Electronic Supplementary Information for Dalton Transactions

Coordination chemistry of the sulfur analog of tricatechol siderophores

Birgit Birkmann,[a] Wolfram W. Seidel,[a] Tania Pape,[a] Andreas W. Ehlers,[b] Koop Lammerstma,[b] and F. Ekkehardt Hahn*[a]

Supplementary Information

Experimental Section

General Remarks

All operations were carried out under an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded at 298 K with Bruker AC 200 (200 MHz) or Bruker AMX 400 (400 MHz) spectrometers and are reported relative to TMS as an internal standard or to the residual solvent signal. Mass spectra were obtained with Micromass Quattro LC-Z (ESI) or Bruker Reflex IV (MALDI) spectrometers. Elemental analyses were performed with a Vario EL III CHNS analyzer. Commercially available [Ti(OPr)$_4$] (Aldrich) was used without further purification.

Ligands H_6-**1** and H_2-**2** were synthesized according to previously published methods.[1]

Selected analytical data for

H_6-1: ^{1}H NMR (400 MHz, DMF-*d*$_7$, 25 °C, ppm): δ = 8.63 (t, 1H, N-H), 7.55 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 3H, Ar-H), 7.30 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 3H, Ar-H), 7.05 (t, ^3J = 7.5 Hz, 3H, Ar-H), 4.66 (d, ^3J = 3.8 Hz, 6H, CH_2), 2.54 (s, 9H, CH_3); ^{13}C NMR (100 MHz, DMF-*d*$_7$, 25 °C): δ = 169.4 (C(O)NH), 137.8, 134.0, 133.4, 132.8, 131.7, 126.3, 125.4, 125.0 (Ar-C), 39.7 (CH_2), 16.5 (CH_3); MS (MALDI) *m/z* = 711 [M−H]$^-$. Calcd for $C_{33}H_{33}N_3O_3S_6$: C, 55.67; H, 4.67; N, 5.90; S, 27.02%. Found: C, 55.36; H, 4.43; N, 6.04; S, 25.88.

H_2-2: ^{1}H NMR (400 MHz, DMF-*d*$_7$, 25 °C, ppm): δ = 9.07 (s br, 1H, N-H) 7.60 (d, ^3J = 7.5 Hz, 1H, Ph-H), 7.44 (d, ^3J = 7.5 Hz, 2H, Bz-H), 7.43 (d, ^3J = 7.5 Hz, 1H, Ph-H), 7.36 (t, ^3J = 7.5 Hz, 2H, Bz-H), 7.27 (t, ^3J = 7.5 Hz, 1H, Bz-H), 7.11 (t, ^3J = 7.5 Hz, 1H, Ar-H), 4.59 (d, 2H, CH_2), 3.50 (s br, 2H, S-H); ^{13}C NMR (100 MHz, DMF-*d*$_7$, 25 °C, ppm): δ = 169.7 (C(O)NH), 140.1, 135.4, 134.2, 132.3, 132.0, 129.0, 128.2, 127.6, 126.1, 125.7 (Ar-C), 43.7 (CH_2). Calcd for $C_{14}H_{13}NOS_2$: C, 61.06; H, 4.76; N, 5.09; S, 23.29%. Found: C, 61.11; H, 4.88; N, 4.98; S, 21.96.

Preparation of 3: A sample of [Ti(OPr)$_4$] (19.9 mg, 0.07 mmol) was added to a solution of H$_6$-**1** (50 mg, 0.07 mmol) and Li_2CO_3 (5 mg, 0.07 mmol) in degassed methanol (20 mL). The mixture was stirred at ambient temperature for 12 h and then filtered. Addition of Ph_4AsCl (61 mg, 0.14 mmol) to the filtrate gave a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried in vacuo. Yield 85 mg (0.06 mmol, 80%).

^{1}H NMR (400 MHz, DMF-d_7, 25 °C, ppm): δ = 8.01 (t, 1H, N-H), 7.99–7.81 (m, 40H, As-Ph-H), 7.16 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 3H, Ar-H), 7.09 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 3H, Ar-H), 6.76 (t, ^3J = 7.5 Hz, 3H, Ar-H), 4.66 (d, ^3J = 3.8 Hz, 6H, CH$_2$), 2.47 (s, 9H, CH$_3$); ^{13}C NMR (100 MHz, DMF-d_7, 25 °C, ppm): δ = 169.4 (C(O)NH), 153.6, 153.4, (C$_6$H$_4$S$_2$-C), 137.1 (C$_6$Me$_e$-C), 135.1, 134.2 (AsC$_6$H$_5$-C), 134.2 (C$_6$H$_4$S$_2$), 134.1 (C$_6$Me$_e$-C), 131.7 (AsC$_6$H$_5$-C), 128.7, 122.4 (C$_6$H$_4$S$_2$-C), 122.2 (AsC$_6$H$_5$-C), 121.8 (C$_6$H$_4$S$_2$-C), 39.1 (CH$_2$), 15.7 (CH$_3$); MS (ESI, negative ions): m/z = 376.7 [Ti(**1**)]$^{2-}$. Calcd for $C_{81}H_{67}N_3As_2O_3S_6Ti$: C, 63.98; H, 4.44; N, 2.77; S, 12.63. Found: C, 65.04; H, 4.54; N, 3.39; S, 13.72%.

Complex (Ph$_4$As)$_2$[Ti(**1**)] exhibits a very simple ^{1}H NMR spectrum, indicating C_3-symmetry of the complex dianions [Ti(**1**)]$^{2-}$ in solution (Figure S1). The signal for the amide proton is concealed behind the DMF solvent signal at δ = 8.01 ppm and is slightly highfield shifted compared to the resonance observed for the free ligand H$_6$-**1** (N–H resonance at δ = 8.63 ppm). In case of the formation of N–H···S hydrogen bonds, lowfield shift was expected for the amide proton upon complex formation. We ascribe the observed highfield shift to the shielding effect of the bridging aromatic ring.

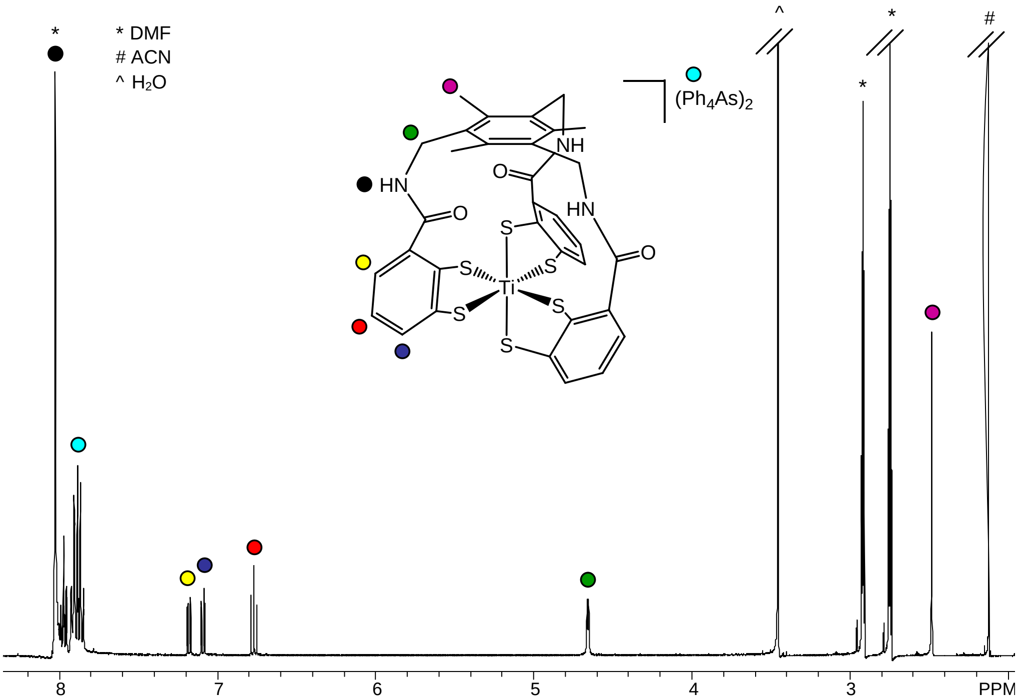


Figure S1 ^{1}H NMR spectrum of (Ph$_4$As)$_2$[Ti(**1**)] in DMF-d$_7$ (∗ = DMF-, # = acetonitrile-, ^ = water-resonances).

Preparation of 4: The compound was prepared as described for $(Ph_4As)_2[Ti(\mathbf{1})]$ from ligand H_2-**2** (50 mg, 0.182 mmol) and $Ti(OPr)_4$ (17 mg, 0.06 mmol). Yield: 96 mg (0.058 mmol, 97 %).

^{1}H NMR (400 MHz, DMF-d_7, 25 °C, ppm): δ = 9.26 (s, 3H, N-H), 7.98–7.78 (m, 40H, As-Ph-H), 7.94 (dd, 3H, Ph-H), 7.40–7.23 (m, 15H, Bz-H), 7.04 (dd, 3H, Ph-H), 6.70 (t, 3H, Ph-H), 4.58 (d, 6H, CH_2); ^{13}C NMR (100 MHz, DMF-d_7, 25 °C, ppm): δ = 169.6 (C(O)NH), 156.3, 150.3, 140.9, 135.1, 134.2, 133.4, 131.7, 129.0, 128.84, 128.80, 127.9, 127.0, 124.7, 121.8 (Ar-C) 43.4 (CH_2); MS (ESI, negative ions): m/z = 433.7 $[Ti(\mathbf{2})_3]^{2-}$. Calcd for $C_{90}H_{73}N_3As_2O_3S_6Ti$: C, 66.13; H, 4.50; N 2.57; S, 11.77%. Found: C, 66.52; H, 4.54; N, 2.39; S, 10.62.

The proton NMR spectrum of complex $(Ph_4As)_2[Ti(\mathbf{2})_3]$ (Figure S2) is very simple, indicating C_3-symmetry of the complex in solution. The signal for the amide proton is slightly shifted downfield compared to the free ligand H_2-**2** ($\Delta\delta$ = 0.19 ppm) and appears at δ = 9.26 ppm.

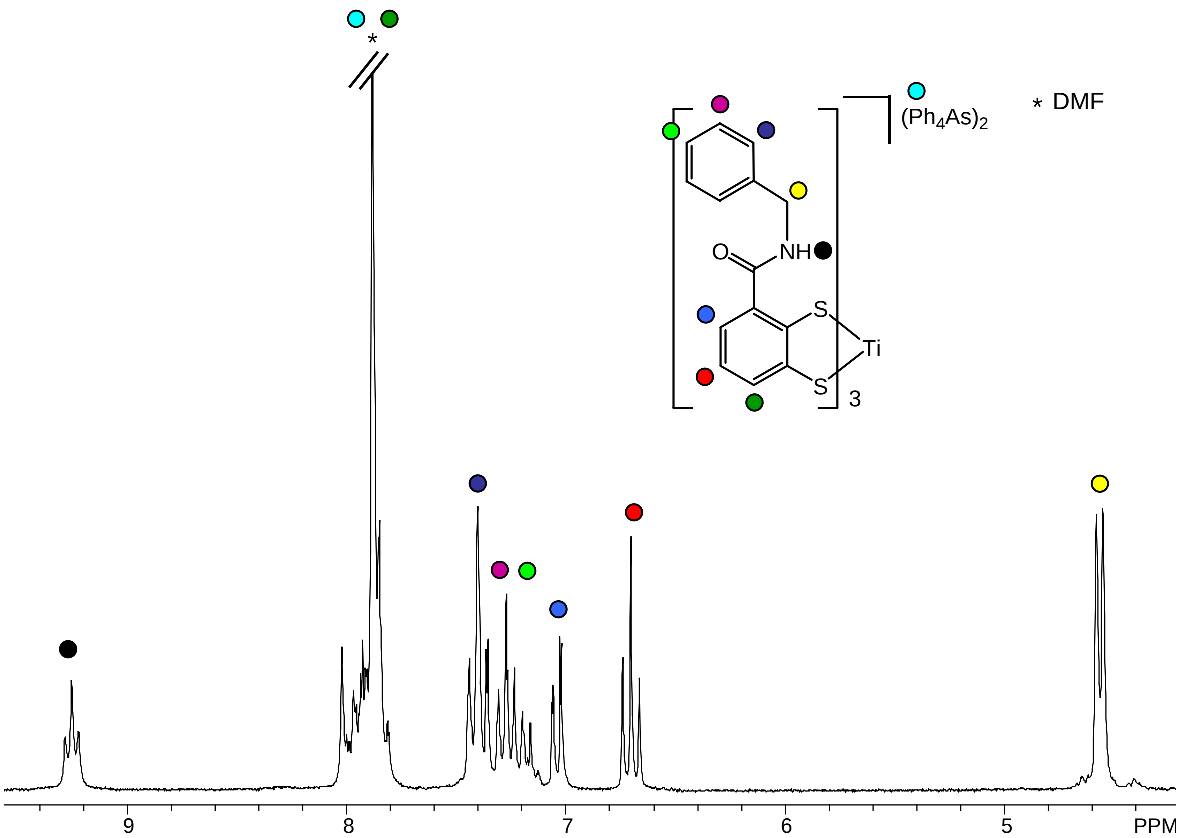
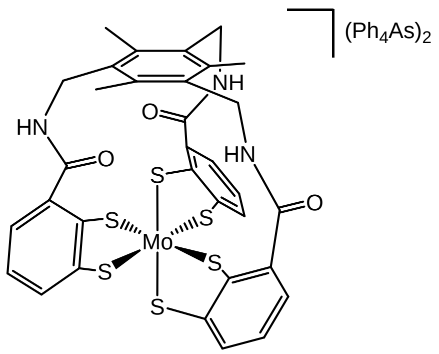


Figure S2 ^{1}H NMR spectrum of $(Ph_4As)_2[Ti(\mathbf{2})_3]$ in DMF-d_7 (* = DMF-resonances).

Preparation of 5: A sample of [$MoCl_4(CH_3CN)_2$] (22.4 mg, 0.07 mmol) was added to a solution of H_6-**1** (50 mg, 0.07 mmol) and Li_2CO_3 (28 mg, 0.38 mmol) in degassed methanol (20 mL). The mixture was stirred at ambient temperature for 12 h and was then filtered. Addition of $Ph_4AsCl{\cdot}H_2O$ (61 mg, 0.14 mmol) to the filtrate yielded a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried in vacuo.



Yield: 64 mg (0.042mmol, 60%), $C_{81}H_{67}N_3As_2MoO_3S_6$ (M = 1568.59 g/mol).

MS (ESI, neagtive ions): m/z = 802.9 [Mo(**1**)]$^{-}$, 401.3 [Mo(**1**)]$^{2-}$; UV-Vis (nm): λ_{max} = 356, 578.

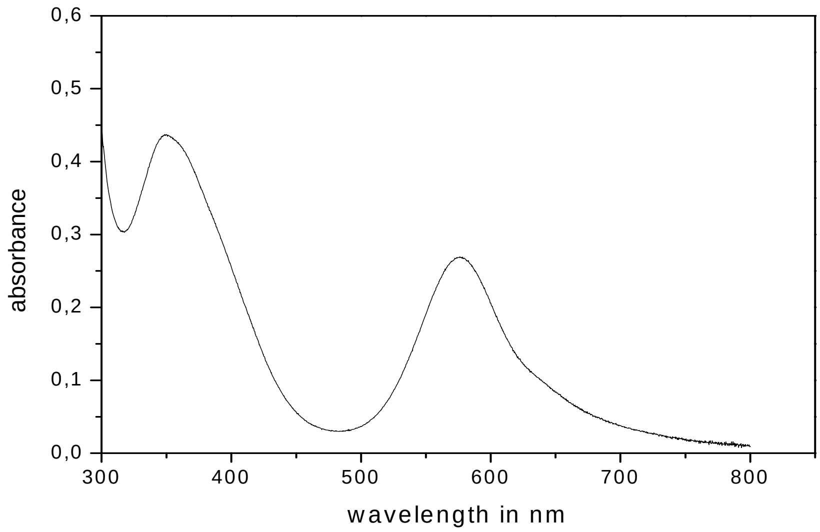
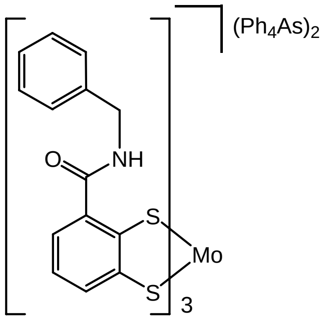


Figure S3 UV-Vis spectrum of complex $(Ph_4As)_2$[Mo(**1**)] at ambient temperature in DMF.

Preparation of 6: A sample of $[MoCl_4(CH_3CN)_2]$ (20.0 mg, 0.06 mmol) was added to a solution of H_2-**2** (50 mg, 0.18 mmol) and Na_2CO_3 (19.0 mg, 0.18 mmol) in degassed methanol (20 mL). The solution was stirred under argon at ambient temperature for 12 h and was then filtered. Addition of $Ph_4AsCl\cdot H_2O$ (61 mg, 0.14 mmol) to the filtrate yields a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried under vacuum.



Yield: 74 mg (0.04 mmol, 72%), $C_{90}H_{73}N_3As_2MoO_3S_6$ (M = 1682.73 g/mol). ^{1}H NMR (400 MHz, DMF-d_7, 25 °C, ppm): δ = 9.58 (t, ^3J = 5.7 Hz, 3H, N-H), 7.96 (m, 8H, As-Ph-H), 7.89 (m, 16H, As-Ph-H), 7.85 (m, 16H, As-Ph-H), 7.56 (d, ^3J = 7.5 Hz, 6H, Bz-H), 7.56 (s b, 3H, Ar-H), 7.41 (s b, 3H, Ar-H), 7.35 (t, ^3J = 7.5 Hz, 6H, Bz-H), 7.22 (t, ^3J = 7.5 Hz, 3H, Bz-H), 6.73 (s b, 3H, Ar-H), 4.73 (d, ^3J = 5.7 Hz, 6H, CH_2); ^{13}C NMR (100 MHz, DMF-d_7, 25 °C, ppm): δ = 169.5 (C(O)NH), 156.9, 151.4 ($C_6H_4S_2$-C), 141.0, 128.9, 128.0, 127.1 (Bz-C), 135.1, 134.2, 131.7, 122.2 (As-C_6H_5-C), 133.0, 128.94, 123.3, 120.4 ($C_6H_4S_2$-C), 43.6 (CH_2). MS (ESI, negative ions): m/z = 917.5 $[Mo(\mathbf{2})_3]^-$, 458.9 $[Mo(\mathbf{2})_3]^{2-}$; UV-Vis (nm): λ_{max} = 362 and 580.

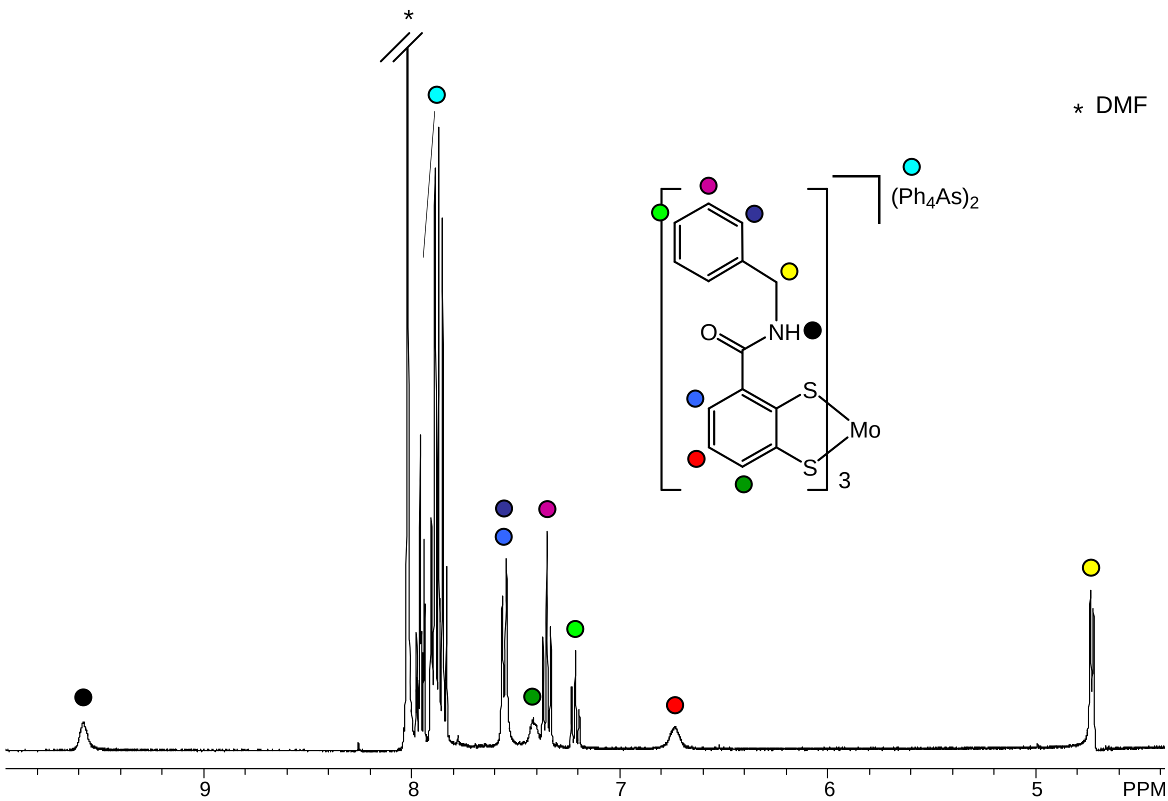


Figure S4 ^{1}H NMR spectrum of complex $(Ph_4As)_2[Mo(\mathbf{2})_3]$ at ambient temperature in DMF-d_7.

Aerobic oxidation of complex $(Ph_4As)_2[Mo^{IV}(\mathbf{2})_3]$ gave the corresponding Mo^{V} species with the associated changes in the electron absorption spectrum (Figure S5, λ_{max} = 392, 480, 603 and 720 nm).

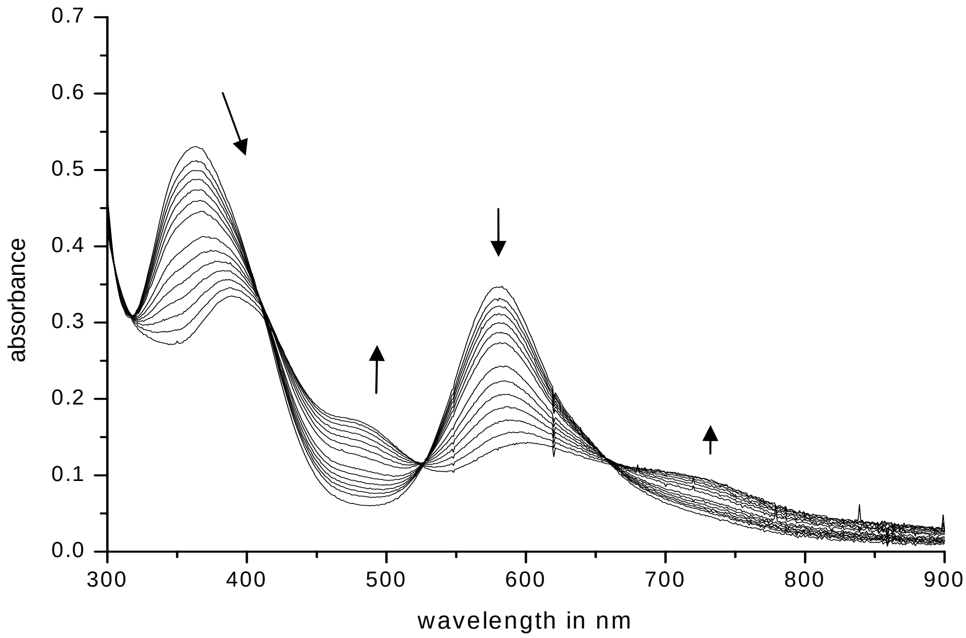


Figure S5 UV-Vis spectra of the time dependent aerobic oxidation of $(Ph_4As)_2[Mo^{IV}(\mathbf{2})_3]$ to $(Ph_4As)[Mo^{V}(\mathbf{2})_3]$ in methanol.

X-ray Data for $(Ph_4As)_2[Ti(1)]\cdot 3H_2O$: $C_{81}H_{73}N_3As_2O_6S_6Ti$, M = 1574.56, triclinic, a = 14.433(3), b = 14.456(3), c = 19.842(4) Å, α = 90.257(4), β = 90.467(4), γ = 119.715(4) °, V = 3595.1(11) Å^3, T = 153 K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 1.264 mm^{-1}, 29245 intensities measured in the 2θ-range 2.0–25.0°, 12643 unique intensities (R_{int} = 0.0663), R = 0.0602, wR = 0.1241 for 8757 observed intensities ($I \geq 2\sigma(I)$). Hydrogen atoms were added to the structure model on calculatd positions with the exception of the hydrogen atom positions at the three water molecules which were not identified.

Computational Studies

All density functional theory calculations (B3LYP)[S2] were performed with the Gaussian03 suite of programs,[S3] using the SDD basis set and pseudopotentials for titanium[S4] and the D95V[S5] basis set for all other atoms. The nature of the transition state structures was confirmed by frequency calculations.

Table S1 Relative energies (in kcal/mol) for the B3LYP/SDD optimized structures of mononuclear tris(benzene-*o*-dithiolato) molybdenum complexes.

complex	*pseudo*-O_h	D_{3h}	C_{3h}	triplet state *pseudo*-O_h
$[Mo(bdt)_3]^{2-}$	0	0.70	---[a]	2.55[b]
$[Mo(bdt)_3]^{-}$	0	---[c]	5.16	---[d]
$[Mo(bdt)_3]$	5.37	---[c]	0	---[d]

[a] Optimization of the C_{3h}-symmetric tris(benzene-*o*-dithiolato) complex resulted in the D_{3h}-symmetric isomer; [b] the triplet state is higher in energy; [c] Optimization of the D_{3h}-symmetric tris(benzene-*o*-dithiolato) complex resulted in the C_{3h}-symmetric isomer; [d] no triplet state exists.

References

[S1] (*a*) F. E. Hahn and W. W. Seidel, *Angew. Chem.*, 1995, **107**, 2938–2941; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2700–2703; (*b*) H. V. Huynh, C. Schulze Isfort, W. W. Seidel, T. Lügger, R. Fröhlich, O. Kataeva and F. E. Hahn, *Chem.–Eur. J.,* 2002, **8**, 1327–1335; (*c*) H. V. Huynh, W. W. Seidel, T. Lügger, R. Fröhlich, B. Wibbeling and F. E. Hahn, *Z. Naturforsch.*, 2002, **57b**, 1401–1408; (*d*) F. E. Hahn, T. Kreickmann and T. Pape, *Eur. J. Inorg. Chem.,* 2006, 535–539.

[S2] [S1] (*a*) A. D. Becke, *Phys.Rev. A,* 1988, **38**, 3098–3100; (*b*) A. D. Becke, *J. Chem. Phys.,* 993, 98, 5648–5652; (*c*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785–789.

[S3] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A.

Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[S4] (*a*) A. Bergner, M. Dolg, W. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.,* 1993, **80**, 1431–1441; (*b*) M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta,* 1993, **85**, 441–450; (*c*) M. Dolg, H. Stoll, H. Preuss and R. M. Pitzer, *J. Phys. Chem.,* 1993, **97**, 5852–5859; (*d*) U. Haeussermann, M. Dolg, H. Stoll and H. Preuss, *Mol. Phys.,* 1993, **78**, 1211–1224; (*e*) W. Kuechle, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.,* 1994, **100**, 7535–7542; (*f*) A. Nicklass, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.,* 1995, **102**, 8942–8952; (*g*) T. Leininger, A. Nicklass, H. Stoll, M. Dolg and P. Schwerdtfeger, *J. Chem. Phys.,* 1996, **105**, 1052–1059; (*h*) X. Y. Cao and M. Dolg, *J. Chem. Phys.,* 2001, **115**, 7348–7355; (*i*) X. Y. Cao and M. Dolg, *J. Mol. Struct.(Theochem),* 2002, **581**, 139–147.

[S5] T. H. Dunning, Jr. and P. H. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer, III, Plenum, New York, 1976 (Vol 3, pp 1–28).