CHEMISTRY LETTERS, pp. 2047-2050, 1991.

Transition Metal Complexes of 1,1'-Bis(2-pyridyl)ferrocene. A Cationic Rhodium(I) and a Silver(I) Complex. Preparation and Structure

Kazuhide TANI,* Takeshi MIHANA, Tsuneaki YAMAGATA, and Taro SAITO†
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

The first transition metal complexes of 1,1'-bis(2-pyridyl)ferrocene (**1**), a cationic rhodium(I) complex, $[Rh(cod)(\mathbf{1})]ClO_4$, (cod=cycloocta-1,5-diene) and a silver(I) complex, $[Ag(\mathbf{1})ClO_4]_2$, were prepared and characterized. X-Ray crystallographic analysis of the silver complex revealed that the complex is a dinuclear highly distorted five-coordinate Ag(I) complex with bridging perchlorate ligands, one of rare examples of five-coordinate Ag(I) complexes.

Although 1,1'-bis(2-pyridyl)ferrocene (**1**) was prepared over 20 years ago,1) its transition metal complexes are little known; only a weak interaction in solution with methylmanganpentacarbonyl has been recognized.2) We therefore planed to prepare some transition metal complexes of **1** and examine their structures and properties.

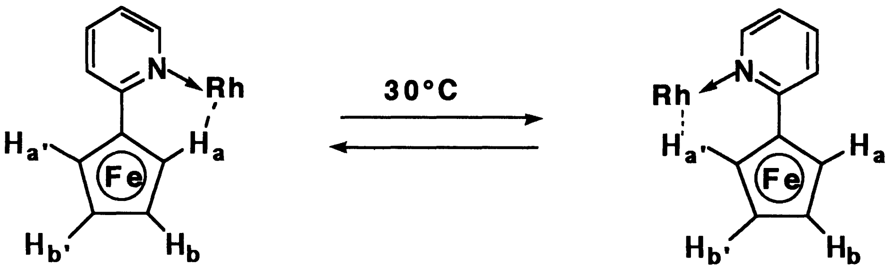
The reaction of $[Rh(cod)Cl]_2$ with **1** in the presence of $AgClO_4$ in acetone gave air-stable orange crystals, mp 170 °C(dec), of chemical formula $[Rh(cod)(\mathbf{1})]ClO_4$ (**2**) in 67% yield.3) Spectroscopic studies,4) mainly ^1H NMR involving ^1H COSY and difference NOE methods, showed that the complex **2** has a usual four-coordinate square-planar structure analogous to conventional cationic diphosphine diene complexes, where both **1** and cod act as *cis* chelating ligands. The complex **2** has a C_s symmetry: the two cp rings and the two pyridyl groups of the ligand **1** are equivalent respectively, but two α- and two β-protons of each cyclopentadienyl ring are nonequivalent. The ir spectrum showed a strong broad absorption at 1080 cm^{-1} for uncoordinated ClO_4 ion. A lower field shift of 6-H of the pyridyl group of **2** compared to that of the free ligand (δ9.49 *vs.* δ8.16) and a higher ν(py C=N) stretching frequency (1600 cm^{-1}) compared to that (1580 cm^{-1}) of the free ligand indicate the coordination of the pyridyl nitrogen.5) The uniquely lower field shift (δ6.50) for one of the cp protons (assigned to Ha, see Eq. 2) indicates the presence of some interactions between the proton and the central Rh atom.6) Irradiation at the signal δ6.50, spin saturation transfer to the signals δ4.66 (assigned to $H_{a'} + H_{b'}$) and δ4.80 (assigned to H_b) were observed at 35°C, which indicates that protons H_a and $H_{a'}$ as well as those H_b and $H_{b'}$ are

---

†Present address: Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113.

equilibrating slowly in solution as shown in Eq. 2. Such spin saturation transfer was not observed below 0 °C.

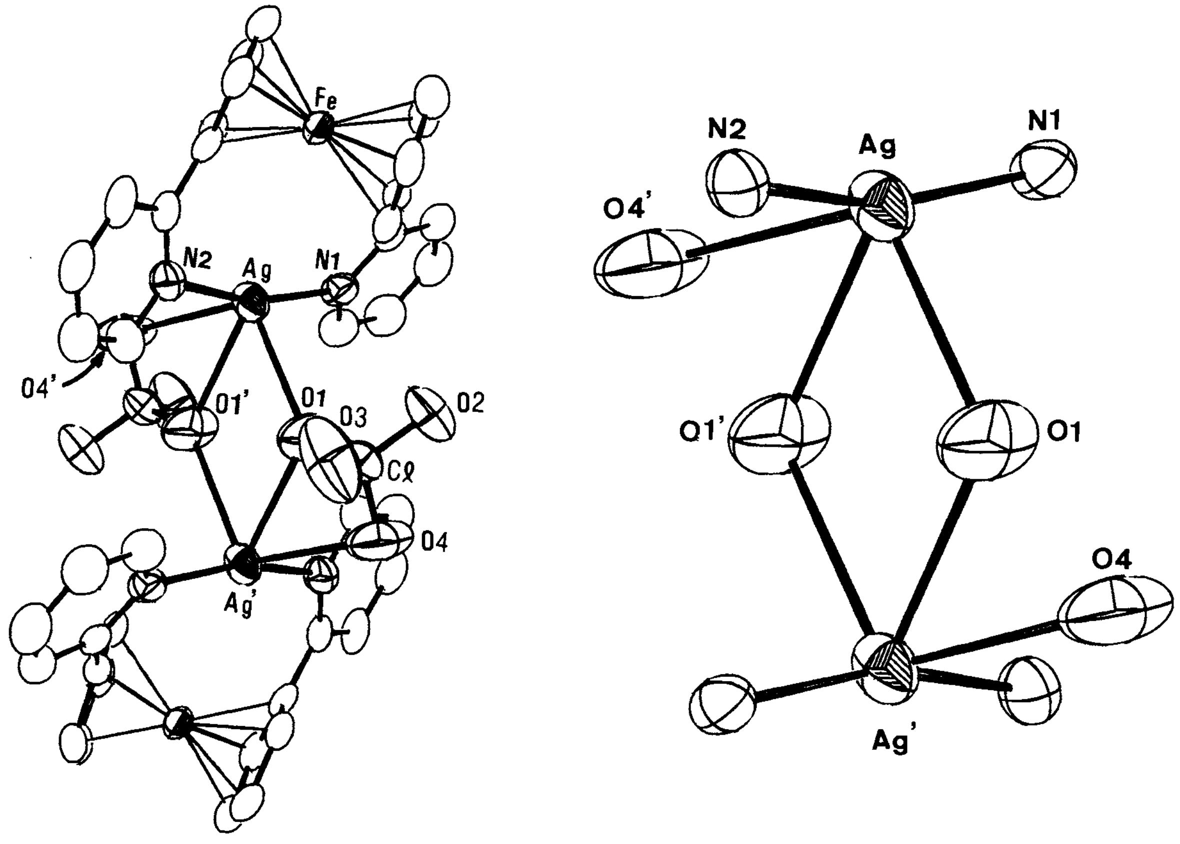
$$[Rh(cod)Cl]_2 \quad + \quad 1 \quad \xrightarrow[\text{acetone}]{AgClO_4} \quad \underset{\mathbf{2}}{[Rh(cod)(1)]ClO_4} \qquad (1)$$



(2)

An attempt to get a cationic Rh(III) complex with the bispyridyl ligand **1** by using $RhCl_3 \cdot 3H_2O$ instead of $[Rh(cod)Cl]_2$ resulted, however, in only isolation of a neutral Ag(I) complex of chemical formula, $[Ag(1)ClO_4]_2$(**3**).7,8) The reaction of $IrCl_3 \cdot nH_2O$ or $RuCl_3 \cdot nH_2O$ with **1** in the presence of $AgClO_4$ gave also the same result. The air-stable orange-red crystalline complex (mp 180 °C(dec)) was isolated in good yield also from the direct reaction of **1** with silver perchlorate in acetone. The IR spectrum showed three strong absorptions at 1033, 1055, and 1100 cm^{-1} for coordinated perchlorate group and a $\nu_{C=N}$ at 1595 cm^{-1}, 15 cm^{-1} higher frequency from that of the free ligand, indicating coordination of the pyridyl group through the nitrogen atom. Lower field shift of 6-H of the pyridyl group of **3** compared to that of the free ligand **1** ($\Delta\delta$ 0.61ppm) also suggests the coordination of **1** through pyridyl nitrogen. X-Ray crystallographic analysis9) shows that the complex **3** has a dinuclear Ag complex having two perchlorate bridges (Fig. 1). The bispyridyl ligand **1** acts as a nearly *trans*-chelating ligand ($\angle$N-Ag-N=163.1(2)°) and the geometry around the silver atoms is a highly distorted 5-coordination with large vacant coordination sites, which are blocked by a ferrocene moiety. This is one of rare examples of five-coordinate silver(I) complexes.10) The two cp rings of the ferrocene moiety remain almost parallel (the dihedral angle between two cp rings is 7.6(4)°) but the pyridine rings are not coplanar with the ferrocene cp rings; the dihedral angles between a cp ring and the connecting py ring are 35.4(4)° and 33.7(4)°, respectively. Although the ligand **1** coordinates unsymmetrically to silver atom in solid state, the two cp and the two pyridyl moieties are equivalent in solution as shown from the ^1H NMR. For example 2-H and 5-H or 3-H and 4-H of the cp group are nonequivalent in the solid state, however, ^1H NMR shows the cp protons at δ4.52 and 4.57 as two triplets of a AA'BB' signal, indicating the presence of equilibration, probably via dissociation of the ligand.

The present results show that the bispyridyl ligand **1** acts as both a *cis* and a *trans* chelating ligand and the coordination ability toward transition metal is in the order, Rh(I) > Ag(I) > Rh(III), Ir(III), or Ru(III). However, the coordination ability toward the higher oxidation metal ions should be examined more carefully.



(a) (b)

Fig.1. ORTEP drawings for 3. (a) Molecular structure with numbering schemes. (b) Core part showing coordination geometry around silver atoms. Selected bond lengths(Å) and angles(°): Ag-N(1) 2.187(5); Ag-N(2) 2.14(1); Ag-O(1) 2.89(1); Ag-O(1)' 2.732(6); Ag-O(4)' 2.97(1); N(1)-Ag-N(2) 163.1(2); O(1)-Ag-O(1)' 68.1(2); O(1)-Ag-O(4)' 113.1(2); O(1)'-Ag-O(4)' 46.4(2); N(1)-Ag-O(1) 97.9(2); N(1)-Ag-O(1)' 100.0(2); N(1)-Ag-O(4)' 104.3(2); N(2)-Ag-O(1) 91.1(2); N(2)-Ag-O(1)' 96.6(2); N(2)-Ag-O(4)' 85.1(2); Ag-O(1)-Ag' 111.9(2).

References

1) K. Schlögel and M. Frried, *Monatsch. Chem.*, **94**, 537 (1963); M. D. Rausch and D. J.Ciappenelli, *J. Organomet. Chem.*, **10**, 127 (1967).

2) M. I. Bruce, B. L. Goodall, and I. Matsuda, *Aust. J. Chem.*, **28**, 1259(1975).

3) *Anal.* Found: C, 51.35; H, 4.48; N, 4.31%. Calcd for $C_{28}H_{28}ClFeN_2O_4Rh$: C, 51.68; H, 4.34; N, 4.30%.

4) ^1H NMR(CD_2Cl_2, 35 °C, 500 MHz): δ2.04(brs, 4H, cod CH_2), 2.80(brs, 2H, cod CH_2), 2.91(brs, 2H, cod CH_2), 4.20(brs, 2H, cod CH=), 4.50(brs, 2H, cod CH=), 4.66(s, 4H, 2-H + 3-H of cp), 4.80(m, 2H, 4-H of cp), 6.50(s, 2H, 5-H of cp), 7.16(d, 2H, 3-H of py), 7.36(m, 2H, 5-H of py), 7.48(m, 2H, 4-H of py), 9.64(brs, 2H, 6-H of py). λ_{max}^{EtOH}(logε): 275(4.30), 295(4.20)sh, 344(3.68)sh, 454(2.88) nm.

5) M. P. Anderson, B. M. Matteson, and L. H. Pignolett, *Inorg. Chem.*, **22**, 2644(1983).

6) T. Yoshida, K. Tani, T. Yamagata, Y. Tatsuno, and T. Saito, *J. Chem. Soc., Chem. Commun.*, **1990**, 292.

7) *Anal.* Found: C, 43.83; H, 2.78; N, 5.19; Ag, 19.32; Fe, 10.37%. Calcd for $C_{40}H_{32}Ag_2Cl_2Fe_2N_4O_8$: C, 43.87; H, 2.95; N, 5.12; Ag, 19.70; Fe, 10.20%.

8) ^1H NMR(CD_2Cl_2, 24 °C, 100 MHz): δ4.64(t, J=2 Hz, 4H, cp), 4.87(t, J=2 Hz, 4H, cp), 7.40-7.51(m, 8H, py), 7.73-7.90(m, 4H, py), 8.83(m, 4H, 6-H of py). λ_{max}^{EtOH}(logε): 235(4.06), 282(3.97), 340(3.34)sh, 462(2.64) nm.

9) Crystal Data: $C_{40}H_{32}Ag_2Cl_2Fe_2N_4O_8$, Fw=1095.052, triclinic, $P\bar{1}$, a=10.489(2), b=11.340(3), c=8.789(2)Å, α=91.60(2)°, β=113.29(1)°, γ=83.52(2)°, V=953.9(4)$Å^3$, Z=1, D_{calcd}=1.906, D_{obsd}=1.901(3) g cm^{-3}, μ(Mo Kα)=1.95cm^{-1}, F(000)=544. The X-ray diffraction data were collected on Rigaku-Denki AFC-4 with graphite monochromatized Mo Kα radiation (λ=0.71069Å, 8kW). A total of 3452 independent reflections were collected up to 2θ=50° by the ω-2θ scan method, among which 3209 are unique. The crystal structure was solved by Patterson and Fourier techniques and refined anisotropically by a block-diagonal least-square method for the non-hydrogen atoms using UNICS programs. All hydrogen atoms were located on the differential Fourier maps and fixed at "idealized" positions with C-H=0.95Å (sp^2 hybridized atoms). The final residuals for 263 variables refined against 1960 reflections for $Fo>6\sigma(Fo)$ were R=3.42%, R_w=3.61% (w=1/$\sigma^2(Fo)$), GOF=1.371, and $\Delta/esd_{(max)}$ = 0.00. A final difference-Fourier was featureless with the largest peak 0.52e/$Å^3$. All calculations were carried out on an ACOS S930 computer at Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

10) R. J. Lancashire, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. A. McClevery, Pergamon Press, Oxford(1987), Vol.5, Chap. 54, p.775

(Received August 22, 1991)