Notes

Crystal Structure and Spectroscopic Data of *fac*-Tricarbonylbromo(3,3′-trimethylene-2,2′-bi-1,8-naphthyridine)rhenium(I), $Re(CO)_3Br(C_{19}H_{14}N_4)$

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Summary: The title compound **1** *was obtained from* $Re(CO)_5Br$ *and the binaphthyridine in heptane. Its X-ray crystal structure determination shows a molecular structure with the two nitrogen atoms in positions 1 and 1′ acting as a bidentate chelate ligand to the Re atom.* ^1H *NMR, UV−vis, and IR spectroscopic data are reported and assigned.*

Introduction

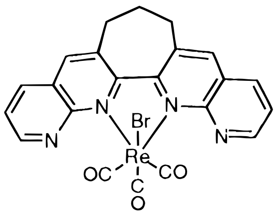
Complexes of polypyridine ligands with d^6 transition metals such as Re(I) have received increasing attention due, at least in part, to the potential versatility of such compounds as catalysts[1−4] and as sensitizers in solar energy conversion schemes.[4,5] One particularly promising class of compounds for these applications are the complexes *fac*-$XRe(CO)_3(L)$ (X = Cl, Br, CN; L = 2,2′-bipyridine and 1,10-phenanthroline and their substituted derivatives), which have been found to act as catalysts for the reduction of carbon dioxide in homogeneous solutions[1−3,6,8,9] and as catalysts bound to electrode surfaces.[7−9]

Luminescence originating from the relaxation of the metal-to-ligand charge-transfer (MLCT) excited state to the ground state provides a convenient alternative to study photophysical decay routes. These properties have been examined to obtain information concerning the mechanisms of intramolecular electron-transfer reactions.[10−12]

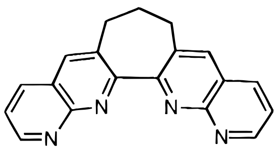
We previously worked with rhenium compounds containing pyridine or biquinoline derivatives as ligands, and the compounds showed luminescence. The emission has been associated with parallel relaxations of two excited states: an intraligand state and a metal-to-ligand charge-transfer state.[13] Complexes similar to those reported here, but containing rhodium instead of rhenium, have been tested as catalysts in the water-gas shift reaction (WGSR) and in the selective reduction of nitrobenzene to aniline under WGSR conditions.[14]

Results and Discussion

Preparation and Spectroscopic Data of 1. When heated in heptane, 3,3′-trimethylene-2,2′-bi-1,8-naphthyridine **(2)** and $Re(CO)_5Br$ yielded the title compound **1**.



1



2

The UV−vis absorption spectrum of **1** in acetonitrile shows essentially three bands with maxima at 260, 374, and 470 nm. The last is associated with a rhenium-to-ligand charge transfer. The two high-energy bands are due to intraligand transitions, since their shapes and positions are similar to bands of the free polypyridine **2**.

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(1) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1244.

(2) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500.

(3) Hawecker, J.; Lehn, J.-M.; Ziessel, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 536.

(4) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

(5) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1981**, *23*, 2104.

(6) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vinig, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414.

(7) Cabrera, C. R.; Abruna, H. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *209*, 101.

(8) O'Toole, T. R.; Margerum, L. D.; Westmoreland, T. D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1416.

(9) Breikss, A. I.; Abruna, H. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *201*, 347.

(10) Danielson, E.; Elliot, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519.

(11) Chen, P.; Westmoreland, T. D.; Danielson, E.; Schanze, K. S.; Anthon, D.; Noveux, P., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116.

(12) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708.

(13) Ferraudi, D.; Feliz, M.; Wolcan, E.; Hsu, T.; Moya, S. A.; Guerrero, J. *J. Phys. Chem.* **1995**, *99*, 4929.

(14) Moya, S. A.; Pastene, R. P.; Sariego, R.; Sartori, R.; Aguirre, P.; Le Bozec, H. *Polyhedron,* in press.

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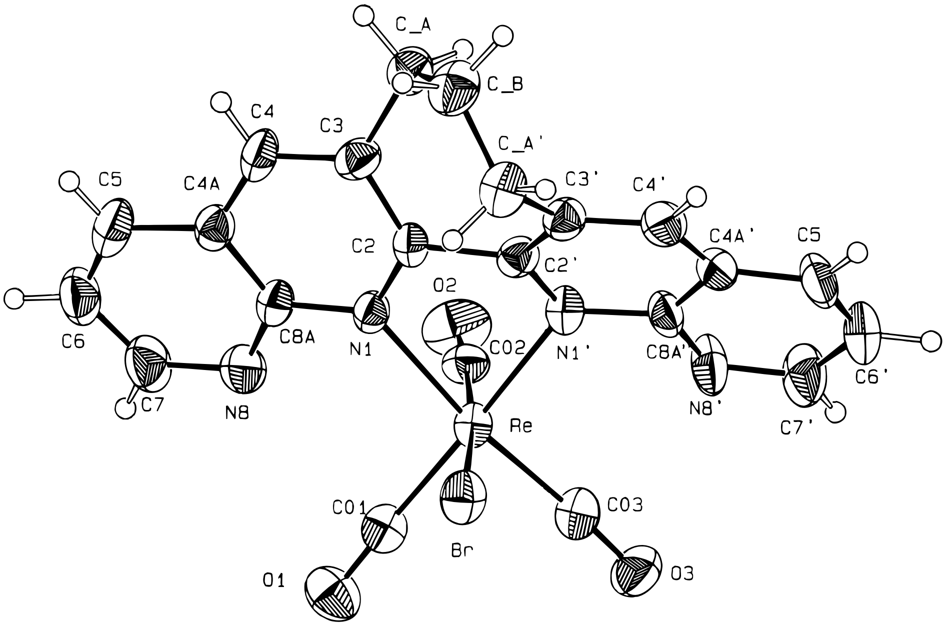

Figure 1. Plot of **1** with thermal ellipsoids (50% probability).

Table 1. Proton NMR Chemical Shifts and Coordination-Induced Shifts in 1[a]

	chem shift					
substrate	$H_7H_{7'}$	$H_6H_{6'}$	$H_5H_{5'}$	$H_4H_{4'}$	H_α	H_β
δ(complex), **1**	9.07 (m)	7.69 (dd)	8.52 (dd)	8.72 (s)	2.83 (m)	2.49 (m)
δ(ligand), **2**	9.11 (dd)	7.48 (dd)	8.26 (dd)	8.05 (s)	2.73 (t)	2.24 (q)
Δδ	−0.04	0.21	0.26	0.67	0.10	0.25

[a] δ in ppm, referenced to TMS in $CDCl_3$ at 200 MHz.

The IR spectrum of **1** in the carbonyl ν(CO) absorption region shows three bands at 2061 (m), 2031 (w), and 1988 (s) cm^{-1}. This is consistent with a facial arrangement of the three carbonyl groups.[15] In comparison to the pentacarbonyl precursor $Re(CO)_5Br$,[16] the frequencies are shifted to lower wavenumbers, indicating an increased Re→CO electron back-donation.

The ^1H NMR chemical shift data (Table 1) of the complex **1** and **2** show the coordination-induced shifts $\Delta\delta = \delta(\text{compl}) - \delta(\text{lig})$. In general, positive Δδ values for the protons are attributed to ligand-to-metal σ-donation, except for protons on carbon atoms adjacent to the coordinating nitrogen atoms; these show negative contributions attributed to metal-to-ligand π-back-donation and to through-space ring-current anisotropy effects.[17] This is in agreement with the coordination occurring through the atoms in "peri" positions.

Table 2. Experimental Crystallographic Data for 1

formula	$C_{22}H_{14}BrN_4O_3Re$
mol wt	648.5
T/K	298(2)
diffractometer	Enraf-Nonius CAD4
λ(Mo Kα radiation)/Å	0.71073
scan type	ω
cryst syst	orthorhombic
space group	$Pca2_1$
a/Å	14.267(2)
b/Å	9.957(1)
c/Å	14.359(5)
V/Å^3	2043.5(4)
rflns cell calcd	$24.1° < \theta < 33.3°$
Z	4
D_{calcd}/g cm^{-3}	2.13
abs coeff μ/mm^{-1}	8.00
F(000)	1232
cryst size/mm	0.04 × 0.02 × 0.01
2θ range/deg	5.0−56.2
hkl ranges	0−18; −13 to +13; −18 to 0
no. of rflns collected	4955
no. of indep rflns	2551
R_{int}	0.028
no. of obsd rflns, $I > 2\sigma(I)$	2407
abs cor	semiempirical (ψ scans)
max and min rel transmissn	1.00 and 0.60
refinement	least squares on F^2
no. of params	280
goodness of fit of F^2	0.985
R_w on F^2 (all data)	0.0597
R on F (obsd rflns)	0.021
weighting scheme	$w = 1/(\sigma^2(F_o^2) + 0.00015F^2)$
residual electron density/Å^{-3}	0.779
computing programs	refs 26−28
scattering factors, Δf′, Δf″	ref 29

X-ray Crystal Structure of 1. Crystals of **1** were obtained by slow evaporation from an acetonitrile−dichloromethane (3:1) solution. Crystallographic data, positional parameters, and selected bond lengths and angles are given in Tables 2 and 3. Figure 1 shows the molecular structure and the atom labeling used in the structure determination. The coordination octahedron of the Re atom is rather distorted due to the chelating effect of the polypyridine ligand. There is no significant difference among the Re−C bond distances. Each of the bipyridyl groups of the ligand is planar within 0.10 Å; the torsion angle between these two groups is 23.4(6)°. Compared with the analogous terpridyl compounds $Re(L)(CO)_3Cl$[18] with L = 3,3′-dimethylene-2,2′-biquinoline,

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(15) (a) Sartori, R.; Guerrero, J.; Pastene, R.; Schmidt, R.; Sariego, R.; Moya, S. A. *Bol. Soc. Chil. Quim.* **1992**, *37*, 311. (b) Wagner, J. R.; Hendricker, D. G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1375.

(16) Brimm, E. O.; Lynch, M. A., Jr.; Sesny, W. J. *J. Am. Chem. Soc.* **1954**, *76*, 3831.

(17) (a) Steel, P. J.; Constable, E. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1389. (b) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinksi, J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761.

(18) Moya, S. A.; Guerrero, J.; Pastene, R.; Schmidt, R.; Sariego, R.; Sartori, R.; Sanz-Aparicio, J.; Fonseca, I.; Maertínez-Ripoll, M. *Inorg. Chem.* **1994**, *33*, 2341.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1

Re−Br	2.626(1)	C(03)−O(3)	1.143(9)
Re−C(01)	1.901(6)	N−C	1.31 to 1.37(1)
Re−C(02)	1.894(8)	C(3)−C(A)	1.51(1)
Re−C(03)	1.910(8)	C(3′)−C(A′)	1.50(1)
Re−N(1)	2.182(6)	C(A)−C(B)	1.53(1)
Re−N(1′)	2.199(6)	C(A′)−C(B)	1.51(1)
C(02)−O(2)	1.144(8)	other C−C	1.35 to 1.42(1)
C(02)−O(2)	1.135(9)		

Br−Re−C(01)	89.0(3)	C(01)−Re−N(1′)	170.6(3)
Br−Re−C(02)	172.9(2)	C(02)−Re−N(1)	90.1(3)
Br−Re−C(03)	94.3(2)	C(02)−Re−N(1′)	97.7(3)
Br−Re−N(1)	83.1(2)	C(03)−Re−N(1)	171.1(3)
Br−Re−N(1′)	82.3(2)	C(03)−Re−N(1′)	97.8(3)
C(01)−Re−C(02)	90.5(3)	N(1)−Re−N(1′)	73.4(2)
C(01)−Re−C(03)	86.4(3)	Re−N(1)−C(2)	116.3(4)
C(02)−Re−C(03)	92.2(3)	Re−N(1′)−C(2′)	114.3(5)
C(01)−Re−N(1)	102.1(3)		

with Re(terpy)$(CO)_3X$[19,20] with X = Cl, Br, and with $Re(CO)_5Br$,[21] there are no significant differences in the bond lengths and bond angles.

Experimental Section

The reactions were performed under a dry nitrogen atmosphere using Schlenk techniques. The solvents were dried by standard methods. ^1H NMR spectra were recorded on a Bruker ACP-200 spectrometer in $CDCl_3$ at ambient temperature. The infrared spectrum was recorded on a Bruker IFS-66 FT spectrometer. The UV−vis spectra were recorded on a Shimadzu UV-160 spectrometer using acetonitrile as solvent and quartz cells at ambient temperature. Elemental analysis was performed at the Facultad de Química, Pontificia Universidad Católica de Chile.

$Re(CO)_5Br$ was obtained by treating $Re_2(CO)_{10}$ with a stirred bromine solution in cyclohexane at ambient temperature for 3 h. **2** was synthesized by the methods described in the literature.[22] **1** was prepared by modification of published procedures.[23−25] $Re(CO)_5Br$ (812 mg, 2.0 mmol) and **2** (563 mg, 2.0 mmol) were heated in 85 mL of dry heptane under reflux for approximately 2 h. The obtained mixture was cooled, its volume was reduced to 30 mL by evaporation, and the red solid which precipitated was filtered. The fine powder was dried in vacuo. Yield: 90%. Anal. Calcd for $C_{22}H_{14}N_4O_3BrRe$: C, 40.75; H, 2.18. Found: C, 42.66; H, 2.32.

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Supporting Information Available: Tables of bond lengths and angles, torsion angles, crystal data and structure refinement details, atomic coordinates, and thermal parameters for **1** (9 pages). Ordering information is given on any current masthead page.

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(19) Abel, E. W.; Dimitrov, V. S.; Long, N. J.; Orrel, K. G.; Osborne, A. G.; Pain, H. M.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 597.

(20) Civitello, E. R.; Dragovic, P. S.; Karpishin, T. B.; Novick, S. G.; Bierach, G.; O'Connell, J. F.; Westmoreland, T. D. *Inorg. Chem.* **1993**, *32*, 237.

(21) Porter, L. H.; Reid, A. H.; Fackler, J. P., Jr. *Acta Crystallogr.* **1992**, *C48*, 908.

(22) Thummel, R. P.; Lefoulon, F. *J. Org. Chem.* **1985**, *50*, 3824.

(23) Tikkanen, W.; Kaska, W. C.; Moya, S. A.; Layman, T.; Kane, R. *Inorg. Chim. Acta* **1983**, *76*, L29.

(24) Moya, S. A.; Pastene, R.; Schmidt, R.; Guerrero, J.; Sartori, R. *Polyhedron* **1992**, *11*, 1665.

(25) Moya, S. A.; Pastene, R.; Schmidt, R.; Guerrero, J.; Sartori, R.; Sariego, R. *Bol. Soc. Chil. Quim.* **1992**, *37*, 43.

(26) Sheldrick, G. M. SHELXS-86, Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1986.

(27) Sheldrick, G. M. SHELXS-83, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1993.

(28) Zsolnai, L. ZORTEP, PC Version of ORTEP; University of Heidelberg, Heidelberg, Germany, 1994.

(29) *International Tables for Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.