

Unexpected Pt^{II} Migration between the Calixarene Oxygen Atoms

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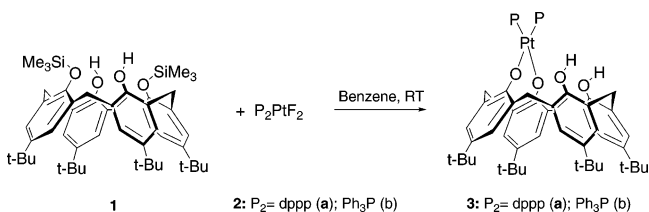
Reaction between the 1,3-bis(trimethylsilyl) ether of calix[4]arene and platinum(II) difluoro complexes unexpectedly results in the formation of the 1,2-bridging platinum(II) calixarene complex, which, upon treatment with 2 equiv of acyl chloride, reinstates the 1,3-disubstitution pattern in the calixarene moiety.

While the coordination of metal ions to the oxygen atoms of the calixarene scaffolds has been extensively studied during the last 2 decades, nearly all of these studies involved highly oxophilic early and middle-row transition metals.^{1,2} In the absence of a pendant soft donor ligand,³ coordination of the Pt group metals to the oxygen atoms competes with the more favorable η^6 coordination to the calixarene aromatic rings.⁴ Such competition was recently exemplified by Ishii and co-workers, who demonstrated that a Rh center can be coordinated to the lower calix[4]arene (calixarene) rim only after one of the metal ions is attached to the phenoxide aromatic ring.⁵ To circumvent this problem, we thought of utilizing a strategy that directs a late transition metal toward oxygen atoms of the lower rim. Silyl-protected calixarene molecules⁶ appear to be a suitable starting point because the protective groups can easily be removed by reaction with the fluoride ion. As late-transition-metal fluoro complexes can serve as sources of highly active fluoride ions,⁷ we were

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- (1) For general references, see: (a) *Calixarenes Revisited*; Gutsche, C. D., Ed.; Springer: New York, 1998. (b) Bohmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713. (c) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713. (d) Ludwig, R. *Fresenius' J. Anal. Chem.* **2000**, *367*, 103.
- (2) For reviews on transition-metal calixarene chemistry, see: (a) Wieser, C.; Dieleman, C. B.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93. (b) Harvey, P. D. *Coord. Chem. Rev.* **2002**, *233–234*, 289. (c) Petrella, A. J.; Raston, C. L. *J. Organomet. Chem.* **2004**, *689*, 4125. (d) Sliwa, W. *Croat. Chem. Acta* **2002**, *75*, 131. (e) Floriani, C.; Floriani-Moro, R. *Adv. Organomet. Chem.* **2001**, *47*, 167.
- (3) Jeunesse, C.; Armspach, D.; Matt, D. *Chem. Commun.* **2005**, 5603.
- (4) Staffilani, M.; Hancock, K. S. B.; Steed, J. W.; Holman, K. T.; Atwood, J. L.; Junega, R. K.; Burkhalter, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 6324.
- (5) (a) Ishii, Y.; Onaka, K.-I.; Hirakawa, H.; Shiramizu, K. *Chem. Commun.* **2002**, 1150. (b) A late transition metal was incorporated inside the calixarene cavity in a bimetallic system: Iwasa, K.; Kochi, T.; Ishii, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3658.
- (6) Anwender, R.; Eppinger, J.; Nagl, I.; Scherer, W.; Tafipolsky, M.; Sirsch, P. *Inorg. Chem.* **2000**, *39*, 4713.
- (7) Grushin, V. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 994.

Scheme 1



interested in investigating the reactivity of platinum(II) difluoro complex dpppPtF_2 ($\text{dppp} = 1,3\text{-diphenylphosphinopropane}$) **2a**⁸ with 1,3-bis(trimethylsilyl) calixarene ether, **1**. The reaction between the two compounds in benzene at room temperature overnight resulted in the formation of TMS–F (as observed by ¹⁹F NMR spectroscopy) and a new Pt complex **3a** (Scheme 1), which showed a single resonance in the ³¹P NMR spectrum at -8.35 ppm ($J_{\text{PtP}} = 3492.6$ Hz). The same product was also observed when the reaction was performed in chloroform.

Surprisingly, the ¹H NMR spectrum of the new compound showed an asymmetric pattern for the bridging CH₂ groups, inconsistent with the expected 1,3-coordination mode. Six sets of doublets were observed in this spectrum for the CH₂ groups. One of these signals appeared at 6.50 ppm, a very low field resonance for this group. The phenolic H atoms showed a sharp singlet at 10.40 ppm,^{5a} again far downfield from the value expected for the disubstituted calixarene molecule. Single crystals of **3a** were obtained, upon slow evaporation of its CH₂Cl₂/pentane solution, and subjected to X-ray analysis.⁹ The structure of **3a** (Figure 1) revealed that the Pt center had indeed replaced both silyl groups in **1**. However, an unprecedented concomitant metal migration to

- (8) Yahav, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.* **2003**, *125*, 13634.
- (9) X-ray structure data for **3a**: C₇₁H₈₀O₄P₂Pt·CH₂Cl₂, $M = 1339.31$, $0.25 \times 0.25 \times 0.15$ mm³, monoclinic, space group $P2_1/c$, $a = 21.0646(3)$ Å, $b = 12.6317(2)$ Å, $c = 24.6998(5)$ Å, $\beta = 94.8104(6)^\circ$, $V = 6549.02(19)$ Å³, $Z = 4$, Nonius Kappa CCD, Mo K α radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 110(2)$ K, 15 672 collected reflections, and 11 587 unique reflections ($R_{\text{int}} = 0.0530$). The structure was determined by direct methods (SIR-97) and refined anisotropically by least squares on F^2 data (SHELXL-97; 746 parameters with no restraints). $R1 = 0.0475$, $wR2 = 0.0753$ for 11 587 data with $I > 2\sigma(I)$, and $R1 = 0.1106$, $wR2 = 0.1249$ for all unique data. One of the t-Bu groups is rotationally disordered and modeled so. The CH₂-Cl₂ solvent located inside the calix suffers also from a significant positional/orientational disorder, which however could not be resolved.

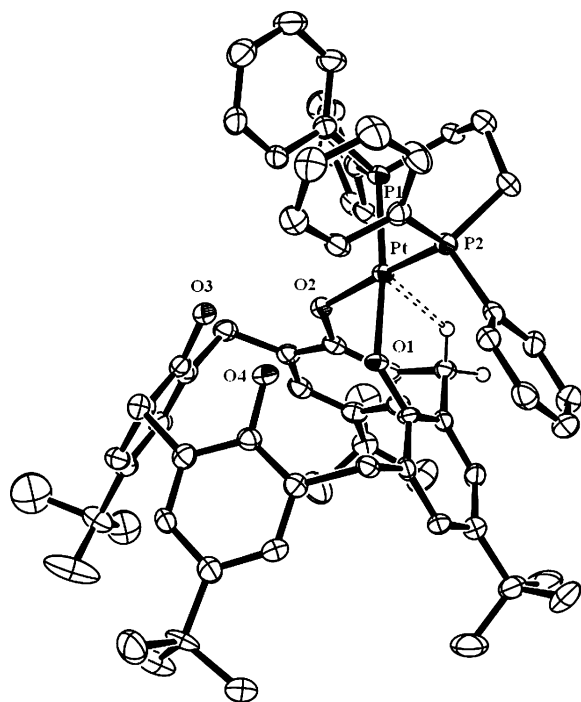
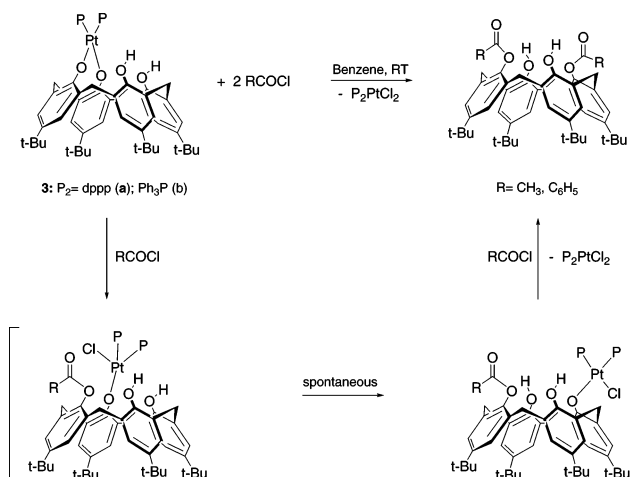


Figure 1. ORTEP drawing of a molecule of **3a** at 50% probability. H atoms and the entrapped solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt–O1, 2.051(3); Pt–O2, 2.061(3); Pt–P1, 2.2293(11); O1–C28, 1.354(5); O3–C17, 1.380(5); O1–Pt–O2, 84.87(12); O1–Pt–P1, 171.70(9); P1–Pt–P2, 91.13(4).

the 1,2-positions also occurred. The complex crystallizes with a solvent molecule (CH_2Cl_2) entrapped inside the calixarene cavity. An interesting crystallographic feature of **3a** is the short distance of 2.254 Å between the metal center and axial H atom of the calixarene bridging CH_2 group (dashed line in Figure 1). This short interaction is responsible for an extreme downfield chemical shift of this H atom, which appears at 6.50 ppm in the ^1H NMR spectrum. The bond distances Pt–O1 and Pt–O2 of 2.051(3) and 2.061(3) Å, respectively, are almost identical with the O1–Pt–O2 and P1–Pt–P2 angles, being close to 90° , demonstrating a nearly perfect square-planar arrangement at the metal center. This arrangement seems to be the driving force for the 1,2 Pt shift because transition-metal complexes with the 1,3-coordination mode are well-known and show high stability. We also reacted **1** with a difluoroplatinum(II) complex bearing monodentate phosphine ligands, $(\text{Ph}_3\text{P})_2\text{PtF}_2$, **2b**. Again, only the 1,2-disubstituted platinum(II) calixarene complex **3b** was obtained in this case, indicating that this substitution pattern is not imposed by the presence of a chelating diphosphine ligand. Because of a larger steric bulk of the triphenylphosphine ligand, the signal of the endocyclic CH_2 group hydrogen now appears even further downfield at 7.39 ppm.

The large downfield shift of the axial hydrogen atom, accompanied by the short metal–H distance, has previously been observed for late-transition-metal calixarene systems.^{5a,10} While regular agostic interactions normally cause an upfield

Scheme 2



shift of the hydrogen resonance,¹¹ there are many instances of the opposite effect in d^8 square-planar complexes.¹² In these cases, the large downfield shift was proposed to be a result of the metal orbital anisotropy effect directed toward an axial or pseudoaxial H atom.¹³ The X-ray structure of **3a** shows that the aromatic rings of the phosphine ligand are far away from the Ar– CH_2 –Ar H atoms and their ring currents are unlikely to be responsible for the large downfield shifts. The axial H atom is also located far away from the oxygen atoms of the calixarene lower rim (>2.7 Å) to interact with their lone pairs.¹⁰

In both cases, **2a** and **2b**, the reaction with the calixarene ligand was complete within several hours at room temperature and no formation of the 1,3-disubstituted product was observed. The same substitution pattern was also obtained with the calixarene ligand lacking the bulky t-Bu groups in the para position to the phenolic oxygen atoms, showing that the Pt^{II} coordination to the lower rim is not driven by steric factors. As complexes **3a** and **3b** represent the first example of a monometallic late-transition-metal calixarene complex with a metal–O coordination mode, we were interested in studying their reactivity. The addition of 2 equiv of acyl halide to either **3a** or **3b** in benzene resulted in a rapid precipitation of the corresponding platinum(II) dichloride complex. Unexpectedly, the formation of the 1,3-disubstituted (and not 1,2-disubstituted calixarene) esters was observed as organic products (Scheme 2). The addition of less than 2 equiv of acyl chloride gave a mixture of the 1,3-disubstituted calixarene ester along with unreacted complex **3**. These data indicate that, in a stepwise reaction, the Pt center migrates to the less sterically hindered position (Scheme 2).

When less reactive electrophiles, such as iodomethane or benzyl bromide, were used, the reactions were sluggish and required long times and a large excess of the reagents. Reaction of **3a** with α -bromoethylbenzene at 50°C for 2

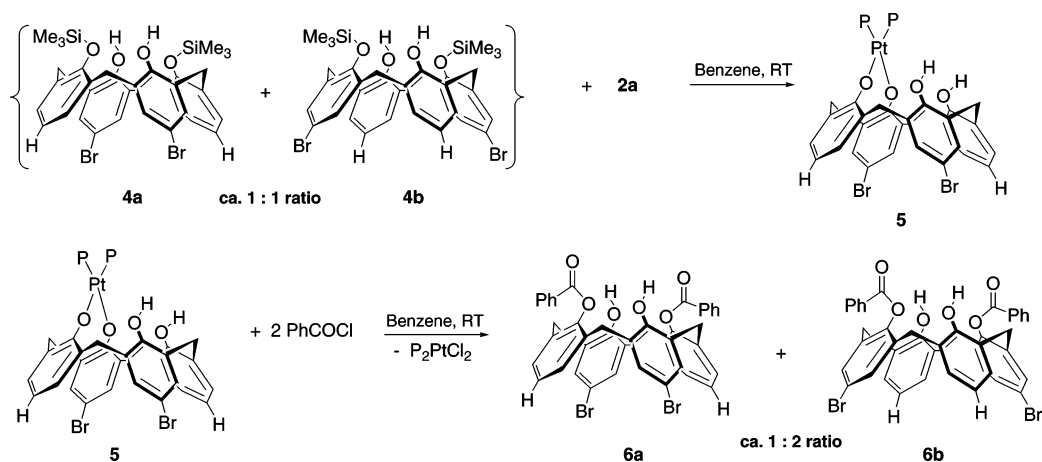
(10) Dieleman, C. B.; Marsol, C.; Matt, D.; Kyritsakas, N.; Harriman, A.; Kintzinger, J.-P. *J. Chem. Soc., Dalton Trans.* **1999**, 4139.

(11) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, 36, 1.

(12) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, 254, 105.

(13) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, 29, 1812.

Scheme 3



days gave a mixture of the monosubstituted and 1,3-disubstituted calixarene; however, a very small amount of styrene was observed in the reaction mixture. These data suggest that the acylation and alkylation of the phenolic oxygen atoms proceed via the nucleophilic substitution mechanism, without the change in the metal's oxidation state. The oxidative addition–reductive elimination mechanism is unlikely to operate in this system because large amounts of styrene would be expected in the reaction with α -bromoethylbenzene. The nonionic character of the Pt–O bonds explains the sluggish reactivity of complexes **3** toward weak electrophiles. It also implies that this reactivity should be dependent on the stability of the Pt–aryl oxide bond. To verify this, we decided to investigate the reactivity of 1,3-bis(trimethylsilyl) ethers of calixarenes bearing nonidentical aromatic rings. The 1:1 mixture of 1,3-bis(trimethylsilyl) ethers of the dibromocalixarene, **4a** and **4b**, was prepared by refluxing a solution of dibromocalixarenetetraphenol with $(\text{TMS})_2\text{NH}$ in *p*-xylene.⁶ As expected, treatment of this mixture with **2a** gave a single complex **5** (Scheme 3). This complex shows two different phenolic proton signals in the ^1H NMR spectrum at 10.1 and 10.5 ppm, indicating that no fluxional processes occur in the platinum calixarene complexes at room temperature. Reaction of **5** with PhCOCl produced two isomeric 1,3-dibenzoyl esters, **6a** and **6b**, in an approximately 1:2 ratio. Thus, the Pt–O bond of the Br-substituted phenolic ring breaks preferentially over the Pt–O bond of the nonsubstituted phenolate.

This preference for the formation of **6b** correlates with the Pt–OAr bond strength¹⁴ rather than the basicity of the phenolates.¹⁵ The Pt–O bond cleavage is followed by rapid Pt migration to the position opposite to the first ester group. Interestingly, direct acylation of the 1,3-dibromo-substituted calixarenetetraphenol with benzoyl chloride under the standard basic conditions¹⁶ affords a 1:1 mixture of **6a** and **6b**.

The results presented herein demonstrate that late-transition-metal fluorides can be used as an efficient entrance point toward the synthesis of O-bound metal calixarene complexes. Unlike more oxophilic early metals, Pt complexes strongly favor the 1,2-binding mode. However, the 1,3-substitution pattern becomes more attractive once the metal is attached to a single phenolic oxygen atom.

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Supporting Information Available: Characterization of complexes **3–5**, including crystallographic data for complex **3a** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Dockter, D. W.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1996**, *118*, 4846.
- (15) Gross, K. C.; Seybold, P. G.; Hadad, C. M. *Int. J. Quantum Chem.* **2002**, *90*, 445.
- (16) van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1990**, *55*, 5639.