Table III. Fundamental Vibrational Frequencies (cm^{-1}) for Gaseous Perfluorovinyldifluoroborane and Perfluorovinyldichloroborane

Approx description		F_2CCFBF_2		$F_2CCFBCl_2$
		A′		
C=C str	ν_1	1725	ν_1	1694
CF str	ν_2	1410	ν_2	1290
CF_2 antisym	ν_3	1390	ν_3	1352
BX_2 antisym str	ν_4	1323	ν_6	981
CF_2 sym str	ν_5	1179	ν_4	1128
B-C str	ν_6	1040	ν_5	1023
BX_2 sym str	ν_7	709	ν_7	864
CF_2 rock	ν_8	679	ν_8	532
BX_2 scissors	ν_9	584	ν_9	404
CF_2 scissors	ν_{10}	370	ν_{10}	329
BX_2 rock	ν_{11}	351	ν_{12}	163
CF bend	ν_{12}	248	ν_{11}	217
CCB bend	ν_{13}	138	ν_{13}	135
		A″		
CF_2 wag	ν_{14}	682	ν_{14}	632
BX_2 wag	ν_{15}	596	ν_{16}	245
CF bend	ν_{16}	335	ν_{15}	323
CF_2 twist	ν_{17}	123	ν_{17}	90
BX_2 torsion	ν_{18}	(69)	ν_{18}	(30)

0.237 cm^{-1} for V_fBF_2 and V_fBCl_2, respectively. If the torsional fundamental for V_fBF_2 is 69 cm^{-1}, the twofold barrier to internal rotation is near 7 kcal/mol, but if this frequency represents double jumps, the barrier would be close to 2 kcal/mol. For V_fBCl_2 a torsional frequency of 30 cm^{-1} corresponds to ~2.7 kcal/mol.

Conclusion

The vibrational spectra of perfluorovinyldifluoroborane and perfluorovinyldichloroborane indicate that both molecules have a plane of symmetry and are probably planar in the fluid and solid phases. It is difficult to determine directly from the vibrational frequencies whether there is π delocalization along the C–B bond. Unfavorable steric factors can be explained by invoking a degree of delocalization.

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Registry No. V_fBF_2, 1511-68-8; V_fBCl_2, 758-99-6.

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Reactions of Tetraborane(10) with Mono- and Dimethylamine

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The reactions of tetraborane(10) with mono- and dimethylamine were found to give $H_2B(CH_3NH_2)_2^+B_3H_8^-$ and $H_2B[(CH_3)_2NH]_2^+B_3H_8^-$, the unsymmetrical cleavage products of tetraborane(10), exclusively. As in the reaction of tetraborane(10) with ammonia, the fast deprotonation of tetraborane(10) proceeds to produce $B_4H_9^-$ ion first and the competing reaction to form the final product proceeds slowly. The latter reaction becomes fast at about −40 °C. The mechanism of the reactions that leads to the exclusive unsymmetrical cleavage of tetraborane(10) by these amines is discussed with reference to the reactions of diborane(6) with the same amines, where both symmetrical and unsymmetrical cleavage products are produced. The strong affinity of the B_3H_7 group toward the bridge hydrogen in the intermediate $H_2B(amine)$–H–B_3H_7 is thought to be responsible for the exclusive formation of the $B_3H_8^-$ salts.

Introduction

Two types of cleavage products, "symmetrical" and "unsymmetrical", are known to form in different proportions in the reactions of diborane(6) with the series of methylamines. Ammonia gives the unsymmetrical cleavage product, $H_2B(NH_3)_2^+BH_4^-$, virtually exclusively under carefully controlled conditions.[1] With increasing methyl substitution on amine nitrogen the amounts of symmetrical cleavage products in the reaction products increase,[2,3] and trimethylamine gives only the symmetrical cleavage product $(CH_3)_3N{\cdot}BH_3$.[4] The observed variation has been correlated with the increasing steric requirement of the amine ligands and the steric effect is considered to be a predominant factor that determines the type of cleavage product in this series of diborane reactions.[2,5]

Although tetraborane(10) is known to give $H_2B(NH_3)_2^+B_3H_8^-$ (unsymmetrical cleavage product)[6] and a 1:1 mixture of $(CH_3)N\cdot BH_3$ and $(CH_3)_3N\cdot B_3H_7$ (symmetrical cleavage products)[7] upon reaction with ammonia and trimethylamine, respectively, the reactions with mono- and dimethylamine have not been reported. It was of interest to complete the series of methylamine reactions with tetraborane(10) to obtain further evidence and information on the factors that influence borane cleavage reactions.

Results and Discussion

The reactions of tetraborane(10) with mono- and dimethylamine were run in diethyl ether and in dichloromethane under reaction conditions similar to those reported for the preparation of the diammoniate of tetraborane(10),[6a] while the ratio of amine to tetraborane(10) in each reaction system was limited to 2:1. Exclusive formation of the unsymmetrical cleavage product was found to take place in the reaction with ammonia under these conditions as it was when an excess amount of ammonia was used. In contrast to the reactions of diborane(6) with mono- and dimethylamine,[2,3] where both symmetrical and unsymmetrical cleavage products are observed, the reactions of tetraborane(10) with these methylamines were found to give the unsymmetrical cleavage products exclusively.

$$B_4H_{10} + 2CH_3NH_2 \rightarrow H_2B(CH_3NH_2)_2{}^+B_3H_8{}^-$$

$$B_4H_{10} + 2(CH_3)_2NH \rightarrow H_2B[(CH_3)_2NH]_2{}^+B_3H_8{}^-$$

The dimethylamine compound is a solid at room temperature and the monomethylamine compound melts at about 22 °C. The products are indefinitely stable in the absence of moisture. The anticipated symmetrical cleavage products of tetraborane(10), $CH_3NH_2\cdot B_3H_7$ and $(CH_3)_2NH\cdot B_3H_7$, have been characterized and reported previously.[8]

The ^{11}B NMR study of the mono- and dimethylamine reaction systems at low temperatures revealed that the deprotonation of tetraborane(10) to form $B_4H_9^-$ ion proceeds rapidly and exclusively at −80 °C first and that the formation of the unsymmetrical cleavage product becomes noticeable at higher temperatures. The latter is complete in a few minutes at −40 °C but is slow below −40 °C. This observation is comparable to that reported for the reaction of tetraborane(10) with ammonia[9] and is represented by the following equations, by analogy to the ammonia reaction:

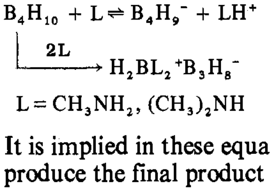
$$B_4H_{10} + L \rightleftharpoons B_4H_9{}^- + LH^+$$

$$\xrightarrow{2L} H_2BL_2{}^+B_3H_8{}^-$$

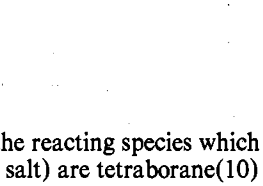
$$L = CH_3NH_2,\ (CH_3)_2NH$$

It is implied in these equations that the reacting species which produce the final product (the $B_3H_8^-$ salt) are tetraborane(10) molecules which are in equilibrium with $B_4H_9^-$ ions.

Earlier, by analogy to the reaction mechanism proposed for the reactions of diborane(6) with ammonia to form the diammoniate of diborane(6),[10] an intermediate $B_4H_{10}NH_3$ was proposed in the reaction of tetraborane(10) with ammonia.[6a] The proposed structure for the intermediate is shown below (in I). The second base attack on B_1 atom followed by the cleavage of B_1–H_b–B_2 bond at B_1–H_b would result in the unsymmetrical cleavage of tetraborane(10), whereas the second base attack on the B_3 moiety (B_2, B_3, or B_4) followed by the cleavage at H_b–B_2 would produce the symmetrical cleavage products. A rearrangement of hydrogen atoms within the B_3 moiety is assumed in the latter case if the attacking site is B_3 or B_4.



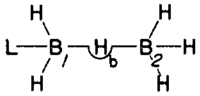
I



II

It is clear that the formation of the unsymmetrical cleavage product does not involve the initial symmetrical cleavage of tetraborane(10) followed by a hydride transfer reaction. This was substantiated by the observation that no change occurred in a 1:1 mixture of $(CH_3)_2NH\cdot BH_3$ and $(CH_3)_2NH\cdot B_3H_7$ in dichloromethane at temperatures from −80 to +20 °C.

Shown in II is an alternative representation of the 1:1 adduct intermediate. No evidence is available to differentiate the two structures. In I, the singly bridged hydrogen (H_b) is considered to be located closer to B_2 than to B_1 due to the strongly acidic nature of B_3H_7. In II, the hydrogen H_b is attached only to B_2 and thus the close association of H_b with B_2 is made manifest. This contrasts with the intermediate in the diborane(6) reaction in which a BH_3 unit is singly bridge bonded to the LBH_2 unit:[10]



Due to the stronger acidity of B_3H_7 as compared with BH_3[7] and also due to the particular boron atom arrangement which is only possible for the B_4H_{10} intermediate, the bridge hydrogen (H_b) would be more strongly bonded to B_2 in the B_4H_{10} intermediate than in the B_2H_6 intermediate. As suggested by Young and Shore,[5] when the reacting base is an amine, the electron-withdrawing effect of the nitrogen atom makes the B_1 atom more susceptible to the second base attack. Thus unsymmetrical cleavage is the favored process with amines unless the steric effect changes the energy balance in favor of symmetrical cleavage. In the tetraborane(10) reactions, because of the strong association of the H_b atom with the B_3H_7 unit, or the relative weakness of the B_1–H_b bond, the steric effect that changes the energy balance appears not to become operative until the amine becomes tertiary.

The unique behavior of trimethylamine in the series of methylamines is also seen in the chloride displacement reaction shown below.[11]

$$LBH_2Cl + L \rightarrow L_2BH_2{}^+Cl^- \quad (L = \text{amines})$$

The reaction proceeds readily at room temperature with ammonia, monomethylamine, or dimethylamine, but not with trimethylamine.

It is noted that *diethylamine*, a secondary amine which is comparable to trimethylamine in size, yields only the unsymmetrical cleavage product, $H_2B[NH(C_2H_5)_2]_2{}^+B_3H_8{}^-$, upon reaction with tetraborane(10) under conditions which are identical with those used for the methylamine reactions. Apparently the specific bulkiness at the immediate vicinity of the nitrogen atom in the amine molecule is primarily responsible for the steric hindrance upon coordination of the second amine to the boron atom.

It is known that tetraborane(10) reacts with tetrahydrofuran (THF) at low temperatures (−70 to −30 °C) to give the unsymmetrical cleavage product, $H_2B(THF)_2{}^+B_3H_8{}^-$, and that the product changes to the symmetrical cleavage products, $THF\cdot BH_3$ and $THF\cdot B_3H_7$, at higher temperatures (above −30 °C).[12] The initial unsymmetrical cleavage was attributed to the inductive effect of the oxygen atom of the coordinated tetrahydrofuran, and the conversion that follows was explained by the inherently weak donor character of tetrahydrofuran compared to hydride ion.[5] It was then speculated,[5b] on the basis of the observed high electrical conductivity of solutions of diborane(6) in tetrahydrofuran, that diborane(6) might undergo unsymmetrical cleavage upon reaction with tetrahydrofuran to give $H_2B(THF)_2^+BH_4^-$. However, our ^{11}B NMR study on the system of diborane(6) and tetrahydrofuran at low temperatures revealed that the reaction to give $THF\cdot BH_3$ was complete at −80 °C and indicated that no BH_4^- ion was present in the system at that temperature. The difference in the cleavage process between the two reaction systems is clear. This difference may be taken as an additional example to which the model presented above can be consistently applied. Tetrahydrofuran in the intermediates would make the B_1 atom more susceptible to base attack. This base, however, is a weak donor relative to amines and its second attack on B_1 followed by B_1–H_b cleavage is possible only when H_b is strongly bonded to B_2 as in the B_4H_{10} intermediate. In the B_2H_6 intermediate the H_b–B_2 bond is not strong enough to allow the formation of dissociatively unstable $H_2B(THF)_2^+$ cation and, therefore, B_2 becomes the effective site of the second base attack to give the symmetrical cleavage. At the higher temperatures the dissociative tendency of the cation, $H_2B(THF)_2^+ \rightarrow$ "$H_2B(THF)^+$" + THF, would become strong and therefore the hydride transfer from $B_3H_8^-$ ion to the BH_2^+ moiety would proceed readily through the formation of the intermediate $H_2B(THF)\leftarrow H-B_3H_7$ which would be cleaved to $THF\cdot BH_3$ and $THF\cdot B_3H_7$ by tetrahydrofuran. The amine-coordinated cations are dissociatively stable enough not to allow such hydride transfer reactions to take place under ordinary conditions.[13]

The reaction of pentaborane(11) with tetrahydrofuran is also known to produce the unsymmetrical cleavage product, $H_2B(THF)_2^+B_4H_9^-$,[14] which is stable only at low temperatures. Tetraborane(8), B_4H_8, also being a stronger acid than BH_3, the formation and the instability of the ionic product can be explained in a manner similar to that described above for the tetrahydrofuran reaction of tetraborane(10). It is noted, however, that the formation of the symmetrical cleavage products of pentaborane(11), $THF\cdot BH_3$ and $THF\cdot B_4H_8$, has not been observed, probably due to the instability of the latter adduct.[14]

The nature of the products in the reactions of tetraborane(10) with amines is sensitive to the reaction conditions, as was observed in the reactions of diborane(6) with ammonia.[15] Unless the reaction mixtures are prepared as uniform, preferably dilute solutions at appropriate low temperatures and the temperature is properly controlled during the reactions, impurities from some side reactions contaminate the products, often making the products less stable and complicating the product analyses. Thus occasionally during the course of this study, small amounts of triborane adducts of the amines were found in the reaction products. Fast addition of reactant, which might cause a localized high concentration of the reactant, and abrupt raising of the temperature of the reaction systems should also be avoided.

Experimental Section

(a) General. Conventional vacuum line techniques were used for the handling of chemicals throughout the experiments and for the preparation of NMR samples. Laboratory stock tetraborane(10), ammonia, and methylamines which had been purified as described in the previous report[8] were used. Reagent grade diethyl ether and dichloromethane were stored over $LiAlH_4$ and molecular sieves, respectively, and were distilled into the vacuum line as needed. The ^{11}B NMR spectra were recorded on a Varian XL-100-15 instrument equipped with a spin-decoupler unit (Gyrocode), operating at 32.1 MHz. Boron chemical shifts are expressed relative to the $BF_3\cdot O(C_2H_5)_2$ signal, *shifts to lower field being taken as positive.*

(b) Reactions of Tetraborane(10) with Mono- and Dimethylamine. B_4H_{10} (1.79 mmol) and 3 mL of diethyl ether were condensed at −196 °C into a 22-mm o.d. Pyrex reaction tube fitted with a standard taper 24/40 male joint, and a solution of the B_4H_{10} was prepared at −80 °C by stirring with a solenoid-operated hopper stirrer. Dimethylamine (3.57 mmol) (molar ratio = 1.99) was measured out and the vapor of the amine was allowed to slowly leak into the reaction tube by opening the connecting stopcock very slightly while the solution was stirred at −80 °C. The absorption of the amine by the solution was virtually complete. The reaction tube was frozen with liquid nitrogen to condense the last trace of the amine vapor, removed from the vacuum system, and stored at −80 °C. After standing at −80 °C for a week, the reaction tube was attached to the vacuum system and opened, and the volatile components (essentially diethyl ether solvent) were removed at 0 °C to isolate the white solid product. In a similar manner 1.21 mmol of B_4H_{10} was treated with 2.53 mmol of monomethylamine (molar ratio = 2.09) in 3 mL of diethyl ether and the white solid product was isolated at 0 °C.

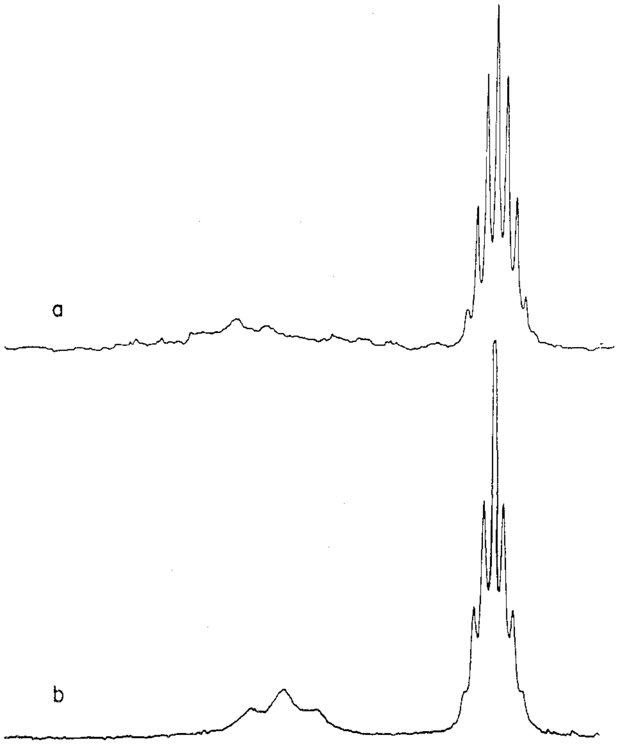


Figure 1. ^{11}B NMR spectra of the unsymmetrical cleavage products (a) $H_2B[(CH_3)_2NH]_2^+B_3H_8^-$ and (b) $H_2B(CH_3NH_2)_2^+B_3H_8^-$ in CH_2Cl_2.

The NMR samples of these reaction products in dichloromethane solution were prepared in standard 5 mm o.d. NMR sample tubes. Each of the ^{11}B NMR spectra of these samples at ambient temperature consisted of a sharp $B_3H_8^-$ multiplet signal at −30.2 ± 0.2 ppm (lit. −30.0 ± 0.5)[16] and a broad triplet signal (see Figure 1). The triplets were observed at −3.0 ppm (J = 131 ± 5 Hz) and −8.5 ppm (J = 111 ± 5 Hz) for the dimethylamine and monomethylamine reaction products, respectively. A shift value of −9.2 ppm was reported for the $H_2B(CH_3NH_2)_2^+$ cation.[2]

(c) NMR Studies of the Reactions. A measured amount of tetraborane(10) (about 0.5 mmol) was condensed in a 10 mm o.d. NMR sample tube, to which a stopcock with a ₮10/30 male joint was attached. A sample of dichloromethane was condensed in the tube to prepare a solution of about 0.3 M concentration. Then a measured amount of the amine vapor (molar ratio of amine/B_4H_{10} = 2:1) was allowed to leak into the tube very slowly through the stopcock while the tube was tilted and shaken to agitate the solution which was kept at −80 °C by immersing the tube in a 2-propanol–dry ice slush. Upon completion of the amine absorption, the tube was frozen with liquid nitrogen, removed from the vacuum line, and stored at −196 °C until the NMR measurements were made. The spectra of each sample were recorded starting at −80 °C in 10 to 20 °C increments up to +30 °C.

The reaction system of tetraborane(10) with ammonia produced a solid in the dichloromethane solution at about −40 °C and no ^{11}B NMR signal could be detected. Below −40 °C the signals of $B_4H_9^-$ ion were clearly seen. One milliliter of diethyl ether was then added to the sample tube and the tube was allowed to warm to room temperature. The spectrum of the resulting solution showed strong signals of $B_3H_8^-$ ion and $H_2B(NH_3)_2^+$ ion. Weak signals of $H_3N{\cdot}BH_3$ and $H_3N{\cdot}B_3H_7$ were also detected. When diethyl ether was used as solvent for this reaction instead of dichloromethane, the solution remained clear at all temperatures of spectrum recording. The initial exclusive formation of $B_4H_9^-$ ion and the conversion of the initial product to $H_2B(NH_3)_2^+B_3H_8^-$, which proceeds rapidly at −40 °C, were evident in the spectra.

The reaction of tetraborane(10) with diethylamine in dichloromethane was studied in the same manner as described immediately above. The reaction began with the initial formation of $B_4H_9^-$ ion and ended with the exclusive formation of $H_2B[(C_2H_5)_2NH]_2^+B_3H_8^-$. The progress of the reaction was also the same as that observed in the dimethylamine reaction. The ^{11}B NMR signal for the $H_2B[(C_2H_5)_2NH]^{2+}$ cation appears at −5.0 ppm as a triplet (J = 115 Hz). The product is a stable, colorless liquid at room temperature.

(d) The System of Dimethylamine–Borane(3) and Dimethylamine–Triborane(7). An equimolar mixture (2.34 mmol each) of $(CH_3)_2NH{\cdot}BH_3$ and $(CH_3)_2NH{\cdot}B_3H_7$ in dichloromethane was prepared in a 10 mm o.d. NMR sample tube. The ^{11}B NMR spectra of the sample at temperatures from −80 to +20 °C showed no evidence of any change in the original compounds. The mixture remained unchanged even after standing for 5 h at room temperature.

(e) The System of Diborane(6) and Tetrahydrofuran. A solution containing 0.30 mmol of B_2H_6 in about 1.5 mL of tetrahydrofuran was prepared in a 10 mm o.d. NMR sample tube at −80 °C. The solution was never warmed above −80 °C before the measurements were initiated. At −80 °C a broad band centered at −2.8 ppm was the only signal that could be observed in the proton spin-decoupled spectrum. As the temperature was raised the signal gradually sharpened and shifted slightly downfield. At +20 °C a well-defined quartet (J = 105 Hz) (or a singlet in the proton-decoupled spectrum) was observed at −1.9 ppm. No other signal could be detected during this whole process. Literature values of the ^{11}B chemical shift for $THF{\cdot}BH_3$ are −0.8 and −0.9 ppm (J = 103 Hz).[17]

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Registry No. $H_2B[(CH_3)_2NH]_2^+B_3H_8^-$, 63937-06-4; $H_2B(CH_3NH_2)_2^+B_3H_8^-$, 63915-42-4; $H_2B[(C_2H_5)_2NH]_2^+B_3H_8^-$, 63937-10-0; B_4H_{10}, 18283-93-7; $(CH_3)_2NH$, 124-40-3; CH_3NH_2, 74-89-5; B_2H_6, 19287-45-7; THF, 109-99-9; $THF{\cdot}BH_3$, 14044-65-6.

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Transition Metal Eight-Coordination. 9. Tetrakis(picolinato)tungsten(IV) and -(V) Complexes[1]

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A series of blue, air and thermally stable, eight-coordinate tungsten(IV) complexes of the type $[WL_4]$ (L = picolinato; 5-methyl-, 5-ethyl-, 3-hydroxy-, and 3,4-benzopicolinato; and 2-pyrazinecarboxylato) has been synthesized anaerobically by high-temperature anhydrous solvent reactions between $W(CO)_6$ and the appropriate ligand. Some were also isolated from sealed-tube melt reactions of the same reactants. These substitution-inert complexes are diamagnetic, and the electronic absorption spectra are dominated by low-energy metal to ligand charge-transfer bands in the range 16 200–18 000 cm^{-1} (ϵ 15 000–23 000), except for tetrakis(1-isoquinolinecarboxylato)tungsten(IV), which has its low-energy maximum at 13 600 cm^{-1} (ϵ ~35 000). The more soluble complexes have been studied by ^1H NMR and exhibit spectra consistent with eight-coordination. Oxidation of the $[WL_4]$ complexes to $[WL_4]X$ salts was accomplished for L = picolinato (pic⁻) and 1-isoquinolinecarboxylato (iqc⁻) by treatment with CCl_4 solution of Cl_2 or Br_2. The golden brown $[W(pic)_4]X$ salts are paramagnetic (μ_{eff} = 1.6 μ_B) and show moderate stability in air but disproportionate rapidly (<10 min) in solution to WL_4 and a tungstate species. The $[W(iqc)_4]Cl$ salt is considerably more resistant to disproportionation. Liquid nitrogen electron spin resonance studies of $[W(pic)_4]Cl$ suggest a low-symmetry configuration of ligands around the metal in an acetone–glass environment. Anisotropic g values of 1.949, 1.863, and 1.763 were obtained under these conditions.

Introduction

Based on the structural and chemical similarities between 8-quinolinol and picolinic acid and the successful synthesis and characterization of a series of tetrakis(8-quinolinolato)tungsten(IV)[2] and -tungsten(V)[3] complexes, an investigation of the possible existence of tetrakis(picolinato)tungsten(IV)[4] and -tungsten(V) complexes was undertaken. In addition to the picolinato ligand (**1**, pic⁻) and its 3-hydroxy (hpic⁻), 5-methyl (mpic⁻), and 5-ethyl (epic⁻) derivatives, the 2-pyrazinecarboxylato (**2**, pzc⁻) and the 1-isoquinolinecarboxylato (**3**, iqc⁻) ligands have been investigated as potential ligands. Tetrakis-8-quinolinolato (**4**, q⁻) tungsten(IV) derivatives have been synthesized[2] for the 5-bromo (bq⁻), the 5,7-dibromo (dbq⁻), the 5,7-dichloro (dcq⁻), the 7-bromo-