Triethyloxonium Tetrafluoroborate as an Ethylating Agent in Aqueous Solution

Sir:

Alkyloxonium salts have been used extensively as alkylating agents in inorganic chemistry.[1] With few exceptions, the alkylations have been conducted in organic solvents that do not effect the solvolysis of the alkyloxonium ion, most commonly dichloromethane.[2] This restriction often leads to the use of a solvent inappropriate to the particular reaction.[3] Here we report on the general use of triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) as an ethylating agent in *aqueous solution*.

The generality of the procedure is exemplified by two paradigms important in inorganic chemistry: (i) the alkylation of a coordinated metal ion and (ii) the alkylation of a coordinated ligand. In addition, the simple aqueous esterification of a carboxylic acid is reported.

Ethyl cobalamin, ((ethyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate, and ethyl benzoate were synthesized in essentially quantitative yield from their unethylated parent compounds and triethyloxonium ion in aqueous solution.

Ethyl cobalamin was synthesized, following the reduction of cyanocobalamin (6.1 mM) with sodium borohydride (66.1 mM) to vitamin B_{12s}, by the addition of $Et_3O^+BF_4^-$ (27.63 mM) to the oxygen-free reaction solution. After 78 min at 25 °C, the product was identified as ethyl cobalamin by ultraviolet and ^1H NMR spectroscopy.[4,5]

((Ethyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate was synthesized from (2-aminoethanethiolato-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate[6] (3.0 mM) and $Et_3O^+BF_4^-$ (74.25 mM) by mixing these reagents in water at 4 °C and immediately placing the reaction at −15 °C. The ethylation is essentially complete in 3 h, and after 16 h the product was identified as ((ethyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate by visible, ultraviolet, and ^1H NMR spectroscopy.[7]

Ethyl benzoate was synthesized by the reaction of the benzoate ion (57.3 mM) with $Et_3O^+BF_4^-$ (1.58 M) in saturated $NaHCO_3$ at 25 °C; the pH was maintained in the range 6.4–8.4 by the addition of 5 N NaOH. After 82 min, the product was dissolved by the addition of ethanol and identified as ethyl benzoate by ultraviolet spectroscopy[8] and by its complete alkaline hydrolysis.

The hydrolysis of $Et_3O^+BF_4^-$ is virtually pH-independent from pH 4 to pH 9, where the half-life is 7.4 min at 25 °C and 1.95 min at 38 °C. Further, the reaction of $Et_3O^+BF_4^-$ with Cl^-, Br^-, and I^- confirms that the reaction is at least largely an S_N1 ionization of Et_3O^+:

$$Et_3O^+ \rightarrow Et^+ + Et\text{–}O\text{–}Et \xrightarrow{\text{nucleophile}} \text{ethylated nucleophile}$$

A comparable reaction is that of the *N,N*-dimethyl-2-phenylaziridinium ion with nucleophiles.[9]

Because Et_3O^+ is so reactive toward nucleophiles, its side reaction with the aqueous solvent can be accommodated by a suitable choice of concentration. The syntheses presented here establish the triethyloxonium ion as an ethylating agent of great utility in inorganic chemistry carried out in aqueous solution and will serve as a basis for our studies of its reactivity toward metal ions and their ligands, particularly those commonly found in proteins.

Acknowledgment. We wish to acknowledge preliminary work on ethyl cobalamin performed by C. Young and to express our gratitude to the Australian Research Grants Scheme and the University of Queensland for financial support. A discussion over dinner with Dr. D. St. C. Black has been one of the principal driving forces in this reaction to enshrined dogma.

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Transition-Metal Hydride Bond Energies: First and Second Row

Sir:

While thermochemistry for transition-metal systems is needed to understand and predict the reactivity and kinetics of metal systems, enumeration of this thermochemistry is a herculean task. Of equal value would be "typical" metal–ligand bond dissociation energies (BDEs) and a means of predicting how these BDEs vary with metal and metal environment. In this paper, we report new values for diatomic transition metal–hydride ion BDEs and analyze the periodic trends to identify such a typical BDE.

The thermochemistry reported here is measured by examining reaction 1 as a function of translational energy. The threshold

$$M^+ + H_2 \rightarrow MH^+ + H \qquad (1)$$

energy for these endothermic processes is determined and related to the metal hydride bond energy, $D(M^+\text{–}H)$. Detailed descriptions of our experimental apparatus[1] and methods of interpretation[2,3] have been published. The metal–hydride BDEs measured here, listed in Table I, typically fall below previously measured values.[4] Part of the difference results from correcting our values for excited electronic states in the reactant metal ion beam.[2,3] For several first-row metals (Cr, Mn, Fe, Co, Ni, and Cu), this is done explicitly by measuring the relative reactivity of these states. Details of these results will be published in subsequent papers.[5]

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Table I. Transition-Metal Hydride Bond Dissociation Energies^a

	$D°_0(M^+–H)$			promotion energy^d	
	this	lit.			
M	work	exptl^b	theory^c	sd^n	d^{n+1}
Sc	55.3 (2)	53 (4)	55.2, 52.7,^{e} 54.4^f	3.5	19.1
Ti	55.1 (2)	59	54.0	6.5	16.1
V	47.3 (1.4)	49	43.6	16.3	15.2
Cr	27.7 (2)	34 (4)	24.3, 22.5^e	45.9	25.3
Mn	47.5 (3.4)	52 (3)	39.6, 40.8,^{g} 37.4^h	13.5	63.7
Fe	47.0 (4)	58 (5)	47.0	11.3	26.7
Co	45.5 (2.3)	51 (4)	43.6	18.9	10.1
Ni	38.5 (1.4)	42 (2)	35.7	31.9	0.0
Cu	21.8 (2.1)	29	20.9	69.9	...
Y	58 (3)			6.4	28.9
Zr	54 (3)			7.7	17.7
Nb	53 (3)			14.1	10.9
Mo	41 (3)			54.1	18.3
Ru		40 (3)		39.6	15.2
Rh		41 (3)		60.6	6.7
Pd	53 (3)	44 (3)		82.2	0.0
Ag	15 (3)			123.9	...

^{a}All values in kcal/mol. Uncertainties in parentheses. ^{b}Reference 4. These values have been corrected to 0 K from 298 K values (0.9 kcal/mol higher). ^{c}Reference 6c, except as noted. ^{d}See text for definition. All values are calculated by using averages over all J levels, which are taken from: Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards: Washington, DC, 1949. ^{e}Reference 6b. ^{f}Reference 6d. ^{g}Reference 6a. ^{h}Reference 6e.

For the remainder of the first-row metals and all of the second row, we correct by the average electronic excitation energy, which assumes that all low-lying electronic states have equal reactivity.[3] Thus, these values could change as more detailed information becomes available. Theoretical values are also available for comparison.[6] These lie an average of 3 kcal/mol below the values presented here (approximately the error expected for the calculations[6c]) and clearly show the same periodic trends.

An early report[4b] of several of the first-row MH$^+$ BDEs noted an inverse correlation with E_p defined as the energy required to promote the metal ion into the lowest electronic state having a $4s3d^n$ electron configuration. A more complete definition of E_p, listed in Table I, includes the loss of spin-exchange energy when the MH$^+$ bond is formed.[4c] Promotion is still to an sd^n configuration, but now the s electron (the bonding orbital on M) is spin-decoupled from the d electrons.[7] Table I also lists an analogous definition for E_p when promotion is to a d^{n+1} configuration. Here the bonding orbital is a $d\sigma$ electron.

In Figure 1, the MH$^+$ BDEs are plotted against $E_p(sd^n)$. For the first row, the correlation is exceptionally good[8] while a similar plot vs. $E_p(d^{n+1})$ shows no correlation. The importance of including the effect of spin-exchange energies is best illustrated by Mn, which has $E_p(sd^5)$ = 13.5 kcal/mol but without exchange has E_p = 0 kcal/mol.[4b] These results suggest that the 4s orbital is a major component of the MH$^+$ bond. However, if E_p is alternatively defined as excitation to an sd^n state *but* where the $d\sigma$ orbital is the bonding orbital and spin-decoupled, a correlation nearly as good as that shown in Figure 1 is obtained. This implies that the sd^n configuration is important in describing the bonding but that the bonding orbital on the metal probably has both 4s and $3d\sigma$ character. This is in qualitative accord with recent ab initio calculations,[6] which go on to demonstrate that 3d character is especially significant on the left side of the periodic table.

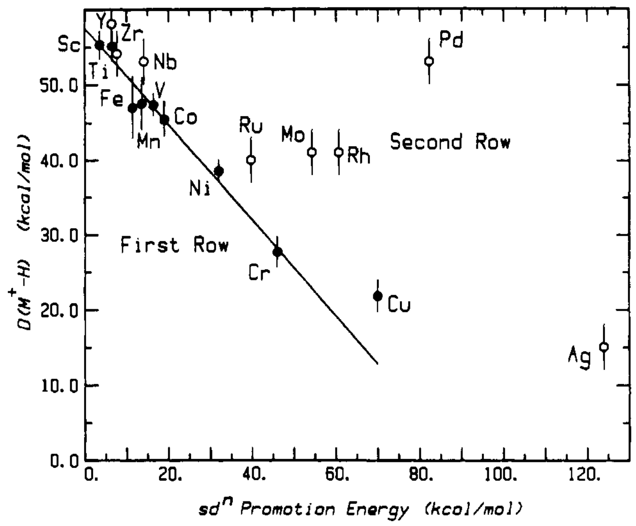

Figure 1. First-row (closed symbols) and second-row (open symbols) transition-metal–hydride ion bond energies vs. atomic metal ion promotion energy to an sd^n spin-decoupled state (see text). The line is a linear regression fit to the first-row data (excluding Cu).

In contrast with the first row, it is obvious that the second row is not well described by a straight line (Figure 1). Other definitions of E_p fare no better at correlating the bond energies. One reasonable explanation for the strong deviation of Pd is to suppose that it utilizes only the 4d orbital to bind H. Note that $E_p(sd^n)$ is quite high (making the 5s orbital energetically inaccessible) while $E_p(d^{n+1})$ is zero. Indeed, this effect may be important for Rh, Mo, and (to a lesser degree) Ru since these also have values of $E_p(d^{n+1})$ that are substantially less than $E_p(sd^n)$. Where $E_p(sd^n)$ is lower or comparable to $E_p(d^{n+1})$, i.e., Y, Zr, and Nb, the second-row MH$^+$ BDEs are consistent with (perhaps slightly higher than) the first-row correlation.

For the metals on the right side, these observations can be verified spectroscopically since the predicted ground state of MH$^+$ differs for the metal sd^n configuration (RuH$^+$, $^5\Delta$; RhH$^+$, $^4\Phi$; PdH$^+$, $^3\Delta$) and the d^{n+1} configuration (RuH$^+$, $^3\Phi$; RhH$^+$, $^2\Delta$; PdH$^+$, $^1\Sigma$).[9] In fact, *neutral* NiH and PdH do have different ground states, $^2\Delta$ and $^2\Sigma$, respectively. Ab initio MO calculations[10] indicate that this is indeed because the bonding in NiH is largely a 4s–1s interaction while in PdH it is 4d–1s.

One significant feature in Figure 1 is that the maximum MH$^+$ BDE is about 58 kcal/mol and occurs near E_p = 0. One useful way of thinking about this maximum is that it may represent any metal–hydride BDE once an orbital on the metal has been prepared for efficient bonding. This preparation probably needs to involve formation of a directional and sterically unhindered metal orbital having a single electron that is electronically decoupled from other electrons. In metal complexes and on metal surfaces, this preparation can be achieved by the electronic environment surrounding the binding site. Indeed, the most commonly cited value for metal–hydride BDEs is ≈60 kcal/mol.[11] The present study provides evidence that this figure is a useful value for *both* first- and second-row metals. Continued work in our labs is directed at characterizing metal environments that might be capable of inducing stronger than typical bonds[11,12] and at deter-

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(9) For metals on the left side of the periodic table, both the sd^n and d^{n+1} configurations lead to the same ground states (YH$^+$, $^2\Delta$; ZrH$^+$, $^3\Phi$; NbH$^+$, $^4\Delta$; MoH$^+$, $^5\Sigma$). See ref 3.

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mining whether the third-row transition metals that activate C–H bonds[13] might behave differently, perhaps because they have filled 4f orbitals shielding the 5d electrons.

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Articles

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Mononuclear Chromium Complexes of the Tripod Ligand (Tripod = 1,1,1-Tris((dimethylphosphino)methyl)ethane)

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Tripod (tripod = 1,1,1-tris((dimethylphosphino)methyl)ethane) reacts with anhydrous $CrCl_3$ or $CrCl_3(THF)_3$ in THF or CH_2Cl_2 to give $CrCl_3$(tripod), which may be crystallized from CH_2Cl_2 as a dichloromethane solvate, *fac*-$CrCl_3$(tripod)·CH_2Cl_2 (**1**), in high yield (>95%). All three phosphorus atoms are coordinated to the Cr atom. The reaction of anhydrous $CrCl_2$ with 2 equiv of tripod in THF yields *trans*-$CrCl_2$(tripod)$_2$ (**2**) in 96% yield. In **2**, each tripod behaves as a bidentate ligand with one uncoordinated $-PMe_2$ group. The reduction of **2** with Na/Hg in THF yields Cr(tripod)$_2$ (**3**) in 70% yield. The coordination geometry about Cr in **3** is that of a trigonal antiprism. X-ray diffraction studies have been performed on *fac*-$CrCl_3$(tripod)·CH_2Cl_2 (**1**), $CrCl_2$(tripod)$_2$ (**2**), and Cr(tripod)$_2$ (**3**). Crystal data for **1** ($CrCl_5P_3C_{12}H_{29}$): $M_r = 495.55$, orthorhombic, *Pbca* (No. 61), $a = 15.602$ (2) Å, $b = 16.718$ (5) Å, $c = 17.030$ (2) Å, $V = 4442$ Å^3, $d_{calcd} = 1.482$ g/cm^3, $Z = 8$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 13.2 cm^{-1}, final $R = 0.046$ ($R_w = 0.049$) from 2351 observed reflections ($I > 3\sigma(I)$) of 4351 measured. Crystal data for **2** ($CrCl_2P_6C_{22}H_{54}$): $M_r = 627.42$, monoclinic, $P2_1/c$ (No. 14), $a = 8.305$ (1) Å, $b = 20.528$ (3) Å, $c = 10.008$ (2) Å, $\beta = 103.799$ (13)°, $V = 1658$ Å^3, $d_{calcd} = 1.257$ g/cm^3, $Z = 2$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 8.0 cm^{-1}, final $R = 0.059$ ($R_w = 0.071$) from 1397 observed reflections ($I > 3\sigma(I)$) of 1546 measured. Crystal data for **3** ($CrP_6C_{22}H_{54}$): $M_r = 556.52$, orthorhombic, *Pnnm* (No. 58), $a = 9.964$ (2) Å, $b = 10.709$ (2) Å, $c = 13.723$ (3) Å, $V = 1464$ Å^3, $d_{calcd} = 1.262$ g/cm^3, $Z = 2$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 7.1 cm^{-1}, final $R = 0.063$ ($R_w = 0.067$) from 815 observed reflections ($I > 3\sigma(I)$) of 1511 measured. Complexes **1**–**3** have also been characterized spectroscopically.

Introduction

The coordination chemistry of potentially multidentate phosphine ligands with transition-metal carbonyl species has been well established.[1] Several complexes involving metals in higher oxidation states have been prepared for the late, first-row transition metals. Examples are known for Ni(I), Ni(II), Co(I), and Co(II) with potentially tri- and quadridentate phosphines, arsines, thioethers, and amide ligands as well as mixed ligands.[2] To date, most examples of chromium halide complexes bearing multidentate phosphines have involved Cr(III). These include CrX_3E (X = F, Cl, Br, I; E = multidentate arsine, phosphine, or thioether).[3] Related chromium(II) halide complexes with multidentate ligands include $[Cr(tetraphos)X]BPh_4$ (X = Cl, Br, I; tetraphos = tris(2-(diphenylphosphino)ethyl)phosphine),[4] $[Cr(QP_3)X]BPh_4$ (X = Cl, Br, I; QP_3 = tris(2-(dicyclohexylphosphino)ethyl)amine), and $[Cr(NP_3)X]PF_6$ (X = Cl, Br; NP_3 = tris(2-(dimethylphosphino)ethyl)amine).[5] This report describes the synthesis and X-ray structures of three tripod (tripod = 1,1,1-tris((dimethylphosphino)methyl)ethane) complexes of Cr(0), Cr(II), and Cr(III). Only three examples of stable Cr(0) hexaphosphorus compounds have previously been described: Cr(dmpe)$_3$[6] (dmpe = 1,2-bis(dimethylphosphino)ethane), $Cr(PF_3)_6$,[7] and $Cr[P(OR)_3]_6$ (R = alkyl group), the last compound being prepared by metal-vapor synthesis.[8] The Cr(0) hexakis(trimethyl phosphite) complex is reportedly active as a catalyst for the hydrogenation of olefins.[8] To our knowledge, Cr(tripod)$_2$ (**3**), reported here, represents the first structurally characterized example of a Cr(0) hexakis(trialkylphosphine) complex.

Experimental Section

General Procedures. All operations were performed under nitrogen or vacuum. Microanalyses were by Schwarzkopf Microanalytical Laboratory, Woodside, NY. THF and hexane were dried over sodium and distilled from the sodium/benzophenone ketyl radical under nitrogen immediately prior to use. Toluene was distilled from sodium, and methylene chloride was dried and distilled from calcium hydride under nitrogen. All solvents were degassed prior to use. $CrCl_3(THF)_3$[9] was

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