ORGANOMETALLICS

Volume 22, Number 4, February 17, 2003

Communications

Chemistry Supported by Preorganized Binucleating Ligands: Synthesis and Structural Characterization of Dititanium(III) *μ*-Methyl *μ*-Hydrido Species

John R. Hagadorn* and Michael J. McNevin

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

Received November 20, 2002

Summary: Binucleating bis(amidinate) ligands based on a 9,9-dimethylxanthene backbone have been used to prepare new dititanium(IV) complexes of the general formula [bis(amidinate)]$Ti_2Cp_2R_4$ (R = CH_3, $^{13}CH_3$, CD_3). Reaction of these methyl derivatives with H_2 affords the dititanium(III) μ-methyl μ-hydrido derivatives [bis(amidinate)]$Ti_2Cp_2(\mu\text{-}R)(\mu\text{-}H)$ (R = CH_3, $^{13}CH_3$, CD_3), which have been characterized by single-crystal X-ray diffraction and NMR and IR spectroscopy. These complexes are rare examples of first-row-transition-metal alkyl hydrido species.

Well-defined bimetallic complexes play important roles in numerous areas of chemistry, including metalloprotein modeling, supramolecular chemistry, and catalysis.[1] A major approach taken toward their development has involved the design and use of preorganized binucleating ligands.[2] These ligands, which generally feature multiple donor groups that are linked together, prevent unwanted fragmentation processes and ideally provide control over molecular structure and reactivity. For applications in early-transition-metal chemistry, relatively few suitable binucleating ligands[3] have been explored, aside from fulvalene[4] and *ansa*-cyclopentadiene dianions.[5] Thus, we[6] have been developing new semirigid bis(amidinate)[7] ligands based on 9,9-dimethylxanthene and dibenzofuran backbones. These ligands have provided access to a wide range of early-metal bimetallics with desired control over key structural features, such as intermetal distance, sterics, and symmetry. In this communication, we report the synthesis and structural characterization of a series of dititanium complexes, including rare examples of a first-row-transition-metal alkyl hydrido species.

As shown in Scheme 1, the bis(amidine) ligand **1** reacted with 2 equiv of $CpTiMe_3$ in toluene solution to

---

[1] Representative reviews on bimetallics in metalloenzyme models: (a) Du Bois, J.; Mizoguchi, T. J.; Lippard, S. J. *Coord. Chem. Rev.* **2000**, *200*−*202*, 443−485. (b) Bosnich, B. *Inorg. Chem.* **1999**, *38*, 2554−2562. Supramolecular chemistry: (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. Catalysis: (d) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998. (e) Rowlands, G. J. *Tetrahedron* **2001**, *57*, 1865−1882.

[2] Selected reviews: (a) Vigato, P. A.; Tamburini, S.; Fenton, D. E. *Coord. Chem. Rev.* **1990**, *106*, 25−170. (b) Kaden, T. A. *Coord. Chem. Rev.* **1999**, *190*−*192*, 371−389. (c) Suzuki, M.; Furutachi, H.; Okawa, H. *Coord. Chem. Rev.* **2000**, *200*−*202*, 105−129. (d) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167−173.

[3] Selected examples include bis(phenolates): (a) Saied, O.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1998**, *37*, 2620−2625. Bis(amidos): (b) Daniele, S.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 1909−1910. (c) Kang, K. K.; Hong, S.-P.; Shiono, T.; Ikeda, T. *J. Polym. Sci.* **1999**, *37A*, 3756−3762. Amidinates: (d) Cotton, F. A.; Wojtczak, W. A. *Gazz. Chim. Ital.* **1993**, *123*, 499−507. (e) Hao, S.; Feghali, K.; Gambarotta, S. *Inorg. Chem.* **1997**, *36*, 1745−1748. (f) Babcock, J. R.; Incarvito, C.; Rheingold, A. L.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 5729−5732.

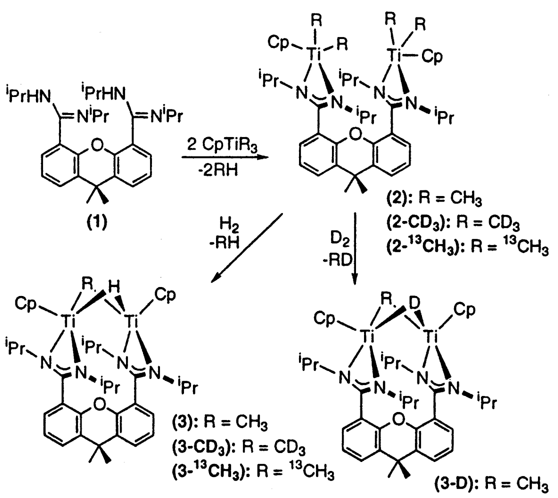
[4] Royo, E.; Royo, P.; Cuenca, T.; Galakhov, M. *J. Organomet. Chem.* **2001**, *634*, 177−184 and references contained therein.

[5] (a) Reddy, K. P.; Petersen, J. L. *Organometallics* **1989**, *8*, 547−549. (b) Green, M. L. H.; Popham, N. H. *J. Chem. Soc., Dalton Trans.* **1999**, 1049−1059 and references contained therein.

[6] Hagadorn, J. R. *Chem. Commun.* **2001**, 2144−2145.

10.1021/om020960p CCC: $25.00 © 2003 American Chemical Society
Publication on Web 01/17/2003

Scheme 1



form air-sensitive **2**, which was isolated as red-orange crystals from hexanes in 75% yield. The ^{1}H NMR spectrum (500 MHz) of **2** acquired in C_6D_6 solution features sharp resonances consistent with overall C_{2v} symmetry for the bimetallic species. Thus, a singlet is observed at δ 6.42 ppm for the pair of equivalent cyclopentadienyl ligands. Another at δ 1.21 ppm is assigned to the four Ti−Me groups. Similar values have been reported by Sita and co-workers for closely related species.[3f,8]

Reaction of **2** with H_2 (1 atm) proceeded at 65 °C over several hours to form **3** as the only observed Ti-containing product (^{1}H NMR). Removal of volatiles afforded **3** as a dark red solid, which was purified by crystallization from Et_2O in 37% isolated yield. We formulate **3** to be a dititanium(III) alkyl hydrido species. To our knowledge, there are only two other reports of first-row-transition-metal alkyl hydrido species.[9] The formulation of **3** is supported by combustion analysis, NMR and IR spectroscopy, isotope labeling studies, and single-crystal X-ray diffraction. Descriptions of these data follow.

The ^{1}H NMR spectrum (500 MHz) of the dititanium(III) complex **3** in C_6D_6 solution features slightly broadened resonances between −2 and 7.5 ppm (Figure S1, Supporting Information). The small amount of paramagnetic line broadening is reflected in the low magnetic moment of 1.14(5) μ_B per dimer (Evans method, 19.5 °C), which indicates a significant amount of antiferromagnetic coupling between the two d^1 centers. A similarly sharp ^{1}H NMR spectrum has been reported for the dititanium(III) hydrido and deuterido species $\{[(Me_3SiNCH_2CH_2)_2NSiMe_3]Ti(\mu\text{-}X)\}_2$ (X = H, D),[10] which feature μ_{eff} values of 1.65 and 1.32 μ_B, respectively.

The ^{1}H NMR spectroscopic data of **3** reveals overall C_s symmetry for the bimetallic complex, with the single mirror operation being oriented perpendicular to the intermetal axis. Thus, the two symmetry-related Cp ligands appear as a singlet at δ 6.25 ppm, yet the pair of Me groups in the 9-position of the xanthene backbone appear as two distinct singlets at δ 1.54 and 1.52 ppm. Conspicuously, the spectrum of **3** also contains a broad resonance at −1.98 ppm ($\omega_{1/2}$ = 54 Hz) with an integrated intensity of 3H, which is assigned to the μ-Me group.[11,12] Consistent with this assignment, the ^{1}H NMR spectrum of **3-CD$_3$** lacked the resonance at −2 ppm. Additionally, the ^{1}H NMR spectrum of **3-^{13}CH$_3$** revealed a broad doublet at −2.04 ppm with a $^1J_{CH}$ value of 110 Hz, which is consistent with an sp^3-hybridized μ-Me group.[11a]

The broadness of the μ-Me resonance appears to be due to its proximity to the paramagnetic Ti centers. For this reason, the ^{13}C{^{1}H} NMR spectra of both **3** and **3-^{13}CH$_3$** failed to reveal any resonances attributable to the μ-Me group. Likewise, the μ-hydrido ligand was not observed by ^{1}H NMR spectroscopy. The ^{2}H NMR spectrum of **3-D**, however, featured a broad resonance at −24.3 ppm ($\omega_{1/2}$ = 100 Hz), which is assigned to the μ-D group. Infrared spectroscopic data provide additional evidence for the presence of a μ-hydrido (μ-deuterido) ligand in **3** (**3-D**). As shown in Figure S2 (Supporting Information), comparing the IR spectra of **3** and **3-D** (mineral oil mulls) reveals $\nu(Ti_2(\mu\text{-}D))$ at 1016 cm^{-1}. The analogous $\nu(Ti_2(\mu\text{-}H))$ stretch in **3** is obscured by strong absorptions associated with the bis(amidinate) ligand around 1440 cm^{-1}.

Numerous attempts were made to characterize **3** and closely related species[13] by single-crystal X-ray diffraction. Solution and refinement of these data sets confirmed the general composition of the molecules, yet they proved inadequate for the location and refinement of hydrogen atoms due to disorder in the position of the μ-Me and μ-H groups. This disorder likely arises due to the chemical equivalence of the two positions. To combat this problem, we sought to introduce asymmetry into the supporting ligands. Our approach to this involved using bis(amidine) **4** for the preparation of a 2:1 mixture of ***meso*-5** and ***rac*-5** (Scheme 2), which do not appear to interconvert, due to hindered rotation about the C$_{ipso}$−amidinate bonds. Recrystallization of the mixture from Et_2O solution at −40 °C afforded crystals suitable for X-ray diffraction. The solid-state structure of ***meso*-5** is shown in Figure 1. The high quality of the data allowed for the location and refinement of the hydrogens

---

[7] Other selected bis(amidinates): (a) Whitener, G. D.; Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1249−1255. (b) Chen, C. T.; Rees, L. H.; Cowley, A. R.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2001**, 1761−1767. (c) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782−785. (d) Appel, S.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1990**, *583*, 7−16. (e) Reference 3f.

[8] (a) Sita, L. R.; Babcock, J. R. *Organometallics* **1998**, *17*, 5228−5230. (b) Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183−4190.

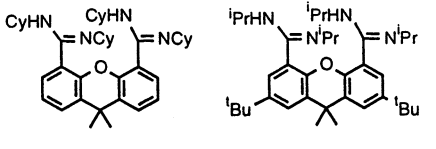
[9] (a) Jonas, K.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 519−520. (b) Henderson, R. A.; Oglieve, K. E. *Chem. Commun.* **1999**, 2271−2272.

[10] Love, J. B.; Clark, H. C. S.; Cloke, F. G. N.; Green, J. C.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1999**, *121*, 6843−6849.

[11] Known dititanium(IV) μ-Me complexes feature comparable upfield-shifted resonances: (a) Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088−2092. (b) Wang, Q.; Gillis, D. J.; Quyoum, R.; Jeremic, D.; Tudoret, M.-J.; Baird, M. C. *J. Organomet. Chem.* **1997**, *527*, 7−14. (c) Kleinhenz, S.; Seppelt, K. *Chem. Eur. J.* **1999**, *5*, 3573−3580.

[12] Related dititanium μ-methylidene species feature downfield-shifted resonances (δ 7−8 ppm): (a) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978−4983. (b) Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922−5923.

[13] Through the use of the two ligands shown below in place of **1**, dititanium(III) μ-Me μ-H species closely related to **3** were prepared: Hagadorn, J. R.; McNevin, M. J. Unpublished results.



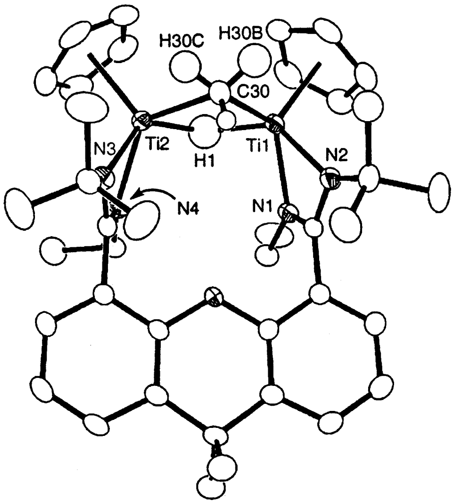
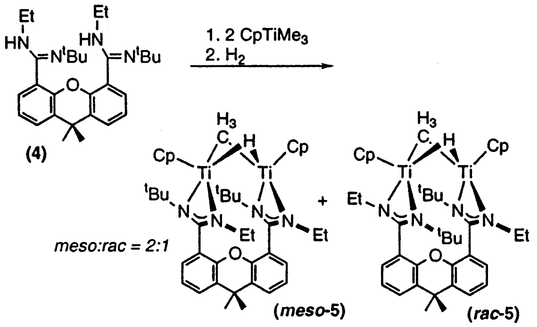


Figure 1. Molecular structure of ***meso*-5** with 50% thermal ellipsoids. Nonrefined hydrogens and cocrystallized Et_2O are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1−Ti2, 2.9788(6); Ti1−N1, 2.062(2); Ti1−N2, 2.193(2); Ti1−C30, 2.270(3); Ti1−H1, 1.81(4); Ti2−N3, 2.199(2); Ti2−N4, 2.058(2); Ti2−C30, 2.277(3); Ti2−H1, 1.89(4); C30−Ti1−H1, 86.3(11); C30−Ti2−H1, 84.3(11); Ti1−C30−Ti2, 81.85(9); Ti1−H1−Ti2, 106.9(18).

Scheme 2



of the μ-Me and μ-hydrido groups. The structure confirms the formulation of the series. The μ-Me is best described as a symmetric pyramidal bridge with an acute Ti1−C30−Ti2 angle of 81.85(9)°. The only other structurally characterized dititanium complex with a μ-Me group is anionic $Ti_2Me_9^-$,[11c] which has an unsymmetrical linear μ-Me group.[14] The Ti−C(30) distances of 2.270(3) and 2.277(3) Å are ca. 0.1 Å longer than related distances for terminal Ti(III) methyls.[15] It is unlikely that the Ti−μ-Me bonds have agostic character. While two of the Ti···$H_{\mu-Me}$ distances are relatively short (Ti1−H30B = 2.26(4) Å, Ti2−H30C = 2.13(3) Å), there is no IR or NMR spectroscopic evidence for such an interaction. The μ-hydrido ligand symmetrically bridges the two Ti centers with an angle of 106.9(18)°. The complex also features an intermetal separation of 2.9788(6) Å, which may indicate a modest amount of direct metal−metal interaction.[3d,e,10,16]

In conclusion, we have prepared several new dititanium complexes supported by binucleating bis(amidinate) ligands. The development of these and related bimetallic complexes for use in catalytic bond-forming reactions is in progress.

Acknowledgment. We thank Dr. Richard K. Shoemaker for his assistance acquiring NMR spectra and the University of Colorado and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supporting Information Available: Text and tables giving synthetic details and characterization data for all new compounds and X-ray crystallographic data for compounds **4** and ***meso*-5**; crystallographic data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020960P

---

(14) For a structurally related Ti−Rh heterobimetallic species, see: (a) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402−6404. Related dizirconium species: (b) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397−398.

(15) (a) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485−1494. (b) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893−894.

(16) Ti−Ti bonding has been proposed in some complexes with very short intermetal separations: (a) Cummins, C. C.; Schaller, C. P.; Van Duyne, G.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985−2994. (b) Horácek, M.; Kkupfer, V.; Thewalt, U.; Stepnicka, P.; Polásek, M.; Mach, K. *J. Organomet. Chem.* **1999**, *584*, 286−292.