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Registry No. $(C_5H_5)_2Mo(C_2H_2)$, 53337-45-4; $(C_5H_5)_2Mo(CH_3C{\equiv}CH)$, 65982-70-9; $(C_5H_5)_2Mo(C_2H_4)$, 37343-05-8; $(C_5H_5)_2MoCl_2$, 12184-22-4; ^{13}C, 14762-74-4.

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Preparation and Characterization of Five-Coordinate Iron(II) Chelates and Their Reaction with Dioxygen[1]

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New iron(II) complexes with pentadentate Schiff base ligands have been isolated and characterized by elemental analyses, magnetic susceptibility measurements, and vibrational and electronic spectral techniques. The compounds are stable in the solid state and are compared to other metal complexes with the same type of ligands. They do not form stable adducts with nitrogenous bases but do react with molecular oxygen in solution. This reactivity toward oxygen is different for different ligand derivatives. Two μ-oxo compounds have been isolated and characterized. Their formation is discussed in terms of a dioxygen-complex intermediate.

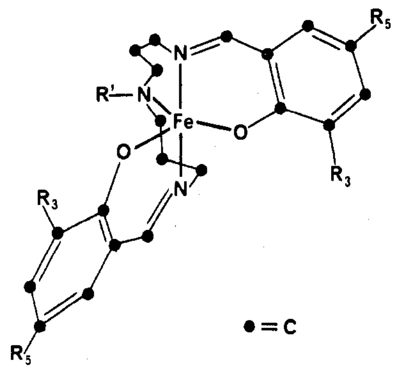
Introduction

The preparation of iron(II) complexes with multidentate ligands has received considerable attention in the past few years. One reason for this is the interest in finding compounds that will reversibly coordinate dioxygen.[2a] Such compounds could then be used as models for more complex molecules such as hemoglobin, myoglobin, or hemerythrin.[2b] Toward this end we have synthesized several new iron(II) complexes with pentadentate Schiff base ligands (Figure 1). Although these compounds do not react reversibly with oxygen, they do represent a class of iron chelates about which little is known. For example, in 1969 Sacconi and Bertini[3] reported a series of complexes employing the same type of ligands. Of the metals studied (Zn(II), Cu(II), Ni(II), Co(II), and Mn(II)), iron was not included. The only mention of the ferrous compounds in the literature is in a 1946 paper by Calvin and Barkelew[4] which deals with the magnetic properties of a number of Schiff base complexes.

In contrast to the relatively few data available for the iron compounds, the corresponding cobalt and nickel complexes have received extended study. *N,N′*-(3,3′-Dipropylamine)-bis(salicylideniminato)cobalt(II), Co(SALDPT), and its derivatives have been used as model compounds due to their reactivity with dioxygen to form stable adducts.[5,6] Some of these compounds have been found to be reversible oxygen carriers.[7,8] Recent work[9] involving the reaction of dioxygen with the manganese complexes has also appeared in the literature. Such reports provided a precedent for studying the iron compounds in a similar manner. Herein we convey our results regarding the characteristics of these complexes.

Experimental Section

Materials. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and ferrous chloride ($FeCl_2{\cdot}4H_2O$) were purchased from Fischer Scientific Co. Salicylaldehyde (SAL), 3-methoxysalicylaldehyde ($3\text{-}CH_3OSAL$), and bis(3-aminopropyl)amine (DPT) were purchased from Aldrich Chemical Co. and distilled prior to use. 5-Nitrosalicylaldehyde



Compound	R'	R_3	R_5
Fe(SALDPT)	H	H	H
Fe(3-CH_3OSALDPT)	H	CH_3O	H
Fe(5-NO_2SALDPT)	H	H	NO_2
Fe(SALMeDPT)	CH_3	H	H
Fe(3-CH_3OSALMeDPT)	CH_3	CH_3O	H
Fe(5-NO_2SALMeDPT)	CH_3	H	NO_2
Fe(SALEtDPT)	CH_3CH_2	H	H
Fe(SALPrDPT)	$CH_3CH_2CH_2$	H	H

Figure 1. Abbreviated nomenclature and schematic representation of the iron(II) complexes.

(5-NO_2SAL) was purchased from Eastman Organic Chemicals and used without further purification. Bis(3-aminopropyl)methylamine (MeDPT), bis(3-aminopropyl)ethylamine (EtDPT), and bis(3-aminopropyl)-*n*-propylamine (PrDPT) were obtained from a catalytic reduction of the corresponding cyano compounds.[10] In a typical reaction, 0.10 mol of the bis(nitrile) was added to 150 mL of ethanol. The solution was purged with ammonia for 15 min after which Raney nickel (approximately 5 g) was added to the flask. Hydrogen was introduced into the flask at a pressure of 60 psi and the contents were shaken overnight at room temperature. The flask was then depressurized and the catalyst filtered off. The solvent was removed by rotary evaporation and the residue distilled under reduced pressure. The starting materials, bis(2-cyanoethyl)methylamine, bis(2-cyanoethyl)ethylamine, and bis(2-cyanoethyl)-*n*-propylamine were obtained from reactions in which acrylonitrile was slowly added to an aqueous solution of methyl-, ethyl-, or propylamine.[10] After the solution was stirred for 48 h, water and unreacted acrylonitrile were removed by rotary evaporation, and subsequent distillation afforded the bis(nitrile) as well as a lower boiling fraction arising from mono addition. All other chemicals and solvents were reagent grade or better and all gases were used without further purification.

Preparation of the Iron(II) Complexes. General Procedure. A 250-mL round-bottomed flask was fitted with a nitrogen intake and stirring bar. The Schiff base ligand was made in situ prior to the addition of the metal. An alcoholic solution of the salicylaldehyde (0.020 mol) was added to the flask. To this was added 0.010 mol of the triamine in alcohol with stirring. An equimolar amount of triethylamine was added and after connecting a condenser, the mixture was refluxed for 30 min under nitrogen. The flask was allowed to cool to room temperature and the condenser was removed. A pressure-equalizing dropping funnel with a course frit was then connected and 0.010 mol of solid ferrous sulfate was added through the top of the dropping funnel. The salt was dissolved by adding deoxygenated water and this solution was then reacted with the Schiff base. A precipitate was formed by slow addition of the metal to the stirred solution of the ligand. The dropping funnel was removed and a fritted filter equipped with connecting joints was attached. The contents of the flask were filtered and the precipitate was washed with deoxygenated hexane. All operations were carried out under nitrogen. The funnel was stoppered and evacuated. The complex was dried under vacuum overnight.

Specific Preparations. Fe(SALDPT)·H_2O, *N,N'*-(3,3'-Dipropylamine)bis(salicylideniminato)iron(II)–Water. SAL (2.44 g) and DPT (1.31 g) were reacted in 40 mL of *tert*-butyl alcohol and 10 mL of isopropyl alcohol. $FeSO_4·7H_2O$ (2.79 g) in 50 mL of H_2O was added and the precipitate was stirred 45 min.

Fe(3-CH_3OSALDPT)·1.5H_2O, *N,N'*-(3,3'-Dipropylamine)bis(3-methoxysalicylideniminato)iron(II)–1.5-Water. The ligand was prepared from 6.08 g of 3-CH_3OSAL and 2.62 g of DPT in 150 mL of ethanol. $FeSO_4·7H_2O$ (5.6 g) in 25 mL of H_2O was added and the precipitate was stirred for 2 h.

Fe(5-NO_2SALDPT), *N,N'*-(3,3'-Dipropylamine)bis(5-nitrosalicylideniminato)iron(II). The ligand precipitated when 1.67 g of 5-NO_2SAL and 0.66 g of DPT were reacted in 100 mL of methanol. The ligand went into solution upon addition of 0.56 g KOH in 25 mL of CH_3OH. The metal was added as 0.99 g of $FeCl_2·4H_2O$, and the precipitate was stirred for 1 h.

Fe(SALMeDPT)·0.5H_2O, *N,N'*-(3,3'-Dipropylmethylamine)bis(salicylideniminato)iron(II)–0.5-Water. SAL (2.44 g) and MeDPT (0.45 g) were reacted in 75 mL of isopropyl alcohol. $FeSO_4·7H_2O$ (2.79 g) in 25 mL of H_2O was added and the precipitate was stirred for 15 min.

Fe(3-CH_3OSALMeDPT)·0.75H_2O, *N,N'*-(3,3'-Dipropylmethylamine)bis(3-methoxysalicylideniminato)iron(II)–0.75-Water. The ligand was prepared by reacting 3.04 g of 3-CH_3OSAL and 1.45 g of MeDPT in 150 mL of isopropyl alcohol. The metal was added as 2.79 g of $FeSO_4·7H_2O$ in 30 mL of H_2O. The precipitate was stirred for approximately 1 h.

Fe(5-NO_2SALMeDPT), *N,N'*-(3,3'-Dipropylmethylamine)bis(5-nitrosalicylideniminato)iron(II). The ligand was dissolved by adding 0.56 g of KOH to 1.67 g of 5-NO_2SAL and 0.73 g of MeDPT in 150 mL of methanol. An equimolar amount of $FeCl_2·4H_2O$ was added to the solution and the precipitate stirred 30 min.

Fe(SALEtDPT)·0.25H_2O, *N,N'*-(3,3'-Dipropylethylamine)bis(salicylideniminato)iron(II)–0.25-Water. SAL (2.44 g) and EtDPT (1.9 g) were mixed in 100 mL of ethanol. The complex precipitated immediately upon addition of 2.79 g of $FeSO_4·7H_2O$ in 25 mL of H_2O. The reaction mixture was filtered after 1 h.

Fe(SALPrDPT)·0.5H_2O, *N,N'*-(3,3'-Dipropylpropylamine)bis(salicylideniminato)iron(II)–0.5-Water. The ligand was formed from 4.88 g of SAL and 3.46 g of EtDPT in 200 mL of ethanol. After addition of 5.6 g of $FeSO_4·7H_2O$ in 25 mL of H_2O, the reaction mixture was stirred for 20 min, whereupon a precipitate soon formed.

Preparation of the μ-Oxo Complexes. The procedure for the preparation of [Fe(5-NO_2SALDPT)$]_2$O·C_3H_6O, μ-oxo-[*N,N'*-(3,3'-dipropylamine)bis(5-nitrosalicylideniminato)iron(III)]-acetone, and [Fe(5-NO_2SALMeDPT)$]_2$O·C_3H_6O, μ-oxo-[*N,N'*-(3,3'-dipropylmethylamine)bis(5-nitrosalicylideniminato)iron(III)]-acetone, is as follows. A saturated acetone solution of Fe(5-NO_2SALDPT) or Fe(5-NO_2SALMeDPT) was placed in a large tubular flask. Oxygen was rapidly bubbled through the solution via a long pipet. The solvent was evaporated in this manner until it was reduced to half of the original volume. The orange crystalline precipitate was filtered and allowed to dry.

Physical Measurements. Carbon, hydrogen, and nitrogen analyses were performed at the Center for Trace Characterization, Texas A&M University. Infrared spectra were taken as Nujol mulls between KBr plates on a Perkin-Elmer Model 237B grating spectrophotometer which was calibrated with polystyrene. Near-IR and visible spectra were measured on a Cary 14 spectrophotometer. Magnetic susceptibility data were obtained by the Gouy method using $HgCo(CNS)_4$ as a standard.

Results and Discussion

The analytical data for the iron(II) complexes are presented in Table I. The compounds precipitate from reaction mixtures involving the addition of a ferrous salt to the previously formed Schiff base. The precipitates appear crystalline and are usually maroon or burgundy. Most of the compounds are hydrated with various amounts of water either trapped in the crystal lattice or hydrogen bonded. The presence of water is confirmed by a broad band in the infrared spectra centered around 3300 cm^{-1}. The shape and position of the peak indicate that

Table I. Elemental Analysis of the Iron(II) Complexes

	% C		% H		% N	
Compd	Calcd	Found	Calcd	Found	Calcd	Found
Fe(SALDPT)·H_2O	58.39	58.40	6.08	6.27	10.21	9.84
Fe(3-CH_3OSALDPT)·1.5H_2O	54.99	54.49	6.25	6.09	8.75	8.91
Fe(5-NO_2SALDPT)	49.69	49.62	4.35	4.33	14.49	14.23
Fe(SALMeDPT)·0.5H_2O	60.57	60.29	6.25	6.00	10.09	10.01
Fe(3-CH_3OSALMeDPT)·0.75H_2O	57.44	57.30	6.21	6.14	8.74	8.90
Fe(5-NO_2SALMeDPT)	50.70	50.97	4.63	4.62	14.08	13.83
Fe(SALEtDPT)·0.25H_2O	62.37	61.88	6.49	6.36	9.92	9.68
Fe(SALPrDPT)·0.5H_2O	62.16	62.50	6.31	6.62	9.46	9.33

Table II. Magnetic Susceptibility of the Iron(II) Complexes

Compd	$10^6\chi_g$, cgsu	μ_{eff}, μ_B
Fe(SALDPT)·H_2O	10 920	5.22
Fe(3-CH_3OSALDPT)·1.5H_2O	9 150	4.88
Fe(5-NO_2SALDPT)	9 510	5.34
Fe(SALMeDPT)·0.5H_2O	10 750	5.07
Fe(3-CH_3OSALMeDPT)·0.75H_2O	9 220	4.97
Fe(5-NO_2SALMeDPT)	9 200	5.25
Fe(SALEtDPT)·0.25H_2O	10 350	4.90
Fe(SALPrDPT)·0.5H_2O	10 130	5.12

the water is not coordinated. Those compounds, Fe(5-NO_2SALDPT) and Fe(5-NO_2SALMeDPT), which are not hydrated were prepared in a completely alcoholic medium. The infrared spectra of all of the compounds show the Schiff base stretching frequencies around 1600 cm^{-1}. For complexes in which the amine is unsubstituted, the N–H stretch is also observable as a medium-weak sharp peak just below 3200 cm^{-1}.

The room-temperature magnetic susceptibility data for the individual complexes can be found in Table II. All of the compounds are high spin with magnetic moments between 4.88 and 5.34 μ_B. Such data suggest that the complexes are five-coordinate, whereas six-coordinate ferrous compounds normally have higher moments due to incomplete quenching of angular momentum. Since Fe(SALDPT) etc. do not react with oxygen in the solid state, the low susceptibility is not the result of ferric contamination. The high-spin nature of this type of chelate was initially established by Calvin and Barkelew.[4] They reported χ_g as 10 300 × 10^{-6} and 11 000 × 10^{-6} cgsu for Fe(3-ClSALDPT) and Fe(3-CH_3CH_2OSALDPT), respectively. However, Fe(3-CH_3OSALDPT) was reported to have a χ_g of 15 000 × 10^{-6} cgsu. This value seems unreasonably high and is in disagreement with our findings. Since the preparation and analytical data for the compounds were not given in their paper, the high susceptibility reported for Fe(3-CH_3OSALDPT) may be the result of an impure sample.

The electronic absorption spectra of the ferrous complexes are very similar. Figure 2a shows the type of spectrum observed is exemplified by that of Fe(5-NO_2SALDPT). There is a d–d transition at about 24 000 Å and another just below 15 000 Å. The shoulder around 5000 Å and all other higher energy bands are probably charge-transfer or ligand–ligand transitions. Although there is little with which to compare these spectra, they most closely resemble that of [FeBr(Me_6tren)]Br.[11] This compound contains a "tripod" ligand which produces a trigonal-bipyramidal complex.[12] The spectrum shows two strong bands at 20 000 and 10 200 Å. These have been attributed to the spin-allowed transitions $^5E \rightarrow {}^5A$ and $^5E \rightarrow {}^5E$, respectively. There are also higher energy bands of low intensity resulting from spin-forbidden transitions from the ground state to the first excited triplet states.

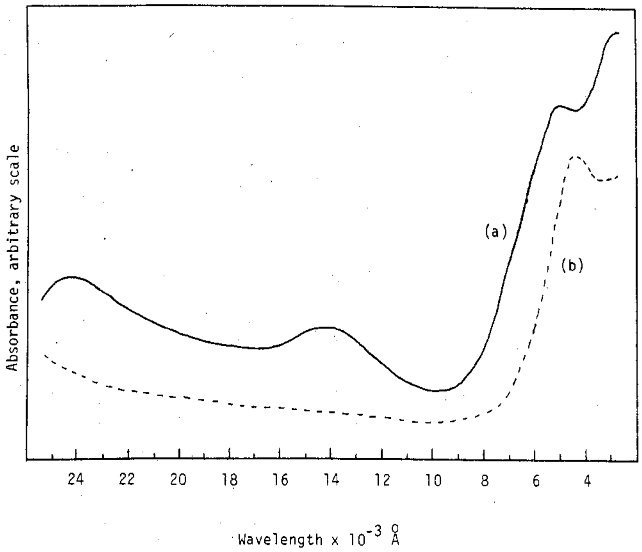


Figure 2. Solid-state electronic absorption spectra: (a) Fe(5-NO_2SALDPT), —; (b) [Fe(5-NO_2SALDPT)]$_2$O·C_3H_6O, ---.

Table III. Elemental Analyses of μ-Oxo Compounds

	% C		% H		% N	
Compd	Calcd	Found	Calcd	Found	Calcd	Found
[Fe(5-NO_2SALDPT)]$_2$O·C_3H_6O	48.86	48.91	4.55	4.46	13.25	13.09
[Fe(5-NO_2SALMeDPT)]$_2$O·C_3H_6O	50.56	50.16	4.87	5.10	13.11	12.71

The shift in the peak positions in the spectrum of Fe(SALDPT) is probably the result of a slightly different structure. This may be due to the fact that this type of compound only approaches trigonal-bipyramidal geometry. X-ray analysis of analogous compounds Ni(SALDPT)[13] and Ni(SALMeDPT)[14] reveals distorted trigonal-bipyramidal symmetry resulting from constraints imposed by the pentadentate ligands. Thus, a lowering of symmetry in the iron chelates from that observed in [FeBr(Me_6tren)]Br may be partly responsible for the difference in the spectra. Also, in Ni(SALDPT) and Ni(SALMeDPT), the metal ion is located in the equatorial plane. In [FeBr(Me_6tren)]Br, the metal is outside the equatorial plane. As a matter of comparison, the square-pyramidal complexes such as [Fe(ClO_4)($OAsMe_3$)$_4$]ClO_4[15] have only a single broad band around 10 000 Å, and with this added information one may conclude that the pentadentate ligands are not inclined to coordinate in this fashion around the iron(II) center.

The propensity of these compounds to be five-coordinate is indicated by the inability to isolate six-coordinate adducts with nitrogenous bases such as pyridine, piperidine, and propylamine. Addition of these ligands to the reaction medium results in compounds with the same characteristics as those obtained in their absence. These results are similar to what has been found for the cobalt(II) complexes.[3] Those compounds exhibit the same five-coordinate spectra in both coordinating and noncoordinating solvents. However, upon reaction with oxygen, the spectral characteristics change and six-coordinate cobalt dioxygen adducts are isolated.[6]

The ferrous complexes also react with oxygen, and although no dioxygen adducts were isolated even at −100 °C in aprotic solvents, they are apparently formed as intermediates leading to μ-oxo binuclear complexes. In at least two cases μ-oxo complexes have been isolated and characterized. These were prepared by dissolving the ferrous compounds in acetone and exposing the solutions to oxygen. For the 5-nitro derivatives, orange crystalline precipitates were soon formed. Analytical data (Table III) for the materials isolated suggest the formulation $[Fe(L)]_2O{\cdot}C_3H_6O$, where L = 5-NO_2SALDPT or 5-NO_2SALMeDPT. This type of oxidation is frequently encountered in iron(II) chemistry. For example, another iron(II) Schiff base complex, Fe(SALEN), reacts with oxygen to give the μ-oxo complex $[Fe(SALEN)]_2O$.[16] This compound has been well characterized and exhibits a metal–oxygen asymmetric stretching vibration at 825 cm^{-1} in the infrared spectrum. The room-temperature magnetic moment is 1.86 μ_B, consistent with the oxidation to low-spin iron(III).[17]

The μ-oxo complexes with pentadentate ligands give similar results. $[Fe(5\text{-}NO_2SALDPT)]_2{\cdot}C_3H_6O$ has a room-temperature magnetic moment of 1.89 μ_B while that of $[Fe(5\text{-}NO_2SALMeDPT]_2O{\cdot}C_3H_6O$ is 1.91 μ_B. Comparison of the infrared spectra of these compounds to that of the iron(II) complex reveals a new peak which has been assigned to the Fe–O stretching mode. This peak occurs at 810 cm^{-1} in the spectrum of $[Fe(5\text{-}NO_2SALDPT)]_2O$ and at 815 cm^{-1} in the spectrum of the methyl derivative. In both spectra there is a new band, just below 1700 cm^{-1}, which is the carbonyl stretching of the solvated acetone. The electronic spectra of these compounds are also different from that of the precursor (see Figure 2b). $[Fe(5\text{-}NO_2SALDPT)]_2O$ has a band at 4300 Å and $[Fe(5\text{-}NO_2SALMeDPT)]_2O$ has a band at 4000 Å plus a slight shoulder at 5000 Å. These spectra are very similar to that of $[Fe(SALEN)]_2O$ which also exhibits a single band in this area.

Solution spectra of Fe(SALDPT) and other derivatives show similar changes when exposed to oxygen. However, an interesting feature of these spectra is that there is an apparent difference in the reactivity of Fe(SALDPT) as compared to the methyl, ethyl, and propyl derivatives. For example, a chloroform solution of Fe(SALDPT) prepared in air gives only the iron(III) spectrum. A solution of Fe(SALMeDPT) prepared in a similar manner gives the same spectrum as the obtained in the solid state. This spectrum changes over a period of several minutes as the sample reacts with oxygen. The initial spectra of Fe(SALEtDPT) and Fe(SALPrDPT) are also the same as observed for the solid state and change with time, but more slowly than that of the methyl derivative. If oxygen is bubbled through the solution, the spectra immediately change. The reaction is irreversible even after purging with nitrogen.

In order to understand the significance of all this, one needs to compare the corresponding cobalt complexes. It has also been found that the reaction of oxygen is slower for Co(SALMeDPT) than for Co(SALDPT).[8] From the x-ray structure[18] of $[Co(SALDPT)]_2O_2{\cdot}C_6H_5CH_3$ it was determined that the position of attack is cis to the central nitrogen donor. Placing a methyl group on this nitrogen somewhat blocks this cis coordinate site, thus decreasing reactivity. It was also suggested[8] that the methyl group prevents dimerization and therefore μ-peroxo complexes are not formed with this type of derivative. However, the formation of a μ-oxo complex with Fe(5-NO_2SALMeDPT) suggests either that a rearrangement is taking place so that dimerization is more sterically favored or that an additional mode of attack is operating for the iron compounds.

In summary, iron(II) complexes with pentadentate Schiff base ligands are similar to other metal chelates of this type. These ferrous compounds, however, do not provide good models for biological oxygen carriers since reaction with oxygen in solutions leads to irreversibly oxidized ferric complexes. Of interest are the relative stability of these complexes with amine substituents and the inertness of all the pentadentate complexes toward oxidation in the solid state.

Registry No. Fe(SALDPT), 65802-41-7; Fe(3-CH_3OSALDPT), 65802-42-8; Fe(5-NO_2SALDPT), 65802-40-6; Fe(SALMeDPT), 65802-39-3; Fe(3-CH_3OSALMeDPT), 65802-38-2; Fe(5-NO_2SALMeDPT), 65802-37-1; Fe(SALEtDPT), 65802-36-0; Fe(SALPrDPT), 65802-35-9; $[Fe(5\text{-}NO_2SALDPT)]_2O$, 65802-34-8; $[Fe(5\text{-}NO_2SALMeDPT)]_2O$, 65802-33-7; SAL, 90-02-8; DPT, 56-18-8; 3-CH_3OSAL, 148-53-8; 5-NO_2SAL, 97-51-8; MeDPT, 105-83-9; EtDPT, 2372-77-2.

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A One-Step Synthesis of $B_{11}H_{14}^-$ Ion from $NaBH_4$

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A facile synthesis of tetradecahydroundecaborate(1−) ion, $B_{11}H_{14}^-$, is described from $BF_3{\cdot}O(C_2H_5)_2$ and salts of $B_3H_8^-$ ion or from $B_3H_8^-$ ion prepared in situ from $BF_3{\cdot}O(C_2H_5)_2$ and $NaBH_4$.

Introduction

The synthesis of tetradecahydroundecaborate(1−) ion, $B_{11}H_{14}^-$, was first accomplished by the reaction of metal borohydrides with decaborane(14).[1,2] Later it was shown that

$$MBH_4 + B_{10}H_{14} \xrightarrow[R_2O]{90\,^\circ C} MB_{11}H_{14} + 2H_2 \qquad (1)$$

$B_{11}H_{14}^-$ ion could be prepared directly from sodium borohydride and diborane(6) or pentaborane(9) in high-pressure equipment,[3] and in low yield from diborane(6) in the presence of dimethyl sulfide.[3] These methods suffer from the necessity of utilizing as starting materials hazardous and expensive boron hydrides.

We report here the facile synthesis of $B_{11}H_{14}^-$ ion from