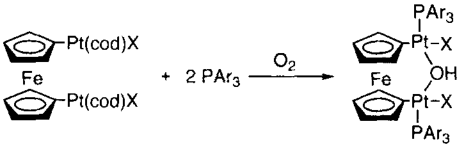
Reactions of 1,1′-Ferrocenediylbis{chloro-[(1,2,5,6-η)-1,5-cyclooctadiene]}diplatinum with Triarylphosphane and Molecular Oxygen[**]

Toshiya Yoshida, Shigeaki Tanaka, Tomohiro Adachi,
Toshikatsu Yoshida, Kiyotaka Onitsuka,
and Kenkichi Sonogashira*

In the chemistry of transition metal complexes containing metallocenes, intramolecular metal–metal interactions involving the metal atom of the metallocene have become one of the most interesting topics in recent years.[1] As part of our studies of ferrocenyl transition metal complexes[2] we have investigated the reactivities of the 1,1′-ferrocenediyldiplatinum complexes $[\{C_5H_4Pt(cod)X\}_2Fe]$ (X = Cl, Br; cod = cyclooctadiene) (**1**).[3] These complexes react with two mole equivalents of PAr_3 (Ar = Ph, p-$CH_3OC_6H_4$) and oxygen to give the novel paramagnetic μ-hydroxo complexes **2**. We wish to report here the chemistry of these and related complexes.

The μ-hydroxo-1,1′-ferrocenediyldiplatinum complexes **2** were prepared in yields of 46 to 62% as air-stable green crystals by ligand exchange reaction of the corresponding 1,1′-ferrocenediyldiplatinum complexes **1**, in which each Pt atom has a cyclooctadiene ligand, with two equivalents of PAr_3 in CH_2Cl_2 in the presence of molecular oxygen at room temperature for 6 h [Eq. (1)].[4]



(1)

1a X = Cl
1b X = Br

2a X = Cl, Ar = Ph
2b X = Br, Ar = Ph
2c X = Cl, Ar = p-$C_6H_4OCH_3$
2d X = Br, Ar = p-$C_6H_4OCH_3$

The IR spectrum of complex **2a** shows an absorption at 3440 cm^{-1} due to the stretching of the OH group.[5] In the ^{1}H NMR spectrum of **2a** the characteristic broad signal of the μ-OH unit appears at much higher field ($\delta = -23.5$) than those of other μ-hydroxo complexes,[6] and disappeared upon addition of a few drops of D_2O. The broad signals attributed to the cyclopentadienyl protons are observed at $\delta = 36.6$ and 26.6 owing to the paramagnetism of the ferrocenediyl group,[7] which was confirmed by the detection of a paramagnetic resonance in the ESR spectrum of **2a**. The cyclic voltammogram of **2a** in CH_2Cl_2 shows a reversible reduction peak ($E_{1/2} = -0.62$ V) ascribed to the reduction of Fe^{III} to Fe^{II} accompanied by decomposition to give an unknown product ($E_a = -0.37$ V) (Fig. 1). In an effort to obtain information about the origin of the μ-hydroxo group, we carried out several experiments. Treatment of **1a** with one equivalent of triphenylphosphane per platinum atom in thoroughly degassed and anhydrous solution did not lead the formation of **2a**. ^{1}H and ^{31}P NMR spectra of this reaction mixture indicated the presence of reactive diamagnetic intermediates such as **3** and **4**. Complex **2a** was not obtained when H_2O was added to this system, but it was generated by the introduction of dry air. These results suggest that the reactive intermediate is easily oxidized by molecular oxygen. Thus, we believe that the oxygen atom of complex **2** arises from O_2, though we have no indications of the origin of the hydrogen atom of the μ-hydroxo group.

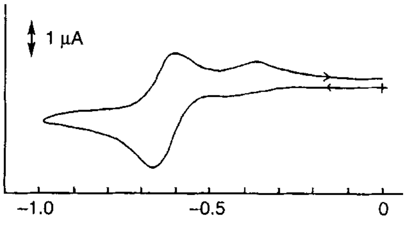
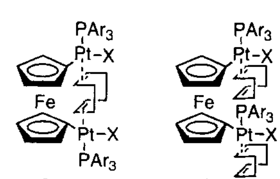


Fig. 1. Cyclic voltammogram of **2a** (10^{-3} M in CH_2Cl_2); scan rate 100 mV s^{-1}, supporting electrolyte tetrabutylammonium hexafluorophosphate (10^{-1} M), working electrode Pt disk (2 mm diameter).



3 **4**

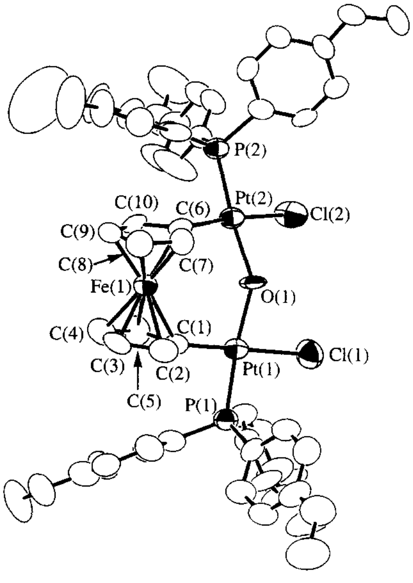


Fig. 2. Crystal structure of **2a**. Selected bond lengths [Å] and angles [°]: Pt(1)–Cl(1) 2.390(5), Pt(1)–P(1) 2.224(5), Pt(1)–O(1) 2.127(9), Pt(1)–C(1) 2.00(2), Pt(2)–Cl(2) 2.386(5), Pt(2)–P(2) 2.241(5), Pt(2)–O(1) 2.13(1), Pt(2)–C(6) 2.01(2); Cl(1)-Pt(1)-O(1) 83.5(3), P(1)-Pt(1)- O(1) 172.6(3), O(1)-Pt(1)-C(1) 93.0(5), Cl(2)-Pt(2)-O(1) 82.7(3), P(2)-Pt(2)-O(1) 177.3(3), O(1)-Pt(2)-C(6) 91.2(6), Pt(1)-O(1)- Pt(2) 138.9(5).

A single-crystal X-ray structure analysis of **2c**[8] confirms the presence of an OH group bridging the two platinum atoms in a bent fashion. The unit cell contains two independent molecules with essentially the same structure, one of which is shown in Figure 2. The coordination around each platinum atom is square planar, and the dihedral angle between the two Pt coordination plane is 146.9°. These planes form dihedral angles of 87.1 and 63.8° with the adjacent cyclopentadienyl ligands. The roughly equal Pt–O bond lengths (2.127(9) and 2.13(1) Å) are longer

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[*] Prof. Dr. K. Sonogashira, T. Yoshida, S. Tanaka, Dr. K. Onitsuka
Department of Applied Chemistry, Faculty of Engineering
Osaka City University, Sumiyoshi-ku, Osaka 558 (Japan)
Telefax: Int. code + (6)605-2769

T. Adachi, Prof. Dr. T. Yoshida
Department of Chemistry, Faculty of Integrated Arts and Sciences
University of Osaka Prefecture (Japan)

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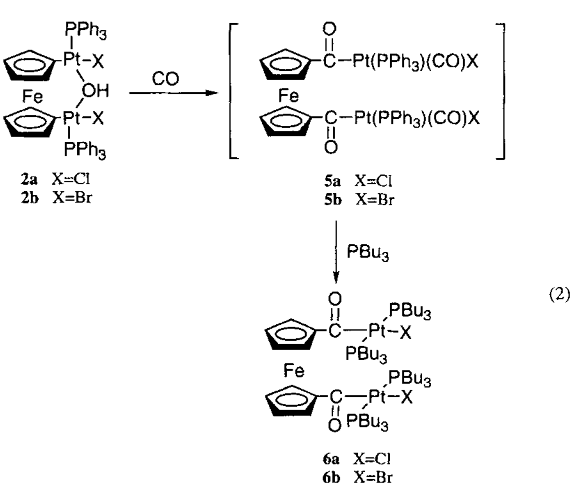
than that of $[NBu_4][\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (2.07(2) Å)[9] but agree with the average value found in $[\{Pt(PEt_3)_2(\mu\text{-}OH)\}_2]$ (2.130 Å).[10] The Pt-O-Pt angle of 138.9(5)° is significantly larger than those of the other μ-hydroxodiplatinum complexes (92(2)–101.4(6)°).[9, 10] The Pt–C bond lengths of 2.00(2) and 2.01(2) Å are within the range expected for a normal Pt–C bond in a σ-ferrocenylplatinum complex.[11] The Pt–Fe distances of 3.728(3) and 3.725(3) Å and the Pt–Pt distance of 3.990(2) Å indicate the absence of any direct M–M interaction. The separation of 3.49(1) Å between the oxygen atom and the iron atom does not reflect any bonding interaction. The ferrocenediyl group has a staggered conformation, and the dihedral angle between the two cyclopentadienyl ligands is 8.5°.

The reaction of **2a** with CO (30 kg cm^{-2}) in dichloromethane at room temperature gave the brown-red solid **5a**. Although we were not able to purify **5a**, its structure was assigned based on IR and ^{1}H NMR spectra. Subsequent treatment of **5a** with excess tri(n-butyl)phosphane led to the formation of stable orange crystals of **6a** [Eq. (2)]. In the IR spectrum of **6a** a CO stretching band at 1600 cm^{-1} indicates that CO inserted into the Pt–C bonds of **2a**. ^{1}H and ^{13}C NMR spectra reveal that the two cyclopentadienyl ligands are equivalent, and the *trans* arrangement of the Pt moieties is supported by a singlet in the ^{31}P NMR spectrum and the ^2J(P,C) coupling of the CO signal in the ^{13}C NMR spectrum. These data are consistent with the structure of **6a** which is produced by the insertion of one molecule of CO into each Pt–C bond of **2a**. The analogous reaction of **2b** gave insertion product **6b**.



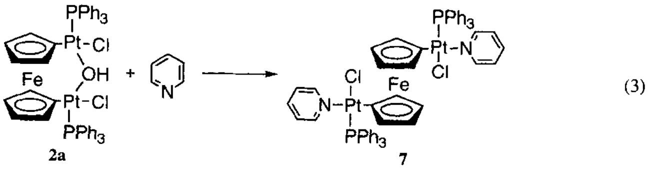
2a X=Cl
2b X=Br

5a X=Cl
5b X=Br

6a X=Cl
6b X=Br

(2)

When complex **2a** was treated with pyridine, the red complex **7** was isolated [Eq. (3)]. The structure of **7** determined by X-ray crystallography is shown in Figure 3.[8] Apparently pyridine has cleaved the hydroxo bridge in **2a** following reduction of the complex; the pyridine ligand at each platinum atom is *trans* to the cyclopentadienyl ligand. The fate of the bridging hydroxo group is not known. The Pt atoms have the expected square-planar coordination with Pt–C σ bonds to the 1,1′-ferrocenediyl moieties and coordination to PPh$_3$, pyridine, and Cl ligands. The 1,1′-ferrocenediyl group adopts an eclipsed conformation with the Pt planes in a transoid orientation, which minimizes steric interaction across the ferrocene molecule. The tilt angle between the two cyclopentadienyl rings is 1.6°. The bond lengths and angles lie in the expected range.



2a

7

(3)

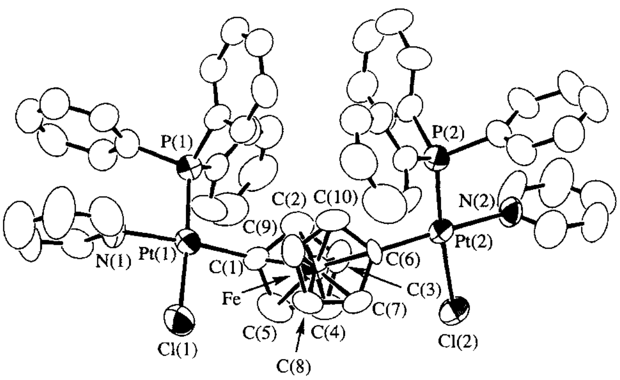


Fig. 3. Crystal structure of 7. Selected bond lengths [Å]: Pt(1)–C(1) 2.02(1), Pt(1)–Cl(1) 2.362(4), Pt(1)–P(1) 2.216(4), Pt(1)–N(1) 2.15(1), Pt(2)–C(6) 2.03(1), Pt(2)–Cl(2) 2.361(4), Pt(2)–P(2) 2.208(4), Pt(2)–N(2) 2.15(1).

In conclusion, we have synthesized a novel paramagnetic μ-hydroxo 1,1′-ferrocenediyldiplatinum complex **2**, in which the 1,1′-ferrocenediyl group functions not only as a bridging ligand fixing the two platinum atoms at an appropriate distance but also as an electron pool. Complexes **2** are reduced by CO and pyridine to give diamagnetic complexes **6** and **7**, respectively. We are now exploring further reactions of these complexes.

Experimental Procedure

2a: To a solution of **1a** (101 mg, 0.117 mmol) in CH$_2$Cl$_2$ (20 mL) was added PPh$_3$ (63 mg, 0.240 mmol). The reaction mixture was stirred at room temperature for 6 h, during which time the color gradually turned from red to green. After removal of the solvent, the green residue was dissolved in 1,2-dichloroethane. Slow evaporation of this solution provided green crystals of complex **2a** (100 mg, 62%). M.p. 235–240 °C (decomp); IR (Nujol): $\tilde{\nu}$ = 3440 cm^{-1} (OH); ^{1}H NMR (CD$_2$Cl$_2$): δ = 36.56 (br, 4H; C$_5$H$_4$), 26.59 (br, 4H; C$_5$H$_4$), 12.80 (br, 12H; Ph), 10.89 (br, 12H; Ph), 10.15 (br, 6H; Ph), −23.49 (br, 1H; OH); ^{31}P NMR (CD$_2$Cl$_2$, PPh$_3$): δ = −84.88 (s); MS (FAB): m/z: 1168 $[M - OH]^+$; UV/Vis (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-2}$) = 774 (6.05), 637 (4.03), 406 nm (27.0).

6a: A solution of **2a** (48 mg, 0.0347 mmol) in 10 mL of CH$_2$Cl$_2$ was placed in a 100 mL autoclave, which was then charged with CO (30 kg cm^{-2}). The reaction mixture was allowed to stand for 24 h at room temperature. Then tri(n-butyl)phosphane (70 mL, 0.281 mmol) was added and the solution stirred for 4 h at room temperature. The solvent was removed, and the residue was purified by column chromatography on silica gel (15 mm × 100 mm) with CHCl$_3$ as eluent. Recrystallization from hexane gave orange crystals of **6a** (19 mg, 37%). M.p. 131–132 °C; IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1} (CO); ^{1}H NMR (CDCl$_3$): δ = 4.61 (s, 4H; C$_5$H$_4$), 4.23 (s, 4H; C$_5$H$_4$), 1.83 (br, 12H; CH$_2$), 1.67 (br, 12H; CH$_2$), 1.49–1.39 (m, 48H; CH$_2$), 0.92 (t, J = 7.3 Hz, 36H; CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 213.62 (t, ^2J(P,C) = 5.3 Hz; CO); 97.92 (t, ^3J(P,C) = 4.2 Hz; C$_5$H$_4$ *ipso*), 70.54, 69.49 (C$_5$H$_4$), 25.97, 24.23, 21.72, 13.81 (PBu$_3$); ^{31}P NMR (CDCl$_3$, PPh$_3$): δ = 11.72 (J(Pt,P) = 3034 Hz).

7: A solution of **2a** (35 mg, 0.0295 mmol) in 10 mL of pyridine was stirred for 48 h at room temperature. The green solution gradually turned orange, and then a red orange precipitate (35 mg, 90%) was obtained. M.p. 237–241 °C (decomp).

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[8] Crystal data for **2c**: 0.80 × 0.60 × 0.10 mm, monoclinic, space group $P2_1/a$, $a = 18.36(1)$, $b = 17.64(2)$, $c = 38.313(8)$ Å, $\beta = 97.04(3)^{\circ}$, $V = 12311(16)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.608\ \text{g cm}^{-3}$, $\mu(\text{Mo}_{K\alpha}) = 51.06\ \text{cm}^{-1}$, ω-2θ scan, $6.0^{\circ} < 2\theta < 50.1^{\circ}$. All non-hydrogen atoms were refined anisotropically by full matrix least squares refinement against $|F|^2$; $R = 0.040$ and $Rw = 0.045$ for 8717 reflections with $I > 6.0\sigma(I)$ out of 17916 unique reflections (reflection/parameter ratio = 6.96), empirical absorption correction using DIFABS [12], GOF = 3.07, residual electron density = −0.89 to 1.04 e Å^{-3}. For **7**: 0.70 × 0.30 × 0.10 mm, monoclinic, space group $P2_1/c$, $a = 10.22(2)$, $b = 24.907(7)$, $c = 22.175(9)$ Å, $\beta = 96.00(7)^{\circ}$, $V = 5614(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.711\ \text{g cm}^{-3}$, $\mu(\text{Mo}_{K\alpha}) = 54.73\ \text{cm}^{-1}$, ω-2θ scan, $6.0^{\circ} < 2\theta < 45.1^{\circ}$. All non-hydrogen atoms were refined anisotropically by full matrix least squares refinement against $|F|^2$; $R = 0.038$ and $Rw = 0.041$ for 4449 reflections with $I > 9.0\sigma(I)$ out of 7564 unique reflections (reflection/parameter ratio = 7.10), empirical absorption correction using DIFABS [12], GOF = 3.17. Further details of the crystal structure may be obtained from the Director of the Cambridge Crystallographic Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

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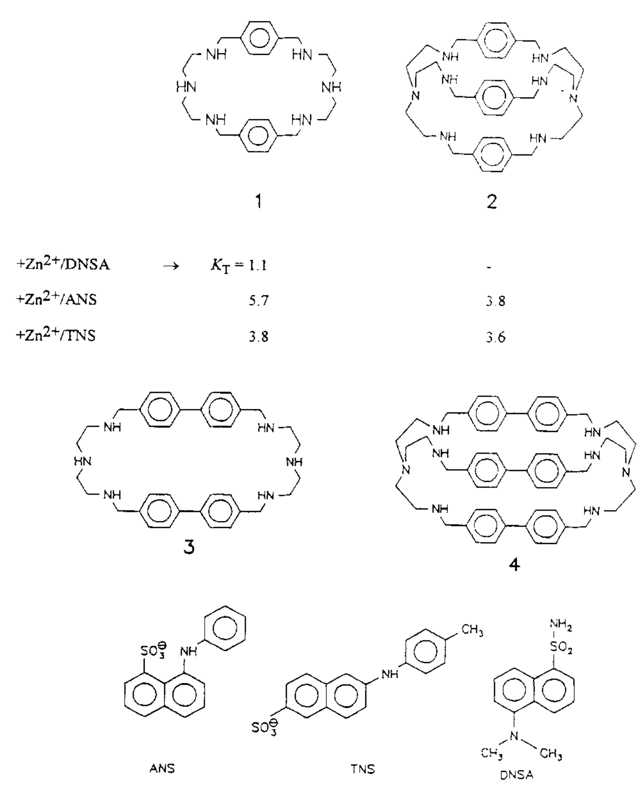
Complexes from Polyazacyclophanes, Fluorescence Indicators, and Metal Cations—An Example of Allosterism through Ring Contraction[**]

Ralf Baldes and Hans-Jörg Schneider*

Synthetic host–guest systems can be relatively easily designed to have a receptor containing several conformationally strongly coupled binding sites that may also bind organic substrates.[1] We report here on ternary complexes in which the cavity for a lipophilic guest molecule is fitted spacially by *contraction* of the hollow space, which is initiated by the binding of metal cations.

Molecular mechanics simulations (force-field CHARMm[3]) of polyazacyclophanes **1** and **2** (Scheme 1)—obtained by published procedures[2]—indicate an almost spherical shape with a wide cavity in the absence of complexing metal cations (Fig. 1a). When metal ions, for example zinc ions, are bound to the ethylene diamine moieties, the cavities become smaller and more strongly anisotropic (Fig. 1b), thus allowing an optimal enclosure of guest molecules of the naphthalene type (Scheme 2, Fig. 1c). The potential energy necessary for the formation of the smaller cavity is provided by the high stability constants[4] of metal complexes of the corresponding polyamine ligands. Unfortunately, the complexes of the new derivatives of **1** and **2** with biphenyl instead of benzene moieties (**3** and **4**, Scheme 1) are too insoluble in water, and we can only discuss here the allosteric properties of the well-known[2] polyazacyclophanes **1** and **2**. Because of the low solubility of these systems, the complexation reactions could not be monitered by NMR spectroscopy. However, using fluorescence spectroscopy and suitable indicators[5] (ANS (8-anilinonaphthalene-1-sulfonic acid), TNS (6-*p*-toluidino)-2-naphthalenesulfonic acid), DNSA (5-dimethylaminonaphthalene-2-sulfonic acid), Scheme 1), the expected cooperative effects could be quantified. At the same time this presented new possibilities for the detection of, for example, zinc ions in aqueous solution.



		1	2
$+Zn^{2+}$/DNSA	→	$K_T = 1.1$	-
$+Zn^{2+}$/ANS		5.7	3.8
$+Zn^{2+}$/TNS		3.8	3.6

Scheme 1. Structures of the host ligands L and guest molecules G (fluorescence indicators) and their equilibrium constants (in units of $10^{-3}\,\text{M}^{-1}$; water, 25 °C) for the ternary complex L·G·Zn^{2+}.

The addition of a solution of **1** (5×10^{-3} M, at pH 7.0 present as **1** × $4H^+$) with $ZnCl_2$ (5×10^{-3} M) to a solution of the fluorescent dye DNSA (10^{-5} M) in water at pH 7.0 led to a considerable increase in the fluorescence emission *F*; from the saturation curve (Fig. 2) a constant $K_T = 1.1 \times 10^3\ \text{M}^{-1}$ with a scattering of about 8% could be calculated for the formation of the ternary complex L·G·M (**1**·DNSA·Zn^{2+}) from a nonlinear fitting

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[*] Prof. Dr. H.-J. Schneider, Dipl.-Chem. R. Baldes
Fachrichtung Organische Chemie der Universität des Saarlandes
D-66144 Saarbrücken (Germany)
Telefax: Int. code + (681)4105

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