Novel titanium(II) amine complexes L₄TiCl₂[L = 1/2 N,N,N',N'-tetramethylethylenediamine (TMEDA), 1/2 N,N,N'-trimethylethylenediamine, pyridine, 1/2 2,2'-bipyridine]: synthesis and crystal structure of monomeric trans-(TMEDA)₂TiCl₂


Published in:
Inorganic Chemistry

DOI:
10.1021/ic00002a002

Published: 01/01/1991

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

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substantial internal micropore volume, we examined the water collapsing the framework, i.e. if it were possible to generate any about a crystallographic 2-fold phosphate group, which is partially responsible for determining the size and shape of the tunnel, about a crystallographic 2-fold axis (Figure 1b).

The structure of (CH₃)₂NH₃[Mo₂O₇(PO₄)₂(H₂PO₄)] was examined with a single-crystal X-ray diffraction study. Figure 1 shows the structure of 2 viewed both parallel and perpendicular to the MoOPO₄-like layers, and the interlamellar phosphate groups are obvious. There is a slight disorder of the PO₄ portion of the P(OH)₂ group about a crystallographic 2-fold axis. All of the Mo atoms are in the +5 oxidation state and display the characteristic short Mo–O molybdenyl contacts (1.61 Å). While the analytical data discussed above leave no doubt that there are stoichiometric amounts of MeNH₃⁺ cations in the molybdenum phosphate framework of 2, we could find no trace of the cation in the crystal structure. All of the significant peaks in the final difference map (+1.70 to −1.41 eÅ⁻³) were near the Mo or P atoms. The simulation of the powder X-ray diffraction measurements indicated that the MoOPO₄-like layers, and the interlamellar phosphate groups to access essentially all of the internal volume of the solids when water is used as the probe molecule.

In summary, a new class of molybdenum phosphates based on the Mo₅O³(PO₄)₂(H₂PO₄) framework can be easily prepared by the reaction of a Mo⁶⁺ source in the presence of phosphoric acid. Unlike many other open framework solids, which yield a specific structure when hydrothermally prepared in the presence of a specific templating cation, the Mo₅O³(PO₄)₂(H₂PO₄) framework is very accommodating in terms of formation in the presence of cations of varying sizes and shapes. Absorption isotherms indicated it was possible, after decomposition of the entrained organic cation, to access essentially all of the internal volume of the crystals via a tortuous pathway.

**Acknowledgment.** We are grateful to Professor A. Clearfield for sharing his related results on this system prior to publication and to Drs. J. W. Johnson and A. J. Jacobson for useful discussions.

**Supplementary Material Available:** Table S1, listing experimental crystallographic details, positional and thermal parameters, and bond distances and angles (9 pages); Table S2, listing calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

**Novel Titanium(II) Amine Complexes L₄TiCl₄ [L = 1/2 N,N,N',N'-Tetramethylthelylenediamine (TMEDA), 1/2 N,N,N',N'-Trimethylthelylenediamine, Pyridine, 1/2 2,2'-Bipyridine] Synthesis and Crystal Structure of Monomeric trans-(TMEDA)₂TiCl₄**

Interest in the chemistry of divalent titanium has been stimulated by the very diverse aspects of its chemical reactivity, including activation of small molecules (N₂, CO₂, CO₂, H₂), and further...
coupling of olefins and acetylenes, and a possible role played in Ziegler–Natta catalysis. However, apart from the bispentadienyl and related systems, the chemistry of divalent titanium is poorly known and is limited to a few examples. Only three pentadienyl and related systems, the chemistry of divalent titanium is poorly known and is limited to a few examples. Only three pentadienyl and related systems, the chemistry of divalent titanium is poorly known and is limited to a few examples.

The lack of suitable Ti(II) starting compounds has probably been the limiting factor in the development of this chemistry. Recent results have shown that amines have an unexpected stabilizing effect on low-valent vanadium, and due to the fact that these compounds are versatile starting materials for studying the poorly known chemistry of V(II), we were especially interested in testing a similar synthetic strategy for the chemistry of low-valent group 4 transition metals. In this paper we wish to report the synthesis and crystallographic characterization of a novel class of trans-cl2Ti(amine)4 complexes.

As illustrated in Scheme I the reduction of TiCl3(THF) with an excess of lithium in the presence of 6 equiv of TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) proceeded slowly at room temperature, initially forming a mixed-valence Ti(II)/Ti(III) species (I) as a very insoluble, air-sensitive, light brown solid. The solid dissolved within 2 days of stirring in the presence of metallic Li, forming a dark brown reddish solution from which air-sensitive, light violet crystals of trans-(L)2TiCl2(L = pyridine) were obtained (yield 85%) after filtration, concentration, and cooling at −30 °C.

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Figure 1. ORTEP drawing of 2, showing the labeling scheme. Selected bond distances (Å) and angles (deg): Ti-Cl = 2.477 (2), Ti-N1 = 2.381 (7), Ti-N2 = 2.377 (7), Cl-Ti-N1 = 90.3 (2), Cl-Ti-N2 = 90.0 (2), N1-Ti-N2 = 79.2 (3).

The structure of the TMEDA adduct 2 has been demonstrated by X-ray analysis. The molecule (Figure 1) possesses the same trans halide octahedral geometry previously observed for trans-L4VCl2, and trans-(dme)2TiCl2 with comparable values of the Ti-Cl distance [Ti-Cl = 2.477 (2) Å]. Conversely, the Ti-N distances are slightly longer than for the isostructural vanadium complex, probably as a result of a more efficient Ti-Cl π bonding.

The solution chemistry of 2 is characterized by a remarkable lability of the coordinated TMEDA ligands, allowing facile ligand replacement reactions with several amines, and formation of the corresponding trans-cl2TiL4 derivatives (L = pyridine (4), (1/2), 2,2'-bipyridine, (5) in crystalline form. The lability of the coordinated amine is probably responsible for the thermal instability of 2–4 toward the disproportionation to higher oxidation states. For instance, light violet crystals of 2 dissolve in both THF and toluene, yielding golden yellow solutions, which darken slowly at room temperature. The only identifiable reaction product was the isomeric-valence species 1, obtained as light brown

14 A red suspension of TiCl3(THF) (30.5 g, 0.082 mol) in THF (350 mL) was stirred with metallic lithium (1.9 g, 0.27 mol) in the presence of an excess of TMEDA (58 g, 0.497 mol). A brown insoluble microcrystalline material separated after 3 hours. The solid slowly dissolved during 48 h of stirring, forming a light violet crystalline solid. The mixture was diluted with THF (200 mL), filtered, and concentrated. Light violet crystals of 2 (24.6 g, 70 mmol, 85%) separated upon standing at low temperature (−30 °C).
15 Crystal data for C32H32Cl2N,Ti(2) at room temperature: monoclinic, space group P21/n with a = 9.784 (2), b = 12.492 (2), c = 9.335 (2), β = 97.49 (5), V = 923.4 (3) Å3, Z = 2, and dcalc = 1.261 g cm−3. Of 1459 unique reflections collected by using Mo Kα (λ = 0.71073 Å) radiation (2θmax = 44.8°), 966 with I > 2σ(I) were used in the final refinement. R = 0.072, R = 0.084, and GOF = 1.60. The highest residual peak in the final difference Fourier map was 0.500 e Å−3. Due to the conformational disorder, atoms C3 and C4 were isotropically refined with an occupancy of 50%.
needles upon standing 24 h at room temperature (Scheme II). Very fast reaction was observed in boiling THF. A similar fate was observed for the pyridine complex 4, whose royal blue solutions turned brown at room temperature within 24 h, forming olive green needles of TIC13(py)3 upon cooling. Complex 3 decomposes only slowly in boiling toluene. Conversely, complex 5 and the mixed-valence species I are thermally robust and can be refluxed in THF for several days without observing any appreciable decomposition. That I is a Ti(II)/Ti(III) mixed-valence species has been indicated by its quantitative formation from TIC13(THF)2 with TiCl4(TMEDA)2 (1:1 ratio). In accordence, chemical degradation of I with pyridine gave a mixture of olive green TIC13(py)3 and royal blue TIC13(py)4, which have been identified after fractional crystallization. While the 1:1 ratio has been confirmed by analytical data,16 the dimeric structure has been tentatively assigned on the basis of the close similarities with the results obtained in the chemistry of analogous vanadium derivatives.16 Satisfactory elemental analyses have been obtained for all the complexes.16

The low value of the magnetic moment of 1.9384, and the g anisotropy observed at 2.67 GHz, are consistent with the presence of one unpaired electron per dimeric unit. The ESR spectrum at X-band frequency at 295 K showed an isotropic spectrum characteristic of an octahedral species $S = 1/2$ ($g = 1.9384$), and the g anisotropy observed at 77 K ($g_1 = 1.9485$, $g_2 = 1.9264$) confirmed that the complex has an axial symmetry.17 These observations suggest also that a strong Ti–Ti interaction (probably bonding) may be present in complex I. With the only exception of 5, which is diamagnetic, the other complexes are paramagnetic, with values of $\mu_B$16 as expected for a high-spin d2 electronic configuration.

The general tendency of 2 to take part in aggregation reactions with MX$_2$ species (M = Al, Zn, Mg, Li; X = Cl, Me, Et, OR, H) is present under investigation in view of its relevance to Ziegler–Natta modeling studies.

Acknowledgment. This work has been supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the Petroleum Research Fund, administered by the American Chemical Society. The Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) is gratefully acknowledged for providing a visiting scholarship (J.J.H.E.).

Supplementary Material Available: Text giving experimental details for the preparation of all the complexes and listings of crystallographic details, atomic positional and thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (6 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Activated Molybdenum–Molybdenum Quadruple Bonds. 2. First Example of Alkyne Additions to Metal–Metal Quadruple Bonds

Quadruply-bonded dimetal complexes have been known for more than 26 years;1 however, their use in activation of alkynes and other small molecules has received little attention.1,6 Pre-viously, we reported that ethylenediamine (en) solutions of Mo$_2$(O$_2$CMe)$_4$ (4) produced an "activated" quadruply-bonded dimolybdenum dication, [Mo$_2$(en)$_4$(O$_2$CMe)$_4$]$^{2+}$[(O$_2$CMe)$_3$]$^{-}$en, that showed unusual reactivity toward a variety of inorganic and organic substrates.1,6 As a continuation of these studies, we describe here the first alkyne derivatives of a metal–metal quadruply-bonded complex. The alkyne ligands in these compounds are thermally hydrogenated and extruded as alkenes via an unusual amine-to-alkyne hydrogen-transfer reaction.

Addition of the terminal aryl alkyne 4-R$_2$H$_2$C=C=CH (R = H, Me, i-Pr) to en solutions of Mo$_2$(O$_2$CMe)$_4$ at room temperature affords the alkyne adducts 2 (R = H), 3 (R = Me), and 4 (R = i-Pr) of empirical formula [Mo$_2$(μ-4-R$_2$H$_2$C=C(μ-O$_2$CMe)(en)$_4$]$^{2+}$[O$_2$CMe)$_3$]$^{-}$en. The three compounds are formed in two isomeric configurations, a and b, in approximately a 1:1 ratio (eq 1), as determined by $^1$H NMR spectroscopy.10

$$\text{Mo}_2\text{(C}_2\text{H}_4\text{C}=\text{CH)} + 4\text{RCH}_2\text{C} = \text{CH} \rightarrow \text{R}_2\text{H}_2\text{C} = \text{CH} \text{(1)}$$

The details of the formation of other alkyne derivatives will be described in a full paper: Kerby, M. C.; Eichhorn, B. W.; Doviken, L. Manuscript in preparation.


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(10) To an orange-red solution of 1 (90 mg, 0.21 mmol) in en (anhydrous, 2 mL) was added 4-MeH$_2$C=C=CH (29 mg, 0.25 mmol), producing an immediate color change to dark red. After several days, red-purple crystals of 3a and 3b coprecipitated and were dried in vacuo (74 mg; 44%, based on 1). The same procedure is used for the synthesis of 2a, 2b, 3a, and 3b. Selected NMR data for an appropriate equimolar mixture of 2a and 2b as follows: 1H NMR (DMSO-d$_6$, 25 °C): $\delta$ 8.44 (s, 1 H), 7.13 (s, 1 H) (C$_2$H$_4$C=CH); 6.84 (t, 1 J = 7.5 Hz, 2 H, meta); 7.22 (d, J = 7.7 Hz, 2 H, ortho); $\delta$ 7.13 (t, J = 7.0 Hz, 1 H, para); 7.06 (t, J = 7.6 Hz, 2 H, meta); 6.92 (t, J = 7.1 Hz, 1 H, para); 6.99 (d, J = 8.0 Hz, 2 H, ortho) (CH$_2$C=CH). 13C NMR (DMSO-d$_6$, 25 °C): $\delta$ 141.5, 127.2 (C$_2$H$_4$C=CH). Selected spectroscopic data for an approximate equimolar mixture of 3a and 3b are as follows: 1H NMR (DMSO-d$_6$, 25 °C): $\delta$ 8.40 (s, 1 H), 7.10 (s, 1 H) (4-MeH$_2$C=C=CH); 6.90 (d, J = 8 Hz, 2 H, 2H); 6.67 (d, J = 8 Hz, 2 H) (4-MeH$_2$C=C=CH); 6.29 (s, 1 H) (4-MeH$_2$C=C=CH). 13C NMR (DMSO-d$_6$, 25 °C): $\delta$ 141.6, 127.3 (4-MeH$_2$C=C=CH). Molar conductivity (DMSO, 25 °C): 32.0 Ω$^{-1}$ cm$^2$ M$^{-1}$. Anal. Calcd for C$_2$H$_4$N$_2$O$_2$: C, 33.50; H, 7.57; N, 18.58. Found: C, 33.64; H, 7.85; N, 19.68. Selected NMR data for an approximate equimolar mixture of 4a and 4b are as follows: 1H NMR (DMSO-d$_6$, 25 °C): $\delta$ 8.48 (s, 1 H) (4-Pr$_2$CH$_2$C=C=CH); 6.71 (d, J = 8 Hz, 2 H) (4-Pr$_2$CH$_2$C=C=CH); $\delta$ 8.62 (d, J = 8 Hz, 2 H) (4-Pr$_2$CH$_2$C=C=CH); 6.12 (d, J = 9 Hz, 6 H), 1.20 (d, J = 9 Hz, 6 H) (4-Pr$_2$CH$_2$C=C=CH). 13C NMR (DMSO-d$_6$, 25 °C): $\delta$ 25.4, 23.9 (4-Pr$_2$CH$_2$C=C=CH).