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-tBu-calix[4]arene-(OH)$_4$ (**1**) in THF was treated with nBuLi (3 equiv) and then allowed to react with [Ph$_4$P][ReOCl$_4$] (1.5 equiv),[8] an anionic complex tentatively formulated as [Ph$_4$P][ReCl(O){p-tBu-calix[4]arene-(O)$_4$}]·CH$_2$Cl$_2$·0.5 Et$_2$O (**2**·CH$_2$Cl$_2$·0.5 Et$_2$O) 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 [D$_6$]acetone solution) prevented spectroscopic full characterization of **2**, its analytical, EPR, and IR ($\tilde{v}$ = 929 cm^{-1}, v(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.
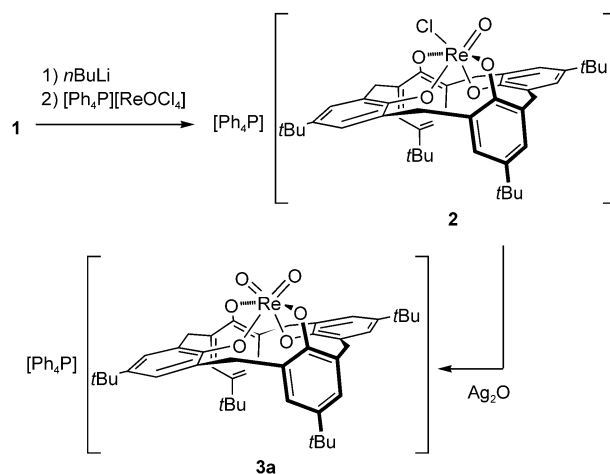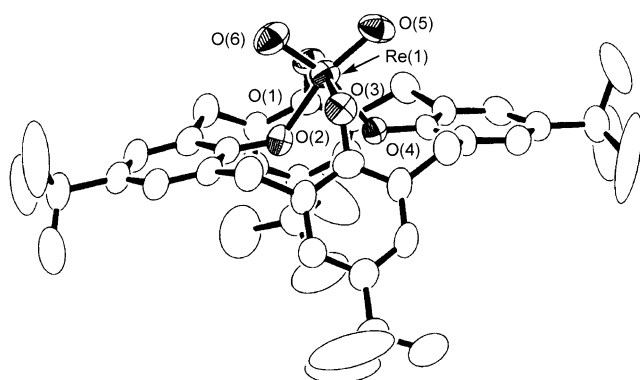
Re–Pd Calixarene Complexes

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-transition-metal 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-transition-metal 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

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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

When complex **2** was treated with excess Ag$_2$O in THF at room temperature, the Re^{VII} complex [Ph$_4$P][ReO$_2${p-tBu-calix[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 ^{1}H NMR spectrum of **3a** shows two aromatic and two tBu signals at δ = 7.06, 6.96 ppm and δ = 1.29, 1.07 ppm, respectively, as well as one set of CH$_2$ signals at δ = 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_{2v} symmetry. The structure of this anion was crystallographically determined via the PPN salt [PPN][ReO$_2${p-tBu-calix[4]arene-(O)$_4$}]·2 Me$_2$CO·0.5 C$_6$H$_6$ (**3b**·2 Me$_2$CO·0.5 C$_6$H$_6$) (Figure 1; PPN = (Ph$_3$P)$_2$N).[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**·2 Me$_2$CO·0.5 C$_6$H$_6$. 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(η³-C$_3$H$_5$)(Me$_2$CO)$_x$](OTf) (OTf = OSO$_2$CF$_3$),[13] the Re–Pd complex [ReO$_2${*p*-*t*Bu-calix[4]arene-(O)$_4$}Pd(η³-C$_3$H$_5$)] (**4**) was obtained in 75% yield (Scheme 2). The
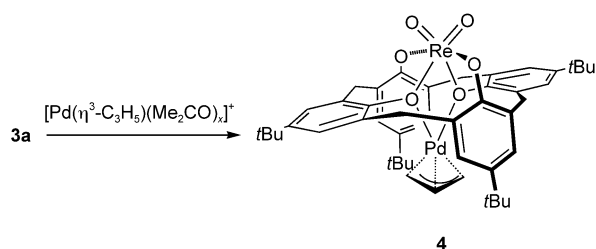
Scheme 2. Synthesis of heterobimetallic complex **4**.

¹H NMR signals for the allyl protons of **4** appear at δ = 4.01 (tt, *J* = 11.7, 6.6 Hz, 1H), 2.20 (d, *J* = 6.6 Hz, 2H), and 1.20 ppm (d, *J* = 11.7 Hz, 2H), and exhibit an extraordinary high-field shift compared with those of [{Pd(η³-C$_3$H$_5$)Cl}$_2$] (Δδ = 1.5–1.9 ppm). This observation strongly suggests that the {Pd(η³-C$_3$H$_5$)$^+$} fragment is encapsulated in the calixarene pocket and surrounded by the aromatic rings. The signals for the calix[4]arene CH$_2$ protons are observed as a pair of doublets at room temperature (δ = 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 (δ = 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(η³-C$_3$H$_5$)$^+$} fragment is situated in the cavity and coordinated by the two phenoxy
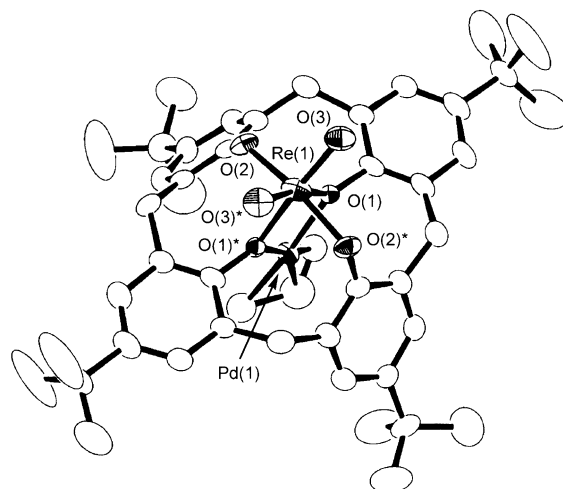
Figure 2. ORTEP diagram for complex **4**. Thermal ellipsoids were set at 50%.

oxygen atoms situated *trans* to the Re=O groups. The heterobimetallic {RePdO$_2$} 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(η³-C$_3$H$_5$)$^+$} 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(η³-C$_3$H$_5$)(Me$_2$CO)$_x$]$^+$, 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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[8] The use of 3 equiv of *n*BuLi and 1.5 equiv of [PPh$_4$][ReOCl$_4$] 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**·2 Me$_2$CO·0.5 C$_6$H$_6$: C$_{89}$H$_{97}$NO$_8$P$_2$Re: (M_r = 1556.90); crystal size 0.20 × 0.35 × 0.35 mm^3, triclinic, space group $P\bar{1}$, a = 13.044(2), b = 14.168(3), c = 22.880(5) Å, α = 80.51(2), β = 88.96(2), γ = 72.17(1)°, V = 3967(1) Å^3, Z = 2, ρ_{calcd} = 1.303 g cm^{-3}, $2\theta_{max}$ = 45.0°, T = 294(2) K; 10865 reflections measured, 10361 unique (R(int) = 0.027) and 7693 $I > 3\sigma(I)$; Rigaku AFC7R four-circle automated diffractometer, Mo$_{K\alpha}$ radiation (λ = 0.71069 Å), graphite monochromator, Lorentz-polarization and absorption corrections (μ = 16.28 cm^{-1}, range of transmission = 0.80–1.00). The structure was solved by heavy-atom Patterson methods and refined with the full-matrix, least-squares 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 e 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$_6$PdRe (M_r = 1010.57); crystal size 0.15 × 0.40 × 0.35 mm^3, monoclinic, space group $C2/c$, a = 24.763(3), b = 9.308(2), c = 19.239(2) Å, β = 108.154(10)°, V = 4213(1) Å^3, Z = 4, ρ_{calcd} = 1.593 g cm^{-3}, $2\theta_{max}$ = 55.0°, 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 (λ = 0.71069 Å), graphite monochromator, Lorentz-polarization and absorption corrections (μ = 33.46 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 e Å^{-3}. The allyl group was found to be disordered around the C_2 axis, and the corresponding C and H atoms were included as fixed atoms with a 50% occupancy. CCDC-205916 (**3b**·2 Me$_2$CO·0.5 C$_6$H$_6$) 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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