

Metallic Carbonyl Complexes Containing Heterocycle Nitrogen Ligands. 2. Tricarbonylbromo(3,3'-R-2,2'-biquinoline)rhenium(I) Compounds

Sergio A. Moya,* Juan Guerrero, Rubén Pastene, Ricardo Schmidt, and Renato Sario

Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile,
Casilla 307-2, Santiago, Chile

Rebeca Sartori

Departamento de Bioquímica, Facultad de Medicina, Universidad de Chile,
Casilla 70086-7, Santiago, Chile

J. Sanz-Aparicio, I. Fonseca, and M. Martínez-Ripoll

UEI de Cristalografía, Instituto Rocasolano, CSIC Serrano 119, E-28006 Madrid, Spain

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Several $\text{BrRe}(\text{CO})_3\text{L}$ complexes (where L groups are 2,2'-biquinoline substituted in the 3 and 3' positions) were prepared. Their pseudooctahedral *fac* structure was established by using FTIR, UV-vis, and $^1\text{H-NMR}$ and confirmed by X-ray analysis. A good correlation between the electrochemical parameters and the MLCT electronic transition was found. The crystalline compound, $\text{BrRe}(\text{CO})_3(3,3'\text{-trimethylene-2,2'-biquinoline})$ belongs to triclinic space group $P\bar{1}$ with $a = 9.113(11)$ Å, $b = 10.192(4)$ Å, $c = 12.825(5)$ Å, $\alpha = 73.23(4)^\circ$, $\beta = 81.30(7)^\circ$, and $\gamma = 66.55(5)^\circ$. The volume of the unit cell is $1048(1)$ Å³ with $Z = 2$. The structure was refined to $R = 0.040$.

Introduction

The photochemical properties of d^6 metal complexes with polypyridine ligands have motivated a considerable amount of research on these compounds.¹⁻⁶ Rhenium(I) tricarbonyl-bipyridyl complexes are very attractive in this regard, because they are chemically stable and easily synthesized.⁷⁻¹⁶ Furthermore, these Re(I) complexes catalyze efficiently and selectively the photoreduction and electroreduction of CO_2 to CO ,^{5,17-19} a process of interest in the conversion and storage of solar energy, and serve as models for natural photosynthesis. The control of

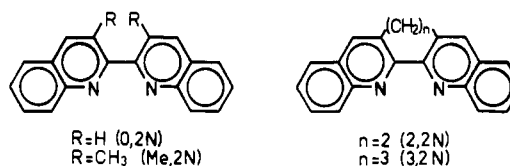


Figure 1. Ligands derived from biquinoline used in this study.

the excited state resulting from metal-to-ligand charge transfer (MLCT) and the redox properties of these complexes, through structural and electronic modifications in the polypyridine ligand, has been proposed as a way to improve the photocatalytic properties of these compounds. We have recently reported the preparation and characterization of these kind of complexes with derivatives of 1,8-binaphthyridine.^{20,21} In this set of complexes changes in the π density of the ligand, in their steric effects, or in the nature of the 3,3' bridge can be studied.

In this paper we have extended our previous work. We now report new complexes of type $\text{ReBr}(\text{CO})_3\text{L}$ containing other 2,2'-biquinoline ligands (Figure 1). The preparation, spectroscopy, redox properties, and, in one case, crystallographic analysis of these complexes are described here. The goal of our work is to extend the availability of rhenium-carbonyl-polypyridine compounds and to evaluate the steric and electronic effects provided by the annelated derivatives of 2,2'-biquinoline on the complexes.

Experimental Section

Physical Measurements. IR spectra were obtained by using a Bruker IFS-66 V FT-IR spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on a 300-MHz Bruker spectrometer. Absorption spectra were measured on a Shimadzu UV-160 spectrophotometer using different solvents, in

- * Abstract published in *Advance ACS Abstracts*, March 15, 1994.
- (1) Belsler, P.; von Zelewsky, A. *Helv. Chim. Acta* 1980, 63, 1675.
 - (2) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G.; von Zelewsky, A. *Inorg. Chem.* 1988, 27, 3652.
 - (3) Hino, J. K.; Della, L.; Dressick, W.; Sullivan, B. P. *Inorg. Chem.* 1992, 31, 1072.
 - (4) Kober, E. M.; Marsahall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* 1985, 24, 2755.
 - (5) Hawecker, J.; Lehn, J. M.; Ziessel, R. J. *Chem. Soc., Chem. Commun.* 1983, 536.
 - (6) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belsler, P.; von Zelewsky, A. *Coord. Chem. Rev.* 1988, 84, 85.
 - (7) Sacksteder, L. A.; Zipp, A. P.; Brown, E. A.; Streich, J. J.; Demas, N.; DeGraff, B. A. *Inorg. Chem.* 1990, 29, 4335 and references therein.
 - (8) Van Wallendael, S. R.; Shaver, J. D.; Rillema, P. B.; Yoblinski, J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* 1990, 29, 1761.
 - (9) Sahai, R. D.; Rillema, P.; Shaver, R.; Van Wallendael, S.; Jackman, D. C.; Boldaji, M. *Inorg. Chem.* 1989, 28, 1022.
 - (10) Winslow, L. N.; Rillema, D. P.; Welch, J. H.; Singh, P. *Inorg. Chem.* 1989, 28, 1596.
 - (11) Glezen, M. M.; Less, A. J. *J. Am. Chem. Soc.* 1988, 110, 3892.
 - (12) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* 1974, 96, 998.
 - (13) Juris, A. J.; Campagna, S.; Bidd, I.; Lehn, J. M.; Ziessel, R. J. *Chem. Soc., Chem. Commun.* 1985, 796.
 - (14) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* 1983, 87, 952.
 - (15) Feliz, M.; Ferraudi, G.; Miller, H. J. *J. Phys. Chem.* 1992, 96, 257.
 - (16) Shaw, J. R.; Schmeil, R. H. *J. Am. Chem. Soc.* 1991, 113, 1991.
 - (17) Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* 1987, 6, 553.
 - (18) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* 1984, 1244.
 - (19) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* 1985, 1414 and references therein.

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

(21) Moya, S. A.; Pastene, R.; Schmidt, R.; Guerrero, J.; Sario, R.; Sartori, R. *Bol. Soc. Chil. Quim.* 1992, 37, 41.

Table 1. Characterization of New Rhenium(I) Complexes

complexes	mp, °C	IR, cm ⁻¹		elemental anal., %: found (calc)			conduct, μmho cm ²
		ν _{CO} in KBr (CHCl ₃) ^c	ν _{ReBr} in polyethylene	C	N	H	
ReBr(CO) ₃ (0,2N)	>350	2016, 1894 ^a (2027, 1927, 1901)	189.6	41.20 (41.59)	4.36 (4.60)	1.87 (1.90)	0.0
ReBr(CO) ₃ (Me,2N)	265–266 ^d	2017, 1918, 1889 (2025, 1924, 1901)	186.3	42.83 (43.54)	3.92 (4.41)	2.54 (2.50)	0.0
ReBr(CO) ₃ (2,2N)	265–266 ^d	2016, 1898 ^a (2026, 1927, 1900)	190.4	43.97 (43.67)	4.41 (4.40)	1.98 (2.20)	8.7
ReBr(CO) ₃ (3,2N) ^b	270–273 ^d	2017, 1901 ^a (2026, 1926, 1900)	189.8	42.70 (43.37)	3.67 (4.21)	2.29 (2.49)	5.7

^a Broad. ^b Monohydrated. ^c 10⁻⁴ mol·L⁻¹ solutions at 25 °C. ^d Decomposition.

Table 2. UV-Visible Data for Rhenium(I) Complexes and Their Free Ligands at 298 K

comps	solv	λ _{abs} , nm (10 ⁻² ε, L·mol ⁻¹ ·cm ⁻¹)	
0,2N	CHCl ₃	343 (sh)	327 (175.15)
Me,2N	CHCl ₃	320 (128.53)	307 (108.00)
2,2N	CHCl ₃	360 (91.18)	345 (81.25)
3,2N	CHCl ₃		319 (98.84)
ReBr(CO) ₃ (0,2N)	CH ₃ C ₆ H ₅	464 (24.15)	377 (162.54)
	CHCl ₃	452 (31.27)	375 (218.49)
ReBr(CO) ₃ (Me,2N)	(CH ₃) ₂ CO	438 (30.75)	374 (235.30)
	CH ₃ C ₆ H ₅	430 (17.63)	
ReBr(CO) ₃ (2,2N)	CHCl ₃	418 (30.30)	359 (215.90)
	(CH ₃) ₂ CO	418 (sh)	359 (54.87)
ReBr(CO) ₃ (3,2N)	CH ₃ C ₆ H ₅	465 (26.52)	394 (198.41)
	CHCl ₃	450 (32.37)	394 (233.21)
ReBr(CO) ₃ (3,2N)	(CH ₃) ₂ CO	437 (29.60)	392 (209.43)
	CH ₃ C ₆ H ₅	450 (31.52)	369 (sh)
	CHCl ₃	435 (28.52)	371 (151.55)
	(CH ₃) ₂ CO	418 (28.52)	369 (153.89)

quartz cells at room temperature. Molar extinction coefficients were calculated from a least-square linear regression of absorbance data at different concentrations. Elemental analyses were performed by the Departamento de Química Orgánica, Facultad de Química y Farmacia, Universidad de Chile. Molar conductivities were determined in CHCl₃ at 25 °C using a Cole-Parmer 01481 conductivity meter.

Electrochemical measurements were carried out on a classical three-electrode potentiostatic setup consisting of a Bank-Wenking POS 73 potentiostat and a XY Linseis Model LX 17100 recorder. Working and auxiliary electrodes were a modified Pt flat disk electrode and a Pt wire, respectively. The reference electrode (an aqueous saturated sodium chloride calomel, SCE) was connected to the electrolysis cell by a Vycor bridge (porous glass No. 7930) filled with saturated KCl solution. The solvent employed was spectrophotometric grade acetonitrile previously treated according to a literature procedure.²² The solutions were 10⁻⁴ mol·L⁻¹ in rhenium complex and 10⁻¹ mol·L⁻¹ in tetrabutylammonium perchlorate, and all of them were deaerated with argon. The coulometry experiments were carried out using a Bank-Wenking potentiostat (Model HP72) connected to a Bank-Wenking generator (Model USG72) and to a Bank-Wenking integrator (Model WVI 80).

X-ray fluorescence spectra were obtained on a Philips EDAD PV-9500 X-ray spectrophotometer (energy dispersion type) at 20 kv and 150 μA. X-ray crystallographic analyses were performed by the UEI de Cristalografía, Instituto Rocasolano, CSIC, Madrid, Spain.

Materials. Solvents and chemicals were reagent grade and purified according to described procedures.²² The precursor compounds aminobenzaldehyde, diketone, and pentacarbonylbromorhenium(I) complex were obtained according to the literature.^{23–26} The ligands 2,2'-biquinoline, (0,2N); 3,3'-dimethyl-2,2'-biquinoline, (Me,2N); 3,3'-dimethylene-2,2'-biquinoline, (2,2N); and 3,3'-trimethylene-2,2'-biquinoline, (3,2N), were prepared by the procedure already described in the literature.²⁷

Synthesis of the Rhenium Complexes. The complexes were prepared in high yield (over 80%) by substitution of two CO groups from the precursor BrRe(CO)₅. The rhenium carbonyl precursor complex was dissolved in a mixture of 1:1 petroleum benzene (100/140 °C) and toluene at 50 °C under inert atmosphere. Subsequently a stoichiometric quantity of the corresponding polypyridinic ligand, dissolved under similar

Table 3. Electrochemistry of the Complexes^a

complexes	E _{1/2} , V	
	redn	oxidn ^b
ReBr(CO) ₃ (0,2N)	-0.94	-1.29 (i)
ReBr(CO) ₃ (Me,2N)	-1.05	-1.35 (i)
ReBr(CO) ₃ (2,2N)	-0.95	-1.30 (i)
ReBr(CO) ₃ (3,2N)	-0.99	-1.58 ^c

^a Potential measurements are referred to the SCE, in 10⁻¹ mol·L⁻¹ TBAP/acetonitrile solution at room temperature. The scan rate was 200 mV·s⁻¹. ^b Values represent anodic peak potentials. ^c ΔE_p: 110 mV.

conditions, was added and heated under reflux. After 2 min of reaction a deep red solid was observed. The mixture was filtered and dried.

Results and Discussion

The compounds crystallize from chloroform as small red crystals. The products are slightly soluble in most common solvents and stable in air, either in the solid state or in solution. The absorption spectra in solution under nitrogen atmosphere show no change during several days. The formulation proposed for the products, ReBr(CO)₃L, is supported by elemental analysis, X-ray fluorescence (which was used to determine the presence of the metal and the halogen), melting points, and conductivity (Table 1).

Most of the characterized complexes of this type correspond to the facial isomer,^{28,29} and so far, there is only one crystallographically defined mer geometry reported in the literature.³⁰

UV-Visible Spectroscopy. The absorption spectra of the complexes (Table 2) can be interpreted by comparison with other Re(I) complexes with ligands structurally related to those used in this work.^{12,31–33} The broad lowest energy absorption band,

- (22) Gordon, A. I.; Ford, R. A. *The Chemist's Companion*, J. Wiley and Sons: New York, 1972.
 (23) Opie, J. W.; Smith, C. T. *Organic Syntheses*; Wiley: New York, 1965; Collect. Vol. III, p 56.
 (24) Vanderhear, R. W.; Voter, R. C.; Banks, C. V. *J. Org. Chem.* **1949**, *14*, 883.
 (25) Reiman, R. H.; Singleton, E. J. *Organomet. Chem.* **1973**, *59*, 309.
 (26) Hieber, W.; Fuchs, H. *Z. Anorg. Allg. Chem.* **1941**, *248*, 256.
 (27) Thummel, R. P.; Lefoulon, F. *J. Org. Chem.* **1985**, *50*, 666.

- (28) Chen, P.; Westmoreland, T. D.; Danielson, E.; Schanze, K. Z.; Anthon, D.; Neveux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116.
 (29) Tikkanen, W.; Kaska, W. C.; Moya, S. A.; Layman, T.; Kane, R. *Inorg. Chim. Acta* **1983**, *76*, L-29.
 (30) Bucknor, S.; Cotton, F. A.; Falvello, L. R.; Reid, H. A., Jr.; Schmulbach, C. D. *Inorg. Chem.* **1986**, *25*, 1021.
 (31) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.
 (32) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7892.
 (33) Juris, A. J.; Campagna, S.; Bidd, I.; Lehn, J. M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.

Table 4. ¹H-NMR Spectral Data for ReBr(CO)₃L Compounds and Free Ligands^a

compds	aliphatic protons			aromatic protons					
	H _a	H _b	H _c	H _{3,3'}	H _{4,4'}	H _{6,6'}	H _{8,8'}	H _{5,5'}	H _{7,7'}
0,2N				8.85 d	8.30 s	7.58 t	8.25 d	7.86 d	7.75 t
Me,2N	2.3 s ^b				8.07 s	7.52 t	8.11 d	7.80 d	7.65 t
2,2N	38.20 s				8.03 s	7.52 t	8.43 d	7.77 d	7.68 t
3,2N	2.70 t	2.20 q			8.00 s	7.54 t	8.35 d	7.81 d	7.69 t
ReBr(CO) ₃ (0,2N)				8.31 d	8.50 s	7.71 t	8.96 d	7.94 m	7.94 m
δ _{compd} - δ _{lig}				-0.50	+0.20	+0.13	+0.71	+0.08	+0.19
ReBr(CO) ₃ (Me,2N)	2.60 s ^b				8.35 s	7.75 t	8.97 d	7.91 m	7.91 m
δ _{compd} - δ _{lig}	2.52 s ^b				+0.28	+0.23	+0.86	+0.11	+0.26
					8.29 s	7.69 t	8.62 d		
					+0.22	+0.17	+0.51		
ReBr(CO) ₃ (2,2N)	3.35 m	3.26 m			8.21 s	7.66 t	8.84 d	7.86 m	7.86 m
δ _{compd} - δ _{lig}					+0.18	+0.14	+0.41	+0.09	+0.18
ReBr(CO) ₃ (3,2N)	2.83 q	2.74 m	2.43 q		8.25 s	7.69 t	8.82 d	7.90 m	7.90 m
δ _{compd} - δ _{lig}					+0.25	+0.15	+0.47	+0.09	+0.21

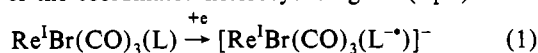
^a Shifts are in ppm from TMS, CDCl₃-d₁. ^b Signal assignable to protons of R = CH₃ groups.

which appears accompanied by a shoulder, shows a maximum in the range 400–500 nm. This band has been assigned to a metal-to-ligand charge-transfer (MLCT) transition. The higher energy bands, observed in the spectrum, have been considered as intraligand transitions because of the similar shape and position of these bands when they are compared to the free polypyridine ligands absorption. The intraligand bands are moved to a lower energy region as a result of complexation.

The lower energy of the CT absorption in these complexes, as compared with those derived from 1,10-phenanthroline and 2,2'-bipyridine,³⁴ can be explained by the more extensive conjugation of the polypyridine ligands. This is in agreement with the position of this band in complexes containing naphthyridine ligands.²⁰ On the other hand, the small differences in the energies of the CT bands of these complexes can be correlated with the amount of distortion from planar configuration of the quinoline groups. The large dihedral and out of plane angles observed in the (3,2N) derivative can be expected to increase in the (Me,2N) derivative and to be smaller in the (0,2N) and (2,2N) derivatives. Correspondingly, the energy of CT bands increases from L = (0,2N) to L = (Me,2N). This is a good indication that the LUMO(π*) orbital of the polypyridine ligand is destabilized when both quinoline units tend to be out of the plane.

Electrochemistry. The electrochemical properties of the carbonyl complexes of Re(I) with polypyridinic ligands were studied by cyclic voltammetry (Table 3).

In the 0.0 to -1.8 V range, two reduction waves were observed: The first reduction wave is reversible, as it was established by linear plots $i_p/v^{1/2}$ and i_p/C , with i_c/i_a values near 1. Coulometric measurements as well as the ΔE_p ($E_{pc} - E_{pa}$) values between 60 and 90 mV are indicative of a one electron transfer process (comparable to those found for the Fc/Fc⁺ couple, used as an internal reversibility standard). This wave can be assigned to the reduction of the coordinated heterocyclic ligand (eq 1). This



experimental observation is in agreement with the fact that the LUMO is the π* orbital of the polypyridinic ligand.^{18,35,36} Further support for the assignment of the first reduction wave comes from the good linear correlation ($E_{\text{abs}} = 0.78 - 2.08 E_{1/2}$) (correlation coefficient, $r = 0.998$) between E_{abs} and $E_{1/2}$ (where E_{abs} corresponds to the metal to ligand charge transfer and $E_{1/2}$ is the first reduction potential).³⁷ The inclusion of data previously

- (34) Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ohsen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111.
 (35) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414.
 (36) Baiano, J.; Carlson, D. L.; Wolosh, G. M.; De Jesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R., Jr. *Inorg. Chem.* **1990**, *29*, 2327.
 (37) In rigor the correlation must be between E_{abs} and $E_{1/2} = E_{1/2}(\text{Re}^{\text{II/I}}) - E_{1/2}(\text{L}^{0/-})$, but the oxidation of the metal gives only anodic peak potentials.

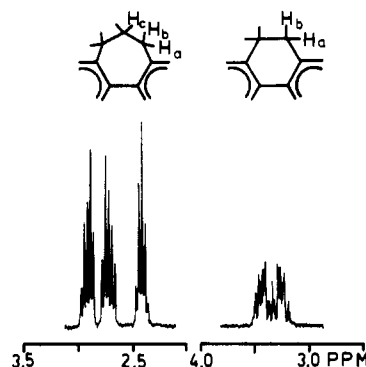


Figure 2. ¹H-NMR high-field region spectra of ReBr(CO)₃(3,2N) and ReBr(CO)₃(2,2N) complexes (in CDCl₃ at 300 MHz).

obtained for analogous compounds fits very well in this correlation.^{20,38}

The second reduction, which can be assigned to a metal-centered process (Re^I/Re⁰), ranges 1.2–1.6 V and does not show any anodic wave. The i_c values differ from those obtained in the first reduction. The high value ($E_{1/2} = -1.58$ V, $\Delta E_p = 110$ mV) found in the complex with (3,2N), makes it possible for this peak to be attributed to a second reduction of the ligand itself. The 540-mV difference between the first and the second reduction potential [$E_{pc}(2) - E_{pc}(1)$] is consistent with those found for similar ligands in complexes with the same electrochemical behavior.^{39–41}

On the other side, all the complexes show an irreversible oxidation wave between 0.0 and +1.6 V, which can be assigned to a Re^I/Re^{II} oxidation process.^{20,42}

The dπ orbitals of the Re atom are facing the ligand π orbitals when the ligand is planar. Therefore, there is a considerable coulombic repulsion between both π clouds. The energy of the dπ orbital decreases in the same amount as the energy of the LUMO increases, when the ligand structure departs from planarity. Such departures are caused by the methylene bridge and the substituents in the 3,3' positions. In this way, the linear relationship between the MLCT energy (dπ → π*) and $E_{1/2}$ (reduction of the ligand) can be explained.

Infrared Spectroscopy. The characteristic bands of the polypyridinic ligands are not strongly affected as a result of

- (38) ReBr(CO)₃L, L = 6,7-dihydrodipyrido[2,3-b:3',2'-j]-1,10-phenanthroline, ($E_{1/2}(\text{red}) = -0.79$ V, $E_{\text{abs}} = 487$ nm), 2,2'-bi-1,8-naphthyridine, ($E_{1/2}(\text{red}) = -0.90$ V, $E_{\text{abs}} = 454$ nm), and 2,7-bis(2'-pyridyl)-1,8-naphthyridine, ($E_{1/2}(\text{red}) = -1.0$ V, $E_{\text{abs}} = 432$ nm).
 (39) Lin, R.; Fu, Y.; Brock, C. P.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 4336.
 (40) De Armond, M. K.; Hanck, K. W.; Wertz, D. W. *Coord. Chem. Rev.* **1985**, *64*, 65.
 (41) Cooper, J. B.; MacQueen, D. B.; Petersen, J. D.; Wertz, D. W. *Inorg. Chem.* **1990**, *29*, 3701.
 (42) Christesen, P.; Hammet, A.; Muir, A. V. G.; Timney, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1455.

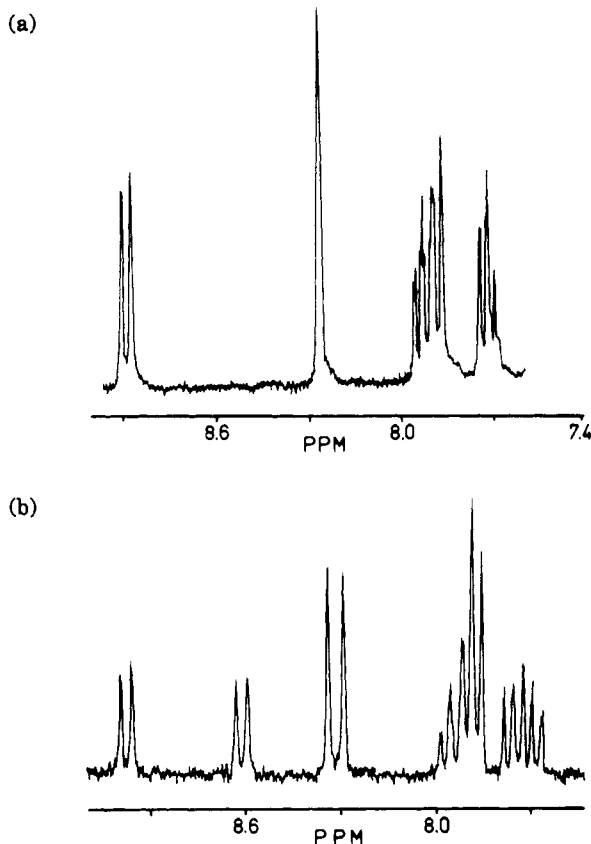


Figure 3. $^1\text{H-NMR}$ spectrum for the aromatic region of (a, top) $\text{ReBr}(\text{CO})_3(2,2\text{N})$ and (b, bottom) $\text{ReBr}(\text{CO})_3(\text{Me},2\text{N})$ complexes (in CHCl_3 at 300 MHz).

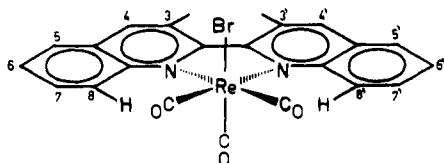


Figure 4. General representation for the (polypyridine)rhenium(I) complexes.

complexation. Some relevant IR data for the carbonyl groups are collected in Table 1. In solution, all the complexes show three strong bands of equal intensity, as expected for a facial structure.^{43,44} In the solid state, except for $\text{BrRe}(\text{CO})_3(\text{Me},2\text{N})$, only two bands are detected, probably because of the superposition of the two bands at low energy.

Protonic Nuclear Magnetic Resonance. The proton NMR spectra of the complexes and free ligands are summarized in Table 4. The assignments of the complex signals were made by considering the data reported previously for the free ligands.²⁷

For complexes containing polypyridine ligands bridged in the 3 and 3' positions such as $\text{ReBr}(\text{CO})_3(2,2\text{N})$ and $\text{ReBr}(\text{CO})_3(3,2\text{N})$, the $^1\text{H-NMR}$ analysis was performed in the high-field region. It was previously established that, on the time scale of the NMR instrument, the ligands (2,2N) and (3,2N) are conformationally mobile respect to the bond $\text{C}(2)-\text{C}(2')$.²⁷ The A_4 system for the (2,2N) ligand is converted into an A_2B_2 system and the A_2X_4 system for the (3,2N) ligand is converted into an $\text{A}_2\text{M}_2\text{X}_2$ system when the complexes are formed⁴⁵ (Figure 2). This leads to a restriction of the freedom of movement through

(43) Wagner, J. R.; Hendricker, D. G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1375.

(44) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.

(45) Thummel, R. P.; Lefoulon, F. *Inorg. Chem.* **1987**, *26*, 675.

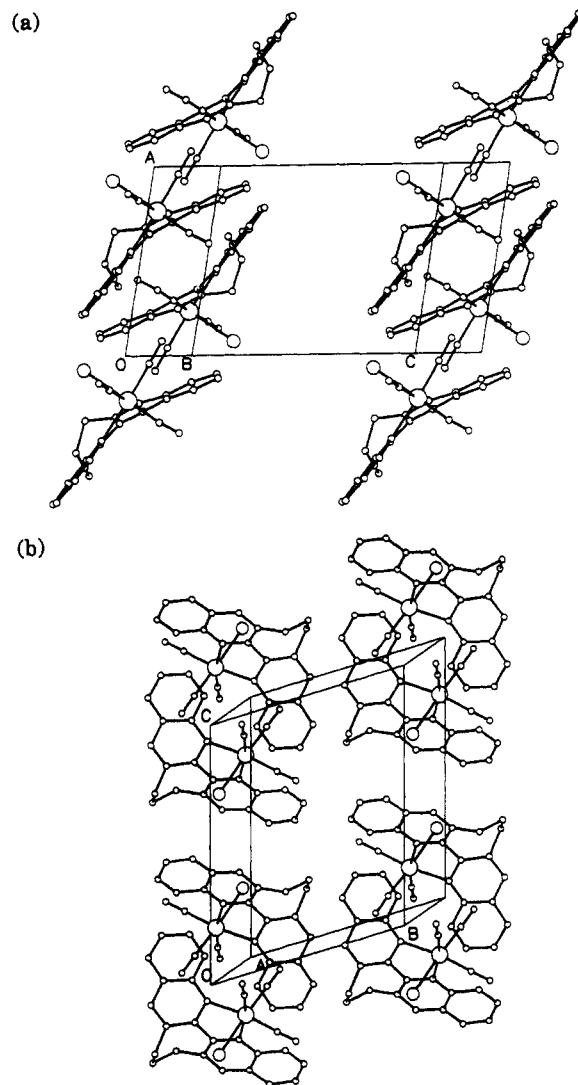


Figure 5. Packing of the molecule $\text{ReBr}(\text{CO})_3(3,2\text{N})$ viewed along the y (a, top) and x (b, bottom) axis.

the $\text{C}(2)-\text{C}(2')$ bond, increasing in this way the coplanarity of both quinoline systems and leading to a distortion in the methylene bridge.

The aromatic proton equivalence shown for each quinoline unit in complexes $\text{BrRe}(\text{CO})_3(0,2\text{N})$, $\text{BrRe}(\text{CO})_3(2,2\text{N})$, and $\text{BrRe}(\text{CO})_3(3,2\text{N})$ is in good agreement with a facial arrangement of the carbonyl groups in the molecule (Figure 3).

As can be seen in Table 4, the ligand aromatic protons undergo a chemical shift to low field after complexation. The displacement of the chemical shifts for each proton are similar through the series. The larger changes to lower fields observed in the complexes are in good agreement with the formation of an $\text{M} \leftarrow \text{N}$ bond which produces an electronic density shift toward the metal. The exception is shown by the H_3 proton of the complex obtained with the (0,2N) ligand, which shows a negative chemical shift difference (-0.50 ppm). This effect can be justified considering the trend of the free ligand to be found in a "anti" position. The increased shielding observed for the $\text{H}_{8,8'}$ protons in this ligand can be explained in the same way. The proton H_8 shows the largest shift to low field in the uncoordinated ligand, which probably is caused by space interaction with the nitrogen occupying the "peri" position. Sterical congestion and paramagnetism of the carbonyl groups produce additional deshielding effects (Figure 4).

The differences between the spectra of *fac*- $\text{BrRe}(\text{CO})_3(\text{Me},2\text{N})$ and *fac*- $\text{BrRe}(\text{CO})_3(2,2\text{N})$, twice the number of resonances in the spectrum of the first complex (Figure 3), suggest a more

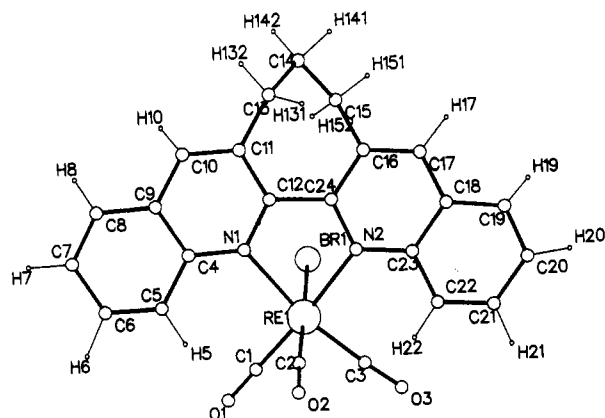


Figure 6. PLUTO⁵² view of the $\text{ReBr}(\text{CO})_3(3,2\text{N})$ molecule showing the atomic numbering.

Table 5. Experimental Data and Structure Refinement Procedures for the $\text{ReBr}(\text{CO})_3(3,2\text{N})$ Complex

Crystal Data	
formula	$\text{C}_{24}\text{N}_2\text{O}_3\text{H}_{16}\text{BrRe}$
cryst size (nm)	$0.21 \times 0.24 \times 0.38$
symmetry	triclinic, $P1$
unit cell determination	least-squares fit from 46 reflns ($6^\circ < 2\theta < 38^\circ$)
unit cell dimens	9.113(11), 10.192(4), 12.825(5) \AA $\alpha = 73.23(4)$, $\beta = 81.30(7)$, $\gamma = 66.55(5)^\circ$
packing: $V(\text{\AA}^3)$, $Z, D_c(\text{g}\cdot\text{cm}^{-3})$, $M, F(000)$, $\mu(\text{cm}^{-1}), \lambda(\text{\AA})$	1048(1), 2, 2.0495, 646.506, 616.0, 77.958, 0.7107
Experimental Data	
technique	four-circle diffractometer: Enraf-Nonius CAD-4, bisection geometry, graphite-oriented monochromator, $\text{Mo K}\alpha$ $\omega/2\theta$ scan
scanning range for θ (deg)	$2 < \theta < 28$
no. of reflns	4950
measd	4120 ($I > 2\theta(I)$ criterion)
obsd	
range of hkl	-12/12, -13/13, 16/0
abs	corr applied
Solution and Refinement	
solution	Patterson and direct methods
refinement	least squares on F_o
no. of variables	280
H atoms	difference Fourier synthesis and geometric calculations
final shift/error	0.006
W-scheme	empirical as to give no trends in ($w\delta^2F$) vs (F_o) and ($\sin \theta$)/ λ
final R and R_w	0.040, 0.046
computer and programs	VAX 11/750, Dirdif, ⁴⁶ Difabs, ⁴⁷ XRAY76, ⁴⁸ pesos, ⁴⁹ parst ⁵⁰
scattering factors	ref 51
anomalous dispersion	ref 51

pronounced departure from a planar biquinoline ligand in the (Me,2N) complex than in the homologous (2,2N). It is not possible to assume a *mer* conformation to explain the differences found in complex $\text{BrRe}(\text{CO})_3(\text{Me},2\text{N})$. In this conformation the H_3 proton should be close to the bromide atom and the H_6 proton close to a carbonyl group. Under these circumstances these protons will show different chemical shifts. Eventually H_7 and H_7' protons might be nonequivalent, but it is unlikely that the rest of the protons of both quinoline systems be nonequivalent because they are far enough from the bromine and carbonyl ligand influences.

Diffraction of X-rays. X-ray crystallography of a single-crystal $\text{ReBr}(\text{CO})_3(3,2\text{N})$ complex was carried out. The structure of the crystal consists of discrete molecules held together by van der Waals forces, the shortest intermolecular distances (not involving

Table 6. Bond Lengths (\AA), Bond Angles (deg), and Torsion Angles (deg) for the $\text{ReBr}(\text{CO})_3(3,2\text{N})$ Complex

(a) Bond Lengths			
$\text{Re}(1)-\text{Br}(1)$	2.628(2)	$\text{C}(8)-\text{C}(9)$	1.43(1)
$\text{Re}(1)-\text{N}(1)$	2.21(1)	$\text{C}(9)-\text{C}(10)$	1.41(1)
$\text{Re}(1)-\text{N}(2)$	2.20(1)	$\text{C}(10)-\text{C}(11)$	1.37(1)
$\text{Re}(1)-\text{C}(1)$	1.92(1)	$\text{C}(11)-\text{C}(12)$	1.41(1)
$\text{Re}(1)-\text{C}(2)$	1.92(1)	$\text{C}(11)-\text{C}(13)$	1.52(1)
$\text{Re}(1)-\text{C}(3)$	1.91(1)	$\text{C}(12)-\text{C}(24)$	1.48(1)
$\text{N}(1)-\text{C}(4)$	1.36(1)	$\text{C}(13)-\text{C}(14)$	1.54(1)
$\text{N}(1)-\text{C}(12)$	1.35(1)	$\text{C}(14)-\text{C}(15)$	1.51(1)
$\text{N}(2)-\text{C}(23)$	1.36(1)	$\text{C}(15)-\text{C}(16)$	1.51(1)
$\text{N}(2)-\text{C}(24)$	1.34(1)	$\text{C}(16)-\text{C}(17)$	1.36(1)
$\text{C}(1)-\text{O}(1)$	1.14(1)	$\text{C}(16)-\text{C}(24)$	1.42(1)
$\text{C}(2)-\text{O}(2)$	1.14(1)	$\text{C}(17)-\text{C}(18)$	1.42(1)
$\text{C}(3)-\text{O}(3)$	1.14(1)	$\text{C}(18)-\text{C}(19)$	1.42(1)
$\text{C}(4)-\text{C}(5)$	1.41(1)	$\text{C}(18)-\text{C}(23)$	1.43(1)
$\text{C}(4)-\text{C}(9)$	1.42(1)	$\text{C}(19)-\text{C}(20)$	1.37(1)
$\text{C}(5)-\text{C}(6)$	1.36(1)	$\text{C}(20)-\text{C}(21)$	1.40(1)
$\text{C}(6)-\text{C}(7)$	1.41(1)	$\text{C}(21)-\text{C}(22)$	1.38(1)
$\text{C}(7)-\text{C}(8)$	1.35(1)	$\text{C}(22)-\text{C}(23)$	1.42(1)
(b) Bond Angles			
$\text{C}(2)-\text{Re}(1)-\text{C}(3)$	91.2(4)	$\text{C}(4)-\text{C}(9)-\text{C}(8)$	119(1)
$\text{C}(1)-\text{Re}(1)-\text{C}(3)$	85.8(4)	$\text{C}(8)-\text{C}(9)-\text{C}(10)$	122(1)
$\text{C}(1)-\text{Re}(1)-\text{C}(2)$	90.7(4)	$\text{C}(4)-\text{C}(9)-\text{C}(10)$	119(1)
$\text{N}(2)-\text{Re}(1)-\text{C}(3)$	96.5(3)	$\text{C}(9)-\text{C}(10)-\text{C}(11)$	121(1)
$\text{N}(2)-\text{Re}(1)-\text{C}(2)$	97.0(3)	$\text{C}(10)-\text{C}(11)-\text{C}(13)$	120(1)
$\text{N}(2)-\text{Re}(1)-\text{C}(1)$	171.9(3)	$\text{C}(10)-\text{C}(11)-\text{C}(12)$	117(1)
$\text{N}(1)-\text{Re}(1)-\text{C}(3)$	167.9(3)	$\text{C}(12)-\text{C}(11)-\text{C}(13)$	122(1)
$\text{N}(1)-\text{Re}(1)-\text{C}(2)$	97.5(3)	$\text{N}(1)-\text{C}(12)-\text{C}(11)$	122(1)
$\text{N}(1)-\text{Re}(1)-\text{C}(1)$	102.4(3)	$\text{C}(11)-\text{C}(12)-\text{C}(24)$	121(1)
$\text{N}(1)-\text{Re}(1)-\text{N}(2)$	74.2(3)	$\text{N}(1)-\text{C}(12)-\text{C}(24)$	116(1)
$\text{Br}(1)-\text{Re}(1)-\text{C}(3)$	88.2(3)	$\text{C}(11)-\text{C}(13)-\text{C}(14)$	115(1)
$\text{Br}(1)-\text{Re}(1)-\text{C}(2)$	177.0(3)	$\text{C}(13)-\text{C}(14)-\text{C}(15)$	111(1)
$\text{Br}(1)-\text{Re}(1)-\text{C}(1)$	86.3(3)	$\text{C}(14)-\text{C}(15)-\text{C}(16)$	116(1)
$\text{Br}(1)-\text{Re}(1)-\text{N}(2)$	86.0(2)	$\text{C}(15)-\text{C}(16)-\text{C}(24)$	119(1)
$\text{Br}(1)-\text{Re}(1)-\text{N}(1)$	83.5(2)	$\text{C}(15)-\text{C}(16)-\text{C}(17)$	122(1)
$\text{Re}(1)-\text{N}(1)-\text{C}(12)$	112(1)	$\text{C}(17)-\text{C}(16)-\text{C}(24)$	118(1)
$\text{Re}(1)-\text{N}(1)-\text{C}(4)$	127(1)	$\text{C}(16)-\text{C}(17)-\text{C}(18)$	121(1)
$\text{C}(4)-\text{N}(1)-\text{C}(12)$	121(1)	$\text{C}(17)-\text{C}(18)-\text{C}(23)$	117(1)
$\text{Re}(1)-\text{N}(2)-\text{C}(24)$	110(1)	$\text{C}(17)-\text{C}(18)-\text{C}(19)$	124(1)
$\text{Re}(1)-\text{N}(2)-\text{C}(23)$	127(1)	$\text{C}(19)-\text{C}(18)-\text{C}(23)$	119(1)
$\text{C}(23)-\text{N}(2)-\text{C}(24)$	119(1)	$\text{C}(18)-\text{C}(19)-\text{C}(20)$	121(1)
$\text{Re}(1)-\text{C}(1)-\text{O}(1)$	179(1)	$\text{C}(19)-\text{C}(20)-\text{C}(21)$	120(1)
$\text{Re}(1)-\text{C}(2)-\text{O}(2)$	174(1)	$\text{C}(20)-\text{C}(21)-\text{C}(22)$	121(1)
$\text{Re}(1)-\text{C}(3)-\text{O}(3)$	177(1)	$\text{C}(21)-\text{C}(22)-\text{C}(23)$	121(1)
$\text{N}(1)-\text{C}(4)-\text{C}(9)$	120(1)	$\text{C}(18)-\text{C}(23)-\text{C}(22)$	118(1)
$\text{N}(1)-\text{C}(4)-\text{C}(5)$	122(1)	$\text{N}(2)-\text{C}(23)-\text{C}(22)$	121(1)
$\text{C}(5)-\text{C}(4)-\text{C}(9)$	118(1)	$\text{N}(2)-\text{C}(23)-\text{C}(18)$	121(1)
$\text{C}(4)-\text{C}(5)-\text{C}(6)$	121(1)	$\text{C}(12)-\text{C}(24)-\text{C}(16)$	124(1)
$\text{C}(5)-\text{C}(6)-\text{C}(7)$	121(1)	$\text{N}(2)-\text{C}(24)-\text{C}(16)$	122(1)
$\text{C}(6)-\text{C}(7)-\text{C}(8)$	120(1)	$\text{N}(2)-\text{C}(24)-\text{C}(12)$	115(1)
$\text{C}(7)-\text{C}(8)-\text{C}(9)$	121(1)		
(c) Torsion Angles			
$\text{N}(1)-\text{Re}(1)-\text{N}(2)-\text{C}(23)$	172(1)	$\text{Re}(1)-\text{N}(2)-\text{C}(24)-\text{C}(12)$	38(1)
$\text{Br}(1)-\text{Re}(1)-\text{N}(2)-\text{C}(23)$	-104(1)	$\text{Re}(1)-\text{N}(2)-\text{C}(24)-\text{C}(16)$	-144(1)
$\text{N}(1)-\text{Re}(1)-\text{N}(2)-\text{C}(24)$	-32(1)	$\text{Re}(1)-\text{N}(2)-\text{C}(23)-\text{C}(18)$	148(1)
$\text{Br}(1)-\text{Re}(1)-\text{N}(2)-\text{C}(24)$	53(1)	$\text{Re}(1)-\text{N}(2)-\text{C}(23)-\text{C}(22)$	-34(1)
$\text{Br}(1)-\text{Re}(1)-\text{N}(1)-\text{C}(4)$	111(1)	$\text{C}(23)-\text{N}(2)-\text{C}(24)-\text{C}(12)$	-163(1)
$\text{Br}(1)-\text{Re}(1)-\text{N}(1)-\text{C}(12)$	-67(1)	$\text{C}(23)-\text{N}(2)-\text{C}(24)-\text{C}(16)$	15(1)
$\text{N}(2)-\text{Re}(1)-\text{N}(1)-\text{C}(12)$	21(1)	$\text{C}(24)-\text{N}(2)-\text{C}(23)-\text{C}(18)$	-6(1)
$\text{N}(2)-\text{Re}(1)-\text{N}(1)-\text{C}(4)$	-162(1)	$\text{C}(24)-\text{N}(2)-\text{C}(23)-\text{C}(22)$	171(1)
$\text{C}(1)-\text{Re}(1)-\text{N}(1)-\text{C}(12)$	-152(1)	$\text{C}(10)-\text{C}(11)-\text{C}(12)-\text{N}(1)$	-6(1)
$\text{C}(1)-\text{Re}(1)-\text{N}(1)-\text{C}(4)$	26(1)	$\text{C}(10)-\text{C}(11)-\text{C}(12)-\text{C}(24)$	-178(1)
$\text{C}(2)-\text{Re}(1)-\text{N}(1)-\text{C}(12)$	116(1)	$\text{C}(13)-\text{C}(11)-\text{C}(12)-\text{N}(1)$	166(1)
$\text{C}(2)-\text{Re}(1)-\text{N}(1)-\text{C}(4)$	-66(1)	$\text{C}(13)-\text{C}(11)-\text{C}(12)-\text{C}(24)$	-7(1)
$\text{C}(3)-\text{Re}(1)-\text{N}(1)-\text{C}(12)$	-20(1)	$\text{C}(10)-\text{C}(11)-\text{C}(13)-\text{C}(14)$	-116(1)
$\text{C}(3)-\text{Re}(1)-\text{N}(1)-\text{C}(4)$	158(1)	$\text{C}(12)-\text{C}(11)-\text{C}(13)-\text{C}(14)$	73(1)
$\text{C}(2)-\text{Re}(1)-\text{N}(2)-\text{C}(24)$	-127(1)	$\text{N}(1)-\text{C}(12)-\text{C}(24)-\text{N}(2)$	-21(1)
$\text{C}(2)-\text{Re}(1)-\text{N}(2)-\text{C}(23)$	76(1)	$\text{C}(11)-\text{C}(12)-\text{C}(24)-\text{N}(2)$	152(1)
$\text{C}(3)-\text{Re}(1)-\text{N}(2)-\text{C}(24)$	141(1)	$\text{C}(11)-\text{C}(12)-\text{C}(24)-\text{C}(16)$	-26(1)
$\text{C}(3)-\text{Re}(1)-\text{N}(2)-\text{C}(23)$	-16(1)	$\text{N}(1)-\text{C}(12)-\text{C}(24)-\text{C}(16)$	161(1)
$\text{Re}(1)-\text{N}(1)-\text{C}(12)-\text{C}(24)$	-8(1)	$\text{C}(11)-\text{C}(13)-\text{C}(14)-\text{C}(15)$	-50(1)
$\text{Re}(1)-\text{N}(1)-\text{C}(12)-\text{C}(11)$	179(1)	$\text{C}(13)-\text{C}(14)-\text{C}(15)-\text{C}(16)$	-33(1)
$\text{Re}(1)-\text{N}(1)-\text{C}(4)-\text{C}(5)$	10(1)	$\text{C}(14)-\text{C}(15)-\text{C}(16)-\text{C}(17)$	-112(1)
$\text{Re}(1)-\text{N}(1)-\text{C}(4)-\text{C}(9)$	-174(1)	$\text{C}(14)-\text{C}(15)-\text{C}(16)-\text{C}(24)$	79(1)
$\text{C}(4)-\text{N}(1)-\text{C}(12)-\text{C}(24)$	174(1)	$\text{C}(15)-\text{C}(16)-\text{C}(24)-\text{C}(12)$	-25(1)
$\text{C}(4)-\text{N}(1)-\text{C}(12)-\text{C}(11)$	1(1)	$\text{C}(15)-\text{C}(16)-\text{C}(24)-\text{N}(2)$	158(1)
$\text{C}(12)-\text{N}(1)-\text{C}(4)-\text{C}(9)$	4(1)	$\text{C}(17)-\text{C}(16)-\text{C}(24)-\text{N}(2)$	-12(1)
$\text{C}(12)-\text{N}(1)-\text{C}(4)-\text{C}(5)$	-173(1)	$\text{C}(17)-\text{C}(16)-\text{C}(24)-\text{C}(12)$	166(1)

H atoms) being 3.03 Å. Representations of the packing along the *x* and *y* axes are displayed in Figure 5, and a perspective view of the rhenium complex molecule with atomic numbering is shown in Figure 6. Crystal data are given in Table 5.⁴⁶⁻⁵² Bond lengths and angles are listed in Table 6.

The overall geometry of the molecule is similar to other compounds with the same substitution pattern.^{29,53-55} The coordination of the rhenium is nearly octahedral with the rhenium atom bonded to the three carbonyl groups in a fac-geometry. The C(1), C(3), N(1), and N(2) atoms form a plane with the Re atom 0.142(2) Å above this plane toward the C(2) atom. The N(1)-Re-N(2) angle is 74.2(3)°, the Br-Re-N(1) and Br-Re-N(2) angles are 83.5(2)°, respectively, and the mean value of the C-Re-C angles (89.2°) is about 90°.

The molecule has an approximate noncrystallographic mirror symmetry about a plane containing Br, C(2), O(2), C(14), and the metal, the two halves of the molecule forming an out of plane angle of 25.9(7)°. The seven-membered ring has a distorted twisted-chair conformation⁵⁶ with a noncrystallographic *C*₂ axis through C(14) and the midpoint of C(12)-C(24).

The estimated value of 50° (obtained from molecular models) for the dihedral angle forming two halves of the uncoordinated

ligand molecule²⁷ is different from the value found from the X-ray structural determination for the complex (21°). The observed difference indicates that the ligand in the complex is forced into a planar arrangement.

The Re-Br bond length, 2.628(2) Å, is similar in all reported compounds, except for [ReBr(CO)₃(NHMe₂)₂],⁵⁵ where it is significantly longer. This could be explained in terms of the steric hindrance of the substituents at the nitrogen atoms. The Re-N distances are shorter in compounds where the N atoms belong to an aromatic ring system. The mean Re-CO distance of 1.91 Å is also very similar for all compounds of this type except for [Re(CO)₃(P(Me₂pz)₂C₆H₅)Br],⁵³ where it is shorter. Nevertheless, due to the large standard deviations in the Re-C distances for this compound, comparison of these distances and angles has only limited value.

Conclusions. The complexes studied in this work have the MLCT band shifted to lower energy as compared to 2,2-bipyridine and 1,10-phenanthroline. This is consequence of the increased delocalization of the π density over the polypyridinic ligands. The energy of this band is slightly dependent on the distortion degree of the polypyridinic ligand. Many Re(diimine)(CO)₃X type complexes have been studied as catalysts for photoinduced reduction of CO₂, always considering the low energy of the available CT band an important step in the catalytic mechanism.^{17,57} The low energy found for this transition in the complexes studied in this work suggests a potential role for these compounds as photocatalysts.

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Supplementary Material Available: Listings of additional bond lengths, additional bond angles, torsion angles, positional and thermal parameters, and other crystallographic data collections parameters and PLUTO diagrams (30 pages). Ordering information is given on any current masthead page.

- (46) Beurskens, P. T.; Bosman, W. P.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Hiltiwanger, R. C. *DIRDIF System of Computer Programs*; Technical Report 1983/1; Crystallography Laboratory Toernooiveld: 6525 ED Nijmegen, The Netherlands 1983.
- (47) Walker, N. *DIFABS. An Empirical Method for Correcting Diffractometer Data for Absorption Effects*; Queen Mary College: London.
- (48) Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. *The XRAY70 System*; Computer Science Center, University of Maryland: College Park, MD, 1974.
- (49) Martinez-Ripoll, M.; Cano, F. H. *PESOS. A Computer Program for the Automatic Treatment of Weighting Schemes*; Instituto Rocasolano, CSIC: Madrid.
- (50) Nardeli, M. *PARST. Comput. Chem.* **1983**, *7*, 95.
- (51) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol 4.
- (52) Motherwell, W. D. S.; Clegg, W. **1978**, *PLUTO. Program for plotting crystal and molecular structures*; Cambridge University: Cambridge, England.
- (53) Cobbleck, R. E.; Dowdell, L. R. J.; Einstein, F. W. B.; Hoyano, J. K.; Peterson, K. *Can. J. Chem.* **1979**, *57*, 2285.
- (54) Couldwell, M. C.; Simpson, J. *J. Chem. Soc., Dalton Trans.*, **1979**, 1101.
- (55) Calderazzo, F.; Vitale, D.; Mavani, I. P.; Marchetti, F.; Bernal, I.; Korp, J. D.; Atwood, J. L.; Rogers, R. D.; Dalton, M. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2523.

(56) Toromanoff, E. *Tetrahedron* **1980**, *36*, 2809.

(57) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161.