2-bis(trimethylsilylimino) analog. The complexes were characterized by elemental analysis, optical spectra, and magnetic measurements. Similar $Pd(HL)Cl_2$, [$Rh(HL)L$]Cl_2 and [$Rh(HL)_2$]Cl_3 complexes were also prepared with

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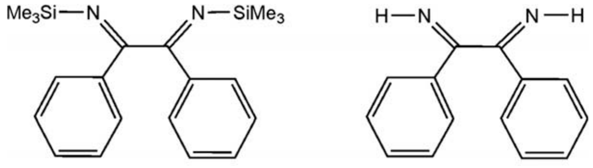


Si_2BDI
1

H_2BDI
2

Fig. 1. Benzil-bis(trimethylsilyl)diimine (**1**) and benzildiimine (**2**).

the same ligands [12] and show considerable π-backbonding within the chelates. Several types of diimine complexes of ruthenium(II) and rhodium(III) of 9,10-phenanthrenequinone were isolated [3b] which have been found to bind DNA avidly by intercalation between base pairs [13,14]. Rhodium(II) complexes containing phi have found a particularly wide range of application as photoactivated probes of local DNA helical conformation [3b].

In spite of these interesting properties, examples of transition metal complexes of **1** as well as **2** are not widely reported and their molecular structures are also unknown till date. So, we were interested to characterize the molecular structure of **1** and synthesize and characterize fully rhodium(III) and iridium(I) complexes of **1** or if not possible, at least of **2**. And indeed, we were successful in the characterization of free **1**, but not in finding **1** as ligand in the complexes, where instead of **1** only **2** was found as bidentate ligand. We present herein the results from the reactions of **2** with Vaska's and Vaska-type complexes *trans*-[$(PPh_3)_2M(CO)Cl$] (M = Ir, Rh) and the characterization of the products by means of IR, mass, ^{1}H, ^{13}C, ^{31}P NMR spectra, elemental analysis and X-ray diffraction. In addition, the solid-state structure of **1** was determined here for the first time by single crystal X-ray diffraction study.

2. Experimental

2.1. General

All reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Solvents were purified by standard procedures; dichloromethane was distilled from calcium hydride and *n*-pentane was distilled from sodium. All solvents were stored under a dry argon atmosphere over 3 Å molecular sieves. The complexes [$MCl(CO)(PPh_3)_2$] (M = Rh, Ir) [15] were prepared and purified according to literature procedures. Si_2BDI was prepared according to the modified literature procedure from benzil with two equivalents of sodium- or lithium-bis(trimethylsilyl)amide followed by quenching with chlorotrimethylsilane [8,9]. The solution of benzil and sodium-bis(trimethylsilyl)amide in benzene was stirred at 70 °C for 7 h. After the addition of chlorotrimethylsilane the mixture was heated at 60 °C for 5 h. Then the solution was filtered and the filtrate was vacuum distilled to yield crystalline solid **1**. It is well soluble in common polar solvents, sparingly soluble in non polar solvents. Other reagents were commercially available and used without further purification. NMR spectra were measured with a Jeol Eclipse 270 spectrometer; the chemical shifts are given relative to external standards (TMS and 85% H_3PO_4). Mass spectra were recorded with a Jeol MStation JMS 700, NBA matrix (FAB^+). IR spectra were recorded from KBr pellets using a Perkin–Elmer Spectrum One FT-IR spectrometer. The melting points, obtained with a Büchi Melting Point B-540 device, are uncorrected. Elemental analysis was performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU, using a Hereaus Elementar Vario El apparatus.

2.2. Synthesis of trans-[bis{(benzildiiminato-N,N′)(triphenylphosphine)}rhodium(III)]-chloride (*3*)

A solution of $(PPh_3)_2Rh(CO)Cl$ (0.052 g, 0.075 mmol) in 10 mL of dichloromethane was added to a dichloromethane solution (10 mL) of Si_2BDI (**1**) (0.053 g, 0.15 mmol). The resulting yellow mixture was heated at 45 °C for 30 min forming a clear yellow solution which was allowed to cool down to room temperature and stirred continued for 1 day at room temperature. Then the solution colour changed from yellow to reddish-brown. The solvent was removed in vacuo. The solid product was washed with pentane and dried under vacuum. Yield: 0.04 g (49.3%), reddish-brown powder. M.p. 240 °C (decomp.). MS-FAB^+: *m/z* (%) 1041 (1.4) [M^+–Cl], 779 (3.8) [M^+–Cl–PPh_3], 573 (16) [$Rh(H_2BDI)(PPh_3)]^+$. ^{1}H NMR (CD_2Cl_2): δ 12.94 (br, 2H, N–H), 7.89–7.81 (m, 12H, Rh–Ph), 7.24–7.19 (m, 18H, Rh–Ph), 7.17–5.99 (m, 20H, H_2BDI–Ph). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 172.37 (d, $^{2}J_{Rh-C}$ = 51.9 Hz, C=N), 135.51 (t, *J* = 5.2 Hz, PPh_3–CH), 131.89 (br, PPh_3–CH), 129.95 (s, PPh_3–CH), 128.13 (t, *J* = 5.2 Hz, PPh_3–CH), 134.93–126.88 (H_2BDI–CH). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 31.1 (d, $^{1}J_{Rh-P}$ = 118.5 Hz, PPh_3). IR (KBr): 3049 (w), 1589 (w), 1571 (w), 1482 (s), 1432 (s), 1096 (m), 938 (m), 745 (m), 692 (vs), 522 (s) cm^{-1}. *Anal.* Calc. for $C_{64}H_{52}ClN_4P_2Rh$ (1077.39): C, 71.34; H, 4.87; N, 5.20. Found: C, 70.31; H, 4.63; N, 4.80%.

2.3. Synthesis of trans-[(benzildiimine-N,N′)-carbonyl-bis(triphenylphosphine)iridium(I)]-chloride (*4*)

A solution of $(PPh_3)_2Ir(CO)Cl$ (0.195 g, 0.25 mmol) in benzene (15 mL) was added to a benzene solution (5 mL) of Si_2BDI (0.088 g, 0.25 mmol). After 30 min the solution color changed from yellow to reddish–brown. The resulting solution was stirred at room temperature for 2 days. The solvent was then removed under reduced pressure and the resulting residue was washed with pentane (20 mL) and dried under vacuum. Yield: 0.075 g (30.4%), light red powder. M.p. 175 °C (decomp.). MS-FAB^+: *m/z* (%) 922 (1.6) [M^+–2H–CO–Cl], 660 (6) [M^+–2H–CO–Cl–PPh_3], 400 (10) [M^+–2H–CO–Cl–2PPh_3]. ^{1}H NMR (CD_2Cl_2): δ 12.11 (br, 2H, NH), 7.97–6.75 (m, 40H, CH–Ph). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 135.34–126.70 (m, CH–Ph). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 28.5 (s, PPh_3). IR (KBr): 3053 (m), 2957 (w), 2925 (w), 1962, 1597 (m), 1571 (w), 1483 (s), 1435 (vs), 1094 (vs), 998 (m), 942 (w), 747 (s), 721 (m), 693 (vs), 522 (s) cm^{-1}. *Anal.* Calc. for $C_{51}H_{42}IrN_2OP_2Cl$ (988.48): C, 61.96; H, 4.29; N, 2.83. Found: C, 60.05; H, 4.51; N, 2.68%.

2.4. X-ray data collection

Crystals of **1** suitable for X-ray analysis were isolated when the vacuum distilled yellow liquid was allowed to cool to room temperature after the synthesis. X-ray quality crystals of the complexes **3** and **4** were grown by slow isothermic diffusion of pentane into solutions of **3** or **4** in CH_2Cl_2 at room temperature within 2 days. Single crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Single crystal X-ray structure analyses were performed by direct methods using the SHELXS software and refined by full-matrix least-squares with SHELXL-97 [16]. Selected bond lengths and angles of **1**, **3** and **4** are given in Tables 1–3, respectively. Hydrogen bonds are given in Table 4. The crystal data and details of the structural refinement can be found in Table 5.

Table 1
Selected bond lengths (Å) and angles (°) for **1**.

N(1)–C(1)	1.268(19)	C(1)–N(1)–Si(1)	137.07(11)
N(2)–C(2)	1.270(19)	C(2)–N(2)–Si(2)	133.17(11)
C(1)–C(2)	1.523(2)	N(1)–C(1)–C(3)	120.71(13)
C(1)–C(3)	1.490(2)	N(1)–C(1)–C(2)	123.0(13)
C(2)–C(9)	1.493(2)	C(3)–C(1)–C(2)	116.29(12)
Si(1)–N(1)	1.737(14)	N(2)–C(2)–C(9)	121.53(13)
Si(2)–N(2)	1.746(13)	N(2)–C(2)–C(1)	122.84(13)
		C(9)–C(2)–C(1)	115.62(12)
		C(3)–C(1)–C(2)–C(9)	86.82(15)
		N(1)–C(1)–C(2)–N(2)	87.90(19)
		N(1)–C(1)–C(2)–C(9)	−92.81(17)
		C(3)–C(1)–C(2)–N(2)	−92.46(17)

Table 2
Selected bond lengths (Å) and angles (°) for **3**.

Rh(1)–N(1)	2.028(3)	N(4)–Rh(1)–N(3)	78.19(11)
Rh(1)–N(2)	2.046(3)	N(1)–Rh(1)–N(2)	78.37(11)
Rh(1)–N(3)	2.038(3)	N(1)–Rh(1)–N(4)	99.59(10)
Rh(1)–N(4)	2.028(2)	N(3)–Rh(1)–N(2)	103.85(12))
Rh(1)–P(1)	2.351(8)	N(4)–Rh(1)–N(2)	177.90(11)
Rh(1)–P(2)	2.367(9)	N(1)–Rh(1)–N(3)	177.48(11)
N(1)–C(1)	1.285(4)	N(2)–Rh(1)–P(2)	89.95(8)
N(2)–C(2)	1.279(4)	N(4)–Rh(1)–P(2)	89.52(7)
N(3)–C(15)	1.284(4)	N(1)–Rh(1)–P(2)	89.07(8)
N(4)–C(16)	1.284(4)	N(4)–Rh(1)–P(1)	88.44(7)
C(1)–C(2)	1.501(5)	N(3)–Rh(1)–P(1)	89.96(8)
C(15)–C(16)	1.499(4)	N(1)–Rh(1)–P(1)	88.78(7)
C(15)–C(17)	1.487(4)	N(2)–Rh(1)–P(1)	92.00(8)
C(16)–C(23)	1.498(4)	N(3)–Rh(1)–P(2)	92.09(8)
C(1)–C(3)	1.496(5)	P(1)–Rh(1)–P(2)	176.75(3)
C(2)–C(9)	1.481(5)	C(1)–N(1)–Rh(1)	114.5(2)
N(2)–H(2)	0.83(4)	C(16)–N(4)–Rh(1)	114.5(2)
N(3)–H(3)	0.86(4)	C(2)–N(2)–Rh(1)	117.4(2)
		C(15)–N(3)–Rh(1)	118.0(2)

Table 3
Selected bond lengths (Å) and angles (°) for **4**.

Ir(1)–N(2)	1.994(2)	C(15)–Ir(1)–N(2)	160.63(10)
Ir(1)–N(1)	2.032(2)	C(15)–Ir(1)–N(1)	96.31(10))
Ir(1)–C(15)	1.872(3)	N(2)–Ir(1)–N(1)	75.26(9)
Ir(1)–P(2)	2.327(10)	C(15)–Ir(1)–P(2)	92.06(8)
Ir(1)–P(1)	2.350(9)	C(15)–Ir(1)–P(1)	95.14(9)
O(1)–C(15)	1.145(3)	N(2)–Ir(1)–P(2)	88.61(7)
N(1)–C(1)	1.333(3)	N(1)–Ir(1)–P(2)	153.14(6)
N(2)–C(2)	1.340(3)	N(2)–Ir(1)–P(1)	103.07(7)
C(1)–C(2)	1.413(3)	N(1)–Ir(1)–P(1)	96.68(7)
C(1)–C(3)	1.484(3)	P(2)–Ir(1)–P(1)	107.96(3)
C(2)–C(9)	1.481(3)	O(1)–C(15)–Ir(1)	177.5(2)
N(1)–H(1)	0.82(3)		
N(2)–H(2)	0.83(3)		

Table 4
Hydrogen bonding for **3** and **4**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
*Compound **3***				
N(2)–H(2)···Cl(1)	0.83(4)	2.60(4)	3.317(3)	145(3)
N(3)–H(3)···Cl(1)	0.86(4)	2.38(4)	3.158(3)	151(3)
*Compound **4***				
N(1)–H(1)···Cl(1)	0.82(3)	2.44(3)	3.263(3)	174(2)

3. Results and discussion

Reaction of two molar equivalents of **1** with one molar equivalent of $RhCl(CO)(PPh_3)_2$ in CH_2Cl_2 at room temperature afforded the cationic rhodium complex $[Rh(PPh_3)_2(HBDI)_2]Cl$ (**3**) with two HBDI ligands within 1 day (Scheme 1). Interestingly, it contains one hydrolyzed and one deprotonated nitrogen of each ligand **2** instead of intact **1**. Rh(I) is oxidized to Rh(III) after the coordination of two ligands and forms the stable d^6 low spin complex **3**. One NH hydrogen atom from each of the ligand **2** is deprotonated and they are reduced to H_2. Attempts to obtain the *mono*-H_2BDI rhodium complex (analogous to **4**) from the reaction using the molar ratio 1:1 resulted also only in complex **3**. As in the literature mentioned before, the two $SiMe_3$ groups of **1** were replaced by two H atoms in complex **3**. Probably traces of H_2O in solvent CH_2Cl_2 and sterical demands initiated the cleavage of bulky $SiMe_3$ and introduction of the H atoms to the bound ligand.

The reaction of equivalent molars of **1** and $IrCl(CO)(PPh_3)_2$ in benzene at ambient temperature afforded the cationic iridium complex $[Ir(PPh_3)_2(CO)(H_2BDI)]Cl$ (**4**) with only one H_2BDI ligand within 2 days (Scheme 1). Attempts to obtain the bis-H_2BDI iridium complex analogous to **3** from a 1:2 metal complex: **1** ratio resulted only in complex **4**. Similar to **3** in complex **4** also both $SiMe_3$ groups were replaced by two H atoms. But, unlike to the synthesis of **3** the CO ligand remained intact in **4** after the reaction. Both complexes are air stable and soluble in polar solvents and insoluble in non polar solvents.

3.1. Crystal structure analysis

*3.1.1. X-ray structure of Si_2BDI (**1**)*

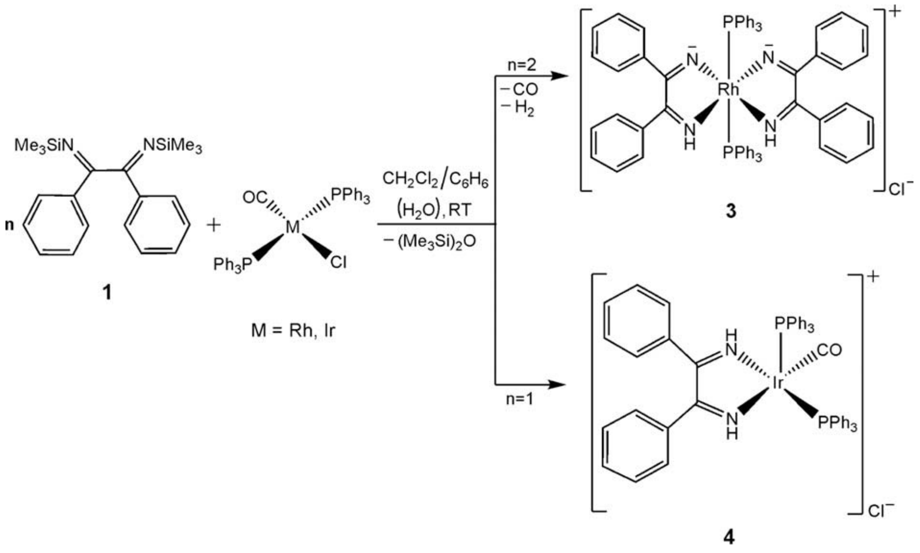
As shown in Fig. 2 the chemically equivalent bonds and angles of the two equal parts of **1** have similar values of bond lengths and angles and compare well with those found in structurally analogous compounds [17,18]. The bond lengths C–N (N1–C1 1.268(19) and N2–C2 1.270(19) Å), Si–N (Si1–N1 1.737(14) and Si2–N2 1.746(13)) and C–C (C1–C2 = 1.523(2), C1–C3 = 1.490(2), C2–C9 = 1.493(2) Å) fall within the expected range of ideal C=N double, Si–N and C–C single bonds. The sum of angles around C1 and C2 is 359.99°, as expected for a sp^2 hybridized carbon. The phenyl ligands are planar (the sum of the angles around C3 and C9 are 359.99° and 359.97°, respectively) and nearly perpendicular to each other with a torsion angle C3–C1–C2–C9 of 86.82(15)°. The atoms N1 and N2 attached with the $Si(CH_3)_3$ groups are nearly in the opposite side to each other and to the phenyl ring as required by the imposed steric interaction of the bulky groups (torsion angles: N1–C1–C2–N2 87.90, N1–C1–C2–C9 −92.81, C3–C1–C2–N2 −92.46°). This may be the reason that **1** can not act as bidentate ligand and is easily cleaved by hydrolysis to form cissoidal **2** which can coordinate to metals as a chelating ligand.

*3.1.2. X-ray structure of $[Rh(HBDI)_2(PPh_3)_2]Cl$ (**3**)*

Complex **3** crystallizes with two molecules of disordered dichloromethane as solvate. The coordination sphere of the Rh center can be described as distorted octahedral (Fig. 3). The phosphine ligands are mutually *trans*-disposed with slightly different Rh–P distances (Rh1–P1: 2.351(8), Rh1–P2: 2.367(9) Å). The two chelating H_2BDI ligands also occupy *trans* positions to each other with similar bite angles (N4–Rh1–N3 78.19(11) and N2–Rh1–N1 78.37(11)). The HBDI and the phosphine ligands are placed in axial positions [(P1–Rh1–P2 176.75(3)°, N1–Rh1–N3 177.48(11)° and N4–Rh1–N2 177.90(11)°]. The rest of the angles between the metal atom and the axial and equatorial donor atoms are in the range of 78.19–103.85°. The four Rh–N distances fall within the reported range [19], two of them (Rh1–N1 and Rh1–N4 2.028(2) Å of two different ligands located on the same side) are almost equal and differ significantly from the other two (Rh1–N3 2.038(3) and Rh1–N2 2.046(3) Å). The bond lengths Rh–P are slightly longer and those of Rh–N are shorter than the bonds observed in other reported examples [20,21]. The bonds N=C (1.279–1.285 Å) of **3** are somewhat longer and those of C1–C2 1.501(5) and C15–C16

Table 5
Crystal data and details of the structure refinement for **1**, **3** and **4**.

Compound	**1**	**3**	**4**
Empirical formula	$C_{20}H_{28}N_2Si_2$	$C_{66}H_{56}Cl_5N_4P_2Rh$	$C_{105}H_{90}Cl_8Ir_2N_4O_2P_4$
Formula weight	352.62	1247.29	2231.81
Temperature (K)	200(2)	195(2)	195(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	9.2022(18)	11.698(2)	9.827(2)
b (Å)	10.195(2)	30.177(6)	13.190(3)
c (Å)	12.093(2)	17.812(7)	19.791(4)
α (°)	82.22(3)	90	86.22(3)
β (°)	85.44(3)	108.33(3)	84.70(3)
γ (°)	69.06(3)	90°	71.72(3)
V (Å^3)	1049.2(4)	5968.98(13)	2423.6(10)
Z	2	4	1
Calculated density (g cm^{-3})	1.1162(4)	1.3879(6)	1.5292(5)
μ (mm^{-1})	0.173	0.608	3.081
F(0 0 0)	380	2560	1114
Crystal size (mm^3)	0.28 × 0.16 × 0.09	0.23 × 0.11 × 0.10	0.12 × 0.10 × 0.06
θ Range (°)	3.27–26.00	3.15–26.00	3.24–27.00
Index ranges	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 11$, $-14 \leqslant l \leqslant 14$	$-14 \leqslant h \leqslant 14$, $-37 \leqslant k \leqslant 37$, $-21 \leqslant l \leqslant 21$	$-12 \leqslant h \leqslant 12$, $-16 \leqslant k \leqslant 16$, $-25 \leqslant l \leqslant 25$
Reflections collected	7694	23 106	21 056
Independent reflections	4116	11 706	10 576
R_{int}	0.0197	0.0382	0.0218
Completeness to θ (%)	99.8	99.8	99.8
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4116/0/223	11 706/0/747	10 576/0/585
S on F^2	1.047	1.028	1.056
Final R indices [I>2σ(I)]	R_1 = 0.0343, wR_2 = 0.0894	R_1 = 0.0463, wR_2 = 0.1106	R_1 = 0.0242, wR_2 = 0.0526
R indices (all data)	R_1 = 0.0433, wR_2 = 0.0947	R_1 = 0.0733, wR_2 = 0.1234	R_1 = 0.0293, wR_2 = 0.0547
Largest difference peak/hole (e Å^{-3})	0.223 and −0.220	1.222 and −0.865	1.595 and −0.898



Scheme 1. Synthesis of the bis-HBDI (**3**) and *mono*-H_2BDI complex (**4**) of rhodium(III) and iridium(I).

1.499(4) Å are slightly shorter compared to the respective bonds of the free ligand **1** (N1–C1 1.268(19), N2–C2 1.270(19), C1–C2 1.523(2) Å). One phenyl ring (C17–C22) of H_2BDI and one (C59–C64) of the phosphine ligand are involved in π–π stacking. The distance between the centroids of stacked phenyl rings is 3.62 Å.

3.1.3. X-ray structure of [Ir(CO)(H_2BDI)(PPh_3)$_2$]Cl (**4**)

Complex **4** was isolated as solid red crystals including dichloromethane as solvate. The molecular view is shown in Fig. 4. Its geometry could be described as distorted square pyramidal or distorted trigonal bipyramidal as the bond angles around the metal center are in the range of 75.26(9)–160.63(10)°. The arrangement, however, resembles more to a highly distorted square pyramide, caused by the strong steric interactions between the two PPh_3 ligands and the two phenyl rings of H_2BDI. Due to this steric repulsion the phosphine ligands forced from the *trans* position to almost *cis* position [P2–Ir–P1 = 107.96(3)°] and the H_2BDI ring strained highly to form the small chelate bite angle N2–Ir1–N1 = 75.26(9)°. The N1 and N2 atoms are pseudo *trans* to the CO ligand (C15–Ir1–N2 160.63(10)°) and P2 of one PPh_3 ligand (N1–Ir1–P2 153.14(6)°), respectively. As the CO ligand is a better σ-donor–π-

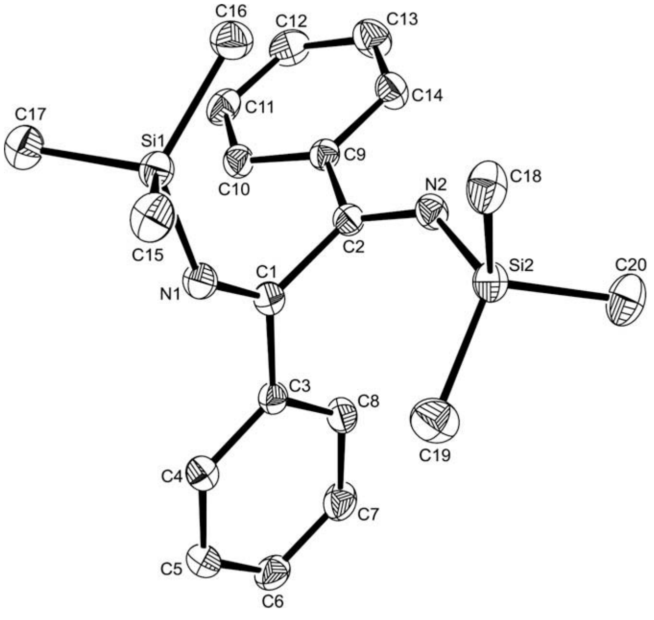


Fig. 2. Molecular structure of **1**. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

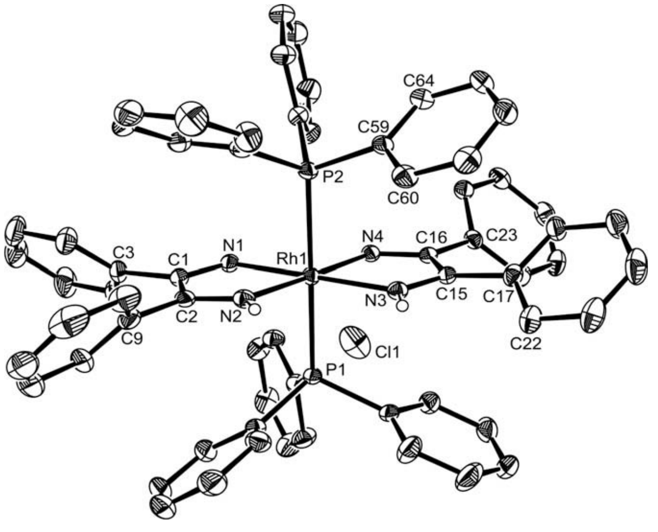


Fig. 3. Molecular structure of **3**. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms of phenyl groups and disordered CH_2Cl_2 solvate molecules are omitted for clarity.

acceptor ligand than the PPh_3 ligand, the Ir1–N2 distance (1.994(2) Å) *trans* to it is shorter than the Ir1–N1 distance (2.032(2) Å) in *trans* position to the PPh_3 ligand. The Ir1–P2 distance (2.327(10) Å) *trans* to the N2 atom is slightly shorter than that of the Ir1–P1 (2.350(9) Å), but both are consistent with reported values [21,22]. The C═N bond distances (N1–C1 = 1.333(3) and C2–N2 = 1.340(3) Å) are somewhat longer and those of C–C (C1–C2 = 1.413(3), C1–C3 = 1.484(3) Å) and C2–C9 = 1.481(3) Å) are slightly shorter than the expected C═N double and C–C single bonds. However, all the bond distances are in the range observed for similar iridium complexes [23,24].

The phenyl rings of H_2BDI in both complexes are essentially planar. As shown in Table 4, one molecule of the complexes (**3** and **4**) is connected to the chloride anion by N–H···Cl hydrogen bond, involving one imine H atom of one H_2BDI and the chloride anion of another complex.

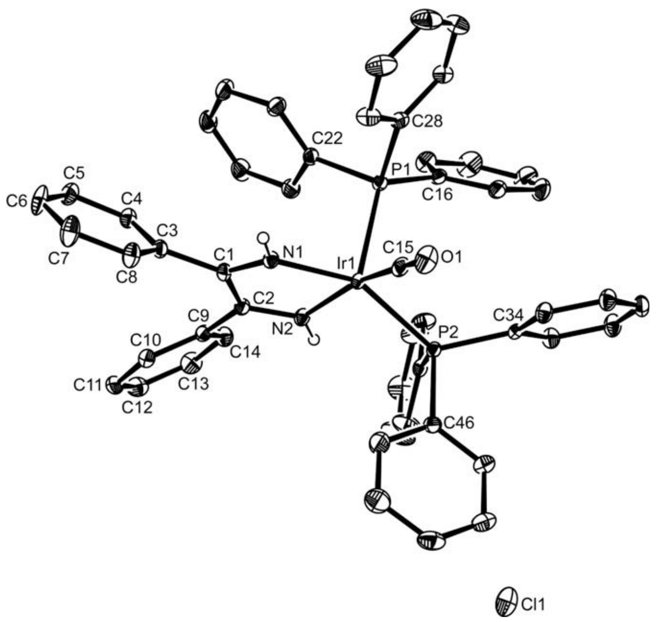


Fig. 4. Molecular structure of **4**. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms of phenyl groups and CH_2Cl_2 solvate molecules are omitted for clarity.

3.2. Spectroscopy

The ^1H NMR spectra of **3** and **4** show distinctive resonances due to imine N–H hydrogen, which is well separated from other parts of the spectrum. The relatively broad N–H resonances are observed at 12.94 (**3**) and 12.11 (**4**) ppm, making it simple to determine protonation of the Si_2BDI. The spectra of **3** and **4** also show signals in the range 7.89–7.19 and 7.17–5.99 and 7.97–6.75 ppm, respectively, indicating the presence of phenyl protons of PPh_3 and H_2BDI ligands.

In the ^{13}C NMR spectrum of **3** all phenyl carbons are well resolved [135.51–128.13 ppm (PPh_3) and 134.9–126.8 ppm (Ph–H_2BDI)]. The C═N carbon is observed at 172.37 ppm as a doublet by coupling with ^{103}Rh. But, in the case of complex **4** overlapping phenyl carbon signals are observed in the range 135.34–126.70 ppm. There is a very weak broad signal at 170–175 ppm indicating the C═N carbon, but a better assignment was not possible.

The signals in both ^1H and ^{13}C NMR spectra are shifted further upfield as compared to the free ligand (**1**), which suggests an electron enriched system, because of the more strongly electron donating PPh_3 ligands. (^1H: 7.80–7.32 ppm, ^{13}C: 174.2 ppm (CN), 138.28–128.14 (Ph–C) ppm, **1** recorded in CD_2Cl_2).

The ^{31}P NMR spectra of **3** and **4** exhibit a doublet at 31.1 ppm with a coupling constant of about 118.5 Hz (**3**) and a singlet at 28.5 (**4**) ppm respectively, indicating equivalent phosphine ligands environment.

The IR spectra (KBr disc) of **3** and **4** exhibit weak vibrations within 3053–2925 cm^{-1} assigned to the ν(N–H) and ν(C–H), respectively. A significant low frequency of ν(C═N) appearing at 1589, 1571(**3**) and 1597, 1571 (**4**) cm^{-1} in comparison to the free ligand **1** (1652 and 1646 cm^{-1}) suggests the involvement of imine nitrogens of the (C═N) groups in coordination with the metal. The ν(C═C) absorptions were observed between 1482 and 1432 cm^{-1}. The strong bands at 692, 522 (**3**) and 693, 522 (**4**) cm^{-1} are indicative of M–PPh_3 ligation in the complexes [25].

In the positive-ion FAB mass spectrum of **3** the [M^+–Cl] peak was observed at m/z = 1041. Other peaks resulting from the fragmentation of **3** are observed at m/z = 779 and 573, assigned to

$[M^{+}-Cl-PPh_3]$ and $[Rh(H_2BDI)(PPh_3)]^{+}$, respectively. On the other hand, for complex **4** instead of the molecular peak, the $[M^{+}-2H-CO-Cl]$ peak was observed at $m/z = 922$. Other peaks resulting from the successive loss of both PPh_3 ligands are observed at $m/z = 660$ and 400.

Supplementary material

CCDC 736240, 736241 and 736242 contain the supplementary crystallographic data for **1**, **3**, and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] G. Van Koten, K. Vrieze, Adv. Organomet. Chem. 21 (1982) 151. and references cited therein.
[2] G. Van Koten, K. Vrieze, Recl. Trav. Chim. Pays-Bas 100 (1981) 129. and references cited therein.
[3] (a) A.H. Krotz, L.Y. Kuo, J.K. Barton, Inorg. Chem. 32 (1993) 5963;
(b) A.M. Pyle, M.Y. Chiang, J.K. Barton, Inorg. Chem. 29 (1990) 4487;
(c) A.M. Pyle, J.K. Barton, Inorg. Chem. 26 (1987) 3820.
[4] J. Sundermeyer, H.W. Roesky, M. Noltemeyer, Can. J. Chem. 67 (1989) 1785.
[5] N. Weis, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. 1 (1999) 7.
[6] I. Matsuda, T. Takahashi, Y. Ishii, Chem. Lett. 12 (1977) 1457.
[7] R. Neidlein, D. Knecht, Helv. Chim. Acta 70 (1987) 1076.
[8] G. Tuchtenhagen, K. Rühlmann, Liebigs Ann. Chem. 711 (1968) 174.
[9] B.N. Diel, T.L. Hubler, W.G. Ambacher, Heteroat. Chem. 10 (1999) 423.
[10] (a) D. Walther, M. Teutsch, Z. Chem. 16 (1976) 118;
(b) D. Walther, Z. Anorg. Allg. Chem. 8 (1974) 405.
[11] K. Schlosser, E. Hoyer, Z. Chem. 10 (1970) 439.
[12] K. Schlosser, E. Hoyer, Z. Anorg. Allg. Chem. 387 (1972) 91.
[13] A.M. Pyle, J.P. Rehmann, R. Meshoyrer, C.V. Kumar, N.J. Turro, J.K. Barton, J. Am. Chem. Soc. 111 (1989) 3051.
[14] A.M. Pyle, E.C. Long, J.K. Barton, J. Am. Chem. Soc. 111 (1989) 4520.
[15] P. Serp, M. Hernandez, B. Richard, P. Kalck, Eur. J. Inorg. Chem. 9 (2001) 2327.
[16] G.M. Sheldrick, SHELX-97, an Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.
[17] B.N. Diel, P.J. Deardorff, C.M. Zelenski, Tetrahedron Lett. 40 (1999) 8523.
[18] S. Nishigaki, H. Yoshioka, K. Nakatsu, Acta Crystallogr. 34 (1978) 857.
[19] A. Alvarez, R. Macias, M.J. Fabra, M.L. Martin, F.J. Lahoz, L.A. Oro, Inorg. Chem. 46 (2007) 6811.
[20] M.T. Youinou, R. Ziessel, J. Organomet. Chem. 363 (1989) 197.
[21] L. Dahlenburg, M. Kuhnlein, Eur. J. Inorg. Chem. 9 (2000) 2117.
[22] R.D. Gilbertson, T.L.S. Lau, S. Lanza, H.P. Wu, T.J.R. Weakley, M.M. Haley, Organometallics 22 (2003) 3279.
[23] A. Tiripicchio, M.T. Camellini, M. Ghedini, G. Dolcetti, Transition Met. Chem. 5 (1980) 102.
[24] P. Dapporto, G. Denti, G. Dolcetti, M. Ghedini, J. Chem. Soc. 4 (1983) 779.
[25] M. Shakir, S. Khatoon, S. Parveen, Y. Azim, Transition Met. Chem. 32 (2007) 42.