Synthesis, Crystal Structure, and Photoluminescent Properties of a Tetracarbonyl(naphthyridylcarbamoyl)rhenium(I) Complex and a Highly Emissive Tetracarbonyl(naphthyridylamido)rhenium(I) Complex

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The reactions of $Re(CO)_5X$ (X = Cl, Br) with 7-amino-2,4-dimethyl-1,8-naphthyridine (H_2L^1) and 7-[2-(6-chloropyridyl)-amino]-2,4-dimethyl-1,8-naphthyridine (HL^2) in the presence of *t*BuOK afforded the η^1-naphthyridylcarbamoyl complex $[Re(CO)_4(HL^1CO)]$ (**1**) and the naphthyridylamido complex $[Re(CO)_4(L^2)]$ (**2**), respectively. The structures of HL^2, **1**·$CHCl_3$, **1**·HL^3·$2CH_2Cl_2$ [HL^3 = (7-chloronaphthyridyl)(5,7-dimethylnaphthyridyl)amine], and **2** have been determined by X-ray crystallography. Complex **1** displays a weak emission at 453 nm in an EtOH/MeOH (1:4, v/v) glassy solution at 77 K; complex **2** exhibits an intense (quantum yield: 0.22 in CH_2Cl_2) and long-lived emission (46 μs in CH_2Cl_2), with a solvent-sensitive λ_{max}, in degassed solutions at room temperature.

Introduction

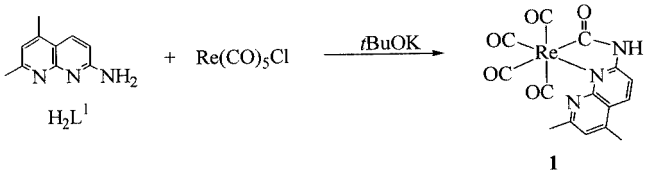
Carbonylrhenium(I) complexes have been the subject of extensive photochemical and photophysical studies over the past several decades. These complexes display interesting photochemical,[1] and rich photoluminescent and electroluminescent properties.[2−4] Recent studies have also demonstrated their applications as luminescent probes for chemosensing.[5] In the course of our studies on the photoluminescent properties of carbonylrhenium(I) complexes, we have paid attention to the species containing tetracarbonylrhenium(I) units. This class of carbonylrhenium(I) complexes, such as the $[Re(CO)_4(bpm)]^+$ cation (bpm = 2,2′-bipyrimidine) and some neutral *ortho*-metalated species, exhibits substantially long emission life-times and high emission quantum yields compared with the extensively studied tricarbonylrhenium(I) species $Re(CO)_3(L-L)X$ (L−L = a bidentate *N*,*N*′-chelating ligand such as 1,10-phenanthroline and 2,2′-bipyridine; X = a monodentate anionic ligand such as Cl^- or Br^-).[6]

In the present paper, we report on the synthesis and the photophysical properties of the tetracarbonyl(η^1-naphthyridylcarbamoyl)rhenium(I) complex $[Re(CO)_4(HL^1CO)]$ (**1**, H_2L^1 = 7-amino-2,4-dimethyl-1,8-naphthyridine), and the naphthyridylamido complex $[Re(CO)_4L^2]$ {**2**, HL^2 = 7-[2-(6-chloropyridyl)amino]-2,4-dimethyl-1,8-naphthyridine}, both of which have been characterized by X-ray crystallography. The η^1-carbamoyl complex **1** was prepared from the reaction between $Re(CO)_5Cl$ and H_2L^1, probably by an interesting intramolecular migratory insertion of CO into the Re^I−amide bond. The amido complex **2** exhibits an intense, long-lived emission in degassed solutions at room temperature.

Results and Discussion

Synthesis and Spectral Features

Treatment of $Re(CO)_5Cl$ with naphthyridylamine H_2L^1 in dichloromethane in the presence of *t*BuOK afforded complex **1** in a 40% yield (Scheme 1). The η^1-carbamoyl group in this complex probably results from the migratory insertion of CO into the rhenium(I)−amide bond. We propose that the reaction might first generate the amine intermediate **I** (Scheme 2), followed by the deprotonation of the coordinated amine ligand in **I** by *t*BuOK to give the arylamide intermediate **II**.[7] This then readily undergoes an intramolecular migratory insertion of CO into the Re−amide bond, giving complex **1**. The synergistic action of the naph-



H_2L^1 **1**

Scheme 1. Synthesis of the η^1-naphthyridylcarbamoyl complex **1**

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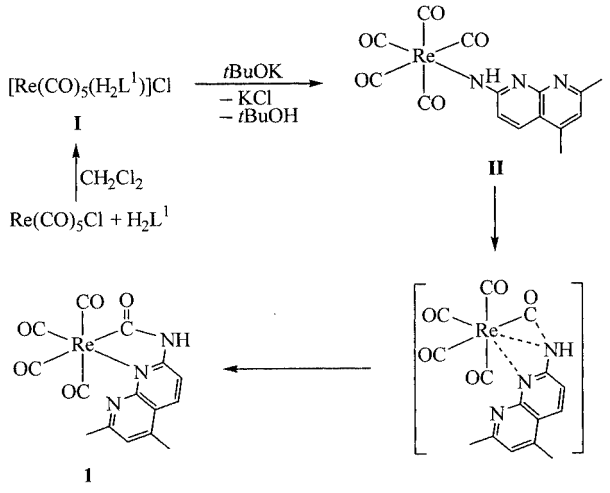
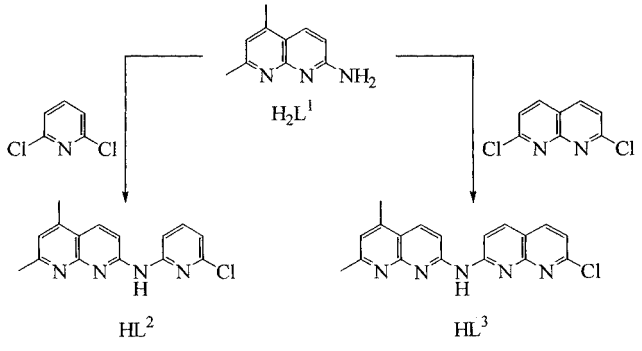


Scheme 2. Proposed mechanism for the formation of complex **1** by migratory insertion of CO into a Re−amido bond

thyridyl group should facilitate such CO insertion processes.

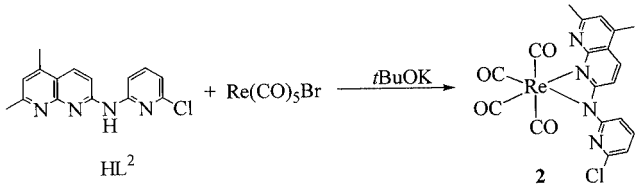
Migratory insertion of CO into a low-valent metal−nitrogen bond is not unprecedented,[8a,9] but is less common than the migratory insertion of CO into an M−R or M−H bond (which has been widely encountered in organometallic chemistry).[10] The mechanism we propose here (Scheme 2) is similar to that of the *ortho*-metalation of the (arylamido)iridium(I) complex *trans*-$Ir(PPh_3)_2(CO)(NHAr)$,[8] and to the formation of the (η^1-carbamoyl)dicarbonylrhenium complex $[(CO)_2RReC(=O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]$ by insertion of CO into an Re−N bond.[9a]

We speculate that replacement of the H atom of the NH group in **II** by a bulky group may prevent or retard the foregoing CO insertion reaction. To test this possibility, we converted H_2L^1 into two new naphthyridylamine ligands HL^2 and (7-chloronaphthyridyl)(5,7-dimethylnaphthyridyl)-amine (HL^3), according to the reactions shown in Scheme 3. Indeed, reaction of $Re(CO)_5Br$ with HL^2 under conditions similar to those for the reaction between $Re(CO)_5Cl$ and H_2L^1 did not give an η^1-carbamoyl complex. Instead, the reaction afforded the amido complex **2** in an 80% isolated yield (Scheme 4).



Scheme 3. Synthesis of HL^2 and HL^3

The reaction of HL^3 with $Re(CO)_5Br$ was also examined, but no identifiable rhenium complexes were obtained in this case. Ligand HL^3 was found to be less reactive than H_2L^1 and HL^2. For example, treatment of $Re(CO)_5Br$ with a 1:1 mixture of HL^3 and H_2L^1 in dichloromethane produced a mixture of **1** and free HL^3, and gave crystals of $\mathbf{1}\cdot HL^3\cdot 2CH_2Cl_2$ on recrystallization from dichloromethane/hexane.



Scheme 4. Synthesis of the naphthyridylamido complex **2**

All the new compounds in this work display parent ion peaks in their mass spectra. The IR spectra of complexes **1** and **2** show CO stretches at frequencies ranging from 1928 to 2103 cm^{-1}; this ν(CO) frequency range is similar to that of the cyclometalated tetracarbonylrhenium(I) complex $[Re(CO)_4\{\mu_2\text{-}C(NHR)(NHC_6H_4)\}]$ (1916−2081 cm^{-1}),[11] but different from the typical ν(CO) frequency range of tricarbonylrhenium(I) complexes (ca. 1700−2000 cm^{-1}).[12] The ν(CO) band at 2087 cm^{-1} for **1**, and at 2103 cm^{-1} for **2**, could be assigned to the *trans*-$Re(CO)_2$ subunits of the $Re(CO)_4$ moieties in the two complexes, since the strong *trans* influence of CO would weaken the Re−CO π-back bonding and thus increase the ν(CO) frequency. However, we cannot exclude the possibility of mixing between the stretching vibrations of the *trans*- and *cis*-$Re(CO)_2$ subunits.

Crystal Structures

Table 6 shows the crystal and refinement data for HL^2, $\mathbf{1}\cdot CHCl_3$, $\mathbf{1}\cdot HL^3\cdot 2CH_2Cl_2$, and **2**. The ORTEP drawings or unit cell diagrams for these crystals are depicted in Figures 1−5. Selected bond lengths and angles are compiled in Tables 1−4.

The free ligand HL^2 is basically planar (Figure 1) and adopts a configuration that is similar to the *anti-syn* configuration of the dimer of 2,2′-dipyridylamine.[13] The N(2)−C(6) and N(2)−C(8) distances are 1.378(6) and 1.400(6) Å, respectively (see Table 1). These are longer than the corresponding C−N distances in pyridine or naphthyridine.

Complex **1** exhibits a distorted octahedral rhenium(I) center and has a strained five-membered metallacycle involving the Re(1), N(1), C(6), N(2), and C(1) atoms (Figure 2) and the Re1, N2, C6, N1, and C5 atoms (Figure 3). The C−Re−N angle in the metallacycle is 76.2(3)° for $\mathbf{1}\cdot CHCl_3$ (Table 2), and 75.8(2)° for $\mathbf{1}\cdot HL^3\cdot 2CH_2Cl_2$ (Table 3). The average Re−CO bond length for the terminal CO groups *trans* to the HL^1CO ligand (1.952 Å) is shorter than the average Re−CO bond length of the *trans*-$Re(CO)_2$ subunit (1.994 Å). The Re−C(carbamoyl) bond lengths of 2.146(7) Å in $\mathbf{1}\cdot CHCl_3$, and of 2.158(7) Å in $\mathbf{1}\cdot HL^3\cdot 2CH_2Cl_2$, are similar to that in $[(CO)_2BrReC(=O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]$ (2.19 Å).[9a] There are hydrogen bonds between complex **1** and the free ligand HL^3 in $\mathbf{1}\cdot HL^3\cdot 2CH_2Cl_2$

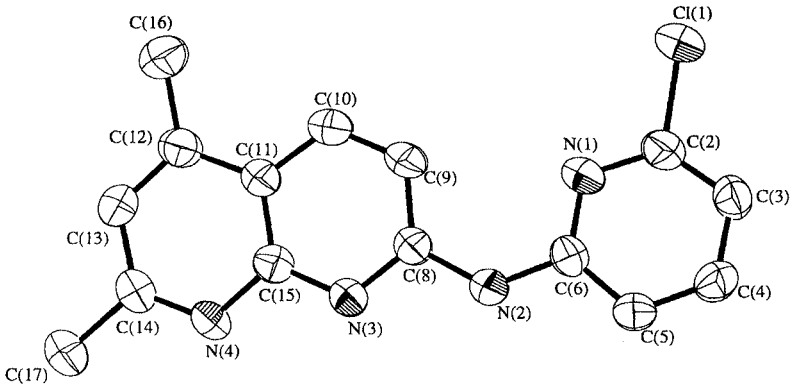


Figure 1. Molecular structure and atomic numbering scheme of HL^2 (probability level of thermal ellipsoids: 50%); hydrogen atoms are not shown

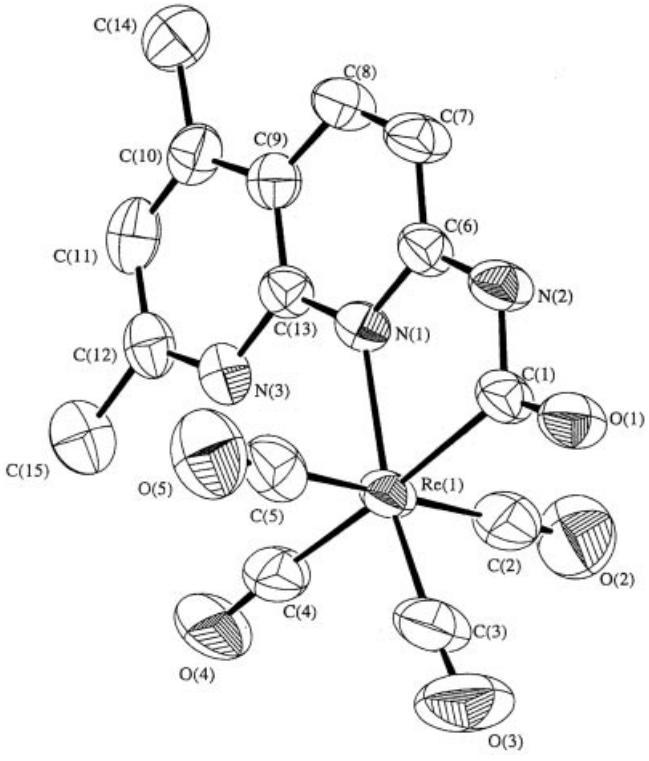


Figure 2. Molecular structure and atomic numbering scheme of **1**·$CHCl_3$ (probability level of thermal ellipsoids: 50%); the hydrogen atoms and the solvent molecules are not shown

[N(1)−H(1)···N(7)* 3.17 Å, O(5)*···H(2)−N(6) 2.86 Å], as shown in Figure 4. Accordingly, the HL^3 ligand in this crystal can be considered as an organic guest incorporated into the host complex **1** (incorporation of an organic guest into organometallic complexes may be potentially useful for nonlinear optical, conducting and ferromagnetic materials[14]).

Complex **2**, which also exhibits a distorted octahedral rhenium(I) center, features a highly strained four-membered metallacycle consisting of the Re(1), N(1), C(10), and N(2) atoms with an N(1)−Re−N(2) angle of 59.5° (Figure 5). The average Re−CO distance for the CO groups *trans* to the naphthyridylamide ligand (1.932 Å) is shorter, while the average Re−CO bond length of the *trans*-$Re(CO)_2$ subunit (2.04 Å) is longer than the corresponding average Re−CO distances in **1**·$CHCl_3$ and **1**·HL^3·$2CH_2Cl_2$. The Re−N(amide) and Re−N(naphthyridine) distances are 2.206(5) and 2.152(5) Å, respectively, which are similar to the average Re−N(bpm) distance of 2.16 Å in [$Re(CO)_4$(bpm)][BF_4].[6] The conformation of the naphthyridylamido ligand L^2 in **2** is similar to that in the free amine HL^2. However, the N(1)−C(5) [1.358(8) Å] and N(1)−C(10) [1.351(8) Å] bonds of the ligand L^2 in **2** are shorter than the corresponding N−C bonds [1.378(6) and 1.400(6) Å, respectively] in the free ligand HL^2.

Electronic Absorption Spectra

Table 5 shows the UV/Vis spectroscopic data of complexes **1** and **2**, together with those of the free ligand HL^2. The absorptions of **1** and **2** at $\lambda < 330$ nm are similar to those of the (carbonyl)(diimine)Re^I complexes;[6,15] we assign these bands mainly to $\pi\rightarrow\pi^*$ transitions. In dichloromethane solution, complex **2** exhibits a broad lower energy absorption band at λ_{max} = 415 nm ($\varepsilon = 1.7\cdot10^4$ $mol^{-1}\cdot dm^3\cdot cm^{-1}$) and a shoulder at 432 nm ($\varepsilon = 1.5\cdot10^4$ $mol^{-1}\cdot dm^3\cdot cm^{-1}$), both of which are absent in the spectra of HL^2 in the same solvent. The 415-nm absorption is solvent-sensitive and is blue-shifted to 410 nm in acetonitrile (see Table 5). We assign this absorption to the $d\pi(Re)\rightarrow\pi^*$ (heterocyclic ligand) transition.[16] Note that on going from **2** to **1** the lowest-energy absorption band shifts to considerably higher energies (from 432 to 358 nm). This may be attributed to the different electronic properties of the coordinated naphthyridylamido and -carbamoyl groups. For example, the partial delocalization of electron density from the metal center to the carbamoyl moiety in complex **1** would raise the energy of the MLCT transition, whereas in complex **2**, the Re($d\pi$) orbitals would be destabilized due to coordination of the electron-rich naphthyridylamido group to Re^I, leading to a reduction in MLCT transition energy.

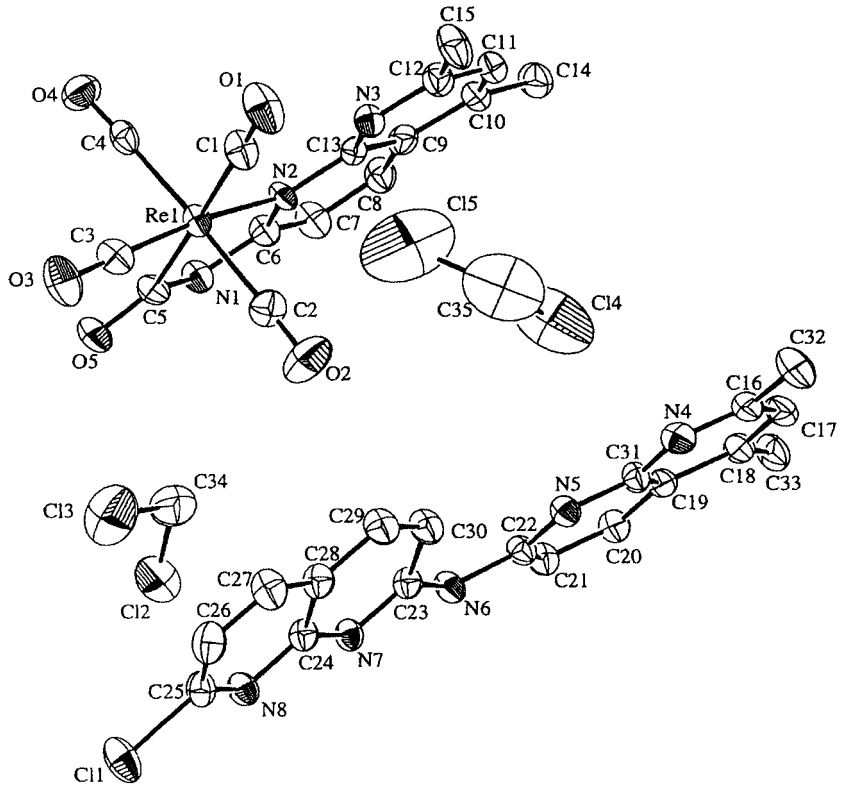


Figure 3. Molecular structure and atomic numbering scheme of **1**·HL^3·$2CH_2Cl_2$ (probability level of thermal ellipsoids: 50%); hydrogen atoms are not shown

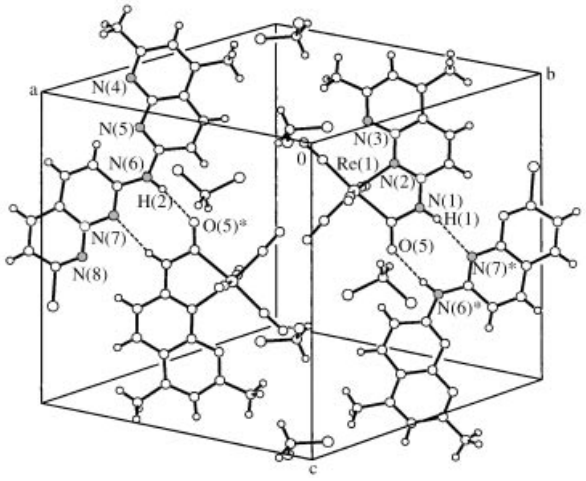


Figure 4. Unit cell diagram for **1**·HL^3·$2CH_2Cl_2$

Photoluminescent Properties

Complex **1** displays a weak emission at λ_{max} = 453 nm in an EtOH/MeOH (1:4, v/v) glassy solution at 77 K. However, no emission was detected when this complex was dissolved in dichloromethane or acetonitrile at room temperature.

On excitation at 400−430 nm, complex **2** exhibits an intense structured emission in an EtOH/MeOH (1:4, v/v) glassy solution at 77 K (λ_{max} = 499 and 533 nm), with a vibrational shift of 1280 cm^{-1} (Figure 6). The emission of **2** in dichloromethane at 77 K is intense and structured (λ_{max} = 512 and 550 nm). On the basis of previous work,[15,17] we tentatively assign the structured 77 K emission to be $^3(\pi\pi^*)$ in nature.

Complex **2** emits strongly in fluid solutions as well. A broad emission analogous to the ^{3}MLCT emission of $[Re(CO)_4(bpm)]^+$ or $[Re^I(CO)_3(L-L)X]$ (L−L = aromatic diimines)[17] was observed at λ_{max} = 520 nm in dichloromethane, 535 nm in acetonitrile, 522 nm in toluene, 505 nm in benzene, and 515 nm in tetrahydrofuran at room temperature (Table 5). We suggest that this solvent-dependent broad emission has an admixture of ^{3}IL and ^{3}MLCT characters (the ^{3}MLCT emissions from (carbonyl)Re^I complexes of aromatic diimines are also solvent-dependent).

Note that the free ligand HL^2 gives a broad emission at λ_{max} = 400 nm in acetonitrile at room temperature. This emission has a substantially higher energy than that of complex **2**, and is assigned to be a $^1(\pi\pi^*)$ emission in nature. As expected, the intraligand fluorescence of HL^2 has a short life-time ($\leq 10^{-3}$ μs, Table 5).

It is interesting to note the very long emission life-times (25−46 μs in degassed solutions, 142 and 150 μs in EtOH/MeOH and CH_2Cl_2 glassy solutions at 77 K) and high emission quantum yields (up to 0.22) for complex **2** (Table 5), which are in contrast to those reported for $[Re(CO)_4(L-L)]^+$ (life-time < 10 μs and quantum yield < 0.05).[15] The long emission life-time is characteristic of an organic triplet emission and reflects substantial ^{3}IL character in the excited state.

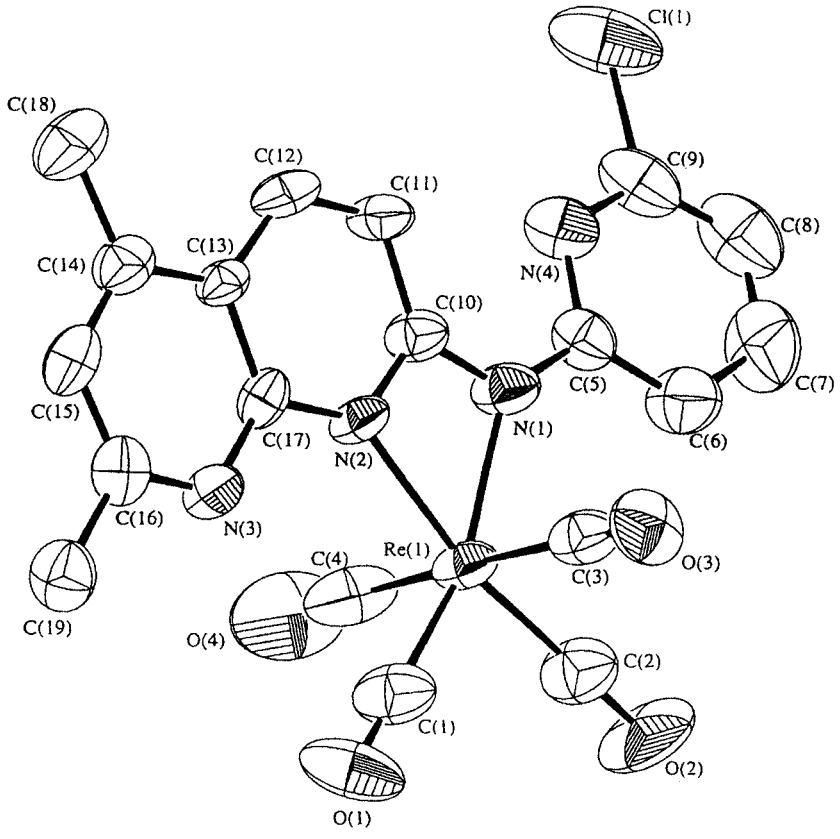


Figure 5. Molecular structure and atomic numbering scheme of **2** (probability level of thermal ellipsoids: 50%); hydrogen atoms are not shown

Table 1. Selected bond lengths and angles in ligand HL^2

Bond lengths [Å]			
Cl(1)−C(2)	1.761(5)	N(1)−C(2)	1.330(7)
N(1)−C(6)	1.336(6)	N(2)−C(6)	1.378(6)
N(2)−C(8)	1.400(6)	N(3)−C(8)	1.335(6)
N(3)−C(15)	1.347(7)	N(4)−C(14)	1.321(7)
N(4)−C(15)	1.375(6)		
Bond angles [°]			
C(2)−N(1)−C(6)	117.0(5)	C(6)−N(2)−C(8)	130.2(4)
C(8)−N(3)−C(15)	117.6(4)	C(14)−N(4)−C(15)	117.6(4)
Cl(1)−C(2)−N(1)	115.8(4)	Cl(1)−C(2)−C(3)	117.7(4)
N(1)−C(2)−C(3)	126.5(5)	C(2)−C(3)−C(4)	115.3(5)
N(1)−C(6)−N(2)	119.8(5)	N(1)−C(6)−C(5)	121.9(5)

Table 2. Selected bond lengths and angles in complex **1**·$CHCl_3$

Bond lengths [Å]			
Re(1)−N(1)	2.205(6)	Re(1)−C(1)	2.146(7)
Re(1)−C(2)	1.99(1)	Re(1)−C(3)	1.91(1)
Re(1)−C(4)	2.000(9)	Re(1)−C(5)	2.00(1)
O(1)−C(1)	1.228(9)	O(2)−C(2)	1.13(1)
O(3)−C(3)	1.14(1)	O(4)−C(4)	1.13(1)
O(5)−C(5)	1.13(1)	N(2)−C(1)	1.41(1)
Bond angles [°]			
N(1)−Re(1)−C(1)	76.2(3)	N(1)−Re(1)−C(2)	91.3(3)
N(1)−Re(1)−C(3)	168.6(3)	N(1)−Re(1)−C(4)	99.6(3)
N(1)−Re(1)−C(5)	90.1(3)	C(1)−Re(1)−C(2)	88.7(3)
C(1)−Re(1)−C(3)	92.4(3)	C(2)−Re(1)−C(3)	88.3(5)
C(2)−Re(1)−C(4)	91.7(4)	C(2)−Re(1)−C(5)	177.5(4)
C(4)−Re(1)−C(5)	90.2(4)	C(1)−N(2)−C(6)	120.4(6)
Re(1)−C(1)−O(1)	132.1(6)		

Experimental Section

General: 7-Amino-2,4-dimethyl-1,8-naphthyridine (H_2L^1) and 2,7-dichloro-1,8-naphthyridine were prepared by literature methods.[18] All reactions were performed under nitrogen using standard Schlenk techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker DPX 300 or DRX 500 FT NMR spectrometer. Chemical shifts were referenced to tetramethylsilane. Fast atom bombardment (FAB) mass spectra were obtained with a Finnigan Mat 95 mass spectrometer using a 3-nitrobenzyl alcohol matrix. UV/Vis absorption spectra were measured with a Perkin−Elmer Lambda 19 UV/Vis spectrophotometer. Elemental analyses were performed by Butterworth Laboratory. Steady-state emission measurements were performed with a SPEX Fluorolog-2 spectrophotometer. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability. Quantum yields of the complexes were determined relative to quinine sulfate in 1.0 N sulfuric acid at 298 K ($\Phi = 0.54$). Emission lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG laser (pulse output 355 nm, 8 ns). The fluorescent lifetimes were obtained by a picosecond laser spectrophotometer equipped with a C4334 streakscope connected to the C4792-01

Tble 3. Selected bond lengths and angles in complex $1{\cdot}HL^3{\cdot}2CH_2Cl_2$

Bond lengths [Å]			
Re(1)−N(2)	2.204(5)	Re(1)−C(1)	1.983(8)
Re(1)−C(2)	1.992(9)	Re(1)−C(3)	1.916(9)
Re(1)−C(4)	1.993(9)	Re(1)−C(5)	2.158(7)
Cl(1)−C(25)	1.771(8)	O(1)−C(1)	1.15(1)
O(2)−C(2)	1.14(1)	O(3)−C(3)	1.16(1)
O(4)−C(4)	1.116(9)	O(5)−C(5)	1.236(9)
N(1)−C(5)	1.396(9)	N(1)−C(6)	1.362(9)
N(2)−C(6)	1.345(9)	N(2)−C(13)	1.393(8)
N(6)−C(22)	1.389(8)	N(6)−C(23)	1.388(9)
Bond angles [°]			
N(2)−Re(1)−C(1)	99.4(3)	N(2)−Re(1)−C(2)	88.0(3)
N(2)−Re(1)−C(3)	170.1(3)	N(2)−Re(1)−C(4)	90.7(2)
N(2)−Re(1)−C(5)	75.8(2)	C(1)−Re(1)−C(2)	91.2(4)
C(1)−Re(1)−C(3)	90.4(3)	C(1)−Re(1)−C(4)	92.9(3)
C(1)−Re(1)−C(5)	174.8(3)	C(2)−Re(1)−C(3)	90.2(4)
C(2)−Re(1)−C(4)	175.8(3)	C(2)−Re(1)−C(5)	90.8(3)
C(3)−Re(1)−C(4)	90.3(3)	C(3)−Re(1)−C(5)	94.4(3)
C(4)−Re(1)−C(5)	85.0(3)	C(5)−N(1)−C(6)	119.7(6)
Re(1)−N(2)−C(6)	114.0(4)	Re(1)−N(2)−C(13)	127.4(4)
C(6)−N(2)−C(13)	118.6(6)	C(22)−N(6)−C(23)	130.3(6)

Table 4. Selected bond lengths and angles in complex **2**

Bond lengths [Å]			
Re(1)−N(1)	2.206(5)	Re(1)−N(2)	2.152(5)
Re(1)−C(1)	1.925(9)	Re(1)−C(2)	1.94(1)
Re(1)−C(3)	2.06(1)	Re(1)-C(4)	2.02(1)
Cl(1)−C(9)	1.751(8)	O(1)−C(1)	1.15(1)
O(2)−C(2)	1.15(1)	O(3)−C(3)	1.07(1)
O(4)−C(4)	1.11(1)	N(1)−C(5)	1.358(8)
N(1)−C(10)	1.351(8)	N(2)−C(10)	1.349(9)
N(2)−C(17)	1.363(8)		
Bond angles [°]			
N(1)−Re(1)−N(2)	59.5(2)	N(1)−Re(1)−C(1)	162.4(2)
N(1)−Re(1)−C(2)	107.5(3)	N(1)−Re(1)−C(3)	89.3(3)
N(1)−Re(1)−C(4)	91.6(3)	N(2)−Re(1)−C(1)	102.9(3)
N(2)−Re(1)−C(2)	166.9(3)	N(2)−Re(1)−C(3)	90.9(2)
N(2)−Re(1)−C(4)	90.1(2)	C(1)−Re(1)−C(2)	90.1(3)
C(1)−Re(1)−C(3)	91.0(4)	C(1)−Re(1)−C(4)	88.3(4)
C(2)−Re(1)−C(3)	90.4(3)	C(2)−Re(1)−C(4)	88.7(3)
C(3)−Re(1)−C(4)	178.9(3)	Re(1)−N(1)−C(5)	136.9(5)
Re(1)−N(1)−C(10)	95.7(4)	C(5)−N(1)−C(10)	127.3(6)
Re(1)−N(2)−C(10)	98.3(4)	Re(1)−N(2)−C(17)	138.6(5)

streak trigger. The decay signal was recorded with a R928 PMT (Hamamatsu), which was connected to a Tektronix 2430 digital oscilloscope. Solutions for the photophysical experiments were degassed by at least four freeze-pump-thaw cycles.

Syntheses

7-[2-(6-Chloropyridyl)amino]-2,4-dimethyl-1,8-naphthyridine (HL^2): A suspension of H_2L^1 (1.73 g, 0.01 mol), 2,6-dichloropyridine (1.48 g, 0.01 mol), and powdered KOH (0.7 g, 0.012 mol) in toluene (300 mL) was refluxed for 24 h. On removal of the solvent, the residue was washed with water and diluted aqueous HCl, followed by chromatography on a silica gel (70−230 mesh) column using petroleum ether (boiling range 40−60 °C) and ethyl acetate (4:1, v/v) as the eluent. The pale yellow fraction was collected and the solvents were evaporated to give a pale yellow product. Yield: 1.19 g (42%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.6−2.7 (s, 6 H, CH_3), 7.0−8.5 (m, 6 H, aryl H), 7.6 (s, 1 H, NH) ppm. FAB-MS: *m/z* = 285 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 3233, 1587, 1505, 1458, 1344, 983, 784, 713, 554 cm^{-1}.

Table 5. Spectroscopic and photophysical properties of HL^2, **1**, and **2**

Compound	Medium (T [K])	λ_{max}^{abs} [nm] ($\varepsilon \times 10^{-4}$ [$dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$])	λ_{max}^{em} [nm]/τ [μs]	φ_{em}
HL^2	CH_2Cl_2 (298)	259 (4.0), 345 (3.1), 357 (3.5)		
	CH_3CN (298)		400/≤ 10^{-3}	0.30
1	CH_2Cl_2 (298)	241 (3.6), 327 (0.99), 342 (1.1), 358 (0.98)	non-emissive	
	CH_3CN (298)	236 (4.6), 307 (0.81), 342 (0.99), 356 (0.83)	non-emissive	
	EtOH/MeOH[a] (77)		weak emission (453 nm)	
2	CH_2Cl_2 (298)	289 (2.6), 317 (1.0, sh), 415 (1.7), 432 (1.5, sh)	520/46	0.22
	CH_3CN (298)	286 (3.0), 316 (1.4, sh), 410 (1.7), 426 (1.6, sh)	535/26	0.19
	$C_6H_5CH_3$ (298)		522/25	0.11
	C_6H_6 (298)	290 (3.0), 317 (1.3, sh), 416 (1.6), 436 (1.4, sh)	505/26	0.16
	THF (298)	291 (2.4), 318 (1.0, sh), 415 (1.3), 437 (1.1, sh)	515/31	0.06
	EtOH/MeOH[a] (77)		499/150 533/150	
	CH_2Cl_2 (77)		512/142 550/142	

[a] 1:4 (v/v).

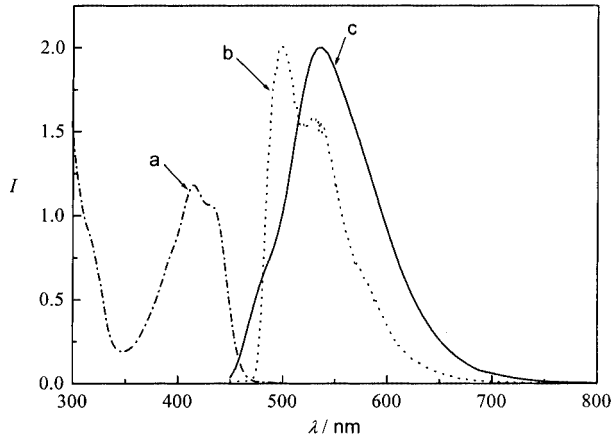


Figure 6. Electronic absorption spectrum (a) and emission spectra (b, c) of **2**; the absorption spectrum was measured in CH_3CN at 298 K, whereas the emission spectra were measured in EtOH/MeOH (1:4, v/v) glassy solutions at 77 K (b) and in degassed acetonitrile at 298 K (c); I = intensity (arbitrary units)

(7-Chloronaphthyridyl)(5,7-dimethylnaphthyridyl)amine (HL^3): This ligand was prepared according to the same procedure as that for HL^2, except that 2,7-dichloro-1,8-naphthyridine was used instead of 2,6-dichloropyridine and the eluent for the chromatography was methanol/dichloromethane (5:95, v/v). Yield: 1.18 g (35%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.6−2.7(s, 6 H, CH_3), 6.7−8.1(m, 7 H, aryl H), 8.3 (s, 1 H, NH) ppm. FAB-MS: m/z = 336 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 3223, 3046, 1674, 1593, 1486, 1313, 1147, 850, 789, 595, 462 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε): 253 ($2.1\cdot10^4$), 329 ($1.1\cdot10^4$), 359 ($1.8\cdot10^4$), 375 ($2.6\cdot10^4$), 419 ($5.9\cdot10^3$), 443 nm ($6.8\cdot10^3$).

$[Re(CO)_4(HL^1CO)]$ (1): A mixture of H_2L^1 (173 mg, 1 mmol), $Re(CO)_5Cl$ (362 mg, 1 mmol), and *t*BuOK (112 mg, 1 mmol) in CH_2Cl_2 (20 mL) was refluxed overnight. After filtration and concentration, a yellow solid was obtained. The solid was washed with toluene and recrystallized from chloroform/pentane. Yield: 203 g (40%). $C_{15}H_{10}N_3O_5Re\cdot0.5H_2O$ (507.47): calcd. C 35.5, H 2.2, N 8.3; found C 35.4, H 2.3, N 8.7. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.67 (s, 3 H, CH_3), 2.75 (s, 3 H, CH_3), 7.15 (s, 1 H, aryl H), 7.30 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, aryl H), 8.23 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, aryl H), 10.37 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 500 MHz): δ = 18.1 (CH_3), 23.7 (CH_3), [109.7, 116.1, 122.7, 136.2, 146.2, 153.7, 161.2] (aryl C), 163.5 (carbamoyl C), [187.1, 190.1, 191.8] (terminal CO) ppm. FAB-MS: m/z = 498 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 3310 (w), 2087 (s), 2008 (s), 1928 (s), 1653 (m), 1614 (s), 1593 (s), 1538 (s), 1044 (s), 862 (s), 701 (s), 615 (s), 580 (s) cm^{-1}.

$[Re(CO)_4L^2]$ (2): A mixture of HL^2 (284 mg, 1 mmol) and *t*BuOK (112 mg, 1 mmol) in CH_2Cl_2 (20 mL) was heated under reflux for 30 min, followed by the addition of $Re(CO)_5Br$ (406 mg, 1 mmol). The mixture was then stirred for 6 h. After filtration and concentration, a yellow solid was obtained, which was chromatographed on a silica gel column using dichloromethane as the eluent. Recrystallization from dichloromethane/hexane afforded complex **2** as yellow prismatic crystals. Yield: 466 mg (80%). $C_{19}H_{12}ClN_4O_4Re$ (581.98): calcd. C 39.2, H 2.1, N 9.6; found C 39.5, H 2.2, N 9.4. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.58 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3), 6.62−8.29 (m, 6 H, aryl H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 500 MHz): δ = 17.8 (CH_3), 25.2 (CH_3), [113.4, 114.8, 115.0, 120.6, 135.7, 140.1, 145.4, 148.4, 152.5, 159.6, 162.1, 177.7] (aryl C), [185.6, 189.2, 189.3, 191.0] (terminal CO) ppm. FAB-MS: m/z = 581 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2925 (w), 2103 (m), 2009 (s), 1981 (s), 1946 (s), 1931 (s), 1682 (m), 1579 (m), 1455 (s), 1336 (m), 1152 (m), 776 (m), 626 (w), 585 (m) cm^{-1}.

Table 6. Crystal and refinement data

	HL^2	**1**·$CHCl_3$	**1**·HL^3·$2CH_2Cl_2$	**2**
Empirical formula	$C_{15}H_{13}ClN_4$	$C_{16}H_{11}Cl_3N_3O_5Re$	$C_{35}H_{28}Cl_5N_8O_5Re$	$C_{19}H_{12}ClN_4O_4Re$
Formula mass	284.75	617.85	1004.13	581.99
Crystal size [mm]	0.15×0.07×0.25	0.30×0.10×0.07	0.15×0.07×0.20	0.05×0.30×0.35
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/a$
a [Å]	13.292(2)	7.419(1)	12.761(2)	9.176(2)
b [Å]	7.497(2)	10.684(2)	13.560(3)	13.378(2)
c [Å]	14.322(3)	14.668(2)	13.829(3)	16.754(3)
α [°]	90	106.06(1)	105.88(2)	90
β [°]	102.74(2)	98.18(1)	101.80(2)	98.73(2)
γ [°]	90	105.56(1)	114.82(2)	90
V [$Å^3$]	1392.1(5)	1046.4(7)	1944(1)	2032.8(6)
Z	4	2	2	4
D_c [g cm^{-3}]	1.359	1.961	1.715	1.901
F(000)	592	588	988	1112
μ [cm^{-1}]	2.69	62.23	35.22	61.44
T [K]	301	301	301	301
$2\theta_{max}$ [°]	51.0	50.0	51.2	51.2
hkl range	$0 \le h \le 16$	$-8 \le h \le 8$	$0 \le h \le 15$	$0 \le h \le 11$
	$0 \le k \le 7$	$0 \le k \le 12$	$-16 \le k \le 14$	$0 \le k \le 16$
	$-16 \le l \le 15$	$-17 \le l \le 16$	$-15 \le l \le 14$	$-20 \le l \le 19$
Measured reflns	13412	3916	17861	18515
Unique reflns	1826	3700	6645	3934
Reflns with $I > 3\sigma(I)$	1006	2966	5526	3081
Parameters	184	248	493	262
R, $_wR$	0.055, 0.064	0.035, 0.045	0.049, 0.063	0.044, 0.059
Goodness of fit	2.09	1.709	1.43	1.81
(D map) max./min. [e·$Å^{-3}$]	0.23/−0.25	1.18/−1.22	1.35/−2.36	1.67/−1.47

X-ray Crystallography: The data of HL^2, **1**·HL^3·$2CH_2Cl_2$, and **2** were collected with a Mar diffractometer equipped with a 300-mm image plate detector, whereas those of **1**·$CHCl_3$ were collected with a Rigaku AFC7R diffractometer, using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å for **1**·$CHCl_3$ and **2**, and 0.71069 Å for the others; data see Table 6). The structures were solved by direct methods (SIR92:[19] HL^2 and **1**·HL^3·$2CH_2Cl_2$) or by Patterson methods (PATTY:[20] **1**·$CHCl_3$ and **2**), expanded by Fourier methods, and refined by full-matrix least squares using the software package TeXsan[21] with a Silicon Graphics Indy computer. Note that the chlorine atoms of the $CHCl_3$ solvent molecule in **1**·$CHCl_3$ were disordered, with Cl(1), Cl(1′), Cl(2), Cl(2′), Cl(3), and Cl(3′) each having an occupation number of 0.5. In the least-squares refinements, all the non-H atoms, except C(16) and the disordered Cl atoms in **1**·$CHCl_3$, were refined anisotropically. The H atoms bonded to the N(2) atom in HL^2 and to the N(1) and N(6) atoms in **1**·HL^3·$2CH_2Cl_2$ found in the difference Fourier synthesis were refined. All the other H atoms placed at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. CCDC-176086 (HL^2), -176087 (**1**·$CHCl_3$), -176088 (**1**·HL^3·$2CH_2Cl_2$), and -176089 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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