COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Ti–Mo heterobimetallic thiacalix[4]arene complex containing an unusual α-agostic μ_2-η^5:η^2-cyclopentadienyl ligand

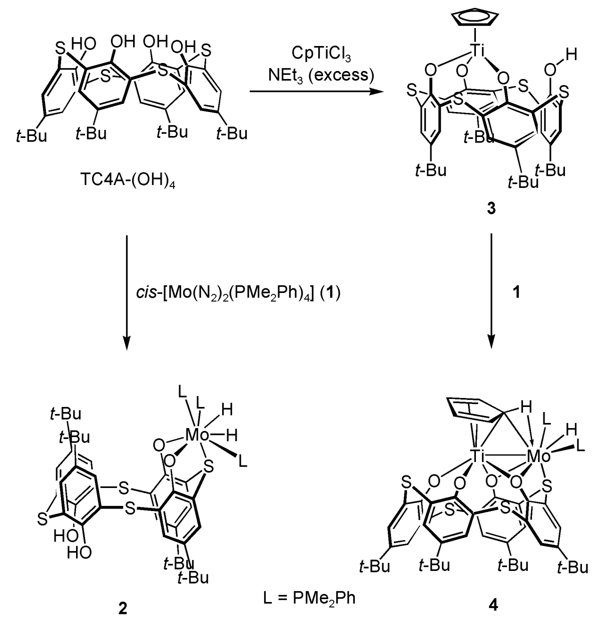
Shin Takemoto†,[b] Shinpei Tanaka,[a] Yasushi Mizobe[b] and Masanobu Hidai*[a]
[a] *Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan. E-mail: hidai@rs.noda.tus.ac.jp*
[b] *Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan*

Received (in Cambridge, UK) 6th January 2004, Accepted 3rd February 2004
First published as an Advance Article on the web 26th February 2004

A stepwise reaction of *p-tert*-butylthiacalix[4]arene (TC4A–(OH)$_4$) with [CpTiCl$_3$]–NEt$_3$ and *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] afforded a new Ti–Mo heterobimetallic complex [TC4A–(O)$_4$Ti(μ_2-C$_5$H$_5$)MoH(PMe$_2$Ph)$_2$] which shows an unusual α-agostic μ_2-η^5:η^2-coordination of a cyclopentadienyl ligand.

Well-defined bimetallic complexes have been the subject of intense research activity because they exhibit diverse patterns of bonding and reactivity that are not observed for monometallic complexes.[1] A major strategy taken toward their development has involved the use of preorganised binucleating ligands with the ability to coordinate to several metal ions.[2] Among such ligands, thiacalixarenes and their derivatives have recently attracted much attention.[3,4] Similarly to the conventional methylene-bridged calixarenes,[5] they are able to act as macrocyclic aryloxy ligands, and the incorporation of S-donor atoms between the phenol units has offered a number of new ligand characteristics, including the increased number of metal binding sites and an enhanced affinity toward soft low-valent metals, as exemplified by an ion extraction study[6] and the crystallographic characterization of polynuclear complexes.[7,8]

Recently, we have reported the reaction of *p-tert*-butylthiacalix[4]arene (TC4A–(OH)$_4$) with the Mo(0) dinitrogen complex *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**1**), which affords the Mo(IV) dihydride complex **2** *via* double oxidative addition of the phenolic O–H bonds to the low valent Mo centre (Scheme 1).[9] Here we describe the synthesis and structural characterization of a Ti–Mo heterobimetallic complex [TC4A–(O)$_4$Ti(μ_2-η^5:η^2-C$_5$H$_5$)MoH(PMe$_2$Ph)$_2$] (**4**). The preparation involves incorporation of a cyclopentadienyl titanium fragment into the thiacalix[4]arene ligand to obtain a partially *O*-metallated derivative [TC4A–(OH)(O)$_3$TiCp] (**3**), followed by its reaction with the molybdenum complex **1**. To the best of our knowledge, complex **4** represents the first heterobimetallic complex incorporating a thiacalixarene ligand. Additionally, we have found an unprecedented α-agostic μ_2-η^5:η^2-coordination of the cyclopentadienyl ligand in the Ti–Mo heterobimetallic complex **4**.



Scheme 1

The mononuclear titanium complex **3**‡ was prepared in 30% yield from the reaction of TC4A–(OH)$_4$ with [CpTiCl$_3$] in THF in the presence of triethylamine. An X-ray diffraction study revealed the coordination of three aryloxy groups to the Ti centre (Fig. 1).§ The remaining phenol unit as well as the four thioether sulfur atoms exhibit no direct bonding interaction with Ti.

Complex **3** reacts smoothly with the molybdenum complex **1** in THF at 60 °C. After subsequent chromatographic workup and recrystallization, the Ti–Mo heterobimetallic complex **4** was isolated in 23% yield as dark blue microcrystals.[10] The ^{1}H NMR spectrum of **4** exhibits a hydride resonance at δ −0.50 ppm that appears as a triplet due to coupling with two phosphorus nuclei. The ^{1}H non-decoupled ^{31}P NMR spectrum shows a doublet at δ 32.5 ppm with the same J_{PH} value for the hydride resonance. These spectroscopic features are consistent with the incorporation of {MoH(PMe$_2$Ph)$_2$} unit in the molecule. The heterodinuclear structure of **4** was unequivocally determined by an X-ray diffraction study (Fig. 2).§ The Ti atom is coordinated by the four aryloxy groups of the thiacalix[4]arene ligand, whereas the Mo unit is incorporated by the coordination of tridentate diaryloxo/thioether donor set.

An interesting feature of the structure of **4** is the μ_2-coordination of the cyclopentadienyl ligand. It is η^5-bonded to Ti, and η^2 to Mo. The bonding with Mo contains the α-agostic C–H···Mo interaction (Mo–H(2) = 2.121(9) Å). While the five ring carbon atoms constitute an almost planar ring, the agostic C–H group is bent away from Mo by 23° out of the mean plane of the cyclopentadienyl ring. Furthermore, the four non-bridging carbon atoms exhibit two short (1.31(2) and 1.33(2) Å) and one long (1.47(2) Å) C–C bond distances similar to the η^4-diene ligands bound to weakly π-basic metals.[11] These structural features suggest that the bridging carbon atom, C(21), possesses considerable degree of sp^3 character, and the negative charge of the cyclopentadienyl ligand is localized on this carbon atom. In agreement with this formulation, the four non-bridging carbon atoms exhibit much longer Ti–C bonds than the Ti–C(21) bond. The latter is comparable to those in the bridging alkyl complex of Ti.[12] The Mo–C(21) distance is slightly longer than the Mo–C bond length for the η^1-C$_5$H$_5$ ligand in [(η^5-

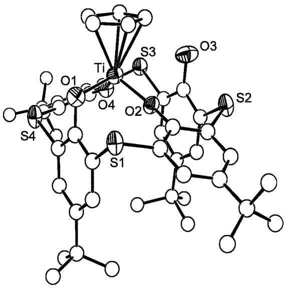


Fig. 1 ORTEP diagram of **3**.

---

† *Present address*: Department of Chemistry, Faculty of Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan.

DOI: 10.1039/b316972c

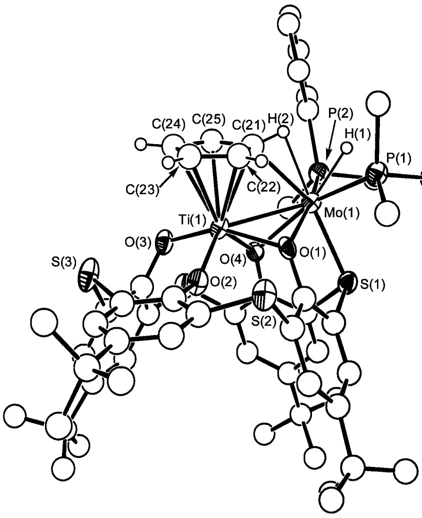


Fig. 2 ORTEP diagram of **4**: Ti(1)–Mo(1) 2.730(3), Ti(1)–O(1) 1.983(9), Ti(1)–O(2) 1.925(9), Ti(1)–O(3) 1.996(10), Ti(1)–O(4) 2.084(9), Ti(1)–C(21) 2.285(15), Ti(1)–C(22) 2.410(16), Ti(1)–C(23) 2.444(17), Ti(1)–C(24) 2.419(17), Ti(1)–C(25) 2.319(16), Mo(1)–O(1) 2.154(9), Mo(1)–O(4) 2.191(9), Mo(1)–S(1) 2.373(4), Mo(1)–P(1) 2.562(5), Mo(1)–P(2) 2.402(4), Mo(1)–C(21) 2.325(17), Mo(1)–H(1) 1.78(11), Mo(1)–H(2) 2.121(9), C(21)–C(22) 1.36(2), C(21)–C(25) 1.43(2), C(22)–C(23) 1.33(2), C(23)–C(24) 1.47(2), C(24)–C(25) 1.31(2) Å.

$C_5H_5)_2(\eta^1\text{-}C_5H_5)Mo(NO)]$.[13] The σ- and π-coordinating μ_2-cyclopentadienyl ligand has been observed in $[(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-}C_5H_5)Sc]_2$,[14] but the α-agostic μ_2-cyclopentadienyl is unprecedented. Such agostic interaction in the bimetallic cyclopentadienyl complex would provide some insights into the mechanism of the formation of ring metallated cyclopentadienyl derivatives such as lithioferrocene,[15] although we have no evidence for C–H bond cleavage in the present system. The Ti–Mo distance of 2.730(9) Å in **4** indicates some bonding interactions between these metals, which may include the Ti–C(21)–Mo three-centre-two-electron bonding and Mo–Ti dative interaction.

In the ^{1}H NMR spectrum of **4**, the cyclopentadienyl resonances appear as considerably broadened signals around δ 6.48 and 2.38 ppm in *ca.* 4 : 1 intensity ratio. The latter is tentatively assigned as the agostic C–H resonance.

In summary, we prepared a new Ti–Mo heterobimetallic complex that exhibits unique structural features, including an unprecedented α-agostic μ_2-η^5:η^2-coordination of a cyclopentadienyl ligand. The present work demonstrates the usefulness of thiacalix[4]arene as binucleating ligand for the synthesis of heterobimetallic complex. Further investigation into the chemical properties of **3** and **4**, as well as preparation of other heterobimetallic complexes are now in progress.

The authors are grateful to the Japan Society for the Promotion of Science (JSPS) for financial support.

Notes and references

‡ *Synthesis and characterization of* **3**: A 50 mL Schlenk flask was charged with TC4A–$(OH)_4$ (900 mg, 1.25 mmol), $[CpTiCl_3]$ (275 mg, 1.25 mmol), and THF (25 mL), and the mixture was stirred for several minutes to form an orange solution. Triethylamine (0.70 mL, 5.0 mmol) was then added to the solution, which caused a rapid change in color to dark red. The reaction mixture was stirred at room temperature for 24 h, and then filtered. The volatiles were removed under reduced pressure, and the residue was extracted with THF (20 mL). Concentration of the extract to 5 mL followed by slow diffusion of hexanes (30 mL) gave **3** as orange crystals. Yield 290 mg, 28%. Anal. Calcd for $C_{45}H_{50}O_4S_4Ti$: C, 65.04; H, 6.06. Found: C, 65.34; H, 6.31%. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.51, 7.36, 7.04, 6.72 (m, 2H each, Ar), 6.96 (s, 5H, C_5H_5), 1.36 (s, 18H, *t*-Bu), 1.10, 0.68 (s, 9H each, *t*-Bu). Crystal data for **3**: triclinic, space group $P\bar{1}$, a = 13.483(3), b = 16.930(8), c = 20.649(6) Å, α = 109.90(3)°, β = 95.721(19)°, γ = 93.84(3)°, V = 4384(3) Å^3, T = 296 K, Z = 2, $\mu(MoK\alpha)$ = 4.26 cm^{-1}, 16123 reflections measured, 15406 unique (R_{int} = 0.1122), $R1$ = 0.0645, $wR2$ = 0.2249, GOF = 1.037.

Synthesis and characterization of **4**: A THF solution (10 mL) containing **1** (141 mg, 0.20 mmol) and **3** (166 mg, 0.20 mmol) was stirred at 60 °C for 12 h. The resultant greenish brown solution was loaded onto a column of alumina. Elution with diethyl ether gave a blue band, which was collected and evaporated to dryness. Recrystallization of the residue from dichloromethane–hexanes afforded **4** as dark blue microcrystals. Yield 55 mg, 23%. Anal. Calcd for $C_{61}H_{72}O_4P_2S_4MoTi$: C, 60.89; H, 6.03. Found: C, 60.56; H, 6.35. ^{1}H NMR (CD_2Cl_2, −40 °C): δ 7.48, 7.43, 7.36, 7.25 (m, 2H each, Ar), 7.26–7.18 (m, 10H, PMe_2Ph), 6.48 (br, 4H, C_5H_5), 2.38 (br, 1H, C_5H_5), 1.63, 1.34 (t, 6H each, PMe_2Ph), 1.17, 1.16 (s, 18H each, *t*-Bu), −0.50 (t, $^2J_{PH}$ = 92 Hz, Mo–H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 32.5 (s). Crystal data for $\mathbf{4}\cdot(C_6H_6)_{0.5}$: orthorhombic, space group *Pbca*, a = 23.430(10), b = 23.594(11), c = 22.051(9) Å, V = 12190(9) Å^3, T = 296 K, Z = 8, $\mu(MoK\alpha)$ = 5.72 cm^{-1}, 70858 reflections measured, 10290 unique (R_{int} = 0.2589), $R1$ = 0.1726, $wR2$ = 0.2878, GOF = 1.280.

§ CCDC 228239 and 228240. See http://www.rsc.org/suppdata/cc/b3/b316972c/ for crystallographic data in .cif or other electronic format.

1 *Metal Clusters in Chemistry*, eds. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, 1999; *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, eds. R. D. Adams and F. A. Cotton, Wiley-VCH, New York, 1998; M. Hidai in *Perspectives in Organometallic Chemistry*, eds. C. G. Screttas and B. R. Steele, Royal Society of Chemistry, Cambridge, UK, 2003, p. 62.

2 D. G. McCollum and B. Bosnich, *Inorg. Chim. Acta*, 1998, **270**, 13; R. M. Bullock and C. P. Casey, *Acc. Chem. Res.*, 1987, **20**, 167.

3 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971.

4 Derivatives of thiacalixarenes: N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari and S. Miyano, *Tetrahedron Lett.*, 1998, **39**, 7559; P. Rao, M. W. Hosseini, A. D. Cian and J. Fischer, *Chem. Commun.*, 1999, 2169; H. Katagiri, N. Iki, T. Hattori, C. Kabuto and S. Miyano, *J. Am. Chem. Soc.*, 2001, **123**, 779.

5 C. Floriani and R. Floriani-Moro, *Adv. Organomet. Chem.*, 2001, **47**, 167; C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93.

6 N. Iki, N. Morohashi, F. Narumi and S. Miyano, *Bull. Chem. Soc. Jpn.*, 1988, **71**, 1597.

7 T. Kajiwara, N. Kon, S. Yokozawa, T. Ito, N. Iki and S. Miyano, *J. Am. Chem. Soc.*, 2002, **124**, 11274; N. Morohashi, T. Hattori, K. Yokomakura, C. Kabuto and S. Miyano, *Tetrahedron Lett.*, 2002, **43**, 7769; H. Akdas, E. Graf, M. W. Hosseini, A. D. Cian, A. Bilyk, B. W. Skelton, G. A. Koutsantonis, I. Murray, J. M. Harrowfield and A. H. White, *Chem. Commun.*, 2002, 1042; G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. M. Harrowfield, B. W. Skelton and A. H. White, *Chem. Commun.*, 1999, 373.

8 Complexes of thiacalixarene derivatives: H. Katagiri, N. Morohashi, N. Iki, C. Kabuto and S. Miyano, *Dalton Trans.*, 2003, 723; T. Kajiwara, S. Yokozawa, T. Ito, N. Iki, N. Morohashi and S. Miyano, *Angew. Chem., Int. Ed.*, 2002, **41**, 2076.

9 S. Takemoto, K. Otsuka, T. Otsuka, H. Seino, Y. Mizobe and M. Hidai, *Chem. Lett.*, 2002, 6.

10 An attempt to synthesize **4** from **2** and $[CpTiCl_3]$ in the presence of triethylamine was unsuccessful.

11 R. L. Harlow, P. J. Krusic, R. J. McKinney and S. S. Wreford, *Organometallics*, 1982, **1**, 1506.

12 J. R. Hagadorn and M. J. McNevin, *Organometallics*, 2003, **22**, 609.

13 J. L. Calderon, F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, 1969, **91**, 2528.

14 P. Bougeard, M. Mancini, B. G. Sayer and M. J. McGlinchey, *Inorg. Chem.*, 1985, **24**, 93; J. L. Atwood and K. D. Smith, *J. Am. Chem. Soc.*, 1973, **95**, 1488.

15 *Ferrocenes*, eds. A. Togni and T. Hayashi, Wiley-VCH, Weinheim, 1995; M. J. Mayor-Lopez, J. Weber, B. Mannfors and A. F. Cunningham Jr., *Organometallics*, 1998, **17**, 4983.