Synthesis and Structures of *p-tert*-Butyltetrathiacalix[4]arene-dihydrides of Mo(IV) and W(IV)

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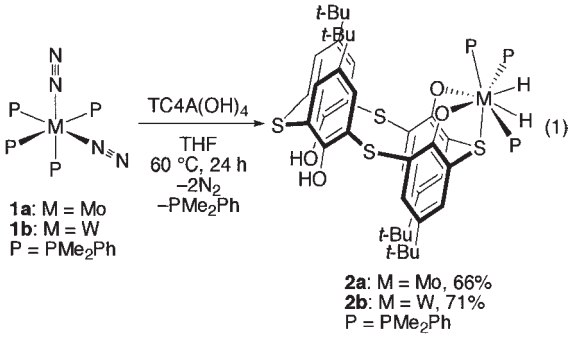
The reaction of zero-valent molybdenum and tungsten dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) with 1 equiv of *p-tert*-butyltetrathiacalix[4]arene ($TC4A(OH)_4$) gave novel dihydrido complexes $[TC4A(OH)_2(O_2MH_2(PMe_2Ph)_3)]$ (M = Mo, W). The structures were determined by X-ray crystallography.

During the last decade calixarene-based molecules have become eminent in supramolecular chemistry as versatile building blocks for functional molecular materials.[1] Of particular interest in this area is their use as a ligand for the construction of mono- and poly-nuclear transition-metal complexes for which the metal-ligand communications are anticipated.[2] As the metallic counterparts, metal-hydrido functionality is intriguing since transition-metal hydrides are well known to participate in numerous catalytic transformations. However, studies on the transition-metal calixarene complexes that contain hydrido ligands are quite limited.[3] The known examples are platinum monohydrido and rhodium dihydrido complexes with calix[4]-arene-based phosphine ligands.[5,6] Herein we report the synthesis and characterization of the dihydrides of Mo(IV) and W(IV) obtained from the reaction of zero-valent dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**1a**: M = Mo; **1b**: M = W) with *p-tert*-butyltetrathiacalix[4]arene ($TC4A(OH)_4$) (eq 1). The practical preparative method of $TC4A(OH)_4$ has recently been developed by Miyano et al., who demonstrated its binding ability toward soft transition-metal centers through the metal-sulfur ligation.[7,8] Isolation and structural characterization of several metal complexes containing tetrathiacalix[4]arene and the related tetrasulfonylcalix[4]arene have already been described in the literatures.[9–11]



When a THF solution containing **1a** and 1 equiv of $TC4A(OH)_4$ was stirred at 60 °C for 24 h under nitrogen, the reaction proceeded cleanly to form **2a** as judged by the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. The product was isolated as yellow-brown crystals in 66% yield after recrystallization from THF–hexane.[12] The tungsten analogue **2b** was similarly prepared by using **1b** in 71% yield.[13] The $^{31}P\{^1H\}$ NMR spectrum of **2a** shows a doublet and a triplet in 2:1 intensity ratio at δ 32.1 and 27.7, respectively, which is indicative of the presence of three phosphorus nuclei on a molybdenum center with the two occupying the equivalent positions. In the ^1H NMR spectrum of **2a**, the methyl resonances of the PMe_2Ph ligands appear as a doublet (δ 1.90) and two virtually coupled triplets (δ 1.57 and 1.29) with equal intensities. The former is assignable to the methyl groups in the unique PMe_2Ph ligand, while the latter are due to the presence of chemically inequivalent methyl groups in the remaining two equivalent PMe_2Ph ligands. The resonances assignable to the aromatic protons and the *t*-Bu groups of the TC4A moiety were observed as two pairs of *meta*-coupled doublets and as two singlets, respectively. This suggests the existence of two kinds of aryl rings in the TC4A moiety. The sharp singlet at δ 8.53 ppm is due to the O–H protons. Noteworthy is that a broad signal appears at δ −3.31 ppm with 2H intensity. This indicates the presence of Mo–H bonds, which is further confirmed by the observation of a band at 1830.3 cm^{-1} in the infrared spectrum. As shown in Figure 1, the hydrido signal begins to split into two peaks at ca −20 °C and appears as two distinct doublets of triplets at −60 °C. The tungsten complex **2b** exhibits similar spectral features to **2a**.

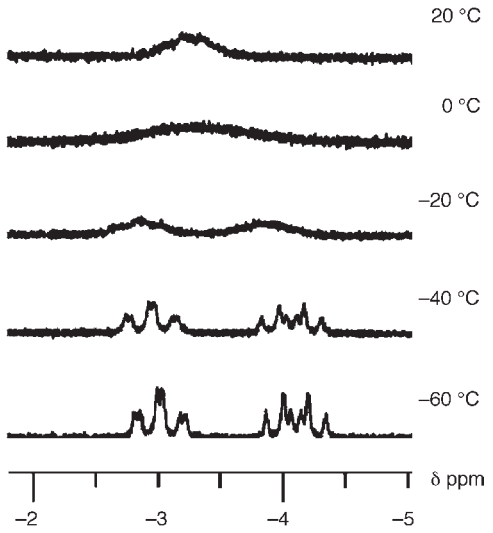


Figure 1. Temperature dependence of the hydride signals in the ^1H NMR spectra of **2a** (toluene-d_8, 400 MHz).

The molecular structures of **2a** and **2b** were determined by X-ray crystallography.[14] An ORTEP drawing of **2a** is shown in Figure 2. The tungsten complex **2b** is isostructural with **2a**. The *p-tert*-butyltetrathiacalix[4]arene moiety adopts 1,2-alternate conformation and is coordinated to the molybdenum center as a tridentate diaryloxo–thioether ligand. Occasionally, we have

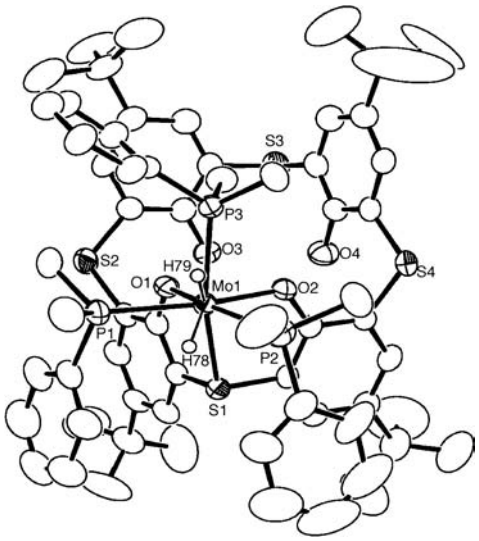


Figure 2. ORTEP drawing of **2a**. Selected bond lengths (Å) and angles (deg): Mo(1)–S(1), 2.4895(9); Mo(1)–O(1), 2.185(2); Mo(1)–O(4), 2.150(2); Mo(1)–P(1), 2.4495(10); Mo(1)–P(2), 2.4597(11); Mo(1)–P(3), 2.4384(9); Mo(1)–H(78), 1.54(5), Mo(1)–H(79), 1.67(5), O(1)–Mo(1)–O(4), 82.73(10); O(1)–Mo(1)–P(1), 76.07(7); P(1)–Mo(1)–P(2), 121.62(4), P(2)–Mo(1)–O(4), 79.41(8); S(1)–Mo(1)–P(3), 154.51(3); H(78)–Mo(1)–H(79), 57(2).

obtained another crystals of **2b** in which partial cone conformation of the *p-tert*-butyltetrathiacalix[4]arene moiety was observed.[15] This observation suggests that the two phenol rings of the TC4A(OH)$_2$(O)$_2$ ligand in **2b** are conformationally mobile in solution, since the NMR spectra of the crystals of the partial cone and 1,2-alternate conformers are identical when dissolved in C_6D_6. The remarkable structural feature around the molybdenum atom is a widely opened P(1)–Mo(1)–P(2) bond angle (121.62(4)°), which implies the presence of the two hydrido ligands at this position. In fact, the two hydrogen atoms were found in the difference Fourier map at the final stages of the refinement, which are refined isotropically. The H(78)–Mo(1)–H(79) plane is almost perpendicular to that defined by P(1), Mo(1), and P(2) atoms, and each hydrogen atom lies at the opposite sides of the P(1)–Mo(1)–P(2) plane. This location of the two hydride ligands is consistent with the ^{1}H NMR spectra observed at low temperature (*vide infra*). Including these hydrido ligands, the molybdenum atom adopts an eight-coordinate distorted dodecahedral geometry.

In summary, we have synthesized and characterized novel molybdenum and tungsten dihydrido complexes containing a tetrathiacalix[4]arene ligand. Application of these complexes in hydrogen transfer reactions are now under investigation.

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Dedicated to Prof. Teruaki Mukaiyama on the occasion of his 75th birthday.

References and Notes

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12 A THF solution (20 mL) containing **1a** (176 mg, 0.250 mmol) and TC4A(OH)$_4$ (180 mg, 0.250 mmol) was stirred at 60 °C for 24 h. The resultant dark yellow solution was concentrated to ca. 5 mL, on which hexane (20 mL) was layered to give **2a** as yellow-brown crystals. Yield 131 mg, 66%. Anal. Calcd for $C_{64}H_{81}O_4S_4P_3Mo$: C, 62.42; H, 6.63%. Found: C, 62.40; H, 6.86%. ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 8.53 (s, 2H, OH), 7.92, 7.81, 7.64, 7.14 (d, 2H each, Ar), 7.29–7.25 (m, 3H, PMe$_2$*Ph*), 7.15–6.99 (m, 12H, PMe$_2$*Ph*) 1.90 (d, 6H, P*Me*$_2$Ph), 1.57, 1.29 (t, 6H each, P*Me*$_2$Ph), 1.15, 1.14 (s, 18H each, *t*-Bu), −3.31 (brs, 2H, MoH). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 32.1 (d, J = 22.1 Hz, 2P), 27.7 (t, J = 22.1 Hz, 1P). IR (KBr): 1830.3 cm^{-1} (Mo–H).
13 Anal. Calcd for $C_{64}H_{81}O_4S_4P_3W$: C, 58.26; H, 6.19%. Found: C, 57.87; H, 6.49%. ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 7.90 (s, 2H, OH), 7.87, 7.80, 7.58, 7.12 (d, 2H each, Ar), 7.41–7.37 (m, 3H, PMe$_2$*Ph*), 7.2–6.9 (m, 12H, PMe$_2$*Ph*) 1.93 (d, 6H, P*Me*$_2$Ph), 1.69, 1.44 (t, 6H each, P*Me*$_2$Ph), 1.15, 1.14 (s, 18H each, *t*-Bu), −0.74 (br s, 2H, WH). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 8.16 (d, J = 9.2 Hz, 2P), 3.84 (t, J = 9.2 Hz, 1P). IR (KBr): 1878.5 cm^{-1} (W–H).
14 All measurements were performed on a Rigaku Mercury CCD system. Structures were solved by direct method (SHELXS-97) and refined by least squares method on F^2 (SHELXL-97). Crystal data for **2a**: tetragonal, $I\bar{4}$(#82), a = 34.7650(11), c = 10.8041(5) Å V = 13057.9(7) Å^3, Z = 8, Fw = 1229.43, D_{calc} = 1.251 g·m^{-3}, μ = 4.45 cm^{-1}, T = 293 K, 14924 unique reflections (R_{int} = 0.044), 693 refined parameters, R1 = 0.050 ($I > 2\sigma(I)$), wR2 = 0.112 (all data), GOF = 1.055. Crystal data for **2b**: tetragonal, $I\bar{4}$(#82), a = 34.787(4), c = 10.8125(11) Å V = 13084.9(20) Å^3, Z = 8, Fw = 1317.34, D_{calc} = 1.337 g·m^{-3}, μ = 20.12 cm^{-1}, T = 293 K, 14938 unique reflections (R_{int} = 0.051), 693 refined parameters, R1 = 0.047 ($I > 2\sigma(I)$), wR2 = 0.102 (all data), GOF = 1.090.
15 Unit cell parameters for the partial cone conformer of **2b**: monoclinic, $P2_1/n$ (#14), a = 14.114(5), b = 24.353(6), c = 23.466(6) Å β = 98.61(2)°, V = 7974(3) Å, Z = 4.