Communications

Re–Pd Calixarene Complexes

Stepwise Construction of a Re–Pd Heterodinuclear Core Inside the Cavity of *p*-tBu-Calix[4]arene**

Kentarou Iwasa, Takuya Kochi, and Youichi Ishii*

Metallocalixarenes have recently received much interest as molecular models of metal species bound on polyoxo surfaces,^[1] as well as metalloreceptors with controlled structures.^[2,3] The majority of the metallocalixarenes so far developed are oxophilic group 4-6 transition-metal derivatives; few examples have been reported for late-transitionmetal complexes of unmodified calixarenes.^[3-6] However, recent studies have revealed that late transition metals can also form stable aryloxo and alkoxo complexes that have intriguing reactivities.^[7] This background prompted us to investigate the synthesis and properties of late-transitionmetal derivatives of calixarenes, and we have recently found that calix[4]arenes undergo site-selective and stepwise complexation with two $\{M(cod)^+\}$ fragments (M = Rh, Ir; cod =1,5-cyclooctadiene), where the first metal center is coordinated to the arene ring and the second is coordinated to the phenolic oxygen atoms at the narrow rim.^[4] With the intention to construct heterodinuclear late-transition-metal cores on

[*]	Prof. Dr. Y. Ishii
	Department of Applied Chemistry
	Faculty of Science and Engineering, Chuo University
	Kasuga, Bunkyo-ku, Tokyo 112-8551 (Japan)
	Fax: (+81) 3-3817-1895
	E-mail: ishii@chem.chuo-u.ac.jp
	K. Iwasa, T. Kochi
	Institute of Industrial Science
	The University of Tokyo
	Komaba, Meguro-ku, Tokyo 153-8505 (Japan)
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the calixarene scaffold, we have turned our attention to the synthesis and reactivities of high-valent rhenium derivatives of calixarenes. Herein we describe the synthesis and characterization of mononuclear rhenium p-tBu-calix[4]arene complexes and their use in the stepwise construction of a phenoxo-bridged Re–Pd heterodinuclear core inside the cavity of the calix[4]arene.

When a solution of *p*-*t*Bu-calix[4]arene-(OH)₄ (1) in THF was treated with *n*BuLi (3 equiv) and then allowed to react with [Ph₄P][ReOCl₄] (1.5 equiv),^[8] an anionic complex tentatively formulated as [Ph₄P][ReCl(O){*p*-*t*Bu-calix[4]arene-(O)₄]]·CH₂Cl₂·0.5 Et₂O (**2**·CH₂Cl₂·0.5 Et₂O) was obtained in 54% yield after repeated recrystallization (Scheme 1).^[9] Although the paramagnetism of the Re^{VI} center (μ_{eff}/μ_B = 1.3 in [D₆]acetone solution) prevented spectroscopic full characterization of **2**, its analytical, EPR, and IR ($\tilde{\nu}$ = 929 cm⁻¹, ν (Re=O)) data are in agreement with the chloro– oxo structure. Further characterization of the rhenium complex has been achieved by oxidation to a Re^{VII} species.



Scheme 1. Synthesis of rhenium complexes 2 and 3 a.

When complex 2 was treated with excess Ag₂O in THF at room temperature, the Re^{VII} complex [Ph₄P][ReO₂{*p*-*t*Bucalix[4]arene-(O)₄]] (3a) was obtained in 89% yield (Scheme 1). The formation of Re=O bonds is confirmed by the characteristic strong IR bands at 902 and 910 cm⁻¹. The ¹H NMR spectrum of **3a** shows two aromatic and two *t*Bu signals at $\delta = 7.06$, 6.96 ppm and $\delta = 1.29$, 1.07 ppm, respectively, as well as one set of CH₂ signals at $\delta = 4.51$ and 3.29 ppm (d, J = 13.7 Hz). This spectral feature is in full agreement with a formulation with an apparent $C_{2\nu}$ symmetry. The structure of this anion was crystallographically determined via the PPN salt [PPN][ReO₂{p-tBu-calix[4]arene- $(O_{4}]$ $2 Me_{2}CO \cdot 0.5 C_{6}H_{6}$ (**3b** $2 Me_{2}CO \cdot 0.5 C_{6}H_{6}$) (Figure 1; PPN = $(Ph_3P)_2N$.^[10] The rhenium atom is coordinated by the four phenolic oxygen atoms of the calix[4]arene ligand and two cis oxo ligands, in a distorted octahedral geometry. The Re(1)-O(5) and Re(1)-O(6) bond lengths at 1.717(5) and 1.714(5) Å, respectively, are typical for Re^{VII}=O double bonds.^[11] Two of the facing aromatic rings of the calix[4]arene ligand are very open, with a dihedral angle of 168.8°, so that



Figure 1. ORTEP diagram for the anionic part in $3b-2Me_2CO-0.5C_6H_6$. Thermal ellipsoids were set at 50%.

the calix[4]arene ligand adopts an elliptical cone conformation where the O(2) and O(4) atoms of the splayed phenoxo residues are mutually *cis* and occupy the *trans* positions of the oxo ligands. It should be noted that complexes **1** and **2** are the first calixarene–rhenium complexes in which the metal atom is directly bound to the body of calixarene, although several calixarene derivatives having a rhenium complex moiety as a pendant group have been synthesized.^[12]

Taking advantage of the anionic nature of the dioxorhenium species, complexation of a second transition-metal fragment with **3a** was examined. When an EtOH solution of **3a** was treated with the solvated allyl–palladium complex $[Pd(\eta^3-C_3H_5)(Me_2CO)_x](OTf)$ (OTf = OSO₂CF₃),^[13] the Re–Pd complex $[ReO_2[p-tBu-calix[4]arene-(O)_4]Pd(\eta^3-C_3H_5)]$ (**4**) was obtained in 75% yield (Scheme 2). The



Scheme 2. Synthesis of heterobimetallic complex 4.

¹H NMR signals for the allyl protons of **4** appear at $\delta = 4.01$ (tt, J = 11.7, 6.6 Hz, 1 H), 2.20 (d, J = 6.6 Hz, 2 H), and 1.20 ppm (d, J = 11.7 Hz, 2 H), and exhibit an extraordinary high-field shift compared with those of $[\{Pd(\eta^3-C_3H_5)Cl\}_2]$ ($\Delta\delta = 1.5-1.9$ ppm). This observation strongly suggests that the $\{Pd(\eta^3-C_3H_5)^+\}$ fragment is encapsulated in the calixarene pocket and surrounded by the aromatic rings. The signals for the calix[4]arene CH₂ protons are observed as a pair of doublets at room temperature ($\delta = 4.61$, 3.53 ppm, J = 14.4 Hz), indicating the dynamic behavior of the allyl group. These signals coalesce at -40 °C and split into four doublets at -80 °C ($\delta = 3.48$, 3.58, 4.32, 4.44 ppm, J = 14.8 Hz), which is in full agreement with the expected C_s symmetry of **4**.

The molecular structure of **4** was established by X-ray crystallography.^[10] An ORTEP drawing is shown in Figure 2, which clearly confirms that the $\{Pd(\eta^3-C_3H_5)^+\}$ fragment is situated in the cavity and coordinated by the two phenoxy



Figure 2. ORTEP diagram for complex **4**. Thermal ellipsoids were set at 50%.

oxygen atoms situated trans to the Re=O groups. The heterobimetallic {RePdO₂} core is planar, and the long Re(1)…Pd(1) interatomic separation at 3.4383(8) Å excludes any metal-metal bonding interaction. The dihedral angle of the two bridging phenoxo groups at 170.7° is comparable to that of **3b**, and the conformation of the calix[4] arene moiety is deformed only slightly by the coordination of the {Pd(η^3 - C_3H_5)⁺ fragment. Although a few alkali-metal salts of anionic calixarene complexes such as [Ta(OPh)₂{*p*-*t*Bu-calix[4]arene-(O)₄]Na(thf)₂] have been reported to adopt a similar coordination structure,^[14] complex **4** provides the first example where a heterodinuclear core composed of two different transition metals has been constructed inside the cavity of a calixarene ligand. Interestingly, complex 4 was the only bimetallic product detected in the reaction of 3a with $[Pd(\eta^3-C_3H_5)(Me_2CO)_x]^+$, and coordination of the terminal Re=O groups in 3a to the palladium center has not been observed.

In conclusion, we have synthesized mononuclear Re^{VI} and Re^{VII} complexes of **1** and found that the Re^{VII} dioxo complex **3** can be used to construct a Re–Pd heterodinuclear core inside the cavity of the calixarene. Although several homopolymetallic complexes of calixarenes have been described in literature,^[15] a methodology to synthesize heteropolynuclear transition-metal cores on the calixarene scaffold still remains to be developed. The present study opens a potential synthetic route for such a class of complexes.

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Communications

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- [8] The use of 3 equiv of *n*BuLi and 1.5 equiv of [PPh₄][ReOCl₄] gave the best result (54% yield); reactions with 2 and 4 equiv of *n*BuLi resulted in a lower yield of 2 (22–53% yield).
- [9] The preparative procedures and data for complexes **2–4** are explained in detail in the Supporting Information.
- [10] a) $3b \cdot 2Me_2CO \cdot 0.5C_6H_6$: $C_{89}H_{97}NO_8P_2Re$: ($M_r = 1556.90$); crystal size $0.20 \times 0.35 \times 0.35$ mm³, triclinic, space group $P\bar{1}$, a =13.044(2), b = 14.168(3), c = 22.880(5) Å, a = 80.51(2), $\beta =$ 88.96(2), $\gamma = 72.17(1)^{\circ}$, $V = 3967(1) \text{ Å}^3$, Z = 2, $\rho_{calcd} = 1.303 \text{ g cm}^{-3}$, $2\theta_{max} = 45.0^{\circ}$, T = 294(2) K; 10.865 reflections measured, 10361 unique (R(int) = 0.027) and 7693 $I > 3\sigma(I)$; Rigaku AFC7R four-circle automated diffractometer, MoKa radiation ($\lambda = 0.71069$ Å), graphite monochromator, Lorentzpolarization and absorption corrections ($\mu = 16.28 \text{ cm}^{-1}$, range of transmission = 0.80-1.00). The structure was solved by heavyatom Patterson methods and refined with the full-matrix, leastsquares method based on F (teXsan, Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1999), 838 parameters, R = 0.042, Rw = 0.043 for $I > 3\sigma(I)$; residual electron density $0.76/-0.68 \text{ e} \text{ Å}^{-3}$. The C and O atoms in the two solvating acetone molecules were included as fixed atoms; one of these molecules was found to be disordered and the corresponding C and O atoms were treated with 60% and 40% occupancies; b) 4: $C_{47}H_{57}O_6PdRe (M_r = 1010.57)$; crystal size $0.15 \times 0.40 \times 0.35$ mm³, monoclinic, space group C2/c, a =

24.763(3), b = 9.308(2), c = 19.239(2) Å, $\beta = 108.154(10)^{\circ}$, V =4213(1) Å³, Z = 4, $\rho_{calcd} = 1.593 \text{ g cm}^{-3}$, $2\theta_{max} = 55.0^{\circ}$, T =294(2) K; 5233 reflections measured, 4856 unique (R(int) =0.018), and 3885 $I > 2\sigma(I)$; Rigaku AFC7R four-circle automated diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), graphite monochromator, Lorentz-polarization and absorption corrections $(\mu = 33.46 \text{ cm}^{-1})$, range of transmission = 0.61–1.00). The structure was solved by heavy-atom Patterson methods and refined with the full-matrix, least-squares method based on F^2 (teXsan), 236 parameters, R2 = 0.102, wR = 0.159 for all data; residual electron density $2.51/-1.80 \text{ e} \text{ Å}^{-3}$. The allyl group was found to be disordered around the C2 axis, and the corresponding C and H atoms were included as fixed atoms with a 50% occupancy. CCDC-205916 ($3b \cdot 2Me_2CO \cdot 0.5C_6H_6$) and CCDC-205917 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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