(TMSO)Cl]NO_3ClO_4, 59301-97-2; *cis*-[Co(en)$_2$(OH_2)(DMSO)](NO_3)$_2$$ClO_4$, 59301-99-4; *cis*-[Co(en)$_2$(DMSO)$_2$](ClO_4)$_3$, 14781-36-3; *cis*-[Co(en)$_2$(DMSO)$_2$](ClO_4)$_2$$NO_3$, 59302-00-0; *cis*-[Co(en)$_2$(DMSO)N_3]NO_3ClO_4, 59302-02-2; *cis*-[Co(en)$_2$(DMSO)Br](ClO_4)$_2$, 15818-85-6; *cis*-[Co(en)$_2$(DMSO)Br]NO_3ClO_4, 59302-03-3; *cis*-Co(en)$_2$(OH_2)Cl^{2+}, 15693-74-0; (–)-*cis*-[Co(en)$_2$(OH_2)Cl]$^{2+}$, 45837-48-7; *trans*-Co(en)$_2$(OH_2)Cl^{2+}, 14403-92-0; (–)-*cis*-[Co(en)$_2$$CO_3$]$ClO_4$, 38673-77-7; *cis*-Co(en)$_2$(OH_2)(DMSO)$^{3+}$, 59301-98-3.

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(6) The number of determinations is given in parentheses.
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(12) DMSO is spectrochemically very similar to Cl^-; ϵ_{500} ~15 for *trans*-Co(en)$_2$(OH_2)Cl^{2+} was used for the calculation.
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(14) Cf. (–)-*cis*-Co(en)$_2$$Br_2^+$ and (–)-*cis*-Co(en)$_2$(OH_2)Br^{2+} which are oxidized in Cl_2 (0.08 M)–HCl (0.1 M) with 100 ± 2% retention of geometric and optical configuration (W. G. Jackson and A. M. Sargeson, unpublished data).

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Reaction of the Simmons–Smith Reagent with Trimethylamine–Borane

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In the course of seeking alternate syntheses for 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane[1] the reaction of the Simmons–Smith reagent with several boron compounds was investigated.

A methylene-transfer reaction to a boron–nitrogen bond of the four-membered ring system of dimeric $(CH_3)_2NBH_2$ using the Simmons–Smith reagent, an organometallic complex formed between Zn and CH_2I_2 known to be an active methylene-transfer agent to carbon–carbon double bonds,[2–4] was attempted. The carbon atom of the active methylene in the Simmons–Smith reagent exhibits electrophilic character[4] and could compete for the electrons shared between boron and nitrogen in forming the four-membered ring system of dimeric $(CH_3)_2NBH_2$. Although the desired reaction did not occur, it was found that the Simmons–Smith reagent will transfer a methylene group to a boron–hydrogen bond.

Discussion

The Simmons–Smith reagent reacts with $(CH_3)_3N{\cdot}BH_3$ transferring methylene groups to B–H bonds to produce, as the simplest moiety, a B–CH_3 unit.

The production of ethane during aqueous hydrolysis of the nonvolatile portion of the reaction mixtures with 0.1 M HCl confirms the presence of C_2H_5 units in the reaction mixture. The isolation of what is thought to be a high molecular weight alkane or mixture of alkanes suggests the presence of alkyl species containing an unknown number of methylene groups.

If the methylene groups transfer nonselectively to a B–H or a B–CH_3 bond, then on a purely statistical basis the probability of obtaining three methylene transfers to a BH_3 unit before obtaining a methylene group transfer to a resulting B–CH_3 bond is 22.2%. The yield of $B(CH_3)_3$ obtained when the Simmons–Smith reagent was prepared in the presence of $(CH_3)_3N{\cdot}BH_3$ (3 mol:1 mol, respectively) is close to this value (25%). Large excesses of the Simmons–Smith reagent did not increase the yield of $B(CH_3)_3$. Thus, the transfer appears to be essentially nonselective in nature when the Simmons–Smith reagent is prepared in the presence of $(CH_3)_3N{\cdot}BH_3$.

In the reaction of the Simmons–Smith reagent with $(CH_3)_3N{\cdot}BH_3$ in a 1:1 ratio $B(CH_3)_3$ was not produced. Over 68% of the $(CH_3)_3N$ put into the system as $(CH_3)_3N{\cdot}BH_3$ was recovered as a ZnI_2 complex of $(CH_3)_3N$. Thus, the B–N bond is destroyed during the initial stages of the reaction of the Simmons–Smith reagent with $(CH_3)_3N{\cdot}BH_3$.

If the Simmons–Smith reagent was formed in the absence of $(CH_3)_3N{\cdot}BH_3$ and then reacted with $(CH_3)_3N{\cdot}BH_3$, the maximum yield of $B(CH_3)_3$ obtained was 6.9%.

This difference in yields of $B(CH_3)_3$ is thought to be due to a change in nature of the Simmons–Smith reagent with time. This possibility has been mentioned previously[3] but was not seriously considered.

In order to obtain additional information about the reagent the present authors reacted the Simmons–Smith reagent with $(CH_3)_3N$ in hope of isolating an organometallic species. The product obtained was shown to be $[(CH_3)_2NCH_2]ZnI_2[N(CH_3)_3]$ in 7.1% yield. A similar compound has been previously prepared by allowing a $ZnCl_2$ solution in diethyl ether, treated with diazomethane, to react with $(CH_3)_3N$. The product reported was $[(CH_3)_3NCH_2ZnCH_2N(CH_3)_3]^{2+}Cl^-{}_2$.[5]

The new compound prepared here demonstrates that only 7.1% of the active methylene present in the Simmons–Smith reagent after 4 h in refluxing diethyl ether is in a position such that a CH_2ZnI_2 moiety can be trapped by $(CH_3)_3N$.

In the reaction of $(CH_3)_3N{\cdot}BH_3$ with the Simmons–Smith reagent, formed over a 4-h period, it is interesting to observe that the yield of $B(CH_3)_3$ is very close to the amount of Zn–CH_2 trapped by $(CH_3)_3N$ under similar conditions.

It appears that the Simmons–Smith reagent is a methylene-transfer reagent that has a high percentage of a reactive intermediate present upon initial formation that either decomposes or rearranges to a less reactive or more selective species with time. The present authors contend that this feature of the Simmons–Smith reagent should be reconsidered.

Experimental Section

Preparation of the Simmons–Smith Reagent. In a typical synthesis of the Simmons–Smith reagent a sample (3.85 g, 52.7 mmol) of Zn/Cu couple [commercially available from Ventron or prepared by reacting 40-mesh Zn in glacial acetic acid with copper acetate] and CH_2I_2 (13.61 g, 48.2 mmol) were added to a 250-ml one-necked flask, equipped for magnetic stirring and reflux, containing 100 ml of diethyl ether. The mixture was brought to gentle reflux under a nitrogen atmosphere and maintained at reflux for 4 h or until the ^{1}H NMR spectrum showed that all of the CH_2I_2 had been consumed.

Reaction of Trimethylamine–Borane with the Simmons–Smith Reagent—I. A sample of $(CH_3)_3N{\cdot}BH_3$ (1.79 g, 24.5 mmol) was added to CH_2I_2 (19.92 g, 70.6 mmol) and the Zn/Cu couple (5.23 g, 71.6 mmol) in 100 ml of diethyl ether in a 250-ml one-necked flask equipped with a magnetic stirring bar.

This mixture was connected to a large cold finger filled with a dry ice–acetone mixture. The upper outlet was connected to a series of three liquid N_2 traps on the vacuum line to trap any –78 °C non-

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condensables. The lower outlet was attached to a tank of prepurified N_2 and a slow passage of N_2 was continued throughout the experiment to aid in removing the noncondensables.

The mixture was then brought to reflux. After approximately 1.5 h, the ether solution was almost clear with only a slight turbidity. Essentially all of the Zn/Cu couple had gone into solution as some type of intermediate. Shortly after this point was reached, a black fluffy material began to settle out. In a previous experiment it was found that at this point $B(CH_3)_3$ was being evolved in large quantities. After 48 h the reaction was stopped.

Investigation of the traps showed only ether, $B(CH_3)_3$, and decomposition products of the Simmons–Smith reagent. The yield of $B(CH_3)_3$ was 25% based on the $(CH_3)_3N{\cdot}BH_3$ that reacted. Of the original 1.79 g of $(CH_3)_3N{\cdot}BH_3$ added only 0.17 g was obtained unreacted from the remaining ether solution. The $B(CH_3)_3$ was characterized by gas-phase infrared analysis[6] after purification by vacuum-line distillation through a −112 °C trap to remove diethyl ether.

Reaction of Trimethylamine–Borane with the Simmons–Smith Reagent—II. A one-necked flask was charged with Zn/Cu couple (2.76 g, 35 mmol), CH_2I_2 (5.36 g, 20 mmol), $(CH_3)_3N{\cdot}BH_3$ (1.46 g, 20 mmol), diethyl ether (50 ml), and a Teflon-coated stirring bar. After 18 h at gentle reflux, heating was stopped and the reaction vessel was allowed to cool.

The gas produced during the reaction occupied a volume of 145 ± 5 cm^3 at 25 °C and atmospheric pressure. The liquid nitrogen condensable portion was investigated. A gas-phase infrared spectrum was obtained and confirmed the presence of diethyl ether and the usual peaks observed from the gases produced during decomposition of the Simmons–Smith reagent. Absorption bands characteristic of $B(CH_3)_3$ were absent.

The material in the reaction flask consisted of two liquid phases. The denser layer was dried by vacuum evaporation for 1 h at 73 °C and weighed 2.44 g. This material was a very viscous liquid. The top layer was evacuated to dryness and produced a white solid weighing 3.74 g. Trimethylamine–borane (3.6 mmol, 18% recovery) was collected during drying of these two fractions.

The white solid obtained from the top layer of the original filtrate was recrystallized from CH_2Cl_2 solution by adding heptane. This solid gave one peak at 2.62 ppm in the NMR spectrum taken in CH_2Cl_2 solution with internal TMS as reference. The infrared spectrum taken in CH_2Cl_2 solution showed no absorption in the B–H stretching region. Anal. Calcd for $ZnI_2(CH_3)_3N$: C, 9.53; H, 2.40; N, 3.70; Zn, 17.28; I, 67.16. Found: C, 9.31; H, 2.32; N, 3.62; Zn, 15.30; I, 67.37.

The viscous liquid obtained from the bottom layer of the original filtrate was a mixture of the material found in the top layer and boron-containing compounds. Attempts to separate a pure material from this mixture were unsuccessful.

Reaction of Trimethylamine–Borane with the Simmons–Smith Reagent—III. A one-necked flask was charged with Zn/Cu couple (11.8 g, 162.2 mmol), CH_2I_2 (17.78 g, 66.4 mmol), a Teflon-coated stirring bar, and 50 ml of diethyl ether. The mixture was removed to the hood and refluxed gently. Formation of the Simmons–Smith reagent was monitored by NMR spectroscopy. The amount of CH_2I_2 was observed to decrease and finally to become undetectable in the NMR spectrum; this required approximately 1.5 h. During this time a total of 170 ± 5 cm^3 of gas was collected. Using the percentage composition of the gas produced from decomposition of the Simmons–Smith reagent[3] this quantity of gas would correspond to a loss of approximately 15–20 mmol of active methylene-transfer reagent; thus there was approximately 46 mmol of active methylene available for transfer to B–H bonds.

Trimethylamine–borane (0.73 g, 10 mmol) was added to the Simmons–Smith reagent; then the mixture was brought to gentle reflux and the over gas was slowly removed by a steady stream of prepurified nitrogen gas into a series of three liquid nitrogen traps. The nitrogen gas and other noncondensables were allowed to escape from the system through a mineral oil bubbler. After 2.3 h the flow of nitrogen was stopped and the material in the reaction flask was allowed to cool. The only boron-containing compound isolated was $B(CH_3)_3$, 0.63 mmol (6.3% yield), from vacuum-line measurements.

The $B(CH_3)_3$ was condensed into the first liquid nitrogen trap of the series. The system of traps was refilled with nitrogen gas and the reaction mixture was brought to gentle reflux again. After a total reaction time of 23 h the system was treated as before and a total of 0.69 mmol of $B(CH_3)_3$ was isolated. The amount of $B(CH_3)_3$ collected corresponded to a 6.9% conversion of the $(CH_3)_3N{\cdot}BH_3$ added.

Reaction of Trimethylamine with the Simmons–Smith Reagent. Methylene iodide (16.5 g, 62.5 mmol) and Zn/Cu (6 g, 81 mmol) were reacted in the hood in ether solution for 4 h. The reaction flask was then cooled and attached to the vacuum line where $(CH_3)_3N$ (65 mmol) was added at liquid nitrogen temperature. The mixture was allowed to warm to room temperature with stirring. After being stirred for 1 h, the mixture was pumped to remove unreacted $(CH_3)_3N$.

A compound insoluble in benzene but soluble in CH_2Cl_2 was the only product isolated. This compound was recrystallized from CH_2Cl_2 solution by adding heptane. A white solid (2.01 g), mp 165 °C, was obtained. The NMR spectrum in CH_2Cl_2 showed peaks at 3.23, 2.78, and 2.45 ppm in a 8.8:2:9 ratio, respectively, with internal TMS as reference. The infrared spectrum was obtained in CH_2Cl_2 solution: 2980 (m), 2920 (m), 2870 (w), 2810 (vs), 1485 (s), 1110 (m), 1010 (s), 965 (m), 910 (w), 822 (s) cm^{-1}.

Anal. Calcd for $C_7H_{20}N_2I_2Zn$: C, 18.63; H, 4.47; N, 6.21; I, 56.25; Zn, 14.49. Found: C, 18.53; H, 4.44; N, 6.05; I, 56.13; Zn, 14.09. Thus, the empirical formula is in good agreement with a complex containing one $(CH_3)_3N$, one ZnI_2, and a $(CH_3)_3NCH_2$ moiety as the simplest formulation.

Registry No. $B(CH_3)_3$, 593-90-8; $ZnI_2(CH_3)_3N$, 59389-43-4; $C_7H_{20}N_2I_2Zn$, 59389-44-5; $(CH_3)_3N{\cdot}BH_3$, 75-22-9; CH_2I_2, 75-11-6; $N(CH_3)_3$, 75-50-3.

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Ultraviolet Photoelectron Spectra of Nickel, Palladium, and Platinum Diethyl Dithiophosphate Complexes

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Uv photoelectron spectroscopy (UPS) is a powerful technique with which to probe the electronic structure of molecules.[1] Its use in transition metal chemistry has been, by necessity, limited to compounds that can be vaporized without decomposition. However, since the required vapor pressure is <0.1 Torr and the sample inlet probe can be easily heated several hundred degrees, there clearly exists a large number of transition metal complexes amenable to study. Our interest has been in studying the effect of changing the metal within a triad while keeping the ligand system constant. A number of such studies involving organometallic complexes have recently appeared.[2-10]

The electronic structure of planar d^8 metal complexes has been the subject of many discussions.[11-16] We have applied the UPS method to this problem and herein report the photoelectron (PE) spectra of the planar d^8 bis(diethyl dithiophosphato)metal(II) complexes, $M[S_2P(OEt)_2]_2$ (M = Ni, Pd, Pt), and the protonated ligand, $HS_2P(OEt)_2$. (Hereafter

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