The Chemistry of Dinucleating Ligands. Synthesis and Structure of Bromotricarbonyl-2,7-bis(2'-pyridyl)-1,8-Naphthyridinerhenium(I)

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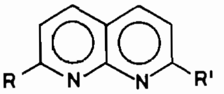
The binucleating properties of 1,8-naphthyridine



R = R' = H (np) are evident with the formation of copper [1, 2], nickel [3] and rhodium [4] complexes. Mononuclear chelate complexes are also observed [5, 6]. In order to promote the binucleating properties of I, the molecule 2,7-bis(2'-pyridyl)-1,8-naphthyridine (R = R' = 2-pyridyl) II, bpnp was synthesized by a series of successive Friedlander condensations [7]. Although II is a potent binucleating ligand [8], mononuclear complexes can be synthesized. Here we report the synthesis and structure of $Re(CO)_3(bpnp)Br$.

Results and Discussion

Treatment of bpnp with $[Re(CO)_3Br(THF)_2]$ at room temperature for 36 hr under nitrogen gives a red solution from which a red solid is precipitated by addition of a five-fold excess of dry diethyl ether in air.

The red solid is soluble in chloroform and THF but insoluble in methanol, benzene, and saturated hydrocarbons. The compound is a non-electrolyte in DMF and CH_2Cl_2; solutions show three bands in the carbonyl stretching region, (2022, 1915, and 1895 cm^{-1}); γ ReBr 170 cm^{-1} (polyethylene mull).

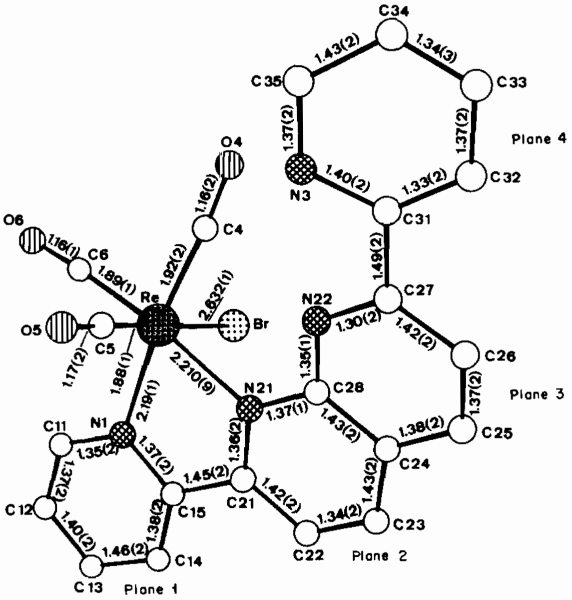


Fig. 1. X-ray molecular structure of bromotricarbonyl-2,7-bis(2'-pyridyl)-1,8-naphthyridinerhenium.

Cyclic voltammetry in acetonitrile with 0.1 *M* tetra-n-butylammonium perchlorate as supporting electrolyte shows a reversible one electron wave at −1.0 V *vs.* S.C.E. The visible spectrum displays a band at 462 nm (ϵ = 830 l/mol/cm). Fluid solutions at room temperature and glasses at −196 °C emit upon excitation of this band. These data suggest a fac $Re(CO)_3(bpnp)Br$ in analogy to the known $Re(CO)_3(np)Br$ [9] and phen $Re(CO)_3(phen)Cl$ [10] which display similar properties.

An X-ray structural determination shows specific coordination of the $Re(CO)_3Br$ moiety to only one of two possible sites on the bpnp ligand.

The crystal chosen for X-ray study had: space group $P2_1/c$; monoclinic, centrosymmetric, a = 10.958(1), b = 19.441(2), c = 11.2709(8); β = 92.058°; Z = 4 for $[Re(CO)_3(bpnp)Br]$; 4667 reflections were collected of which 3345 were used for final refinement with $I > 2\sigma(I)$. The final discrepancy factors R = 0.0495 and R_w = 0.0602 were calculated.

The crystal structure in Fig. 1 shows a fac-tricarbonylrhenium(I) bromide coordinated to the bipyridine fragment of bpnp. The coordination about rhenium atom is a distorted octahedron. The fixed bite of the bipyridine fragment of bpnp is reflected in the N(1)–Re–N(21) angle of 74.6°. The N(1)–Re–Br and N(21)–Re–Br angles are nearly the same, 83.1° and 83.3°, respectively. The C–Re–C angles are all acute, 87.4 ± 0.62° and the Re–N(1), Re–N(21) distances are the same

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2.19(1) and 2.210(9) Å, respectively. These distances are the same as those seen in a fac-tricarbonyl-bis-ethylenediamine complex (2.21 ± 0.04 Å) [11].

The uncomplexed nitrogen of the naphthyridine moiety is not bonded to the rhenium as seen by the Re–N(22) distance of 3.32 Å. The non-bonded C(4)–N(22) distance is 2.87 Å. The Re–Br distance is 2.632 Å. This Re–Br distance is similar to that seen for $(CO)_5ReBr$ (2.62 Å) [12]. The average Re–C and C–O distances of 1.89 ± 0.02 Å and 1.165 ± 0.01 Å, respectively, are similar to those reported for $(C_5H_5)Re(CO)_3$ [13] and other fac-tricarbonylrhenium complexes.

The planes 1 and 2 of the coordinated bipyridyl moiety subtend 8.82° and the angle between the planes 3 and 4 is 15.4°. The naphthyridine planes 2 and 3 subtend 5.14°. The N(21)–C(28)–N(22) angle is 117.4(9)°.

The exclusive formation of a mononuclear product ion has several implications. First: the formation of a five-membered ring is favored over the formation of a more strained four-membered ring, although both species [9, 10] are known for the rhenium(I)-tricarbonyl system. Second: it appears that steric factors are responsible for the formation of a mononuclear complex rather than the desired dinuclear species. This is apparent from the C(4)–N(22) distance of 2.87 Å and the large twisting seen in the non-bonded pyridyl ring, which is twice that seen in a mononuclear tetrahedrally coordinated bpnp-copper(I)bis-triphenylphosphine complex [14]. In this copper complex the cuprous ion resides in the bipy site and shows a Cu–N(22) distance similar to that seen in the title rhenium complex.

The non-planarity of the naphthyridine core of the coordinated bpny is similar to that seen for asymmetrically coordinated mononuclear 1,8-naphthyridine complexes of copper(II) [15, 16].

The similarity of the Re–N distances to those seen in the ethylenediamine complex suggest that the bpnp ligand is acting as a σ donor, with little π accepting behavior. This will be further examined in a later paper in which that emission spectroscopy is discussed.

The C–Re–C angles are somewhat smaller than those seen in cyclopentadienyl-$Re(CO)_3$. Hoffman's calculations [17] show that the C–M–C angle of fac-tricarbonyl complexes is expected to increase on increasing π donor ability of the ligands *trans* to the carbonyls.

In conclusion, the steric demands of the fac-tricarbonyl-rhenium unit prevent the formation of a dinuclear complex by the blocking of the other bipyridine-like site by a carbonyl ligand. The bipyridine site is involved in the formation of a five-membered ring. In other respects (electrochemically and spectroscopically), this complex is similar to the known 1,10-phenanthroline and 2,2′-biquinoline complexes of fac-tricarbonylrhenium(I)-halides.

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