(2)–Tc–P(1)–C(17) = –13.2°, while the P(2) phosphine ligand is slightly rotated in such a way that the P–C(methyl) bond nearly eclipses Tc–N(1) (N(1)–Tc–P(2)–C(23) = –10.7°).

Tc–P distances are similar in the two compounds (Tc–P(1) = 2.431 (1) Å in **1c** and 2.423 (1) Å in **1a**; Tc–P(2) = 2.387 (1) Å in **1c** and 2.391 (1) Å in **1a** but differ inside each complex, Tc–P(1) being on the average longer, without any apparent reason, than Tc–P(2) by 0.038 Å. In the only other P-containing complex of Tc(I) the Tc–P distances have been found to be in the range 2.38–2.44 Å.[17] Tc–CO distances of 1.87–1.88 Å compare well with those reviewed[23] in a variety of Tc(I)–Tc(III) compounds (1.86–1.90 Å). Tc–N distances are 2.202 (2) and 2.203 (2) Å in **1c** and 2.178 (4) and 2.190 (3) Å in **1a**. They are indistinguishable within each compound, which parallels the identity of the two trans CO substituents, while their average is possibly slightly shorter in the triazenido case. The structures of **1c** and **1a** permit an accurate comparison of acetamidinato and triazenido ligands in a strictly comparable molecular environment. The coordination geometries are not perfectly identical, as Tc, N(1), N(2), and N(3) lie strictly on the same plane in **1a**, while in **1c** C(31) is out of the Tc,N(1),N(2) plane by 0.055 Å. Both ligands are symmetrical as far as the pseudoallylic anion is concerned, C(31)–N(1) and C(31)–N(2) being 1.326 (4) and 1.331 (4) Å and N(1)–C(3) and N(2)–C(9) 1.396 (4) and 1.394 (4) Å in **1c** and N(3)–N(1) and N(3)–N(2) being 1.310 (5) and 1.320 (4) Å and N(1)–C(3) and N(2)–C(9) 1.393 (5) and 1.393 (5) Å in **1a**. This can be taken as the indication of a complete delocalization of the π-system in the two anions and agrees with the symmetry of the couples of Tc–N distances. The phenyl and *p*-tolyl groups are slightly out of plane with respect to the mean Tc,N(1),N(2),N(3)/C(31) plane, actual dihedral angles (τ) being 24.7 and 25.6° and 6.7 and 24.3° for the C(3)–C(8) and C(9)–C(14) planes in **1c** and **1a**, respectively. This corresponds to a substantial coupling of the π-systems on the pseudoallyl fragment and the two terminal aromatic rings. In fact, the superposition integral of two p_π atomic orbitals located on adjacent atoms decreases with the cosine of their dihedral angle τ, being 1 for $\tau = 0$ and as high as 0.90 for the maximum τ observed, which is 25.6°. Analysis of literature data shows that in such or similar ligands τ ranges from 5° ($\cos \tau = 0.996$) to 36° ($\cos \tau = 0.81$), indicating a definite tendency to planarity of the whole ligand perturbed by nonbonded interactions but not till decoupling of the π-system occurs.

Table VI collects some structural parameters of the triazenido, acetamidinato, and formamidinato anionic ligands as observed in some mononuclear transition-metal complexes. While the overall precision of the data is not sufficient to establish whether the N–C and N–N distances are different, the angular values inside the ligands seem to indicate a systematic trend. In particular, the N–(C/N)–N angle increases in the series triazenido, acetamidinato, and formamidinato, being respectively 104.7 (6), 109.4 (2), and 114.0 (8)°. It is clear that the effect runs in reverse order with respect to the putative effect of the steric hindrance of the C-substituent; it can be easily rationalized in terms of the VSEPR[30] model, the room taken by the nonbonding pair on N being greater than the room taken by the C–H and C–C bonding pairs and the room taken by the C–CH_3 bonding pair being smaller than that of the C–H bond as the methyl group is less electronegative than hydrogen. The increase of the N–(C/N)–N angle is paralleled by that of the bite of the bidentate ligand (see N–M–N angles in Table VI) and by a change of the (C/N)–N–C angles, which are smaller in the triazenido case.

A last point concerns the values of the C(4)–C(3)–C(8) and C(10)–C(9)–C(14) endocyclic phenyl angles; these are, on average, 117.5 (2)° in **1c** and 117.8 (5)° in **1a**, i.e. significantly smaller than 120°. It may be of interest to compare these values with others in the literature (last column of Table VI). It is found that angles in opposite phenyl rings are always identical within 2σ but that their average value changes: for instance it is close to 120° (e.g. 120.6 (8)° in $\mathrm{Re^I(PPh_3)_2(CO)_2(dpf)}$[10]) or much greater than 120° (e.g. 124.0 (6)° in $\mathrm{Cr^{III}(dpt)_3}$[27]). As it is known that the endocyclic phenyl angle changes from 114 to 125° according to the nature of the ipso substituent, being respectively smaller or larger than 120° for electron-donating or electron-attracting substitutents.[31] it may be tentatively suggested that the value of this angle can be an indirect indicator of the electron density on the pseudoallylic fragment or, more generally, of the π-back-bonding from the metal.

Registry No. **1a**, 99354-91-3; **1b**, 99354-92-4; **1c**, 99354-93-5; **1d**, 99354-94-6; **1e**, 99354-95-7; *mer*-[$\mathrm{Tc(PMe_2Ph)_3(CO)_2Cl}$], 64347-48-4; *trans*-[$\mathrm{Tc(PPh_3)_2(CO)_3Cl}$], 64396-16-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, and structure factor amplitudes for both compounds (45 pages). Ordering information is given on any current masthead page.

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Notes

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Direct Observation of the $HTiO_3^-$ Ion

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The existence of H_2TiO_3, sometimes called metatitanic acid, in the hydrolysis of Ti(IV) halides is supported by thermodynamic[1,2] and kinetic[3] studies. In aqueous solution it ionizes to cations containing the metal,[4] and bases derived from it that contain the metal are not well-characterized. Although the empirical formulas of some minerals of both the ilmenite and perovskite structures correspond to $MTiO_3$, the TiO_3^{2-} ion does not occur as a discrete unit in such minerals.[5] To our knowledge no report exists of the $HTiO_3^-$ ion, although a recent report on formation of calcium titanates contains results for empirical formulas suggesting the existence of the related $HTi_2O_5^-$ ion.[6]

This absence of $HTiO_3^-$ from the literature is vexing in view of the obvious stability of HCO_3^- and of numerous citations of $HSiO_3^-$,[7] ions whose chemistry it could be expected to resemble

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because of periodic relationships. A method exists for the production of HCO_3^- in the gas phase,[8] where several of its properties have been studied in the absence of solvent. We now report observation of the $HTiO_3^-$ ion by negative chemical ionization (NCI) mass spectrometry of titanium tetra-*n*-butoxide (Alfa Chemicals, Danvers, MA) and confirmation of the composition of the ion by its collisionally activated decomposition. Formation of such an ion was anticipated on the basis of prior experience with the formation of monomeric metaphosphate from several phosphate esters,[9] for in our experiments the negative ions have low internal energies and long lifetimes, qualities conducive to the formation of rearrangement products. NCI spectra were obtained on a ZAB-4F four-sector mass spectrometer[10] (BEEB geometry, VG Analytical Ltd., Manchester, U.K.) by introduction of the alkoxide via a partially retracted direct probe into a source at 75 °C with 5×10^{-6} torr Ar (as measured with the source ion gauge) as a buffer gas. Under these conditions the spectrum is dominated by ions from the more efficiently ionized halogen-containing impurities present in the sample from its preparation, but there is a peak of intensity 3% (relative to that of the most abundant negative ion in the spectrum, $(C_4H_9O)_2TiClO^-$; halogen-free ions are all of low abundance) present at m/z 97 with appropriate isotope peaks to contain one Ti. The charge of this ion was reversed by collision (after original acceleration through 7000 V) with thermal He (3×10^{-6} mbar) in a cell between the second and third sectors. The resulting collisionally activated decomposition (CAD) spectrum consisted of four peaks (percentages given are those of fragment ion current, uncorrected): m/z 64, 40%; m/z 65, 17%; m/z 80, 16%; m/z 81, 27%. These ions thus correspond to $^{48}TiO^+$, $^{48}TiOH^+$, $^{48}TiO_2^+$, and $^{48}TiO_2H^+$, by loss of the elements of HO_2, O_2, OH, and O, respectively, from the transitory[11] cation TiO_3H^+.

Structures were modeled by Fletcher–Powell geometry optimization using GAUSSIAN 82[15] and the Ti STO-3G basis set of Hehre.[16] A modification to facilitate convergence was added to the SCF module.[17] The geometry of the $HOTiO_2^-$ form of the anion, which we considered the most likely structure, was minimized by beginning with the Ti–O bonds and then the O–Ti–O angle, the distance from the O–Ti–O plane of the O bonded to H and Ti, the Ti–O–H angle, and the O–H bond length. The bond angles are then as follows: O–Ti–O, 123.9 ± 0.1°; Ti–O–H, 106.9 ± 0.1°; out of plane O (bonded to H and Ti) angle from the O–Ti–O plane, 6.8 ± 0.1°. The H–O–Ti plane bisects this latter O–Ti–O plane. The bond lengths are as follows: Ti–O, 166.1 ± 1 pm; Ti–OH, 191.4 ± 1 pm; O–H, 99.15 ± 1 pm. Since there is a report of a hydrido complex of a titanium(IV) alkoxide,[18] we also considered the form $HTi(O)_3^-$, with a Ti–H bond. Although numerous attempts were made, we could not obtain stable convergence for this form.

The experimental evidence speaks against the existence of the $HTi(O)_3^-$ form: there is no loss of H alone, as is virtually universally observed for H attached to a less electronegative atom. Formation of weak bonds like peroxy O–O bonds from species with stronger bonds is unprecedented in NCI chemistry, so that the forms $HOTi({=}O)OO^-$ and $HOO{-}Ti(O)_2^-$ are unlikely.

Thus calculations suggest that the structure $HOTiO_2^-$ exists in a potential well. Our observation of an ion of appropriate exact mass and of fragments at only the logical masses for the formula and structure confirm its existence for at least tens of microseconds in the absence of solvation.

One may at this point examine expected periodic relationships between HCO_3^- and $HTiO_3^-$, for they both are in old group IV, and assume that the only structural difference between HCO_3^- and $HTiO_3^-$ results from differences in the radii of C(IV) and Ti(IV). Data on HCO_3^- from the crystal structure of $NaHCO_3$[19] or from calculations of the free gaseous ion[8,20] both would have predicted a planar C_{2v} structure for $HTiO_3^-$. Use of the data from the crystal structure of HCO_3^- leads to the prediction of an O–Ti–O angle of 124° and Ti–O bond lengths of 180 and 188 pm; use of the computational results for the gas-phase ion would have generated 129° and 179 and 198 pm, respectively. The differences between this simple analogy and the result of the present computation are not so great, particularly when one considers the comparison with gas-phase HCO_3^-, where the elongated C–OH bond (relative to the bond length in the crystal structure) has drawn some attention.[20] The same pattern of elongation appears in the Ti–OH ion, and indeed the differences between the simplistic model and the computed structure are merely the modest nonplanarity and the somewhat shorter bond lengths of the latter. Our observation of $HTiO_3^-$ and computation of its structure, then, permits some delineation of the degree of periodic relationships in old groups IVA and IVB.

Registry No. $HTiO_3^-$, 98943-14-7; titanium tetra-*n*-butoxide, 5593-70-4.

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Formation of Polynuclear Chlorometalates by the Reduction of Transition-Metal Chlorides with Samarium Metal Slurries: Preparation and EXAFS Structure of $SmNb_3Cl_{14}$

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High-temperature reduction of early-transition-metal halides with metals has been a key technique for the synthesis of metal–metal-bonded polynuclear metal halides.[1] The possibility that similar reactions might take place under mild conditions if the metal reducing agent were in a highly active form has prompted us to investigate the reaction of metal-atomization-generated metal slurries[2] in hydrocarbons with early-transition-metal halides. In this communication we report that samarium metal slurries in methylcyclohexane reduce Nb_2Cl_{10}, Ta_2Cl_{10}, and $TiCl_4$ to form new polynuclear chlorometalate anions. In particular, we describe the characterization of the compound $SmNb_3Cl_{14}$, which contains a linear trinuclear mixed-valance chloroniobate anion.

Samarium metal slurry was prepared by cocondensing samarium metal with methylcyclohexane at liquid-nitrogen temperature in a Planer metal vapor apparatus.[3] After it was warmed to room temperature, the pyrophoric slurry was transferred under argon to a Schlenk tube. The final slurry contained ~10 mg of Sm/mL. Reactions with the metal chlorides were carried out in an He-filled Vacuum Atmospheres glovebox by stirring a portion of the slurry with a large excess of the metal chloride, either neat

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