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Synthesis and Crystal Structure of Binuclear Half-Sandwich Rhodium Carborane Complex[1]

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Abstract—Reaction of unsaturated 16e half-sandwich rhodium carborane complex [Cp*Rh($S_2C_2B_{10}H_{10}$)] (Cp* = pentamethyl-cyclopentadienyl) with half equiv. (*m*-pyridyl)N=C($C_{10}H_6$)C=N(*m*-pyridyl) (*m*Py-Bian, L) afforded a bi-nuclear complex [{Cp*Rh($S_2C_2B_{10}H_{10}$)}$_2$(μ-L)] (**I**), leaving α-diimine moiety of the L ligand as free coordination site. Compounds L and **I** have been characterized by single crystal X-ray diffraction (CIF files nos. 1586584 (L) and 1586585 (**I**)). Compound L crystallizes in the monoclinic space group *C*2/*c* with a = 21.51(3), b = 8.884(13), c = 9.414(14) Å, β = 112.540(19)°, and Z = 4. Complex **I** crystallizes in the orthorhombic space group *Pnma* with a = 15.741(2), b = 34.062(5), c = 14.960(2) Å, and Z = 4.

Keywords: rhodium, carborane, bipyridyl, α-diimine, crystal structure

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INTRODUCTION

The α-diimine compounds RN=C($C_{10}H_6$)C=NR (R = aryl, alkyl) obtained from condensation reactions of acenaphthenequinone and primary amines are an important class of ligands, which could coordinate to various metal ions, such as alkali metal Na [1], alkaline-earth metal Mg [2], and Ni, Cu, Co, Fe, Pd, W, Pt, Ru and other transition metals [3–6]. These structurally diverse and catalytically active metal complexes have attracted great attention during the past decades. For examples, nickel complexes bearing 2,6-dibenzhydryl-*N*-(2-phenyliminoacenaphthylenylidene)-4-methylbenzenamines showed very high activity for ethylene polymerization [7]. A series of redox-active bis(arylimino)acenaphthene (bian)-derived ruthenium complexes were synthesized as efficient and selective precatalysts in transforming a wide variety of alkenes to corresponding epoxides in the presence of PhI(OAc)$_2$ [8]. On the other hand, bipyridyl compounds are common linkers and have been widely employed in self-assembly of supramolecules [9, 10]. It is noted that Reek group designed a pyridyl-bian ligand (*m*Py-Bian, L) for the preparation of palladium catalysts and used them for the tunable CO/4-*tert*-butylstyrene copolymerization, the catalytic activity of the palladium complex and the molecular weight of the copolymer obtained could be tuned by altering the properties of the zinc salphen units coordinated to pyridyl nitrogens of the pyridyl-bian ligand [11]. Competing coordination behavior of pyridyl and α-diimine moieties towards palladium metal center was observed during the direct reaction of [(COD)PdMeCl] (COD = 1,5-cyclooctodiene) and *m*Py-Bian [11]. As a result, the ligand *m*Py-Bian is expected to have rich and complex coordination chemistry because of the existence of both pyridyl groups and α-diimine moiety. Appropriate synthetic routes are needed to design when employing such ligand and limited research has been done related to the *m*Py-Bian ligand up to now according to CCDC searching result. Previously, Jin group reported one pot synthesis of heterometallic macromolecules [$Cp_4^*M_4$(BiBzIm)$_2$(*m*Py-Bian)$_2$Ag(H_2O)](OTf)$_5$ (M = Ir, Rh; H_2BiBzIm = 2,2'-bis(benzimidazole; OTf = OSO_2CF_3) with Ir/Rh coordinated to pyridyl nitrogens and Ag coordinated to bis-α-diimine moieties [12]. Afterwards, we have synthesized a similar complex [(η^6-C_6Me_6)$_4$Ru$_4$(μ-Cl)$_4$(μ- *m*Py-Bian)$_2$Ag](OTf)$_5$ with Ru coordinated to pyridyl nitrogens and Ag coordinated to bis-α-diimine moieties from self-assembly of [(η^6-C_6Me_6)Ru(μ-Cl)Cl]$_2$, AgOTf and *m*Py-bian in methanol [13]. In order to explore the sequential coordination ability of *m*Py-Bian, we herein reported the crystal structure of the compound *m*Py-Bian and synthesis of the *m*Py-Bian bridged bi-nuclear half-sandwich rhodium carborane complex with α-diimine moiety as free coordination site.

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for L and $\mathbf{I} \cdot 2CH_2Cl_2 \cdot n\text{-}C_6H_{14}$

Parameter	Value	
	L	$\mathbf{I} \cdot 2CH_2Cl_2 \cdot n\text{-}C_6H_{14}$
Empirical formula	$C_{22}H_{14}N_4$	$C_{54}H_{82}B_{20}N_4S_4Cl_4Rh_2$
M_r	334.37	1479.30
T, K	293(2)	100(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Pnma$
a, Å	21.51(3)	15.741(2)
b, Å	8.884(13)	34.062(5)
c, Å	9.414(14)	14.960(2)
β, deg	112.540(19)	90
V, Å^3	1661(4)	8021(2)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.337	1.225
μ, mm^{-1}	0.082	0.683
F(000)	696	3024
Crystal size, mm	0.25 × 0.15 × 0.12	0.20 × 0.15 × 0.12
θ Range, deg	2.05–25.99	1.20–27.01
Limiting indices	$-26 \le h \le 12$, $-10 \le k \le 10$, $-11 \le l \le 11$	$-19 \le h \le 19$, $-43 \le k \le 43$, $-8 \le l \le 18$
Reflections collected	3662	43547
Independent reflections (R_{int})	1624 (0.0722)	8841 (0.0423)
Data/restraint/parameters	1624/0/120	8841/27/426
Goodness-of-fit on F^2	0.872	1.064
R indices ($I \ge 2\sigma(I)$)	$R_1 = 0.0477$, $wR_2 = 0.1078$	$R_1 = 0.0581$, $wR_2 = 0.1525$
R indices (all data)*	$R_1 = 0.0768$, $wR_2 = 0.1179$	$R_1 = 0.0719$, $wR_2 = 0.1597$
Largest diff. peak/hole, e Å^{-3}	0.175/–0.195	0.843/–1.080

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

EXPERIMENTAL

Materials and methods. All the operations were carried out under pure argon atmosphere using standard Schlenk techniques. Hexane was distilled from sodium-benzophenone. Dichloromethane was distilled from calcium hydride. 3-Aminopyridine and acenaphthenequinone, were purchased from Acros Co. 16e Half-sandwich rhodium carborane complex [Cp*Rh($S_2C_2B_{10}H_{10}$)] (Cp* = pentamethylcyclopentadienyl) [14] and L [13] were prepared according to the literatures. The ^{1}H NMR spectra were measured on a VAVCE-DMX 400 spectrometer in $CDCl_3$. Elemental analysis was performed on an Elementar Vario EL III analyzer. IR spectra were recorded on the Nicolet FT-IR spectrophotometer.

Synthesis of complex [{Cp*Rh($S_2C_2B_{10}H_{10}$)}$_2$(μ-L)] (I). 16e Half-sandwich rhodium carborane complex [Cp*Rh($S_2C_2B_{10}H_{10}$)] (88.9 mg, 0.20 mmol) and 0.5 equiv. L (33.4 mg, 0.10 mmol) was mixed and stirred in CH_2Cl_2 at room temperature for 10 h, the solvent was removed under vacuum. The crude product was recrystallized in CH_2Cl_2–hexane (v : v = 1 : 3) mixed solvents to afford complex **I** as red block crystals. The yield was 116.2 mg (95%).

IR (KBr; ν, cm^{-1}): 2583 m ν(B–H), 1384 s ν(CH_3).

^{1}H NMR (400 Hz, $CDCl_3$; δ, ppm): 1.62 (s., 30H, Cp*), 2.50 (brs., 20H, BH), 7.05 (d., J = 8.3 Hz, 2H, L), 7.54–7.63 (m., 6H, L), 8.03 (d., J = 2.4 Hz, 2H, L), 8.57 (d., J = 4.9 Hz, 2H, L), 8.68–8.76 (m, 2H, L).

For $C_{46}H_{64}B_{20}N_{42}S_4R$

Anal. calcd., %	C, 45.17	H, 5.27	N, 4.58
Found, %	C, 45.22	H, 5.31	N, 4.50

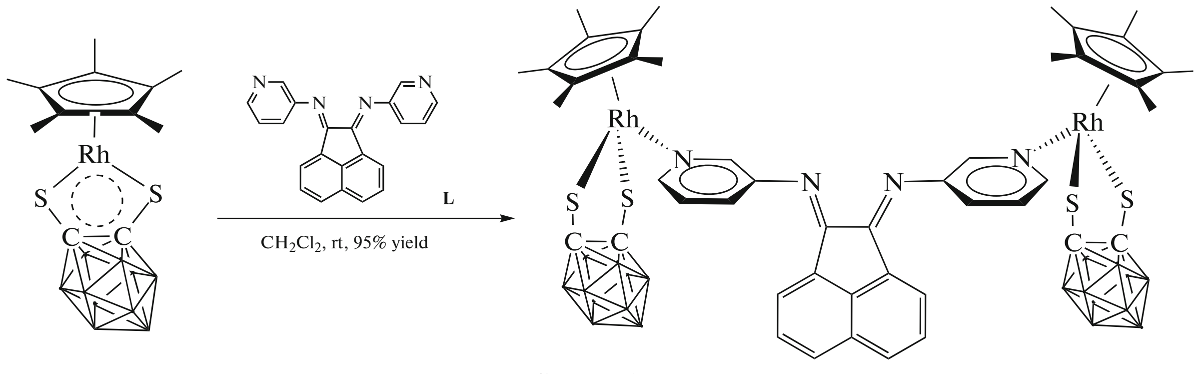
X-ray crystallography. Intensity data of the single crystals were collected on a CCD-Bruker Smart APEX system using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 296(2) K for compound L and CuK_α radiation (λ = 1.5418 Å) at 100(2) K for the crystals of complex $\mathbf{I} \cdot 2CH_2Cl_2 \cdot n\text{-}C_6H_{14}$ (obtained from CH_2Cl_2–hexane mixed solvents). These structures were solved by Direct Methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program [15]. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in Table 1.

Crystallographic data for L and **I** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC nos. 1586584 and 15865845, respectively; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The compound *m*Py-bian (L) was synthesized by heating the mixture of 3-aminopyridine (5 equiv.) and acenaphthenequinone at 150°C for 4 h according to literature [13]. Purification of L was simplified by cooling the ethyl acetate solution of the crude product at –20°C to obtain pure yellow microcrystals in 41% yield. Compound L has a good solubility in common organic solvent, such as dichloromethane, ethanol and methanol, but it is insoluble in hexane. Single crystals of L were obtained by slow evaporation from its ethyl acetate solution. The molecular structure of L is shown in Fig. 1. The characteristic ketoimine bond length of N(1)–C(7) 1.273(3) Å agrees well to those in related α-diimine compounds (*p*Tol)N= C($C_{10}H_6$)-C=N(*p*Tol) (1.269 Å) [16] and PhN=C-($C_{10}H_6$)C=NPh (1.275 Å) [17]. The bond angle of C(7)N(1)C(9) in compound L is 120.24(16)°, comparable to those in compounds (*p*Tol)N=C-($C_{10}H_6$)C=N(*p*Tol) (122.30°) [16] and PhN=C-($C_{10}H_6$)C=NPh (120.50°) [17]. The two pyridyl groups are not coplanar whose dihedral angle is 50.7°, and they have the dihedral angle of 65.3° out of the acenaphthylene plane, which are also similar in aryl substituted α-diimine compounds ArN=C($C_{10}H_6$)-C=NAr [16, 17].

Half-sandwich rhodium carborane complexes have many advantages in organometallic synthesis, such as good solubility, thermally stability, strong coordination ability and easily to crystallize for characterization [18]. Several mono-, bi-, tri-, and tetranuclear half-sandwich rhodium carborane complexes have been reported based on different pyridyl-type ligands [19–21]. So we attempted the reaction of unsaturated 16e complex [Cp*Rh($S_2C_2B_{10}H_{10}$)] and bipyridyl species L in dichloromethane at room temperature to test the coordination behavior of L. Synthesis of bi-nuclear half-sandwich rhodium complex **I** is shown in Scheme 1:



Scheme 1.

(I)

According to the 18e rule, the rhodium metal centers should preferably coordinate to the pyridyl nitrogen to the α-diimine moiety. The expected saturated 18e binuclear rhodium complex **I** was obtained as red block crystals in a quantitive yield (95%). Its IR spectrum shows a band for B–H vibration at approximately

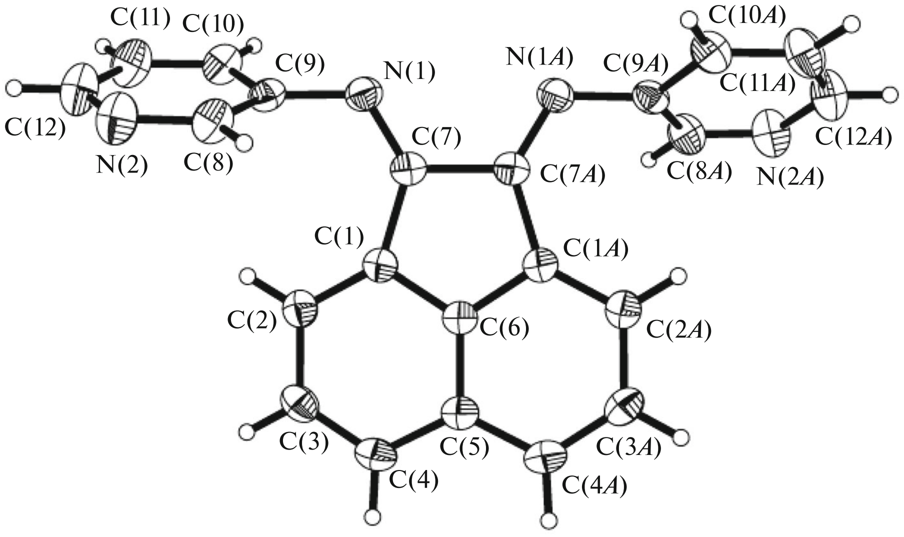


Fig. 1. ORTEP drawing of the molecular structure of L. Selected bond distances and angles: N(1)–C(7) 1.273(3), N(1)–C(9) 1.414(3), N(2)–C(8) 1.328(3), N(2)–C(12) 1.327(3) Å and C(7)N(1)C(9) 120.24(16)°, N(1)C(7)C(1) 132.63(18)°, N(1)C(7)C(7*A*) 120.83(11)°.

2580 cm^{-1}, which is similar to that in related bimetallic half-sandwich rhodium carborane complex $[\{(Cp^*Rh(Cab^{s,s})(CNC_6H_2{}^iPr_2\text{-}2,6))_2\text{-}C{\equiv}C\}\text{-}1,2]$ (2578 cm^{-1}) [18]. A sharp singlet signal around 1.62 ppm in the ^1H NMR spectrum could be ascribed to the methyl groups of the Cp* moiety, the chemical shift of the bridging *m*Py-bian ligand protons in **I** shifted downfield approximately δ = 0.15 ppm relative to free ligand L.

The structure of **I** was further confirmed by single crystal X-ray diffraction. Single crystals of **I** were obtained by slow diffusion of *n*-hexane into concentrated solution of the complex in dichloromethane. The ORTEP diagram for the structure, selected bond distances and angles are shown in Fig. 2. Crystals of **I** go effloresce fast in air at room temperature, X-ray diffraction analysis performed at 100 K presents that there is one *n*-hexane solvent molecule and two dichloromethane solvent molecules in each unit cell of molecule **I**. The Rh(III) centers are located in a three-legged piano-stool conformation. The two metal atoms Rh(1) and Rh(1*A*) are interconnected by the *m*Py-Bian linker to form a stable dimeric structure leaving the α-diimine moiety of L as free coordination site for further modification. The Rh(1)···Rh(1*A*) distance is 11.080 Å.

After coordination of pyridyl nitrogens to rhodiums, the two pyridyl groups in the solid state of **I** are almost in a plane with a small dihedral angle of 3.6°, which is different from that in free ligand L (50.7°). Additionally, the two pyridyl groups have the same dihedral angle (83.1°) towards the acenaphthylene plane, much larger than that in L (65.3°). Usually, the two $[Cp^*Rh(S_2C_2B_{10}H_{10})]$ fragments adopted *trans* conformation in reported bipyridyl bridged half-sandwich Ir/Rh complexes (bipyridyl = 1,2-di(4-pyridyl)ethylene, pyrazine, 4,4′-azopyridine, *N*,*N*′-bis(4-pyridinylmethylene)biphenyl-4,4′-diamine) [19] and bi-isonitrile bridged complex $[\{(Cp^*Rh(Cab^{s,s})\text{-}(CNC_6H_2{}^iPr_2\text{-}2,6))_2\text{-}C{\equiv}C\}\text{-}1,2]$ [18]. However, the two $[Cp^*Rh(S_2C_2B_{10}H_{10})]$ fragments in complex **I** are in a *cis* conformation, which is only observed in complex $[Cp^*RhS_2C_2(B_{10}H_{10})]_2(L)$ (L = 2,5-di(4-pyridyl)-1,3,4-oxadiazole) [19]. The Rh–S bond lengths of 2.3564(11) and 2.3572(11) Å in complex **I** compared well to those in complex $[Cp^*RhS_2C_2(B_{10}H_{10})]_2(L)$ (2.3530(17) and 2.3553(17) Å) [19]. The Rh–N bond length of 2.155(3) Å is also similar to that in complex $[Cp^*RhS_2C_2(B_{10}H_{10})]_2(L)$ (2.148(7) Å) [19]. In complex **I**, the ketoimine bond length of N(1)–C(3) is 1.270(5) Å, almost the same to that in free ligand L (1.273(3) Å), suggesting that the coordination of pyridyl nitrogens has little effect on the α-diimine moiety. The C=N bond lengths in L and **I** are well in the range of those in complexes $[Cp_4^*Rh_4(BiBzIm)_2(m\text{Py-Bian})_2\text{-}Ag(H_2O)](OTf)_5$ (1.246–1.296 Å) [12] and $[(C_6Me_6)_4Ru_4(\mu\text{-}Cl)_4(m\text{Py-Bian})_2Ag](OTf)_5$ (1.258 and 1.286 Å) [13]. In **I**, the bond angle of C(11)N(1)C(3) (120.1(3)°) is similar to that in L (120.24(16)°) and complex $[(C_6Me_6)_4Ru_4(\mu\text{-}Cl)_4(m\text{Py-Bian})_2Ag](OTf)_5$ (121.9° and 121.3°) [13], but a little

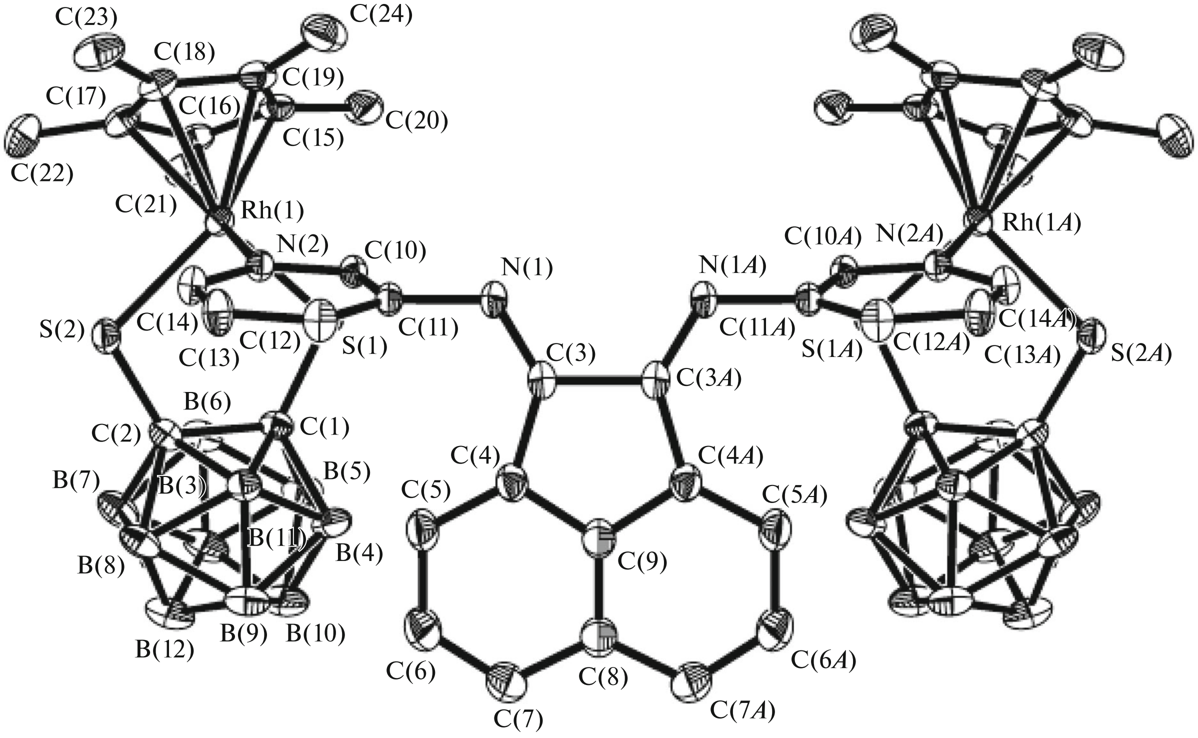


Fig. 2. ORTEP drawing of the molecular structure of complex **I** · 2CH$_2$Cl$_2$ · *n*-C$_6$H$_{14}$. Hydrogen atoms and solvents are omitted for clarity. Selected bond distances and angles: N(1)–C(3) 1.270(5), N(1)–C(11) 1.417(5), N(2)–C(10) 1.333(5), N(2)–C(14) 1.343(5), Rh(1)–S(1) 2.3564(11), Rh(1)–S(2) 2.3572(11), Rh(1)–N(2) 2.155(3) Å and C(3)N(1)C(11) 120.1(3)°, N(1)C(3)C(4) 133.2(3)°, N(1)C(3)C(3*A*) 120.5(2)°, N(2)Rh(1)S(1) 89.94(9)°, S(1)Rh(1)S(2) 90.54(4)°, N(2)Rh(1)S(2) 91.88(9)°.

larger than those in complexes [Cp$^*_4$Rh$_4$(BiBzIm)$_2$(*m*Py-Bian)$_2$Ag(H$_2$O)](OTf)$_5$ (114.14°–117.93°) [12].

In summary, the structure of a bipyridyl compound *m*Py-Bian functionalized with α-diimine moiety was studied by single crystal X-ray diffraction analysis and its coordination behavior was initially investigated. Reaction of *m*Py-Bian and 16e half-sandwich rhodium carborane complex afforded the *m*Py-Bian-bridged binuclear complex quantitively, leaving the α-diimine moiety of *m*Py-Bian as free coordination site for further modification. The two [Cp*Rh(S$_2$C$_2$B$_{10}$H$_{10}$)] moieties in complex **I** are in an unusual *cis* conformation. The design of heterometallic complexes based on sequential coordination reactions employing both α-diimine and pyridyl groups are underway in our lab.

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