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Evidence for the Formation of a $\mathrm{Ru^{III}}$–$\mathrm{Ru^{III}}$ Bond in a Ruthenium Corrole Homodimer[**]

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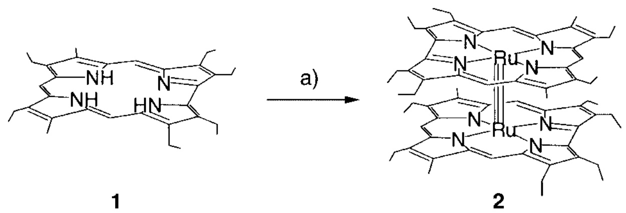
The formation of a ruthenium(II) porphyrin homodimer was first mentioned by Whitten and co-workers in 1975.[1] Nevertheless, the interaction between the two metal centers has been fully evidenced only in 1984 on the basis of an X-ray structure determination of [{Ru(oep)}$_2$].[2, 3] It was shown later that this type of ruthenium porphyrin homodimer can be involved in several catalytic reactions as well as in the coordination of gaseous molecules such as ethylene and carbon monoxide.[4, 5] Furthermore, these complexes are extremely air-sensitive and the one- or two-electron (chemical or electrochemical) oxidation of the dimer easily leads to the formation of the $\mathrm{Ru^{II}/Ru^{III}}$ and $\mathrm{Ru^{III}/Ru^{III}}$ species, respectively.[6] However, until now, no bisruthenium(III) porphyrin homodimer has been obtained by a direct insertion of the $\mathrm{Ru^{III}}$ cation into the porphyrin cavity.

To study the reactivity of tetrapyrrole metal complexes in high oxidation states, we focused on the synthesis and characterization of corrole metal complexes.[7–9] Indeed, the corrole macroring possesses a small four-nitrogen cavity (because of the presence of only three meso carbon atoms) and three NH groups which enhance the stabilization of metal cations in a high oxidation state.[10–12] Although as many as 18 different metal–corrole species are known, ruthenium corroles have never been synthesized. Moreover, many unsuccessful attempts have been made to metalate a corrole with ruthenium(III).[13] Starting from $\mathrm{RuCl_3}$ in dimethylformamide, Boschi et al. observed an insertion of a carbonyl group from the solvent into the pyrrole–pyrrole bond leading, after rearrangements, to a ruthenium(III) porphyrin. The same behavior was noted when using [$\mathrm{Ru_3(CO)_{12}}$] in 2-methoxyethanol, again a carbonyl group insertion, this time from the metal carbonyl complex, occurred affording a ruthenium(III) porphyrin.[13]

We have also attempted the metalation reaction of $\mathrm{H_3}$(hedmc)[3, 14] (**1**) with $\mathrm{RuCl_3}$ in carbonyl group free solvents with different boiling points, such as pyridine, xylene, benzonitrile and trichlorobenzene. No metalation reaction was noted after 72 h at reflux. The complex [{(cod)RuCl$_2$}$_2$][3] does not bear a carbonyl group and is more reactive than $\mathrm{RuCl_3}$ in many metalation reactions.[15] This $\mathrm{Ru^{II}}$ dimer is easily synthesized by the reaction of hydrated $\mathrm{RuCl_3}$ with cod[3] in boiling ethanol for 12 h. The reaction of **1** with an excess [{(cod)RuCl$_2$}$_2$] was carried out in refluxing 2-methoxyethanol with the presence of a trace amount of triethylamine (see Experimental Section). Triethylamine prevents the protonation of **1** by the HCl evolved during the metalation reaction. Furthermore, the reaction is easily carried out in an air atmosphere which enhances the oxidation of $\mathrm{Ru^{II}}$ to $\mathrm{Ru^{III}}$ necessary to form [{Ru(hedmc)}$_2$] (**2**, Scheme 1).[16]



1 **2**

Scheme 1. The formation of [{Ru(hedmc)}$_2$]; a) [{(cod)RuCl$_2$}$_2$], 2-methoxyethanol, triethylamine, reflux, 30 min.

By UV/Vis spectroscopy one can observe after 30 min of reaction the disappearance of the Q bands of the starting free base corrole and a large blue shift of the Soret band from 396 to 336 nm (Figure 1).

The formation of **2** is demonstrated by both the presence in the MALDI/TOF (matrix assisted laser desorption/ionization time of flight) mass spectrum of a peak pattern in the expected region (largest peak at 1186.53)[16] and the results of a single-crystal X-ray diffraction study.[17] No trace of a monomeric species is evidenced by mass spectrometry, thus confirming the presence of the pure, strongly bound dimer **2**. Figure 2a shows the molecular structure of **2** at $T = 112(2)$ K. In spite of the low-temperature X-ray diffraction measurements the atomic thermal parameters are quite large, resulting probably from a rotation of the dimer around the Ru–Ru axis. As

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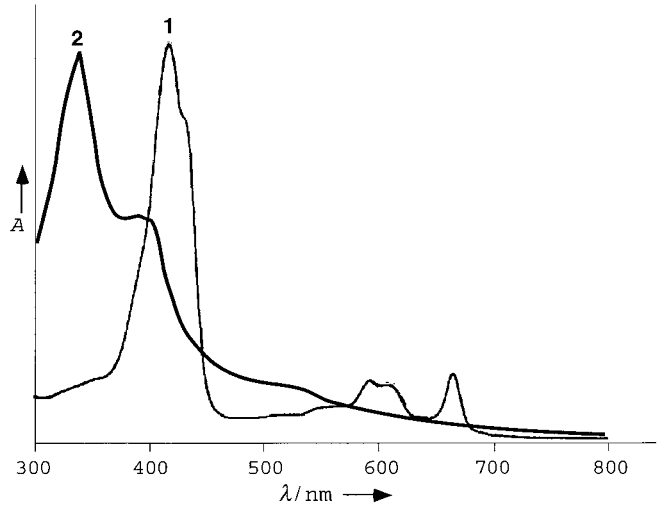

Figure 1. UV/Vis spectra of the corrole free-base **1** and the Ru dimer **2** recorded in dichloromethane.

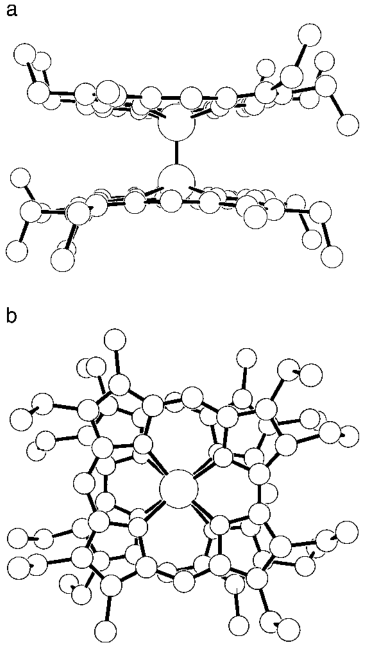

Figure 2. Structure of the ruthenium corrole homodimer **2**; a) viewed from the side, b) viewed from the top; hydrogen atoms are not shown; thermal ellipsoids are omitted for clarity (the corresponding ORTEP drawings are in the Supporting Information). Selected bond length [Å]: Ru–Ru 2.166(1).

suggested on the ORTEP view (see Supporting Information) a rotation about the Ru–Ru axis may be possible. But, as the actual thermal displacement parameter model is not totally satisfactory, a TLS+Ω study (translation, liberation, and screw analysis of the molecule, allowing the intramolecular motion of a particular group, if necessary)[18, 19] at multiple temperatures from room temperature down to 15 K will be undertaken to clarify the dynamics of this system. On the other hand, inspection of the systematic absences leads unambiguously to the space group $P2_1/c$, indicating that only one half of the dimer constitutes the asymmetric unit. This result is in favor of a centrosymmetric *C*s *anti* configuration of the ruthenium dimer. The crystal structure analysis[17] leads to the following main features: a) a Ru–Ru separation of 2.166(1) Å, b) a planar N4 geometry (within 0.011 Å), c) a doming effect, the Ru center being displaced 0.514(4) Å out of the N4 plane, because of the strong Ru–Ru interaction and the steric repulsions (including π-π interactions) between the macrocycles.

The overall number of d electrons for the two ruthenium atoms is ten thus leading to a spin state of zero.[6] One can reasonably assume that the local N4 geometry around the Ru center in **2** is close to that of [(p)Ru]$_2^{2+}$.[3] Therefore, from the qualitative MO diagram developed by Collman and Arnold the metal–metal bond order is expected to be three.[6] These assumptions are corroborated by preliminary ESR measurements which do not show any signals in CH_2Cl_2 at 100 K. Moreover, the diamagnetic character of **2** is further confirmed by the ^{1}H NMR spectrum which shows sharp resonance signals, observed between $\delta = 1.64$ to 8.78.[16] Furthermore, the Ru–Ru bond length of 2.166(1) Å is in accordance with a triple bond and correlates with reported X-ray data.[2, 20] Indeed, Ru–Ru bond lengths of 2.408(1) Å and 2.296(2) Å have been found for [{(oep)Ru}$_2$] (bond order 2) and [{(tpp)Ru}$_2$]$^+$[3] (bond order 2.5), respectively.[2, 20]

Complex **2** is the first ruthenium corrole derivative, and moreover, the first corrole complex exhibiting a metal–metal bond. Further investigations are underway to synthesize other Ru^{III}/Ru^{III} corrole dimers using the same reaction pathway. Such a procedure is applicable to other transition metals, for example, we have recently isolated a corrolatorhodium(III) dimer.[21] Using the "face-to-face" porphyrin-corrole bismacrocycles recently described by our group,[9] the synthesis of heterobinuclear species should be possible.

Experimental Section

A solution of H_3(hedmc) (**1**; 100 mg, 0.2 mmol), [{(cod)RuCl$_2$}$_2$] (226 mg, 0.4 mmol), and triethylamine (c.a. 100 μL) in 2-methoxyethanol was heated under reflux for 30 min. The solvent was evaporated under vacuum, the resulting solid was dissolved in dichloromethane and the excess ruthenium complex was removed by filtration. The product was crystallized from a mixture CH_2Cl_2/CH_3OH (1/1) to give [{Ru(hedmc)}$_2$] (**2**) in 72% yield (172.5 mg, 0.14 mmol).

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[16] Physical data: M.p. >350°C; ^{1}H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta = 8.78$ (s, 1H; H-10), 8.67 (s, 2H; H-5, H-15), 3.95 (m, 4H; H-2a, H-18a), 3.83 (q, 4H; H-3a, H-17a), 3.65 (m, 4H; H-8a, H-12a), 1.87 (t, 6H; H-2b, H-18b), 1.74 (t, 6H; H-3b, H-17b), 1.71 (s, 6H; H-7a, H-13a), 1.64 (t, 6H; H-8b, H-12b); ^{13}C NMR (125 MHz, CDCl$_3$, 25°C, TMS): $\delta = 140.1$, 138.O, 136.8, 136.0, 134.9, 131.5, 129.9, 129.1, 95.6 (C-10), 93.2 (C-5, 15), 21.1, 20.2, 20.1, 19.3, 17.8, 11.9; MALDI/TOF MS (%) m/z: 1186.53 (100), calcd for $C_{66}H_{78}N_8{}^{102}Ru_2$: 1186.45; IR (KBr): $\tilde{\nu} = 2962$ (CH), 2927 (CH), 2896 (CH), 1610, 1450, 1059, 822 cm^{-1}; UV/Vis (CH$_2$Cl$_2$) : λ_{max}[nm](ε) = 336 (103295), 393 (59071), 521 (15481); elemental analysis calcd (%) for $C_{66}H_{78}N_8Ru_2$: C 66.87, H 6.63, N 9.45; found: C 66.93, H 6.69, N 9.50.

[17] X-ray data: $C_{66}H_{78}Ru_2N_8$, crystals were obtained by slow diffusion of methanol in dichloromethane; crystal dimensions $0.40 \times 0.38 \times 0.10$ mm, monoclinic $P2_1/c$, $a = 14.2080(8)$, $b = 13.6160(8)$, $c = 16.1907(7)$ Å, $\beta = 113.322(3)°$, $V = 2876.3(3)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.369$ g cm^{-3}, μ(Mo) = 5.73 cm^{-1}. The measurement of the reflection intensities was carried out on a Enraf-Nonius Kappa-CCD diffractometer ($T = 112(2)$ K, Mo$_{K\alpha}$ radiation $\lambda = 0.71073$ Å); ϕ and ω scans with κ offsets; $2\theta_{max} = 55°$; 15324 measured reflections ($R_{int} = 0.053$). The structure was solved with direct methods and refined with F^2 against all independently observed reflections (4507); heavy atoms with anisotropic, H atoms with isotropic temperature factors); $R1 = 0.0957$, $wR2 = 0.2476$ (for $I > 2\sigma(I)$; total number of parameters 351, $\Delta\rho_{max} = 1.051$ e Å^{-3}, $\Delta\rho_{min} = -0.553$ e Å^{-3}. The programs used for solving and refinement of the structure were SHELXS-97 and SHELXL-97 (G. M. Sheldrick, University of Göttingen) respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141388. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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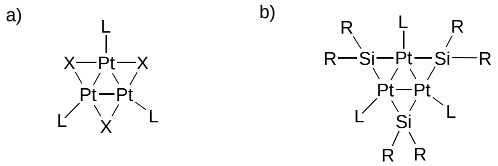
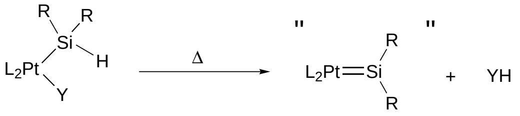
A Triangular Triplatinum Complex with Electron-Releasing SiPh$_2$ and PMe$_3$ Ligands: [{Pt(μ-SiPh$_2$)(PMe$_3$)}$_3$]**

Kohtaro Osakada,* Makoto Tanabe, and Tomoaki Tanase

Triangular complexes composed of three zerovalent transition metal centers are among the most extensively studied cluster compounds. The trinuclear Pt^0 complexes reported so far contain bridging CO or CNR ligands, which have significant π-acceptor character and stabilize complexes with low-valent metal centers (Scheme 1a).[1] Organosilyl ligands have not been commonly used as ligands for these cluster compounds, partly because of the mismatched coordination of a ligand having a significant σ-donor character and negligible π-acceptor capability with electron-rich metal centers. The electronic state and structure of Pt^0 complexes with organosilyl ligands would be of significant interest, but they have not yet been prepared.[2, 3] Since the target structure in Scheme 1b is a trimeric form of a platinum–silylene complex, a synthetic approach that uses such species as precursors might be successful. Owing to their intrinsic instability,[4, 5] mononuclear platinum–silylene complexes were obtained only by using well-designed precursors; however, they were postulated to arise by α-elimination from dialkyl- or diarylsilyl complexes of platinum (Scheme 2).[6, 7] We chose a diaryl-



Scheme 1. Triangular trinuclear complexes of platinum: a) known complexes, where X = CO, CNR, or other neutral ligands; b) target complexes with organosilyl ligands.



Scheme 2. Postulated formation of mononuclear platinum–silylene complexes by α-elimination.

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