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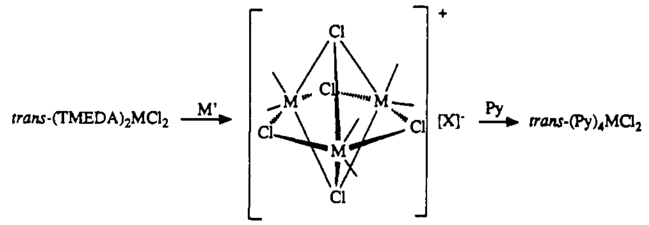
Communications

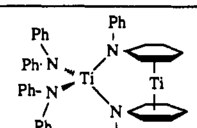
Labile *triangulo*-Trititanium(II) and -Trivanadium(II) Clusters

Triangular trinuclear clusters have stimulated considerable theoretical interest[1] and produced elegant synthetic chemistry,[2-4] since they can be regarded as the basic building blocks of many high-nuclearity polyhedral clusters. A cluster compound contains, by definition, a network of metal–metal bonds that define the coordination polyhedron. However, theoretical work has demonstrated that in *triangulo* clusters the presence of at least three bridging ligands is a very important factor for the stability of the M_3 skeleton.[1] Therefore, the obvious conclusion important to synthetic chemists is that M–M bonds can be rather weak in these species.

We have now prepared cationic *triangulo*-trititanium(II) and -trivanadium(II) clusters with the dual purpose of (i) making an entry into the nonexistent cluster chemistry of divalent vanadium and titanium and possibly (ii) testing the ability of these divalent metals to form M–M bonds [debated in the case of V(II)[5] and extremely rare in the case of Ti(II)[6]]. The choice of *trans*-$(TMEDA)_2MCl_2$ (M = Ti,[7] V[8]; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) as starting materials was determined by their versatility in disproportionation, ligand replacement and clusterification reactions.[9]

Scheme I



M		M'	X	μ_{eff} (μ_B)
Ti	1	$NaNPh_2$		1.81
V	2	$NaNPh_2$	$V(NPh_2)_4$	5.77
V	3	$VCl_3(THF)_3$	$Cl_4V(TMEDA)$	5.01

As shown in Scheme I, the reaction of *trans*-$(TMEDA)_2MCl_2$ with $NaNPh_2$ and $VCl_3(THF)_3$, able to selectively abstract one chlorine atom, proceeds instantaneously at room temperature, leading to the formation of the trimetallic cationic $[(TMEDA)_3M_3Cl_5]^+$ (M = Ti, V).[10] The lower stability of *trans*-$Cl_2Ti(TMEDA)_2$ with respect to the vanadium analogue has so far prevented the preparation of a wider series of titanium derivatives. It is noteworthy that while the same trimetallic frame has been obtained in the case of vanadium upon treatment with $TiCl_3(THF)_3$ and $YCl_3(THF)_3$,[9] reaction with other salts [$ZnCl_2(THF)_2$, $AlCl_3(THF)_3$] capable of forming complex di-

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(6) The existence of Ti–Ti single bonds has been suggested on the basis of Ti–Ti distances of 2.954 and 2.910 Å: (a) Schafer, H.; Laumanns, R.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 325. (b) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *95*, 7870.

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(10) **1** was prepared as follows. Solid NaH (0.34 g, 13.7 mmol) was added to a cooled solution (−60 °C) of Ph_2NH (2.3 g, 13.6 mmol) in THF (70 mL). The addition of $(TMEDA)_2TiCl_2$ (2.28 g, 6.6 mmol) turned the color deep brown. The mixture was stirred for 2 h at −30 °C and at room T for 10 h. After evaporation of the solvent in vacuo, the solid residue was recrystallized from ether (50 mL), yielding deep brown-red crystals of **1** (1.16 g, 0.77 mmol). Anal. Calcd (found) for $C_{70}H_{88}N_{10}Cl_5OTi_5$: C, 55.97 (55.85); H 5.90 (5.78); N, 9.32 (9.28); Cl, 11.80 (11.77); Ti, 15.94 (15.91). **2** was prepared as follows. THF solution (150 mL) of neat Ph_2NH (2.7 g, 16 mmol) was treated with NaH (0.40 g, 16 mmol). The mixture was stirred and warmed for 30 min. The addition of *trans*-$(TMEDA)_2VCl_2$ (2.8 g, 7.8 mmol) to the resulting mixture turned the color to deep red. Stirring was continued for 14 h. The solvent was removed in vacuo and the solid residue recrystallized from toluene (40 mL) containing 10 mL of THF. Olive-green crystals of **1** separated upon cooling at −30 °C (yield 0.85 g, 0.61 mmol, 31%). Anal. Calcd (found) for $C_{66}H_{88}V_4Cl_5N_{10}$: C, 56.47 (56.27); H, 6.27 (6.40); N, 9.98 (9.83); Cl, 12.65 (12.28); V, 14.54 (14.55). **3** was prepared as follows. A suspension of $VCl_2(TMEDA)_2$ (3.12 g, 8.8 mmol) in THF (200 mL) was treated with solid $VCl_3(THF)_3$ (1.46 g, 3.9 mmol). The color turned purple and a gray microcrystalline solid formed during the 6 h of stirring. The gray solid was filtered and extracted with boiling THF, yielding greenish gray crystals of **3** (2.10 g, 2.1 mmol, 73%). Anal. Calcd (found) for $C_{24}H_{64}N_8V_4Cl_9$: C, 29.18 (29.27); H, 6.48 (6.64); N, 11.34 (11.26); V, 20.65 (20.47); Cl, 32.35 (32.57).

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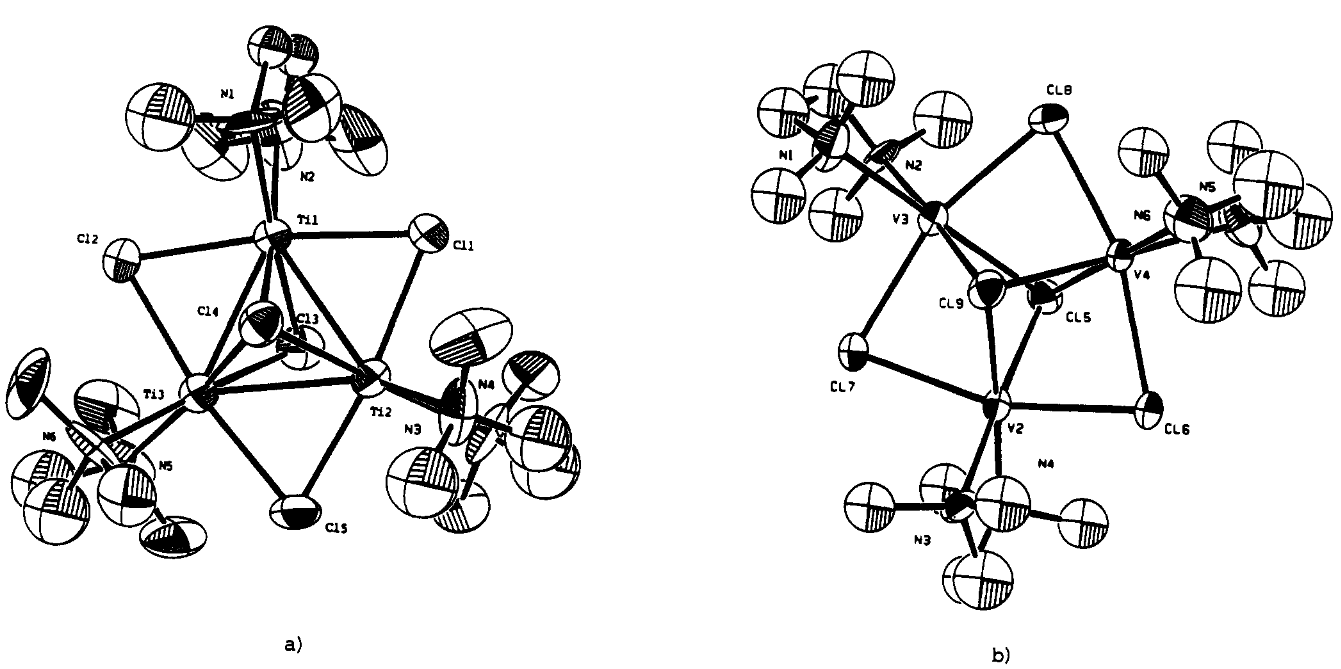

Figure 1. (a) ORTEP drawing of $[(\mathrm{TMEDA})_3\mathrm{Ti}_3\mathrm{Cl}_5]^+$ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: Ti1–Ti2 = 2.761 (4), Ti1–Ti3 = 2.770 (4), Ti2–Ti3 = 2.762 (4), Ti1–Cl1 = 2.474 (5), Ti1–Cl3 = 2.470 (5), Ti1–N1 = 2.317 (11); Ni–Ti1–N2 = 78.5 (4), N1–Ti1–Cl1 = 92.7 (3), Cl1–Ti1–Cl3 = 87.37 (16). (b) ORTEP drawing of $[(\mathrm{TMEDA})_3\mathrm{V}_3\mathrm{Cl}_5]^+$ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: V2··V3 = 3.145 (6), V2··V4 = 3.159 (5), V3··V4 = 3.158 (5), V2–Cl7 = 2.499 (7), V2–Cl5 = 2.510 (7), V2–N3 = 2.20 (2); N3–V2–Cl7 = 97.4 (5), Cl6–V2–Cl7 = 162.3 (7), Cl5–V2–Cl7 = 84.8 (2), V2–Cl7–V3 = 70.2 (2), V2–Cl5–V3 = 77.5 (2).

anions yielded different products having the well-known structure $[(\mathrm{L})_6\mathrm{V}_2\mathrm{Cl}_3]^+$.[11] The reaction with NaNPh_2 appears to be of a different nature. With both metals, the formation of the trimeric species is accompanied by a partial disproportionation reaction and consequent formation of a mixed-valence species. In the case of vanadium, the formation of the anion $[\mathrm{V}(\mathrm{NPh}_2)_4]^-$ is rather straightforward.[12] However, the formation of the dimetallic anion $[N,N'\text{-}\{\mathrm{Ti}[(\eta^6\text{-}\mathrm{C}_6\mathrm{H}_5)\mathrm{PhN}]_2\}\mathrm{Ti}(\mathrm{NPh}_2)_2]^-$ in the case of **1** suggests that the reaction proceeds via a complicated disproportionation mechanism involving the formation of zerovalent species.

The structures of **1** and **3** have been determined by X-ray analysis.[13] The trimetallic structure of the $[\mathrm{M}_3\mathrm{Cl}_5(\mathrm{TMEDA})_3]^+$ cation is basically the same in the Ti and V derivatives (parts a and b of Figure 1, respectively) and is defined by the three metallic centers and three coplanar bridging chlorine atoms. The remaining two μ^3-chlorine atoms are symmetrically placed above and below the molecular plane. The M–Cl distances are slightly different in the two compounds probably as a result of the different electronic configurations of the two metals [ranging from 2.456 (5) to 2.503 (5) Å and from 2.496 (7) to 2.537 (8) Å for **1** and **3** respectively]. Furthermore, while the M–Cl distances formed by the axial (μ^3-) and equatorial (μ^2-) chlorine atoms are quite comparable in **1** [Ti1–Cl1 = 2.474 (5) Å, Ti1–Cl3 = 2.470 (5) Å], a marked difference can be observed in the vanadium derivative **3** [V2–Cl6 = 2.496 (7) Å, V2–Cl9 = 2.526 (8) Å]. The $N,N'\text{-}\{\mathrm{Ti}[(\eta^6\text{-}\mathrm{C}_6\mathrm{H}_5)\mathrm{PhN}]_2\}\mathrm{Ti}(\mathrm{NPh}_2)_2$ anion in complex **1** (Figure 2) consists of a tetracoordinated titanium atom placed in the center of a slightly distorted tetrahedron defined by the nitrogen atoms of four amido groups (N–Ti–N angles ranging from 100.4 to 125.8°). Two rings from two different amido groups are parallel and are attached to one titanium atom, formally zerovalent, forming a $(\eta^6\text{-arene})_2\mathrm{Ti}$ sandwich. No special features were observed for the $\mathrm{VCl}_4(\mathrm{TMEDA})^-$ anion of **3**, which possesses a normal octahedral geometry (Figure 1S).

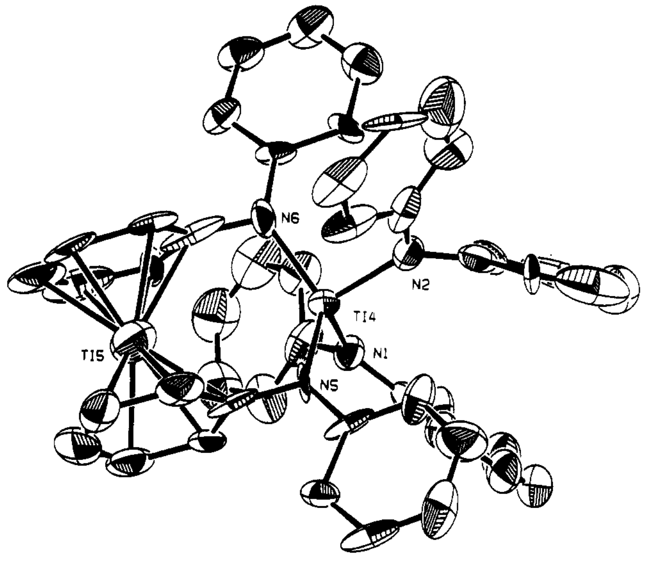

Figure 2. ORTEP drawing of $[N,N'\text{-}\{\mathrm{Ti}[(\eta^6\text{-}\mathrm{C}_6\mathrm{H}_5)\mathrm{PhN}]_2\}\mathrm{Ti}(\mathrm{NPh}_2)_2]^-$ showing the labeling scheme. Selected values of bond distances (Å) and angles (deg) are as follows: Ti4–N7 = 1.990 (11), Ti4–N8 = 2.008 (10); N7–Ti4–N8 = 100.4 (4), N8–Ti4–N10 = 125.8 (4).

The difference between the M–M distances observed in the two cations is striking. The fairly short Ti–Ti bonding distances (average Ti–Ti = 2.764 Å) observed in **1** might be consistent with

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(13) Crystal data for **1** and **3** at room temperature are as follows. **1**: triclinic, $P\bar{1}$, a = 16.809 (4) Å, b = 18.994 (5) Å, c = 12.162 (4) Å, α = 109.13 (2)°, β = 97.16 (2)°, γ = 81.04 (2)°, V = 3830.2 (2) Å^3, Z = 2; least-squares refinement of 538 parameters and 4896 significant reflections [$I \geq 2.5\sigma(I)$] out of 11 316, gave residuals of R = 0.089 (R_w = 0.104). One interstitial molecule of ether was found to be disordered over two positions. **3**: $\mathrm{C}_{24}\mathrm{H}_{64}\mathrm{N}_8\mathrm{Cl}_9\mathrm{V}_4$, fw = 987.67, triclinic, $P\bar{1}$, a = 14.169 (5) Å, b = 18.531 (3) Å, c = 8.695 (1) Å, α = 101.40 (12)°, β = 90.90 (23)°, γ = 90.96 (2)°, V = 2237.2 (9) Å^3, Z = 2; least-squares refinement of 286 parameters and 1750 significant reflections [$I \geq 3.0\sigma(I)$] out of 6536, gave residuals of R = 0.069 (R_w = 0.070).

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the formation of Ti–Ti single bonds.[6] Furthermore, the magnetic moment of **1** ($\mu_{\text{eff}} = 1.81\ \mu_B$), although difficult to interpretate because of the multivalent and polymetallic nature of these compounds, is consistent with the presence of one unpaired electron per molecule. Considering that the anionic fragment of **1** contains one titanium atom bonded to the four amido groups which is probably a d^1 Ti(III), and another which is likely a diamagnetic d^4 Ti(0) atom, the trimetallic Ti(II) frame can reasonably be expected to be diamagnetic. By way of contrast, the V–V distances in the isostructural trivanadium aggregate **3** [ranging from 3.145 (6) to 3.159 (5) Å] are considerably longer and likely not in agreement with the presence of a V–V bond. Assuming a normal d^2 high-spin configuration for the octahedral VCl_4(TMEDA) fragment, the magnetic moment of **3** ($\mu_{\text{eff}} = 5.01\ \mu_B$) indicates that the vanadium atoms of the trinuclear unit should possess a low-spin electronic configuration with less than one unpaired electron per vanadium atom.

There is no doubt that somehow the different electronic configuration of the two metals (d^2 against d^3) should be responsible for the different M–M distances in these two electron-poor clusters.[1] However, in our opinion the low-spin configuration of each vanadium atom in **3** (with two coupled electrons and no V–V bond) makes the existence of a Ti–Ti bond in **1** doubtful, in spite of the short "bonding" distance.

Consistent with this rationale, the cleavage of the trimetallic frames was easily achieved with both **1** and **3** via simple treatment with pyridine at room temperature, forming the monomeric $(\text{pyridine})_4MCl_2$ [M = Ti,[7a] V[7b]] as deep blue and deep red crystalline solids, respectively.

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Supplementary Material Available: Tables listing crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for 1 and 3, an ORTEP diagram (Figure 1S) of the $[VCl_4(\text{TMEDA})]^-$ anion in 3, and a fully labeled ORTEP for the cation 3 (32 pages); tables of observed and calculated structure factors for 1 and 3 (70 pages). Ordering information is given on any current masthead page.

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[Fe(4-imidazoleacetate)$_2$]·2CH$_3$OH: A 2D Antiferromagnetic Iron(II) System Exhibiting 3D Long-Range Ordering with a Net Magnetic Moment at 15 K

Cooperative magnetic phenomena are well-known in solid-state materials but rare in molecular systems. Although substantial efforts have focused on the preparation of ferro- or ferrimagnetic molecular compounds exhibiting long-range magnetic ordering during the past few years, the transition temperature of the ferromagnetic molecular compounds reported so far is extremely low.[1,2] On the other hand, some antiferromagnetic substances exhibit weak ferromagnetism at low temperature resulting from a canting of the spins.[3] Although uncommon, such a situation may occur either in linear chain systems when magnetic interactions between next nearest neighbors occur or in two- or three-dimensional materials.[4] Among this class of compounds, the layered complexes of 1,2,4-triazole with divalent metal thiocyanates,[5] although exhibiting canted spin structures quite similar to that reported in this work, are characterized by low ordering temperature (3–6 K) and hidden canting. The title compound, [Fe(4-imidazoleacetate)$_2$]·2CH$_3$OH, exhibits a net magnetic moment below 15 K, the highest 3D ordering temperature reported so far for a molecular compound characterized by a canted spin structure.

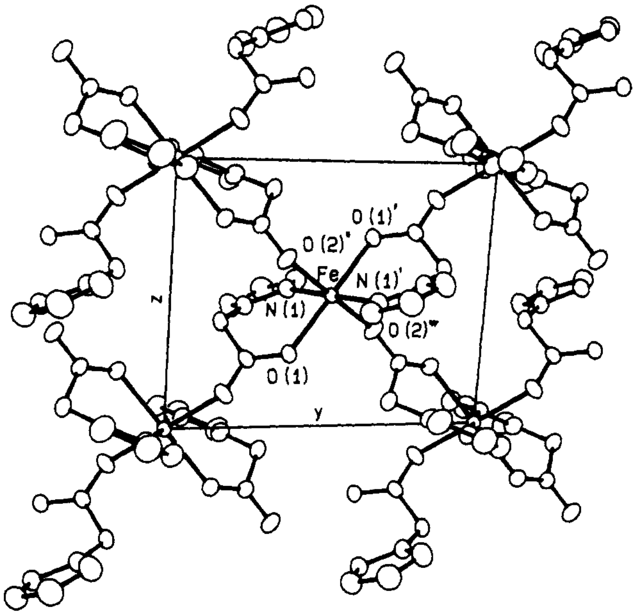

Figure 1. Projection of the unit cell of the [Fe(4-imidazoleacetate)$_2$]·2CH$_3$OH (**1**) complex molecule onto the *yz* plane. For clarity, the methanol molecules have been omitted.

Reaction of a 2:1 molar ratio of sodium 4-imidazoleacetate (Sigma) and ferrous acetate tetrahydrate[6] in deoxygenated methanol for 12 h affords white microcrystals of [Fe(4-imidazoleacetate)$_2$]·2CH$_3$OH (**1**) in 92% yield. Colorless single crystals suitable for X-ray diffraction study[7] were obtained by slow interdiffusion of deoxygenated methanolic solutions of sodium

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(7) Crystals of complex **1** belong to the monoclinic system, space group $P2_1/c$, with a 9.842 (2) Å, $b = 9.522$ (2) Å, $c = 8.144$ (2) Å, $\beta = 96.74$ (2)°, $V = 763$ (1) Å^3, $Z = 2$, and $d_{\text{measd}} = 1.57$ (4) g cm^{-3}. Diffraction data were collected at −6 °C to a 2θ(Mo) maximum of 30° by procedures described elsewhere[9] using an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 4448 reflections were recorded. A linear decay correction (total intensity loss 1.2%) was applied to the data as well as an absorption correction using the numerical method of Coppens.[10] Reflections were corrected for Lorentz and polarization effects,[11] 2074 of which with $I > 2\sigma$ were used in subsequent calculations. The structure was solved by using the heavy-atom method.[12] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the calculations at a fixed distance of 0.95 Å with a mean isotropic temperature factor U = 0.065 Å^2. The atomic scattering factors used were those proposed by Cromer and Waber[13] with anomalous dispersion effects.[14] The final full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.031$ and $R_w = [(\sum w||F_o| - |F_c||)w]/[(\sum |F_o|)w] = 0.043$ with a weighting scheme $w = 1/[\sigma^2(F) + 0.005F^2]^{1/2}$. The goodness of fit was $S = 1.01$.

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