Synthesis of Re(I) complexes bearing tridentate 2,6-bis(7′-azaindolyl)phenyl ligand with green emission properties

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Abstract

The Re(I) complexes bearing 2,6-bis(7′-azaindolyl)phenyl ligand as a tridentate ligand were synthesized by treatment with $Re_2(CO)_{10}$. The structures of the complexes were confirmed by X-ray crystallography. Both 7-azaindolyl ligands of Re(I) complexes are present in butterfly forms. The $Re–C_{ipso}$ bonds showed a partial double bond character by π back-donation between the phenyl moiety and Re atom. In THF solution at room temperature, these complexes exhibited green emission ($\lambda_{em} = 510$ nm), which is considered to be attributable to MLCT ($dz^2(Re) \rightarrow \pi^*$ (7′-azaindolyl group)) transition containing $\pi \rightarrow \pi^*$ (7′-azaindolyl group) transition.
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Keywords: Re(I) complex; Tridentate ligand; Azaindole; Emission

1. Introduction

Cyclometallated compounds bearing nitrogen-containing ligands have attracted considerable interest as a consequence of the wide range of their potential applications in many areas including organic synthesis [1], homogeneous catalysis [2], and photochemistry [3]. In addition, the strong σ donation through a metal–carbon bond increases the electron density on the metal center, resulting in low-energy metal-to-ligand charge transfer [5].

Group 7, especially, Re complexes have been studied for photochemistry. Among them, the $Re(CO)_3(N^{\wedge}N)X$ type complexes ($N^{\wedge}N$: a bidentate N, N'-chelating ligand such as 2,2′-bipyridine or 1,10-phenanthroline, and X = Cl, Br) have been used in a variety of processes including photochemical reduction of CO_2 [6], chemoluminescence [7], electrochemiluminescence [8], exciplex

emission [9], and luminescent probe in curing of epoxy resins [10]. Despite a number of studies on the complexes bearing bidentate N, N'-chelating ligands, only few papers on the tridentate counterparts have been reported [11]. Surprisingly, to the best of our knowledge, only one report appeared on Re complexes containing a Re-carbon bond with a tridentate ligand [12]. In general, Re-carbon bond formation requires severe reaction conditions due to the low reactivity of Re species. For example, the complexes bearing $N^{\wedge}C$ type ligands such as ppy (2-phenylpyridine) were synthesized by treatment with $Re(CO)_5Cl$ in the presence of a proton sponge, although the yields were very low [13]. Another method involves the utilization of alkyl Re species ($R = CH_3$ or $PhCH_2$), which is generated by Na–Hg reduction of $Re(CO)_5X$ followed by the reaction with alkyl halide [14].

Use of a pincer ligand leads to the metal insertion into C–X (X = H, halide, MeO) under mild reaction conditions, providing more stable complexes by chelation to metal [4]. These facts prompted us to investigate the synthesis and photoluminescent properties of the Re(I) complex bearing an N–C–N type tridentate ligand.

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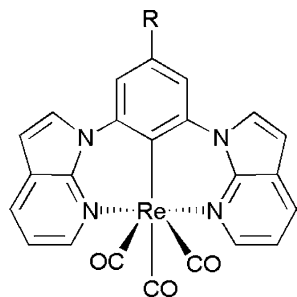*E-mail addresses:* hsakurai@chem.eng.osaka-u.ac.jp (H. Sakurai), hirao@chem.eng.osaka-u.ac.jp (T. Hirao).

Fig. 1. Re(I) complex bearing tridentate 2,6-bis(7'-azaindolyl) phenyl ligend.

We adopted a tridentate ligand containing a benzene moiety as σ-donor and two 7-azaindolyl groups as π-acceptor (Fig. 1). 7-Azaindolyl derivatives is known to provide the fluorescence [15] or luminescence properties [16,17].

2. Results and discussion

2.1. Synthesis of Re(I) complexes 3

Bis(7'-azaindolyl)benzene derivatives **2a–g** were synthesized by Ullmann coupling of the bromobenzene derivatives **1** with 7-azaindole as shown in Scheme 1 [16]. Complexation was carried out by treatment of **2a–g** with $Re_2(CO)_{10}$ in diglyme under refluxing conditions. During the reaction, the solution color changed colorless to brown. The solvent was removed in vacuo, and the resulting solid was washed with CH_2Cl_2 or purified by column chromatography on silica gel to give bis(7'-azaindolyl)benzene-rhenium complexes **3a–g** as colorless
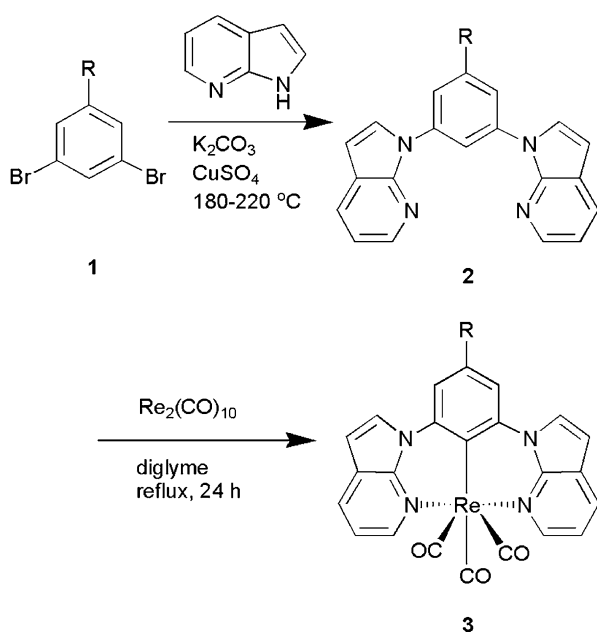
Scheme 1.

Table 1
Synthesis of bis(7-azaindolyl)phenyl-rhenium complexes **3a–g**

R	No.	Isolated yield (%)
H	**3a**	74
F	**3b**	62
Cl	**3c**	65
Br	**3d**	81
CF$_3$	**3e**	68
MeO	**3f**	72
	3g	85
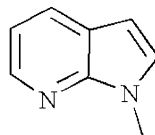
to pale yellow microfine crystals in 62–85% isolated yields (Table 1). In these reactions, neither the additives such as a proton sponge nor the preparation of R–Re(CO)$_5$ (R = CH$_3$ or PhCH$_2$) species were required. Thus-obtained complexes **3a–g** were fully characterized by spectroscopic data, mass spectra, and elemental analyses.

Selected spectroscopic data for the complexes **3a–g** are summarized in Table 2. In a solution state, two $\nu(C\equiv O)$ bands were observed around 2006 cm^{-1} as a sharp absorption and around 1890 cm^{-1} as a broad absorption. In contrast, the IR spectra of all Re(I) complexes **3a–g** in a solid state showed three bands at 1995–2002 (sharp), 1879–1890 (broad), and 1860–1882 cm^{-1} (broad) in the $\nu(C\equiv O)$ frequency region. These bands are assigned to the three IR-active CO stretching modes (2a' + a'') of this type of complexes possessing Cs symmetry [18]. In the ^{13}C NMR spectra, the Re(I) complexes **3a–g** showed two signals at 198.27 ± 0.25 and 195.92 ± 0.24 ppm due to axial and equatorial CO carbon atoms, respectively, suggesting that the complexes possess symmetry in solution [19]. Although the $\nu(C\equiv O)$ stretching frequencies in Re(4,4'-R$_2$-bipy)(CO)$_3$Cl were shifted to higher wavenumber due to the electron-withdrawing group [20], such significant shift effect induced by the substituent of **3a–g** was not detected in both solution and solid states.

2.2. X-ray crystallography

The recrystallization of **3a**, **3b**, **3e**, and **3f** from mixed solvents of DMSO/MeOH at room temperature gave the crystals for X-ray analysis. The crystal data are collected in Table 3. Although these crystals are not isomorphous, their forms are quite similar. These structures are shown in Fig. 2, and some important structural data are listed in Table 4. Although both 7-azaindolyl ligands of Pd(II) and Pt(II) complexes are perpendicular to one another for central metal [17], those in Re(I) complexes are present in butterfly forms.

Table 2
Selected spectroscopic data for complexes 3a–g

	^{13}C NMR C≡O (ppm)[a]		FT-IR vC≡O (cm^{-1})				
			Solid[b]			Solution[c]	
3a	196.12	198.59	1995	1885	1870	2004	1889
3b	195.68	198.17	2002	1893	1882	2005	1889
3c	195.92	198.18	2000	1890	1867	2006	1891
3d	195.90	198.02	1999	1887	1868	2006	1889
3e	195.89	198.02	2002	1888	1880	2007	1894
3f	195.83	198.42	1996	1879	1860	2003	1889
3g	196.09	198.48	1995	1883	1863	2005	1890

[a] DMSO-d$_6$.
[b] KBr.
[c] CH$_2$Cl$_2$.

Table 3
Crystallographic data for 3a, 3b, 3e, and 3f

	3a	3b	3e	3f
Formula	C$_{23}$H$_{13}$O$_3$N$_4$Re	C$_{23}$H$_{12}$O$_3$N$_4$FRe	C$_{24}$H$_{12}$O$_3$N$_4$F$_3$Re	C$_{24}$H$_{15}$O$_4$N$_4$Re
Formula weight	579.59	597.58	647.59	609.61
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space Group	Pbca (No. 61)	C2/m (No. 12)	P2$_1$/n (No. 14)	P$\bar{1}$ (No. 2)
a (Å)	14.6890(3)	14.0228(7)	6.7078(4)	7.2731(4)
b (Å)	14.1024(3)	15.7368(8)	22.297(1)	8.3609(6)
c (Å)	18.7407(3)	9.2122(4)	14.439(1)	17.238(1)
α (°)				89.065(3)
β (°)		103.533(2)	90.437(1)	81.051(3)
γ (°)				82.535(3)
Volume (Å^3)	3882.1(1)	1976.5(2)	2159.6(2)	1026.7(1)
Z	8	4	4	2
D$_{calc}$ (g cm^{-3})	1.983	2.008	1.992	1.972
μ (Mo Kα) (cm^{-1})	62.98	61.96	56.91	59.62
T (K)	269	269	269	269
R[a]	0.041	0.022	0.048	0.031
R$_w$[b]	0.123	0.071	0.138	0.101

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $R_w = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$.

The Re atom is linked to two carbon atoms of CO ligand and two nitrogen atoms of the bis(7'-azaindolyl)phenyl ligand on the equatorial plane, and adopts an approximately octahedral coordination. In order to maintain the octahedral structure, Re(1) atom in these complexes locates 0.5 Å below the N(1)–N(2)–N(3)–N(4) plane, being in contrast to Re atom in Re(CO)$_4$(N∧C) nearly on the plane of phenyl-pyridine [13]. The dihedral angles of the benzene moiety and 7'-azaindolyl groups are about 40° in all cases. *Trans* effect is observed in the CO ligand of 3a, i.e. the distance (Re(1)–C(21)) between Re and CO carbon in axial position is about 0.07 Å longer than those in equatorial positions (Re(1)–C(22) and Re(1)–C(23)). In contrast, axial Re–CO distance in 3b (R = F) and 3e (R = CF$_3$) is 0.05 Å shorter than those in equatorial positions. However, the distance of Re(1)–C(21) in 3f (R = MeO) is very close to the corresponding Re–C distances of other two CO ligands.

The Re(1)–C(1) distances (2.154(4)–2.165(4) Å) in 3a, 3b, 3e, and 3f are nearly the same. The analogous dis-

tances were reported in Re(CO)$_4$(N∧C) (N∧C = ppy: 2.163(7) Å [13c], meppy: 2.168(5) Å [13d], thpy: 2.16(2) Å [13b]). These distances are slightly longer than those of Re=C double bonds (2.125(9) Å) reported for neutral or cationic Re–CO alkylidene complexes [21] and shorter than typical σ-type Re–C single bonds (2.2211(6) Å) reported for neutral or anionic Re–CO complexes [22]. This indicates that a partial double bond character is caused by π back-donation between the phenyl moiety and Re atom.

2.3. Absorption and luminescence spectra

Photophysical properties, especially luminescence profiles, of d$_6$-Re(I) complexes are of interest. The absorption and luminescent data of ligands 2a–g and complexes 3a–g at 298 K are summarized in Table 5. Fig. 3 shows UV–vis spectra of 3a–g in THF. All ligands exhibited strong absorptions between 200 and 300 nm, assignable to π → π* transitions. For complexes 3a–g, two shoulders of low intensity were clearly observed at
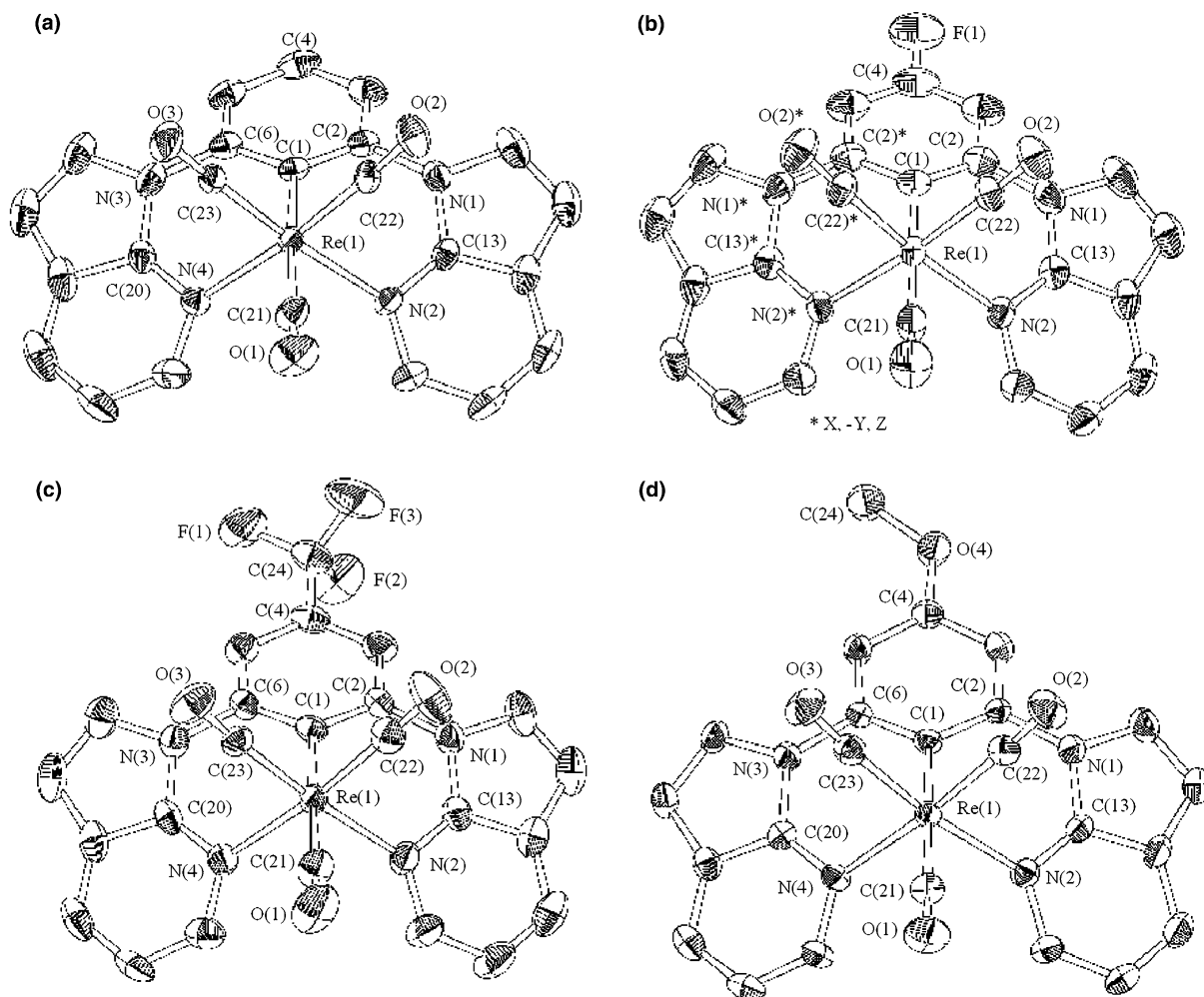
Fig. 2. ORTEP drawing of Re(I) complexes (a) **3a**, (b) **3b**, (c) **3e**, and (c) **3f**. Hydrogen atoms are omitted for clarity. The atoms are drawn with 50% probability thermal ellipsoids.

320 and 370 nm. The former absorption is assigned to $\pi \to \pi^*$ transition of the ligand. On the basis of previous spectral studies on Re(I) complexes, the lower absorption shoulder of **3a–g** at around 370 nm may be assigned to a spin-allowed metal-to-ligand charge-transfer (MLCT) d(Re) $\to \pi^*$ transition [23].

Emission spectra were measured at 298 K in THF solution. As shown in Fig. 4, broad emission bands were observed at $\lambda = 510$ nm for all the complexes **3a–g** in degassed THF solution upon excitation at $\lambda = 370$ nm. These complexes **3a–g** emitted a green color at room temperature. These emissions were not observed in oxygen saturated solution. In addition, **2a–g** exhibited no emission when excited at 370 nm. These findings also support that the emission may be due to d(Re) $\to \pi^*$ (ligand) MLCT excited state. To the best of our knowledge, these complexes appear to be the first examples for neutral Re(I) complexes containing the Re(I)–C bond, which exhibit luminescence in THF at 298 K. Substitution group on the benzene ring of **3a–g** did not affect the emission wavelength.

On the other hand, these complexes in a solid state emitted with orange luminescence. Thin films of the complexes **3a–g** on glass plates were prepared by sublimation under high vacuum (4×10^{-2} Pa). Absorption maxima of about 320 nm in solution states of **3a–g** were 25 nm red-shifted in thin film states. Other absorption maxima were nearly the same. However, absorption maxima of $\pi–\pi^*$ and MLCT bands for **3a–g** were nearly the same in a solid state, suggesting the substituent on benzene ring influences neither to $\pi–\pi^*$ nor to MLCT absorption. Emission maxima ($\lambda_{ex} = 370$ nm) appeared between 550 and 580 nm, which are 20–30 nm red-shifted from the solution state emission (Fig. 5). These emission processes are due to MLCT (dz^2(Re) $\to \pi^*$ (7′-azaindolyl group)) transition. Contribution of $\pi \to \pi^*$ (7′-azaindolyl group) transition cannot be excluded. Emission maxima of all complexes **3a–g** in a solid state are blue-shifted compared with those in a solution state. These observations may be attributed to emission arising from 7′-azaindolyl group, which participates in the intermolecular π interactions

Table 4
Selected bond lengths (Å) and angles (°) for **3a**, **3b**, **3e**, and **3f**

	3a	3b	3e	3f
Bond lengths				
Re(1)–C(1)	2.165(4)	2.154(4)	2.155(7)	2.159(6)
Re(1)–C(21)	1.960(5)	1.957(6)	1.938(8)	1.937(6)
Re(1)–C(22)	1.888(4)	1.900(4)	1.935(9)	1.915(7)
Re(1)–C(23)	1.900(5)		1.891(8)	1.920(6)
Re(1)–N(2)	2.215(4)	2.203(3)	2.204(7)	2.197(4)
Re(1)–N(4)	2.206(4)		2.207(6)	2.203(5)
N(1)–C(2)	1.450(5)	1.425(4)	1.422(10)	1.439(7)
N(3)–C(6)	1.444(6)		1.428(10)	1.436(8)
Bond angles				
C(1)–Re(1)–C(21)	173.4(2)	173.3(2)	176.0(3)	173.9(2)
C(1)–Re(1)–N(2)	81.5(1)	82.2(1)	82.3(3)	82.1(2)
C(1)–Re(1)–N(4)	82.7(1)		81.4(3)	82.1(2)
C(1)–Re(1)–C(22)	93.0(2)	93.5(1)	92.8(3)	94.0(2)
C(1)–Re(1)–C(23)	96.2(2)		93.9(3)	91.9(2)
N(2)–Re(1)–N(4)	95.4(1)	93.9(1)[a]	92.7(2)	93.8(2)
N(2)–Re(1)–C(22)	87.9(2)	88.9(1)	89.8(3)	88.9(2)
C(22)–Re(1)–C(23)	88.4(2)	87.8(6)[b]	87.8(4)	86.5(3)
N(4)–Re(1)–C(23)	88.1(2)		89.3(3)	90.4(2)
C(21)–Re(1)–N(2)	92.9(2)	93.2(2)	94.6(3)	94.1(2)
C(21)–Re(1)–N(4)	94.6(2)		96.3(3)	93.4(2)
C(21)–Re(1)–C(22)	90.2(2)	91.3(2)	89.6(4)	90.7(3)
C(21)–Re(1)–C(23)	89.6(2)		89.4(3)	92.3(3)
Torsion angles				
C(2)–C(1)–Re(1)–N(2)	43.7(3)	41.9(4)	43.6(6)	45.8(5)
C(6)–C(1)–Re(1)–N(4)	39.7(4)		137.0(6)	140.1(5)
C(1)–C(2)–N(1)–C(13)	38.5(6)	35.9(5)	35(1)	25.3(8)
C(1)–C(6)–N(3)–C(20)	34.6(7)		31(1)	23.8(8)
Re(1)–C(1)–C(2)–C(3)	172.6(3)	171.9(3)	168.3(6)	160.3(5)

[a] N(2)–Re(1)–N(2)*, *X, −Y, Z.
[b] C(22)–Re(1)–C(22)*, *X, −Y, Z.

in the solid state. This interaction may lower LUMO and LUMO+1 levels in a solid state compared with those in a solution state.

2.4. DFT calculation

In a solution state, emission maxima were found to be nearly the same wavenumber for all complexes **3a–g**. It might be due to the same initiative process in **3a–g**. In order to understand the nature of the luminescence properties, DFT calculation for **3a–g** was studied at the B3LYP level [24] with the Gaussian 98 program [25]. The HOMO of **3a** mostly consists of the $d(z^2)$ orbital of Re(I) atom and the π orbital of the *trans* CO (Fig. 6). The HOMO-1 and HOMO-2 orbitals of **3a** spread over 7′-azaindolyl group. The interaction between σ orbital of phenyl *ipso*-carbon and orbital of Re(I) atom is in lower energy level. Other complexes **3b**, **3e**, and **3f** possess the similar orbital pattern. LUMO and LUMO+1 orbitals of **3a**, **3b**, **3e**, and **3f** do not spread over the central benzene ring significantly, but over both 7′-azaindolyl groups. Therefore, electron-withdrawing or donating effect on LUMO or LUMO+1 is limited. Thus, the green emission of complexes **3** is most likely due to MLCT (dz^2(Re) → π^* (7′-azaindolyl group)) transition containing $\pi \to \pi^*$ (7′-azaindolyl group) transition.

3. Summary

In summary, the synthesis and structure of Re(I) complexes bearing bis(7′-azaindolyl)phenyl ligand are described here. Their molecular structures were determined by X-ray crystallography to indicate the octahedral coordination through the two carbon atoms of CO and two nitrogen atoms of the bis(7′-azaindolyl)phenyl ligand in the equatorial plane with the one carbon atom
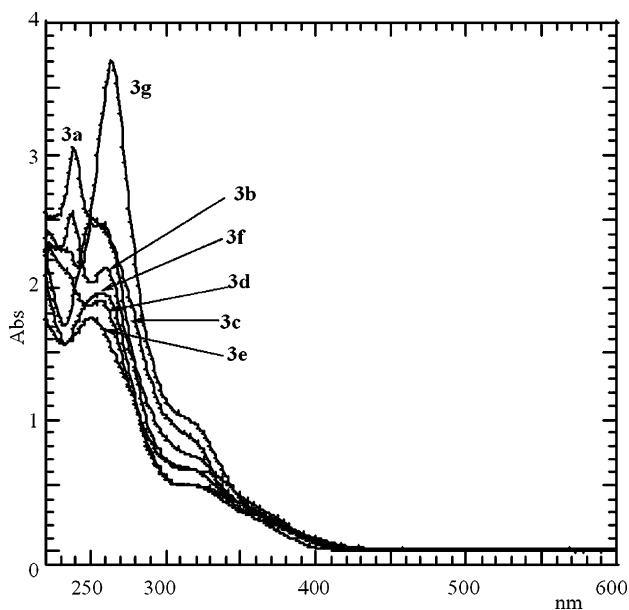
Table 5
UV–vis spectra and luminescent data for ligands **2a–g** and complexes **3a–g**[a]

No.	THF solution[b]		Thin film	
	λ_{max} (nm) log ε	Emission λ_{max} (nm)[c]	λ_{max} (nm) log ε	Emission λ_{max} (nm)[d]
2a	221 (4.54), 239 (4.67), 259 (4.78), 294 (4.43)	358		
2b	224 (4.50), 239 (4.59), 262 (4.76), 292 (4.47)	354		
2c	222 (4.53), 238 (4.62), 263 (4.78), 291 (4.50)	347		
2d	222 (4.60), 237 (4.58), 264 (4.87), 291 (4.50)	344		
2e	223 (4.46), 238 (4.49), 265 (4.76), 291 (4.49)	342		
2f	220 (4.28), 257 (4.68), 291 (4.23)	362		
2g	226 (4.48), 264 (4.77), 290 (4.48)	356		
3a	220 (4.71), 239 (4.79), 258 (4.69), 322 (4.21), 370 (3.71)	512	274, 344, 370	555
3b	223 (4.67), 238 (4.71), 260 (4.63), 322 (4.15), 371 (3.64)	512	274, 343, 370	583
3c	219 (4.65), 253 (4.70), 322 (4.09), 371 (3.74)	511	275, 342, 370	566
3d	217 (4.64), 258 (4.59), 326 (3.99), 372 (3.66)	511	276, 345, 370	583
3e	216 (4.57), 251 (4.55), 318 (4.00), 367(3.62)	509	277, 344, 370	548
3f	223 (4.66), 257 (4.58), 320 (4.09), 371 (3.61)	517	280, 345, 370	578
3g	221 (4.68), 235 (4.66), 263 (4.87), 313 (4.31), 371 (3.69)	517	276, 346, 370	549

[a] 298 K.
[b] 5×10^{-5} M in THF solution.
[c] Excitation λ_{max} 300 nm for **2a–g** and excitation λ_{max} 370 nm for **3a–g**.
[d] Excitation λ_{max} 370 nm.

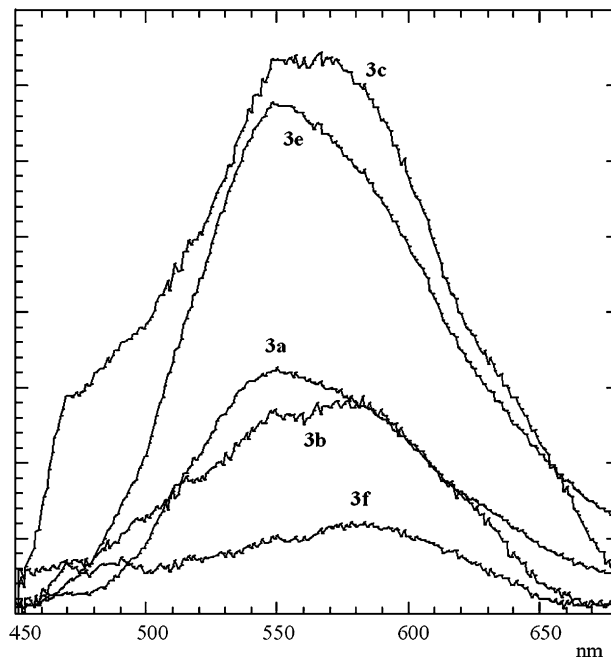Fig. 3. UV–vis spectra of complexes **3a–g** in 5×10^{-5} M THF solution at 298 K.

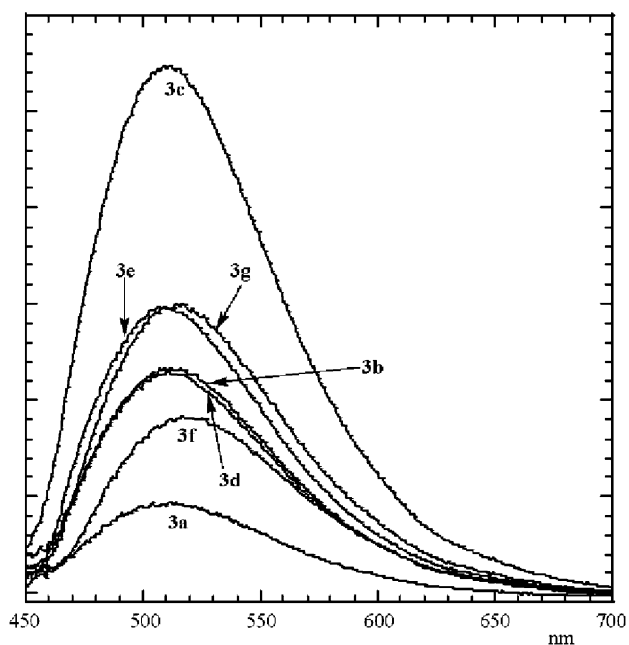Fig. 5. The emission spectra of complexes **3a–g** in thin film at 298 K.

Fig. 4. The luminescence spectra of complexes **3a–g** in 5×10^{-5} M THF solution at 298 K.
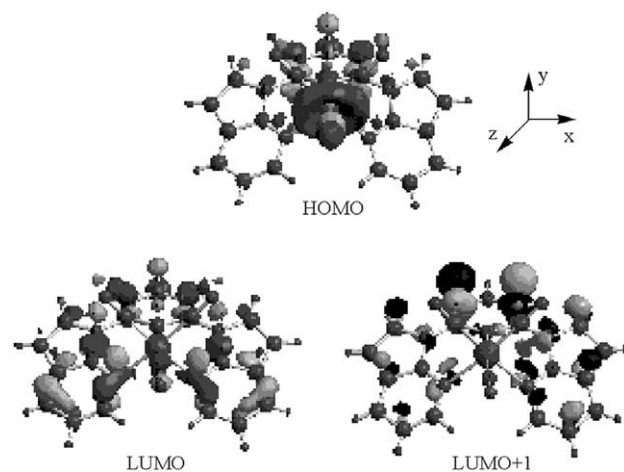

Fig. 6. HOMO, LUMO, and LUMO+1 of **3a**.

4. Experimental section

4.1. General procedures

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 plus. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were recorded on a Varian MERCURY 300 (300 MHz) spectrometer. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. UV–vis spectra were

of CO and one carbon atom of benzene moiety in axial axis. These complexes **3a–g** emitted at $\lambda = 510$ nm, when excited at $\lambda = 370$ nm, and showed green luminescence in THF solution. DFT calculation suggests that these emission processes are due to MLCT (dz^2(Re) $\rightarrow \pi^*$ (7′-azaindolyl group)) transition containing $\pi \rightarrow \pi^*$ (7′-azaindolyl group) transition.

obtained by using a Hitachi U-3500 spectrophotometer at 5×10^{-5} M concentration in THF at 298 K. Emission spectra were taken on a Shimadzu RF-5300PC spectrofluorophotometer at 5×10^{-5} M concentration in THF at 298 K. THF was purchased from KANTO Chemical Co., Ins. Thin films were prepared by sublimation on ULVAC VPC-410 at 65 A and 4×10^{-2} Pa. Emission spectra of thin films on glass were taken on a Shimadzu RF-5300PC spectrofluorophotometer at 298 K. The molecular structures were established by using the crystallographic coordination of the complexes **3a**, **3b**, **3e**, and **3f**. LanL2DZ basis set for Re and 6-31G(d) basis sets for the other elements were used. The orbital diagrams were generated with the Chem3D program. All contour values are ±0.045 au.

4.2. Synthesis of 2,6-bis(7′-azaindolyl)benzene derivatives

4.2.1. 1,3-Bis(7′-azaindolyl)benzene (Bab-H, 2a) [16]

1,3-Dibromobenzene (0.50 ml, 4.13 mmol), 7-azaindole (1.47 g, 12.4 mmol), K_2CO_3 (1.71 g, 12.4 mmol), and cupric sulfate hydrate (0.025 g, 0.10 mmol) were mixed and heated at 220 °C for 5 h under argon. After being cooled to ambient temperature, the reaction mixture was dissolved in CH_2Cl_2 (100 ml) and washed with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel using hexane/AcOEt (5:1, $R_f = 0.18$) as an eluent to give 0.911 g (71%) of **2a** as a colorless solid. ^{1}H NMR (CDCl$_3$) δ 6.64 (d, $J = 3.8$ Hz, 2H), 7.12 (dd, $J = 7.9$ Hz, 4.7 Hz, 2H), 7.60 (d, $J = 3.8$ Hz, 2H), 7.64 (dd, $J = 9.0$ Hz, 7.2 Hz, 1H), 7.74 (d, $J = 1.8$ Hz, 2H), 7.77 (t, $J = 1.8$ Hz, 2H), 7.96 (dd, $J = 7.9$ Hz, 1.7 Hz, 2H), 8.27 (t, $J = 2.1$ Hz, 1H), 8.35 (dd, $J = 4.7$ Hz, 1.7 Hz, 2H). ^{13}C NMR (CDCl$_3$) 101.94, 116.77, 119.24, 121.32, 121.63, 127.70, 129.04, 130.00, 139.22, 143.49, 147.38 ppm.

4.2.2. 1,3-Bis(7′-azaindolyl)-5-fluorobenzene (F-Bab-H, 2b)

1,3-Dibromo-5-fluorobenzene (0.50 ml, 3.97 mmol), 7-azaindole (1.41 g, 11.9 mmol), K_2CO_3 (1.65 g, 11.9 mmol), and cupric sulfate hydrate (0.025 g, 0.10 mmol) were mixed and heated at 200 °C for 9 h under argon. After being cooled to ambient temperature, the reaction mixture was dissolved in CH_2Cl_2 (100 ml) and washed with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel using hexane/AcOEt (2:1, $R_f = 0.50$) as an eluent to give 0.817 g (63%) of **2b** as a colorless solid, m.p. 180–184 °C. IR (KBr) 3140, 3104, 3040, 3010, 1616, 1591, 1522, 1483, 1434, 1412, 1360, 1272, 1208, 1180, 1040, 1002, 892, 877, 846, 791, 764, 732, 674, 516 cm^{-1}. ^{1}H

NMR (CDCl$_3$) δ 6.67 (d, $J = 3.6$ Hz, 2H), 7.17 (dd, $J = 7.8$ Hz, 4.8 Hz, 2H), 7.60 (d, $J = 3.6$ Hz, 2H), 7.62 (dd, $J = 7.8$ Hz, 1.6 Hz, 1H), 7.98 (dd, $J = 7.8$ Hz, 1.6 Hz, 2H), 7.98 (dd, $J = 7.8$ Hz, 1.6 Hz, 2H), 8.27 (t, $J = 1.6$ Hz, 1H), 8.39 (dd, $J = 4.8$ Hz, 1.6 Hz, 2H). ^{13}C NMR (CDCl$_3$) 102.59, 108.05 (d, $J = 25$ Hz), 113.57 (d, $J = 2.9$ Hz), 117.09, 121.80, 127.13, 129.16, 140.13 (d, $J = 12.3$ Hz), 143.60, 147.33, 162.96 (d, $J = 245$ Hz) ppm. GC-MS (m/z) 328 (M$^+$). HRMS Found: 328.1123. $C_{20}H_{13}N_4F$ Calc.: 328.1124.

4.2.3. 1,3-Bis(7′-azaindolyl)-5-chlorobenzene (Cl-Bab-H, 2c)

1,3-Dibromo-5-chlorobenzene (1.35 g, 5.00 mmol), 7-azaindole (1.77 g, 15.0 mmol), K_2CO_3 (2.07 g, 15.0 mmol), and cupric sulfate hydrate (0.031 g, 0.12 mmol) were mixed and heated at 180 °C for 10 h under argon. After being cooled to ambient temperature, the reaction mixture was dissolved in CH_2Cl_2 (100 ml) and washed with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel using hexane/AcOEt (5:1, $R_f = 0.18$) as an eluent to give 0.388 g (23%) of **2c** as a colorless solid, m.p. 185–188 °C. IR (KBr) 3099, 1608, 1594, 1518, 1489, 1465, 1414, 1273, 1226, 892, 857, 840, 792, 771, 755, 727, 714, 676 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.66 (d, $J = 3.8$ Hz, 2H), 7.14 (dd, $J = 7.8$ Hz, 4.7 Hz, 2H), 7.58 (d, $J = 3.8$ Hz, 2H), 7.81 (dd, $J = 7.8$ Hz, 1.7 Hz, 2H), 7.97 (d, $J = 1.9$ Hz, 2H), 8.32 (t, $J = 1.9$ Hz, 1H), 8.38 (dd, $J = 4.7$ Hz, 1.7 Hz, 2H). ^{13}C NMR (CDCl$_3$) 102.61, 116.60, 117.09, 120.75, 121.74, 127.14, 129.14, 135.24, 139.92, 143.63, 147.35 ppm. HRMS Found: 344.0832. $C_{20}H_{13}N_4Cl$ Calc.: 344.0829.

4.2.4. 1-(7′-Azaindolyl)-3,5-dibromobenzene, 1,3-bis(7′-azaindolyl)-5-bromobenzene (Br-Bab-H, 2d) [16] and 1,3,5-tris(7′-azaindolyl)benzene (Tab-H, 2g) [16]

1,3,5-Tribromobenzene (1.26 g, 4.00 mmol), 7-azaindole (1.89 g, 16.0 mmol), K_2CO_3 (2.21 g, 16.0 mmol), and cupric sulfate hydrate (0.025 g, 0.10 mmol) were mixed and heated at 180 °C for 8 h under argon. After being cooled to ambient temperature, the reaction mixture was dissolved in CH_2Cl_2 (200 ml) and washed with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel using hexane/AcOEt (5:1) as an eluent.

4.2.4.1. 1-(7′-Azaindolyl)-3,5-dibromobenzene. Colorless solid (0.553 g, 39%, $R_f = 0.58$), m.p. 73–74 °C. IR (KBr) 3071, 1585, 1558, 1517, 1480, 1452, 1405, 1353, 1278, 1151, 1097, 847, 794, 777, 767, 756, 745, 711, 675, 657 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.63 (d, $J = 3.9$ Hz, 1H), 7.14 (dd, $J = 7.7$ Hz, 4.7 Hz, 1H), 7.45 (d, $J = 3.9$ Hz, 1H), 7.56–7.59 (m, 1H), 7.93 (dd, $J = 7.7$ Hz, 1.5 Hz, 1H),

7.99 (d, $J = 4.2$ Hz, 2H), 8.37 (dd, $J = 4.7$ Hz, 1.5 Hz, 1H). ^{13}C NMR (CDCl$_3$) 103.02, 117.29, 121.69, 123.05, 124.89, 126.61, 129.21, 131.22, 140.31, 143.75, 147.25 ppm. GC-MS (m/z): 352 (M$^+$). HRMS Found: 348.8982. C$_{14}$H$_9$Br$_2$N Calc.: 348.9102.

4.2.4.2. 1,3-Bis(7′-azaindolyl)-5-bromobenzene (Br-Bab-H, 2d) [16]. Colorless solid (0.499 g, 32%, $R_f = 0.38$), m.p. 212–214 °C. ^{1}H NMR (CDCl$_3$) δ 6.66 (d, $J = 3.8$ Hz, 2H), 7.14 (dd, $J = 7.8$ Hz, 4.7 Hz, 2H), 7.58 (d, $J = 3.8$ Hz, 2H), 7.95 (dd, $J = 7.8$ Hz, 1.7 Hz, 2H), 7.97 (d, $J = 1.9$ Hz, 2H), 8.35 (t, $J = 1.9$ Hz, 1H), 8.38 (dd, $J = 4.7$ Hz, 1.7 Hz, 2H). ^{13}C NMR (CDCl$_3$) 102.60, 117.06, 117.11, 121.70, 122.85, 123.53, 127.10, 129.10, 140.01, 143.60, 147.34 ppm.

4.2.4.3. 1,3,5-Tris(7′-azaindolyl)benzene (Tab-H, 2g) [16]. Colorless solid (0.209 g, 12%, $R_f = 0.10$), m.p. 220–222 °C. ^{1}H NMR (CDCl$_3$) δ 6.67 (d, $J = 3.6$ Hz, 3H), 7.14 (dd, $J = 7.7$ Hz, 4.7 Hz, 3H), 7.70 (d, $J = 3.6$ Hz, 3H), 7.97 (dd, $J = 7.7$ Hz, 1.7 Hz, 3H), 8.34 (s, 3H), 8.36 (dd, $J = 4.7$ Hz, 1.7 Hz, 3H). ^{13}C NMR (CDCl$_3$) 102.27, 116.01, 116.92, 121.79, 127.62, 129.05, 139.81, 143.56, 147.50 ppm.

4.2.4.4. 1,3-Dibromo-5-trifluoromethylbenzene (1e) [26]. A solution of 5-(trifluoromethyl)-1,3-phenylenediamine (0.528 g, 3.00 mmol) in aq 48% HBr solution (100 ml) was stirred for 12 h at room temperature. A solution of sodium nitrite (1.67 g, 24 mmol) in water (50 ml) was added dropwise to the reaction mixture over 60 min at 0 °C. After the reaction mixture was stirred at 0 °C for 30 min, a suspension of copper(I) bromide (1.38 g, 9.6 mmol) in aq 48% HBr solution (80 ml) was added dropwise to the mixture over 1 h. After the reaction mixture was stirred at 70 °C for 1 h, the mixture was poured into ice water (100 ml), stirred for 30 min, and extracted with CH$_2$Cl$_2$ (300 ml). The extract was washed with water, dried over anhydrous MgSO$_4$, and concentrated. The residue was chromatographed on silica gel using hexane as an eluent to give 1e (0.554 g, 61%) as a colorless solid; m.p. 41–43 °C. ^{1}H NMR (CDCl$_3$) δ 7.68–7.69 (m, 2H), 7.83–7.84 (m, 1H). ^{13}C NMR (CDCl$_3$) 120.38, 123.33, 127.26 (q, $J = 3.8$ Hz), 133.56 (q, $J = 34$ Hz), 137.47 ppm.

4.2.4.5. 1,3-Bis(7′-azaindolyl)-5-trifluoromethylbenzene (CF$_3$-Bab-H, 2e). The compound 1e (0.492 g, 1.62 mmol), 7-azaindole (0.574 g, 4.86 mmol), K$_2$CO$_3$ (0.672 g, 4.86 mmol), and cupric sulfate hydrate (0.006 g) were mixed and heated at 200 °C for 13 h under argon. After being cooled to ambient temperature, the reaction mixture was dissolved in CH$_2$Cl$_2$ (200 ml) and washed with water. The organic layer was separated, dried over MgSO$_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica

gel using hexane/AcOEt (10:1, $R_f = 0.18$) as an eluent to give 0.449 g (73%) of 2e as a colorless solid, m.p. 137–138 °C. IR (KBr) 3108, 3039, 1613, 1595, 1523, 1489, 1412, 1364, 1300, 1272, 1236, 1153, 1114, 964, 889, 828, 798, 775, 759, 717 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.68 (d, $J = 3.6$ Hz, 2H), 7.16 (dd, $J = 7.8$ Hz, 4.7 Hz, 2H), 7.63 (d, $J = 3.6$ Hz, 2H), 7.97 (dd, $J = 7.8$ Hz, 1.6 Hz, 2H), 8.04 (d, $J = 1.2$ Hz, 2H), 8.37 (dd, $J = 4.7$ Hz, 1.6 Hz, 2H), 8.70 (t, $J = 1.2$ Hz, 1H). ^{13}C NMR (CDCl$_3$) 102.90, 117.16 (q, $J = 3.9$ Hz), 117.23, 121.31, 121.77, 125.30, 126.99, 129.22, 132.43 (q, $J = 33$ Hz), 139.75, 143.74, 147.41 ppm. HRMS Found: 378.1089. C$_{21}$H$_{13}$N$_4$F$_3$ Calc.: 378.1092.

4.2.5. 1,3-Bis(7′-azaindolyl)-5-methoxybenzene (MeO-Bab-H, 2f)
To a suspension of 2c (0.161 g, 0.41 mmol) and copper(I) bromide (0.059 g, 0.41 mmol) in DMF (0.75 ml) was added a solution of sodium (0.095 g, 0.42 mmol) and methanol (15 ml). The mixture was refluxed for 24 h. After being cooled to ambient temperature, the reaction mixture was dissolved in CH$_2$Cl$_2$ (50 ml) and washed with water. The organic layer was separated, dried over MgSO$_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel using hexane/AcOEt (5:1) to give 0.119 g (85%) of 2f as a colorless solid, m.p. 120–122 °C. IR (KBr) 3127, 3034, 2924, 1610, 1522, 1490, 1415, 1356, 1275, 1208, 1057, 756, 708 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 3.92 (s, 3H, CH$_3$O), 6.61 (d, $J = 3.9$ Hz, 2H), 7.11 (dd, $J = 7.7$ Hz, 4.7 Hz, 2H), 7.40 (d, $J = 1.9$ Hz, 2H), 7.58 (d, $J = 3.9$ Hz, 2H), 7.85 (t, $J = 1.9$ Hz, 1H), 7.94 (dd, $J = 7.7$ Hz, 1.6 Hz, 2H), 8.36 (dd, $J = 4.7$ Hz, 1.6 Hz, 2H). ^{13}C NMR (CDCl$_3$) 55.66 (CH$_3$O), 101.84, 107.41, 111.35, 116.67, 121.59, 1127.59, 128.88, 139.83, 143.39, 147.36, 160.50 ppm. HRMS Found: 340.1320. C$_{21}$H$_{16}$N$_4$O Calc.: 340.1324.

4.3. Synthesis of Re(I) complexes 3

4.3.1. Re(Bab)(CO)$_3$ complex (3a)
Re$_2$(CO)$_{10}$ (111 mg, 0.17 mmol) and 2a (106 mg, 0.34 mmol) were refluxed in diglyme (10 ml) for 24 h under argon. After the solvent was removed, the resulting residue was washed with CH$_2$Cl$_2$ (15 ml) to give 147 mg (74%) of 3a as a pale yellow solid, m.p. (dec.) 280 °C. IR (KBr) 1995 (CO), 1885 (CO), 1869 (CO), 1518, 1429, 1227, 803, 711 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 6.93 (d, $J = 3.8$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 2H), 7.38 (dd, $J = 7.6$ Hz, 5.3 Hz, 2H), 8.33 (d, $J = 7.6$ Hz, 2H), 8.53 (d, $J = 3.8$ Hz, 2H), 9.21 (d, $J = 5.3$ Hz, 2H). ^{13}C NMR (DMSO-d$_6$) 104.55, 113.37, 118.19, 123.45, 126.24, 129.18, 132.48, 143.18, 143.50, 147.53, 149.66, 196.12 (CO), 198.59 (CO) ppm. HRMS Found: 586.0624. C$_{23}$H$_{13}$N$_4$O$_3$Re +H$^+$ Calc.: 586.0624. Anal. Found: C, 47.11; H, 2.40; N, 9.50.

$C_{23}H_{13}N_4O_3Re \cdot 0.3H_2O$ Calc.: C, 47.17; H, 2.35; N, 9.57.

4.3.2. Re(F-Bab)(CO)₃ complex (3b)

$Re_2(CO)_{10}$ (111 mg, 0.17 mmol) and **2b** (112 mg, 0.34 mmol) were refluxed in diglyme (10 ml) for 24 h under argon. After the solvent was removed, the resulting residue was purified by column chromatography on silica gel using CH_2Cl_2 to give 126 mg (62%) of **3b** as a pale yellow solid, m.p. (dec.) >300 °C. IR (KBr) 2962, 2921, 2001 (CO), 1893 (CO), 1882 (CO), 1586, 1520, 1468, 1443, 1423, 1359, 1326, 1293, 1260, 1202, 1121, 1080, 1020, 960, 921, 870, 825, 802, 791, 762, 728, 718, 621 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 6.95 (dd, $J = 3.9$ Hz, 1.2 Hz, 2H), 7.32 (d, $J = 11$ Hz, 2H), 7.49 (ddd, $J = 7.8$ Hz, 5.4 Hz, 1.2 Hz, 2H), 8.33 (d, $J = 7.8$ Hz, 2H), 8.52 (d, $J = 3.9$ Hz, 2H), 9.21 (d, $J = 5.4$ Hz, 2H). ^{13}C NMR (DMSO-d_6) 100.67 (d, $J = 24$ Hz), 104.99, 118.38, 123.35, 129.06, 132.52, 136.74 (d, $J = 14$ Hz), 143.19 (d, $J = 11$ Hz), 147.35, 149.58, 195.68 (CO), 198.17 (CO) ppm. HRMS Found: 599.0540. $C_{23}H_{12}N_4O_3FRe$ Calc.: 598.0451.

4.3.3. Re(Cl-Bab)(CO)₃ complex (3c)

$Re_2(CO)_{10}$ (111 mg, 0.17 mmol) and **2c** (117 mg, 0.34 mmol) were refluxed in diglyme (10 ml) for 24 h under argon. After the solvent was removed, the resulting residue was washed with CH_2Cl_2 (10 ml) to give 137 mg (65%) of **3c** as a yellow solid, m.p. (dec.) >300 °C. IR (KBr) 2000 (CO), 1890 (CO), 1867 (CO), 1561, 1468, 1425, 1354, 1315, 1293, 1270, 1203, 837, 792, 716 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 6.96 (d, $J = 3.8$ Hz, 2H), 7.40 (dd, $J = 7.7$ Hz, 5.5 Hz, 2H), 7.46 (s, 2H), 8.34 (dd, $J = 7.7$ Hz, 1.2 Hz, 2H), 8.59 (d, $J = 3.8$ Hz, 2H), 9.22 (dd, $J = 5.5$ Hz, 1.2 Hz, 2H). ^{13}C NMR (DMSO-d_6) 105.24, 112.89, 118.58, 123.59, 129.26, 130.96, 132.70, 144.05, 147.58, 149.79, 195.92 (CO), 198.18 (CO) ppm. HRMS Found: 614.0144. $C_{23}H_{12}N_4O_3ClRe$ Calc.: 614.0155. Anal. Found: C, 44.23; H, 2.14; N, 8.89. $C_{23}H_{12}N_4O_3ClRe \cdot 0.5H_2O$ Calc.: C, 44.34; H, 2.10; N, 8.99.

4.3.4. Re(Br-Bab)(CO)₃ complex (3d)

$Re_2(CO)_{10}$ (137 mg, 0.21 mmol) and **2d** (164 mg, 0.42 mmol) were refluxed in diglyme (15 ml) for 24 h under argon. After the solvent was removed, the resulting residue was washed with CH_2Cl_2 (15 ml) to give 225 mg (81%) of **3d** as a yellow solid, m.p. (dec.) >300 °C. IR (KBr): 1999 (CO), 1887 (CO), 1868 (CO), 1556, 1521, 1467, 1427, 1354, 1314, 1292, 1270, 1202, 802, 766, 728 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 6.94 (d, $J = 3.9$ Hz, 2H), 7.39 (dd, $J = 7.8$ Hz, 5.4 Hz, 2H), 7.56 (s, 2H), 8.35 (dd, $J = 7.8$ Hz, 1.4 Hz, 2H), 8.60 (d, $J = 3.9$ Hz, 2H), 9.23 (dd, $J = 4.5$ Hz, 1.4 Hz, 2H). ^{13}C NMR (DMSO-d_6) 105.18, 115.55, 118.52, 118.86, 123.55, 123.82, 129.24, 132.65, 144.25, 147.55, 149.74, 195.90 (CO), 198.12 (CO)

ppm. HRMS Found: 658.9712. $C_{23}H_{12}BrN_4O_3$ Re + H$^+$ Calc.: 658.9728. Anal. Found: C, 42.58; H, 2.09; N, 8.54. $C_{23}H_{12}BrN_4O_3Re \cdot 0.2H_2O$ Calc.: C, 41.72; H, 1.89; N, 8.46.

4.3.5. Re(CF₃-Bab)(CO)₃ complex (3e)

$Re_2(CO)_{10}$ (111 mg, 0.17 mmol) and **2e** (129 mg, 0.34 mmol) were refluxed in diglyme (10 ml) for 20 h under argon. After the solvent was removed, the resulting residue was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent to give 149 mg (68%) of **3e** as a pale yellow solid, m.p. (dec.) 270 °C. IR (KBr) 2002 (CO), 1888 (CO), 1880 (CO), 1429, 1338, 1208, 1161, 1117, 804, 734 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 6.99 (d, $J = 3.8$ Hz, 2H), 7.41 (dd, $J = 7.7$ Hz, 5.3 Hz, 2H), 7.61 (s, 2H), 8.35 (d, $J = 7.7$ Hz, 2H), 8.72 (d, $J = 3.8$ Hz, 2H), 9.24 (d, $J = 5.3$ Hz, 2H). ^{13}C NMR (DMSO-d_6) 105.50, 108.99, 118.74, 123.63, 129.40, 132.86, 143.95, 147.64, 150.01, 195.89 (CO), 198.02 (CO) ppm one aromatic carbon and CF_3 carbon were not detective due to the low solubility of **3e**. HRMS Found: 648.0413. $C_{24}H_{12}F_3N_4O_3Re$ Calc.: 648.0419. Anal. Found: C, 44.73; H, 2.17; N, 8.25. $C_{24}H_{12}F_3N_4O_3Re$ Calc.: C, 44.51; H, 1.87; N, 8.65.

4.3.6. Re(MeO-Bab)(CO)₃ complex (3f)

$Re_2(CO)_{10}$ (226 mg, 0.35 mmol) and **2f** (236 mg, 0.69 mmol) were refluxed in diglyme (20 ml) for 24 h under argon. After the solvent was removed, the resulting residue was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent to give 302 mg (72%) of **3f** as a pale yellow solid, m.p. (dec.) >300 °C. IR (KBr) 1996 (CO), 1879 (CO), 1860 (CO), 1591, 1427, 1361, 1203, 803 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 3.84 (s, 3H, CH_3O), 6.92 (d, $J = 3.9$ Hz, 2H), 7.00 (s, 2H), 7.37 (dd, $J = 7.7$ Hz, 5.4 Hz, 2H), 8.32 (dd, $J = 7.7$ Hz, 1.4 Hz, 2H), 8.58 (d, $J = 3.9$ Hz, 2H), 9.20 (dd, $J = 5.4$ Hz, 1.4 Hz, 2H). ^{13}C NMR (DMSO-d_6) 55.49 (CH_3O), 100.34, 104.24, 117.89, 123.19, 129.04, 132.10, 132.46, 143.14, 147.38, 149.30, 158.79, 195.83 (CO), 198.42 (CO) ppm. HRMS Found: 611.0723. $C_{24}H_{15}N_4O_4Re$ +H$^+$ Calc.: 611.0729. Anal. Found: C, 46.55; H, 2.64; N, 8.92. $C_{24}H_{15}N_4O_4Re \cdot 0.5H_2O$ Calc.: C, 46.60; H, 2.61; N, 9.06.

4.3.7. Re(Tab)(CO)₃ complex (3g)

$Re_2(CO)_{10}$ (196 mg, 0.30 mmol) and **2g** (171 mg, 0.40 mmol) were refluxed in diglyme (30 ml) for 24 h under argon. After the solvent was removed, the resulting residue was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent to give 237 mg (93%) of **3g** as a pale yellow solid, m.p. (dec.) >300 °C. IR (KBr) 2925, 1995 (CO), 1883 (CO), 1863 (CO), 1588, 1519, 1467, 1453, 1418, 1347, 1300, 1269, 1225, 1205, 894, 802, 765, 715 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 6.74 (d, $J = 3.6$ Hz, 1H), 6.96 (d, $J = 3.8$ Hz, 2H), 7.18 (dd,

$J = 8.0$ Hz, 5.0 Hz, 1H), 7.40 (dd, $J = 7.6$ Hz, 5.5 Hz, 2H), 7.82 (s, 2H), 8.05-8.10 (m, 2H), 8.28 (m, 1H), 8.35 (d, $J = 7.6$ Hz, 2H), 8.60 (d, $J = 3.8$ Hz, 2H), 9.26 (d, $J = 5.5$ Hz, 2H). ^{13}C NMR (DMSO-d_6) 101.27, 104.94, 109.44, 116.73, 118.40, 121.22, 123.53, 129.07, 129.23, 129.29, 132.61, 137.02, 141.47, 143.09, 143.38, 147.21, 147.78, 149.80, 196.09 (CO), 198.48 (CO) ppm. HRMS Found: 697.0999 $C_{30}H_{17}N_6O_3Re + H^+$ Calc.: 697.0998. Anal. Found: C, 51.77; H, 2.79; N, 11.64. $C_{30}H_{17}N_6O_3Re$ Calc.: C, 51.79; H, 2.46; N, 12.08.

4.4. X-ray structure analysis

All measurements for **3a**, **3b**, **3e**, and **3f** were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The structures of **3a**, **3b**, **3e**, and **3f** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-224950 for **3a**, no. CCDC-224951 for **3b**, no. CCDC-224952 for **3e**, and CCDC-224953 for **3f**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int) +44-1223/ 336-033; email: deposit@ccdc.cam.ac.uk].

Acknowledgements

References

[1] A.D. Ryabov, Synthesis (1985) 233.
[2] D.M. Grove, G. van Koten, A.H.M. Verschuuren, J. Mol. Catal. 45 (1988) 169.
[3] Y. Wakatsuki, H. Yamazaki, P.A. Grutsch, M. Santhanam, C. Kutal, J. Am. Chem. Soc. 107 (1985) 8153.
[4] G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[5] Y. Ohsawa, S. Sprouse, K.A. King, M.K. DeArmond, K.W. Hanck, R.J. Watts, J. Phys. Chem. 91 (1987) 1047.
[6] J. Hawecker, J.M. Lehn, R. Ziessel, J. Chem. Soc. Chem. Commun. (1984) 328.
[7] A. Vogler, H. Kunkely, Angew. Chem. Int. Ed. Engl. 20 (1981) 469.
[8] H. Kunkely, A. Merz, A. Vogler, J. Am. Chem. Soc. 105 (1983) 7241.
[9] A. Vogler, H. Kunkely, Inorg. Chim. Acta 45 (1980) L265.
[10] T.G. Kotch, A.J. Lees, S.J. Fuerniss, K.I. Papathomas, Chem. Mater. 4 (1992) 675.
[11] L.E. Helberg, T. Brent Gunnoe, B.C. Brooks, M. Sabat, W.D. Harman, Organometallics 18 (1999) 573.
[12] M.H.P. Rietveld, L. Nagelholt, D.M. Grove, N. Veldman, A.L. Spek, M.U. Rauch, W.A. Herrmann, G. van Koten, J. Organomet. Chem. 530 (1997) 159.
[13] (a) P. Spellane, R.J. Watts, A. Vogler, Inorg. Chem. 32 (1993) 5633;
(b) F.W.M. Vanhelmont, H.U. Güdel, M. Förtsch, H.-B. Bürgi, Inorg. Chem. 36 (1997) 5512;
(c) F.W.M. Vanhelmont, G.F. Strouse, H.U. Güdel, A. Claudia Stückl, H.W. Schmalle, J. Phys. Chem. A 101 (1997) 2946;
(d) F.W.M. Vanhelmont, M.V. Rajasekharan, H.U. Güdel, S.C. Capelli, J. Hauser, H.-B. Bürgi, J. Chem. Soc. Dalton Trans. (1998) 2893.
[14] M.I. Bruce, B.L. Goodall, F.G.A. Stone, J. Organomet. Chem. 60 (1973) 343.
[15] T. Suzuki, U. Okuyama, T. Ichimura, J. Phys. Chem. A. 101 (1997) 7047.
[16] Q. Wu, J.A. Lavigne, Y. Tao, M. D'Iorio, S. Wang, Chem. Mater. 13 (2001) 71.
[17] Pt(II) and Pd(II) complexes bearing 7-azaindolyl groups were reported by Wang D. Song, Q. Wu, A. Hook, I. Kozin, S. Wang, Organometallics 20 (2001) 4683.
[18] L.H. Staal, A. Oskam, K. Vrieze, J. Organomet. Chem. 170 (1979) 235.
[19] M.J. Webb, W.A.G. Graham, J. Organomet. Chem. 93 (1975) 119.
[20] L.A. Worl, R. Duesing, P. Chen, L. Della Ciana, T.J. Meyer, J. Chem. Soc. Dalton Trans. (1991) 849.
[21] E. Frisch, T. Kerscher, K. Polboen, W. Beck, J. Organomet. Chem. 460 (1993) C25.
[22] C.M. Lukehart, J.V. Zeile, J. Organomet. Chem. 140 (1977) 309.
[23] H. Hori, K. Koike, M. Ishizuka, K. Takeuchi, T. Ibusuki, O. Ishitani, J. Organomet. Chem. 530 (1997) 169.
[24] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
(b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200;
(c) A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Gaussian Inc, Pittsburgh, PA, 1998.
[26] B.V. Kunshenko, V.O. Omarov, N.N. Muratov, S.M. Mikhailevskii, L.M. Yagupol'skii, Zh. Org. Khim. 27 (1991) 125.