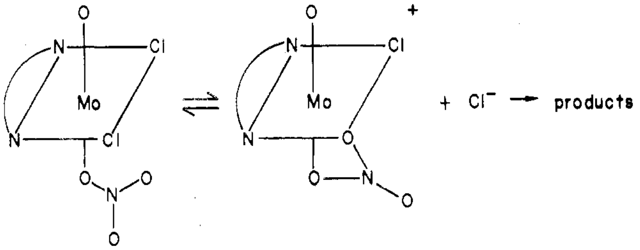
overlap of the Mo(V) d_{xy} orbital (which contains the electron) and the nitrate oxygen π orbital for electron transfer. In the cases of the *cis*-$MoOCl_3$(bpy) and *cis*-$MoOCl_3$(phen) complexes, initial coordination of NO_3^- at the trans position must then be followed by rapid rearrangement or rapid formation of an intermediate chelate nitrato complex:



It was anticipated the reduction of NO_3^- by $MoOCl(CH_3OH)$(sip) would be rapid and would not exhibit Cl^- inhibition, since a coordination site cis to the oxo group is occupied by a weakly bound CH_3OH (or solvent DMF), which should be easily replaced by NO_3^-. While this complex does indeed react more rapidly than the others, the reduction appears still to proceed by a preliminary loss of Cl^-, suggesting the formation of a negatively charged intermediate nitrato complex, $MoOCl(NO_3)(sip)^-$, is not favorable.

Finally, the lack of reduction of NO_3^- by $MoOCl(sal_2phen)$ may be due either to the impossibility of forming an intermediate nitrato complex with the correct orbital overlap or to the thermodynamic instability of the trans Mo(VI) dioxo structure required of the product.[16,22]

The results suggest a possible mechanism for the enzymatic reduction of NO_3^-: NO_3^- is initially bound at a nonaqueous Mo(V) site at an open coordination position or, by displacement of a weakly coordinated ligand, cis to the oxo group, accompanied by dissociation of a second negatively charged group (sulfhydryl or tyrosyl, e.g.), to maintain the original charge at the site (binding might occur at the trans position, followed by rapid rearrangement to the cis structure, but this seems less likely with the protein). After transfer of an oxo group, NO_2 is released and disproportionates in an aqueous region to NO_3^- and NO_2^-. The Mo center subsequently is reduced by the flavin or iron cofactors of the enzyme,[3] with the oxygen forming H_2O or OH^-. Appropriate enzymatic experiments using ^{18}O-labeled NO_3^- and H_2O would provide a possible test of the hypothesis.

Acknowledgment. This work was supported by Grant GM-08437 from the National Institutes of Health and by the American Metal Climax Foundation, Inc., to which thanks are gratefully expressed. We are indebted to Dr. John Enemark and Dr. K Yamanouchi of the Department of Chemistry, University of Arizona, for making available to us unpublished X-ray crystallographic results and synthetic procedures.

Registry No. *cis*-$MoOCl_3$(phen), 38237-92-2; *cis*-$MoOCl_3$(bpy), 35408-53-8; *trans*-$MoOCl_3$(bpy), 35408-54-9; *trans*-$MoOCl(ox)_2$, 67650-70-8; *trans*-$MoOCl(tox)_2$, 67650-71-9; *cis*-$MoOCl(sal_2phen)$, 64085-34-3; *trans*-$MoOCl(CH_3OH)$(sip), 68081-62-9; $MoO_2(tox)_2$, 17926-52-2; MoO_2(sip), 67598-36-1; $(NH_4)_2MoOCl_5$, 17927-44-5; Na_2MoO_4, 7631-95-0; NO_3^-, 14797-55-8.

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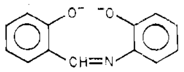
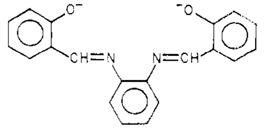
(10) Abbreviations used: bpy = α,α'-bipyridyl; phen = *o*-phenanthroline; ox = 8-hydroxyquinoline (oxine); tox = 8-mercaptoquinoline (thiooxine); sip = *o*-(salicylidenimino)phenol



sal₂phen = *o*-bis(salicylidenimino)benzene



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Three Classes of Seven-Coordinate Tungsten(II) Chelates with Both Hard and Soft Donors

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Received July 7, 1978

Three types of mixed-ligand tungsten(II) chelates have been isolated with simultaneous coordination of hard phenolato oxygen, borderline heterocyclic nitrogen, and soft carbonyl and phosphine donors. The complexes are $W(CO)_2(PPh_3)(dcq)_2$, $W(CO)_3(PPh_3)(dcq)Cl$, and $W(CO)_2(PPh_3)_2(dcq)Cl$, where Ph = C_6H_5 and dcq^- = 5,7-dichloro-8-quinolinolato. A strong base (e.g., proton sponge) is necessary to prepare the bis-dcq^- chelate from $W(CO)_3(PPh_3)_2Cl_2$ and Hdcq. The physical and chemical properties of the diamagnetic chelates are consistent with seven-coordinate geometries.

Introduction

We have been interested in the synthesis of seven-coordinate tungsten(II) complexes of the general form $W(CO)_2(PPh_3)L_2$, where L is an anion of 8-quinolinol, picolinic acid, or related derivative. These complexes might then serve as starting materials for the synthesis of mixed-ligand tungsten(IV)

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complexes $WL_2L'_2$ in a reaction in which L remains coordinated to the W at all times, thereby avoiding the $WL_nL'_{4-n}$ product distribution previously observed using $W(CO)_6$ as the starting material.[1] Similar seven-coordinate species have been synthesized for soft donor ligands (L) such as $S_2CNR_2^-$, S_2COMe^-, and $S_2P(OEt)_2^-$ by ligand substitution starting with $W(CO)_3(PPh_3)_2Cl_2$.[2] For some ligands only the monosubstituted $W(CO)_2(PPh_3)_2LCl$ species could be isolated.[2] We have been able to synthesize mixed-ligand complexes containing both hard and soft donors, to isolate a $W(CO)_3(PPh_3)LCl$ species, and to drive monosubstituted reactions to completion by the addition of "proton sponge".

Experimental Section

Reagent grade solvents were used exclusively. These solvents were deoxygenated with nitrogen prior to use and subsequently used without further purification unless noted. All reactions were carried out under nitrogen atmospheres.

Tricarbonyldichlorobis(triphenylphosphine)tungsten(II). $W(CO)_3(PPh_3)_2Cl_2$ was prepared using a modified version of the synthesis given by Chen, Yelton, and McDonald.[2] The major difference was that excess chlorine from the reaction of $W(CO)_6$ (10.2 g, 29 mmol) and chlorine (60 mL) was allowed to evaporate in vacuo first at 195 K and then at room temperature. At that time, the system was filled with nitrogen and opened to the atmosphere; the solid was quickly powdered to remove any occluded chlorine and then the reaction vessel was closed and reevacuated. Acetone (60 mL) was vacuum distilled from anhydrous calcium sulfate onto the reaction mixture. The dark green-blue solution of $W(CO)_4Cl_2$ was transferred to a nitrogen-filled glovebag and filtered. A solution of triphenylphosphine (PPh_3, 14.6 g, 58 mmol) in 100 mL of acetone was added to the $W(CO)_4Cl_2$ solution, and a yellow precipitate resulted. The mixture was stirred 20 min and then filtered in air, and the yellow solid was washed with acetone and with diethyl ether and was then air-dried; yield 80%.

Dicarbonylbis[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), $W(CO)_2(PPh_3)(dcq)_2$. First $W(CO)_3(PPh_3)_2Cl_2$ (1.73 g, 2.0 mmol), 5,7-dichloro-8-quinolinol (Hdcq, 0.87 g, 4.1 mmol), and proton sponge [Aldrich, 1,8-bis(dimethylamino)naphthalene] (0.88 g, 4.1 mmol) were placed in a round-bottom flask under an N_2 atmosphere, and 215 mL of a 1:1 v/v CH_3OH/CH_2Cl_2 solution was added. The reaction mixture was stirred 2 h to ensure complete reaction. A dark red solution and red crystals were produced. The volume was reduced by approximately one-third in vacuo and the mixture was filtered in air. The red crystals were quickly rinsed twice with ethanol and once with hexane and then dried in vacuo at 56 °C over P_4O_{10}; yield 95%.

Anal. Calcd for $W(CO)_2(PPh_3)(dcq)_2$: C, 49.16; H, 2.50; N, 3.02; Cl, 15.28. Found: C, 49.24; H, 2.61; N, 2.90; Cl, 15.60.

Dicarbonylchloro[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)]bis(triphenylphosphine)tungsten(II), $W(CO)_2(PPh_3)_2(dcq)Cl$. Initially $W(CO)_3(PPh_3)_2Cl_2$ (0.86 g, 1.0 mmol) and 5,7-dichloro-8-quinolinol (0.42 g, 2.0 mmol) were dissolved in 90 mL of 2:1 v/v CH_2Cl_2/CH_3OH. Nitrogen was bubbled through the stirred solution for approximately 6 h. The solution became yellow-brown. Gradual addition of 50 mL of methanol led to the formation of a yellow-orange solid. The product was filtered in air and recrystallized from CH_2Cl_2 by the addition of methanol (typical amounts: 0.2 g of solid, 2 mL of CH_2Cl_2, 2 mL of CH_3OH). The product was dried in vacuo at 56 °C over P_4O_{10}; yield 50%.

Anal. Calcd for $W(CO)_2(PPh_3)_2(dcq)Cl$: C, 55.72; H, 3.39; N, 1.38; Cl, 10.50. Found: C, 55.71; H, 3.42; N, 1.27; Cl, 10.44.

Tricarbonylchloro[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), $W(CO)_3(PPh_3)(dcq)Cl$. $W(CO)_3(PPh_3)_2Cl_2$ (0.86 g, 1.0 mmol) and 5,7-dichloro-8-quinolinol (0.42 g, 2.0 mmol) were placed in a round-bottom flask under a nitrogen atmosphere, and 90 mL of 2:1 v/v CH_2Cl_2/CH_3OH was added. The mixture was stirred for 1 h and the solution turned yellow-brown. The solution was filtered to remove any unreacted $W(CO)_3(PPh_3)_2Cl_2$ and the filtrate was flash-evaporated to approximately 15 mL and filtered. The solid was recrystallized twice from methylene chloride by the addition of hexane (typical amounts: 0.10 g of solid, 1 mL of CH_2Cl_2, 2.5 mL of C_6H_{14}) and dried in vacuo at 56 °C over P_4O_{10}; yield 30%.

Anal. Calcd for $W(CO)_3(PPh_3)(dcq)Cl\cdot0.15CH_2Cl_2$: C, 45.75; H, 2.46; N, 1.77; Cl, 14.80. Found: C, 45.32; H, 2.50; N, 1.78; Cl, 14.80.

Scheme I

$$\mathrm{Hdcq} \rightleftarrows \mathrm{H^+ + dcq^-} \qquad \text{(a)}$$

$$\mathrm{W(CO)_3(PPh_3)_2Cl_2 + dcq^- \rightleftarrows W(CO)_3(PPh_3)(dcq)Cl + PPh_3 + Cl^-} \quad \text{and} \qquad \text{(b)}$$

$$\mathrm{W(CO)_3(PPh_3)_2Cl_2 + dcq^- \rightleftarrows W(CO)_2(PPh_3)_2(dcq)Cl + CO + Cl^-} \qquad \text{(c)}$$

$$\mathrm{W(CO)_3(PPh_3)(dcq)Cl + dcq^- \rightleftarrows W(CO)_2(PPh_3)(dcq)_2 + CO + Cl^-} \qquad \text{(d)}$$

$$\mathrm{W(CO)_2(PPh_3)_2(dcq)Cl + dcq^- \rightleftarrows W(CO)_2(PPh_3)(dcq)_2 + PPh_3 + Cl^-} \qquad \text{(e)}$$

Physical Measurements. Electronic spectra were obtained using a Cary Model 14 spectrophotometer and Thunberg cells. The solvent was refluxed under a stream of nitrogen for 2 h and then distilled directly into the Thunberg cell under a nitrogen atmosphere. The cell was then sealed with the cap containing a weighed amount of sample and then evacuated and backfilled with nitrogen four times before dissolving the sample. By evacuating and backfilling with oxygen it was subsequently possible to record the spectra under that atmosphere as well.

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer as KBr disks.

Conductivity measurements were carried out using an Industrial Instruments Model RC-18 conductivity bridge and an Industrial Instruments dip cell, cell constant = 0.0100 cm^{-1}. The measurements were carried out under a nitrogen atmosphere using spectrograde solvents, which had been deaerated prior to use.

Magnetic susceptibilities were determined by the Faraday technique using a Cahn RH electrobalance and an Alpha Scientific 4-in. electromagnet with $HgCo(SCN)_4$ as the calibrant. Magnetic moments were corrected for the diamagnetism of the ligands using Pascal's constants.[3]

The proton magnetic resonance spectra were recorded using a Varian A-60 spectrometer with deuteriochloroform as solvent with internal Me_4Si as reference.

Elemental analyses were performed by the University of Massachusetts microanalysis laboratory.

Results and Discussion

Synthetic Results. The reactions between $W(CO)_3(PPh_3)_2Cl_2$ and Hdcq are best represented by the equilibria given in Scheme I, where the magnitudes of the arrows indicate the directions toward which the equilibria lie. As indicated by summing Ia and Ib or Ia and Ic, the major contaminant in the synthesis of either $W(CO)_3(PPh_3)(dcq)Cl$ or $W(CO)_2(PPh_3)_2(dcq)Cl$ is the other mono-dcq$^-$ species. The distribution between the two can be varied depending on the reaction conditions; however, in the absence of added base, no significant amount of the bis-dcq$^-$ complex is formed. This is true despite attempts to force reactions Id and Ie by the addition of excess Hdcq and by sweeping the reaction mixture with nitrogen to remove the CO and HCl produced in the reactions.

Addition of base to a yellow solution containing a 1:2 $W(CO)_3(PPh_3)_2Cl_2$ to Hdcq ratio leads to an immediate darkening of the solution with the solution turning red in a matter of minutes because of the formation of $W(CO)_2(PPh_3)(dcq)_2$. Proton sponge has been used as the base for the synthesis because it is noncoordinating and it does not produce water, which might cause side reactions. Addition of less proton sponge than an equimolar Hdcq-to-proton sponge amount leads to a product distribution containing all three of the W^{II}–dcq$^-$ complexes. Furthermore, when the reaction was run in pure methylene chloride, only a yellow solution was obtained which subsequently turned red upon the addition of methanol such that the methylene chloride to methanol ratio was 5:1. From this result and the conductivity data given below, it appears reasonable that the mechanism for these

Table I. Magnetic Properties of Tungsten(II) Complexes[a]

complex	$10^6\chi_g$[b]	$10^6\chi_m^{cor}$[b]	μ
$W(CO)_3(PPh_3)(dcq)Cl$	−0.60 (35)	−80 (350)	0.0
$W(CO)_2(PPh_3)_2(dcq)Cl$	−0.53 (20)	−56 (152)	0.0
$W(CO)_2(PPh_3)(dcq)_2$	−0.48 (24)	1 (225)	0.0

[a] Estimated errors in parentheses. [b] In cgsu.

Table II. Electronic Spectra of Tungsten(II) Complexes

complex	N_2 atmosphere[a]	O_2 atmosphere[a]
$W(CO)_3(PPh_3)(dcq)Cl$	438 (3.74)	no change over 24 h
$W(CO)_2(PPh_3)_2(dcq)Cl$	457 (3.68)	433 (3.58), 351 (sh)
$W(CO)_2(PPh_3)(dcq)_2$	506 (3.83), 419 (sh), 360 (w, sh)	380 (3.72), 332 (w, sh)

[a] Peak positions in nm with the log of the molar extinction coefficients (M^{-1} cm^{-1}) in parentheses; sh = shoulder, w = weak.

Table III. Molar Conductivity of Tungsten(II) Complexes

complex	7:3 v/v CH_3OH/CH_2Cl_2[a]	3:2 v/v $(CH_3)_2CO/CH_2Cl_2$[b]
$W(CO)_3(PPh_3)(dcq)Cl$	64	3
$W(CO)_2(PPh_3)_2(dcq)Cl$	100	4
$W(CO)_2(PPh_3)(dcq)_2$	4[c] 6[d]	

[a] Values given in cm^2 Ω^{-1} $equiv^{-1}$, KI standard = 119. [b] Values given in cm^2 Ω^{-1} $equiv^{-1}$, KI standard = 180. [c] Red solution. [d] Yellow solution; oxidized by oxygen.

Table IV. Carbonyl Stretching Frequencies of W(II) Complexes[a]

complex	frequencies
$W(CO)_3(PPh_3)_2Cl_2$[b]	2020 m, 1940 s, 1895 m
$W(CO)_3(PPh_3)(dcq)Cl$[c]	2017 s, 1939 s, 1904 s
$W(CO)_2(PPh_3)_2(dcq)Cl$[c]	1920 s, 1826 vs
$W(CO)_2(PPh_3)(dcq)_2$[c]	1919 s, 1824 vs

[a] Values given in cm^{-1}; m = medium, s = strong, vs = very strong. [b] From ref 5, as Nujol mull. [c] As KBr disks; uncertainties ±1 cm^{-1}.

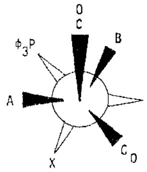

Figure 1. Suggested stereochemistry for the various tungsten(II) complexes, where A = Co or N of dcq^-, B = PPh_3 or N of dcq^-, and X = Cl^- or O^- of dcq^-. See text for details.

reactions is the replacement of Cl^- by the O end of the entering dcq^- followed by replacement of one of the neutral ligands by the N end of the bidentate ligand.

Physical Properties. Table I presents the magnetic properties of these complexes. All are diamagnetic with magnetic moments of essentially zero which is consistent with d^4 seven-coordinate complexes.[4]

The electronic spectra of these complexes are summarized in Table II. Although all of the solids appear to be stable in air for extended periods of time, red solutions of $W(CO)_2(PPh_3)(dcq)_2$ were observed to gradually turn yellow over a period of minutes in either air or oxygen atmospheres. Therefore, the spectra have been recorded for both nitrogen- and oxygen-saturated solutions. Both $W(CO)_2(PPh_3)_2(dcq)Cl$ and $W(CO)_2(PPh_3)(dcq)_2$ exhibit changes in their spectra upon the addition of oxygen. The $W(CO)_2(PPh_3)(dcq)_2$ solution spectra have an isosbestic point at 396 nm. The yellow solutions generated from $W(CO)_2(PPh_3)(dcq)_2$ are nonconductors (vide infra), and the infrared spectrum of a yellow solid isolated from the $W(CO)_2(PPh_3)(dcq)_2$ solutions contains bands attributed to dcq^- and W–O vibrations, but no carbonyl stretches are observed. Further characterization was not attempted.

As shown in Table III, the two mono-dcq^- species behave as 1:1 electrolytes in solutions with high methanol content and as nonelectrolytes in less polar solvents. Both the red and yellow solutions from $W(CO)_2(PPh_3)(dcq)_2$ are nonconductors even under the higher solvent polarity conditions. This behavior is similar to that observed for $W(CO)_2(PPh_3)L_2$ and $W(CO)_2(PPh_3)_2LCl$, where L = $S_2P(OEt)_2^-$,[2] and again is most likely because of the dissociation of chloride in solutions with higher polarities for the mono-L species.

The carbonyl stretching frequencies for these complexes are given in Table IV. In each case the number of carbonyl bands which are observed corresponds to the number of carbonyl groups present. It is interesting to note that replacement of Cl^- and PPh_3 by dcq^- does not lead to appreciable shifts in the carbonyl stretching frequencies. This constancy suggests essentially no change in the net W–CO interactions and is consistent with the substitution mechanism described above occurring with very little change in the overall stereochemistry of the solid ground states.

The ^1H NMR of $W(CO)_2(PPh_3)(dcq)_2$ at ambient temperature is a single doublet for H(2) of dcq^- centered at 8.34 ppm downfield from Me_4Si (J = 8 Hz) indicating chemically equivalent dcq^- ligands on the NMR time scale. Although this could arise from either a capped trigonal prism (CTP) structure or the closely related capped octahedral (CO) structure[6] in which the dcq^- ligands are equivalent, preliminary results of a single-crystal X-ray study indicate that the dcq^- ligands are nonequivalent.[7] Assuming similarity between the solid-state and solution ground-state structures, this equivalency is due to the fluxional behavior of $W(CO)_2(PPh_3)(dcq)_2$ in solution as has been demonstrated for a number of other seven-coordinate complexes.[8]

On the basis of similarities in the carbonyl region of their infrared spectra, $W(CO)_2(PPh_3)(dcq)_2$ and $W(CO)_2(PPh_3)_2(dcq)Cl$ appear to have structures similar to that of $Mo(CO)_2(dpam)_2Br_2$, dpam = bis(diphenylarsino)methane,[9] or $Mo(CO)_2Cl_2(PMe_2)_3$.[10] Both of these have distorted CO/CTP structures[6,10,11] which, when described as CO, have the carbonyl groups in the capping position and in the capped face. Likewise, $W(CO)_3(PPh_3)(dcq)Cl$ has carbonyl stretches similar to those of $W(CO)_3(dpam)_2Br_2$,[9] which again has a CO structure with carbonyls in the capping position and the capped face.[12]

A possible generalized structure is shown in Figure 1, which can be viewed either as a CO with a carbonyl in the capping site or as a CTP with the carbonyls on the unique edge and a PPh_3 on the capping site. Thus stepwise replacement of Cl^- by dcq^- could lead initially to either $W(CO)_3(PPh_3)(dcq)Cl$ or $W(CO)_2(PPh_3)_2(dcq)Cl$ and finally to $W(CO)_2(PPh_3)(dcq)_2$. However, we cannot rule out other isomers with similar structural features.

Structural determinations are currently underway in order to elucidate the solid-state structures, and the chelates are being used as intermediates for inorganic coordination polymers. Light-catalyzed decomposition occurs, even in the solid state, for at least one of these complexes and will be subjected to future elucidation.

Acknowledgment. We gratefully acknowledge the support of the U.S. Army Research Office for support of this research. Analyses were determined by the University of Massachusetts microanalysis laboratory.

Registry No. $W(CO)_2(PPh_3)(dcq)_2$, 68036-87-3; $W(CO)_2(PPh_3)_2(dcq)Cl$, 68036-88-4; $W(CO)_3(PPh_3)(dcq)Cl$, 68036-89-5; $W(CO)_3(PPh_3)_2Cl_2$, 18130-04-6.

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Molecular Addition Compounds. 5. Interaction of *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine with Boron Trifluoride and Monoalkylboranes

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Received September 7, 1978

N,*N*,*N'*,*N'*-Tetramethylethylenediamine (TMED) reacts instantly with boron trifluoride ethyl etherate to give the highly insoluble product TMED·$2BF_3$. This development made it of interest to synthesize and study the addition compounds of TMED with representative monoalkylboranes. TMED reacts readily with typical monoalkylboranes to form both the TMED–monoalkylborane TMED·BH_2R and the corresponding bis adducts TMED·$2BH_2R$. These are air stable and can be stored without apparent change for long periods of time. Boron trifluoride removes TMED from these adducts, rapidly and completely, precipitating TMED·$2BF_3$. In this way the monoalkylboranes can be conveniently purified and stored as their stable adducts with TMED, with rapid convenient generation of the parent monoalkylborane as desired.

Introduction

Recent studies in this laboratory have resulted in a simple procedure for the preparation of triethylamine–monoalkylborane adducts, $Et_3N·BH_2R$, starting from triethylamine–thexylborane, $Et_3N·BH_2Th$ (**1**),[1] and have led to the discovery of promising new applications for these derivatives. The triethylamine component could be removed from these adducts by treatment with either THF·BH_3[2] or $Et_2O·BF_3$[3] to produce the free monoalkylboranes for reduction and hydroboration applications. However, this procedure suffers from certain difficulties. Both $Et_3N·BH_3$ and $Et_3N·BF_3$ are highly soluble in the usual THF medium, making them difficult to separate from the desired product.[2,3] This problem can be circumvented in part by changing to a pentane solution from which $Et_3N·BF_3$ can be precipitated at −50 °C.[3] Furthermore, the $Et_3N·BH_2R$ adducts are liquids of uncertain purity which cannot be purified readily. Moreover, the versatile monoalkylboranes, thexylborane, $ThBH_2$,[4] and 2,4,4-trimethyl-3-pentylborane, diisobutylborane ≡ $(DIB)BH_2$,[5] possess limited stability upon storage in THF at 0 °C or at 25 °C.[5] Consequently they must be synthesized and used shortly thereafter. Hence it appeared highly desirable to develop a derivative which could be stored either neat or in solution for extended periods of time and then conveniently converted to the free borane as and when needed.

In the course of our work on amine–boranes,[6] we discovered that the reaction of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMED) with $Et_3O·BF_3$ affords a white solid which is highly insoluble in the usual organic solvents (THF, Et_2O, $CHCl_3$, pentane, benzene) and only slightly soluble in acetone or water. Despite the fact that many studies have been published concerning addition compounds of polyamines with boron trifluoride, no results on the reaction between $Et_2O·BF_3$ and TMED appear to have been recorded in the literature previously.[7-13] Therefore, it appeared desirable to investigate the reaction between $Et_2O·BF_3$ and TMED and to explore the possibility of utilizing TMED as a stabilizing addendum for monoalkylboranes.

This paper reports the isolation and characterization of TMED adducts of BF_3, $ThBH_2$, $(DIB)BH_2$, and monoisopinocampheylborane, $(IPC)BH_2$, and the facile quantitative removal of the TMED complexing agent from these adducts as the highly insoluble TMED·$2BF_3$ compound.

Experimental Section

The reaction flasks and other glass equipment used for experiments were dried in an oven and assembled in a stream of dry nitrogen gas. Special experimental techniques used in handling air-sensitive material are described in detail elsewhere.[14] All melting points are uncorrected and were determined in evacuated sealed capillary tubes using the Thomas-Hoover capillary melting point apparatus. $Et_2O·BF_3$ and TMED were distilled from calcium hydride. ^1H NMR and ^{11}B NMR spectra were recorded on Varian T-60 and FT-80A instruments, respectively. The ^1H and ^{11}B chemical shifts are in δ relative to Me_4Si and $Et_2O·BF_3$ standards, respectively.

Preparation of Complexes.[15] ***N*,*N*,*N'*,*N'*-Tetramethylethylenediamine Complex with Boron Trifluoride, TMED·$2BF_3$ (2). (a) Determination of Stoichiometry by ^1H NMR Spectroscopy.** Three different reactions were carried out in individual reaction flasks maintained at 25 °C. The flasks were charged with TMED (2.0 mmol), benzene (2.0 mmol, internal standard), and $CDCl_3$ (2.0 mL). An aliquot was taken from the first flask and the amount of TMED was estimated via ^1H NMR spectroscopy. To the second flask, 2.0 mmol of $Et_2O·BF_3$ was added with stirring. The ^1H NMR spectrum of the supernatant liquid indicated that 1.0 mmol of TMED remained unreacted. To the third flask was added with vigorous stirring 4.0 mmol of $Et_2O·BF_3$. The supernatant liquid was withdrawn and its ^1H NMR spectrum determined. No signals attributable to TMED were visible.

(b) Determination of Stoichiometry by GLC. The same reactions were carried out in the THF, Et_2O, and pentane at 25 °C. The following procedure in THF is representative. In a 50-mL centrifuge vial 5.0 mmol of TMED and 3.0 mmol of *n*-dodecane (internal standard) were dissolved in 4.0 mL of THF. The amount of TMED present in the solution was determined by GLC analysis with a 6 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb W. The solution was then treated with 5.0 mmol of $Et_2O·BF_3$ with stirring; a white solid precipitated. GLC analysis of the supernatant liquid indicated that 2.5 mmol of the TMED remained unreacted. The reaction mixture was treated further with 5.0 mmol of $Et_2O·BF_3$.

0020-1669/79/1318-0051\$01.00/0 © 1979 American Chemical Society