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Preparation and Characterization of Compounds Containing the Octamethylditungsten(II) Anion and Partially Chlorinated Analogues

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Abstract: Reactions of methyllithium with tungsten(IV) and tungsten(V) chlorides at temperatures at or below 0 °C in ether allow the isolation of $Li_4W_2Me_8{\cdot}4Et_2O$ (**1**) when a 1–2 molar excess of LiMe is used. When only about a 0.5 molar excess of LiMe is used, nonstoichiometric products of the type $Li_4W_2Me_{8-x}Cl_x{\cdot}4Et_2O$ (**2**) are obtained. The former is red, the latter red purple, and the Et_2O in each can be replaced by THF, giving **3** and **4**. It has not yet been possible to determine the crystal structure of **1** but a sample of **4** with $x \approx 3.2$ has been shown to contain a statistically disordered $W_2Me_{8-x}Cl_x^{4-}$ anion with virtual D_{4h} symmetry and W–W = 2.26 Å. The $W_2Me_8^{4-}$ ion is presumed to be very similar. None of the compounds is thermally stable above 0 °C and the mixed methyl-chloro ones seem unstable above −20 °C. All are exceedingly reactive to air or moisture. The electronic spectra agree well with previously suggested correlations for other $M_2Me_8^{n-}$ ions containing Cr, Mo, and Re.

Since the discovery, in 1964, that quadruple bonds exist,[2-4] a great many compounds of rhenium,[4-8] technetium,[4,9,10] ruthenium,[4] chromium,[4] and especially molybdenum[4,11-16] have been shown to contain quadruple bonds or bonds of similar character in structurally similar circumstances, namely, in ions or molecules of the sort $L_4M{\equiv}ML_4$ (where L_4 may represent a mixed set of ligands) with $M_2(O_2CR)_4$ constituting a very important special case.[4] It is striking that while molybdenum is, on current data, the most prolific former of such bonds, rhenium forms them rather readily and chromium forms analogues to many, though by no means all, of the molybdenum compounds, quadruply bonded pairs of tungsten atoms had never been shown conclusively to exist. A series of compounds, $W_2(O_2CR)_4$, with R = C_6H_5, p-$CH_3C_6H_4$, C_6F_5, C_3H_7, and C_3F_7, were prepared[17] and have been reproduced many times by different workers, but never has a crystalline sample of any of them come into our hands. Hence, direct structural proof of the existence of a quadruple bond in these molecules has not been obtainable.

On the other hand, the isolation of $[MoW(O_2CCH_3)_4]I{\cdot}CH_3CN$ with its Mo–W bond[18] of order 3.5 and the fact that there exist as many, or more, stable compounds containing W–W triple bonds as Mo–Mo triple bonds[19-21] justified some optimism about obtaining and authenticating at least a few compounds containing W–W quadruple bonds. Also, a scattered wave Xα-SCF calculation[10] for the hypothetical $W_2Cl_8^{4-}$ ion gave results qualitatively and quantitatively similar to those for $Mo_2Cl_8^{4-}$.[22]

Efforts to prepare some quadruply bonded ditungsten species were undertaken independently and, initially, without mutual awareness, in our two laboratories. In both cases the explicit objective was the $W_2Me_8^{4-}$ ion, for which the analogues $Cr_2Me_8^{4-}$,[23] $Mo_2Me_8^{4-}$,[24] and $Re_2Me_8^{2-}$ [8] were already known and well characterized.[25] In this paper we report the successful results obtained in both laboratories. A part of this work has already been described in a preliminary note.[26]

Experimental Section

General. All syntheses and other operations were conducted in vacuum or under rigorously oxygen-free nitrogen or argon. The thermal instability of the products precluded combustion analysis and other methods were therefore used. Methyl groups were determined by hydrolysis and measurement of methane in a gas buret. Chlorine was precipitated and weighed as AgCl. Tungsten was determined gravimetrically as WO_3 (Texas) or using a plasma arc emission-absorption instrument (London). Lithium analysis was also done with the latter instrument. For further details, see below.

Starting Materials. Methyllithium was prepared by reaction of lithium metal with methyl chloride in diethyl ether. The tungsten halides were prepared, according to the suggestion of King and McCarley,[27] by reactions of WCl_6 with $W(CO)_6$. For WCl_4 a mole ratio of 2:1 was heated to reflux in chlorobenzene. The WCl_4 precipitated and was isolated by filtration, dried under vacuum, and used without further purification. WCl_5 was obtained by placing 10–20 g of WCl_6 in a glass tube, under argon, adding a slight excess over a 1:5 mole ratio of $W(CO)_6$ and connecting the tube to a mercury bubbler. The tube was then heated to 100 °C in an oil bath. The reaction was allowed to proceed 4–6 h. Unreacted $W(CO)_6$ was removed by connecting the reaction tube to the vacuum line and subliming the material into a cold trap. The remaining product was transferred to a two-compartment tube and the WCl_5 was sublimed away from small amounts of WCl_4 in vacuo at 250 °C. Elemental analyses were made on at least one batch of each halide and gave satisfactory results.

Preparation of $Li_4W_2Me_8{\cdot}4Et_2O$ from WCl_5. This is the procedure developed in London. Into a solution of WCl_5 (5 g, 0.0147 mol), prepared by cooling the WCl_5 at −78 °C and adding 60 mL of melting ether previously frozen in liquid nitrogen, was added at −78 °C slowly under stirring a solution of MeLi (1.1 M) in ether (105.4 mL, 0.0147 × 8 = 0.1176 mol). The reaction mixture was left to warm up slowly. The solution becomes red at −35 °C and deep red at −10 °C. The mixture was left to react further for 1 h at 0 °C and filtered quickly; the filtrate was reduced to 25 mL, and the product was crystallized in the form of bright-red crystals at −78 °C. These were filtered at −78 °C, washed with successive portions of ether at −78 °C, and dried at −20 °C (10^{-3} Torr) to give 2.5 g of pyrophoric red crystals; yield 44% based on WCl_5.

Analysis of a typical batch of product gave CH_4/W and Li/W mole ratios of 3.9 and 2.0, respectively. The ^1H NMR spectrum in benzene had signals at τ 6.53 (quartet) and 8.78 (triplet) due to Et_2O and τ 9.73 (singlet) due to $W{-}CH_3$. The signal intensities were consistent with the formula proposed.

Preparation of $Li_4W_2Me_8{\cdot}4Et_2O$ from WCl_4. This is the procedure developed in Texas. Methyllithium (25 mL of a 1.9 M diethyl ether solution, 47 mmol) was slowly added with stirring to a cold (−78 °C) slurry of tungsten(IV) chloride (2.0 g, 6.1 mmol) in 20 mL of diethyl ether. The reaction mixture was gradually warmed to 0 °C, whereupon it became red, and held there for 10 min. It was then cooled to and maintained at −20 °C for 1 h. The resulting red-purple solution was filtered quickly and then cooled to −78 °C for ca. 12 h. The red-purple crystals deposited from the filtrate were recrystallized from cold diethyl ether to give approximately 1.0 g (1.23 mmol, 40% yield) of product, $Li_4W_2(CH_3)_8{\cdot}4Et_2O$.

Analyses of two different batches gave $CH_4/W/Cl$ mole ratios 4.5:1:0 with an estimated uncertainty of ±0.4 in the CH_4/W ratio.

Preparation of $Li_4W_2Me_8{\cdot}4THF$. To a dark red solution of the diethyl etherate, prepared as above, in diethyl ether at 0 to −20 °C (ca. 1.0 g in 200 mL of Et_2O), was added 1–2 mL of carefully purified THF. The color of the solution immediately became a brighter shade of red. The solution was then cooled to −78 °C and kept there for ca. 12 h. The crop of bright red crystals was collected by filtration at −78 °C, washed with several 10-mL portions of THF at −78 °C, and dried at −10 °C (10^{-3} Torr). The recovery of the tetrahydrofuranate is nearly quantitative.

A typical analysis gave a $CH_4/W/Cl$ ratio of 4.2:1:0. The ^1H NMR spectrum in benzene solution had multiplets due to THF at τ 7.23 and 8.48 and a singlet at τ 9.63 due to $W{-}CH_3$. The signal intensities were proportional to the proposed formula.

Preparation of $Li_4W_2Me_{8-x}Cl_x{\cdot}4Et_2O$. These substances were obtained only in Texas, using either WCl_4 or WCl_5. Using WCl_4, methyllithium (21 mL of a 1.9 M diethyl ether solution, 40 mmol) was slowly added with stirring to a cold (−78 °C) slurry of tungsten(IV) chloride (2.0 g, 6.1 mmol) in 20 mL of diethyl ether. The reaction mixture was gradually warmed to 0 °C, whereupon it became red-purple, and held there for 10 min. It was then cooled to and maintained at −20 °C for 1 h. The resulting red-purple solution was quickly filtered, then cooled to −78 °C for ca. 12 h. The red-purple crystals deposited from the filtrate were recrystallized from cold diethyl ether to give approximately 1.1 g of product, $Li_4W_2(CH_3)_{8-x}Cl_x{\cdot}4Et_2O$.

Using WCl_5, methyllithium (21 mL of a 1.9 M diethyl ether solution, 40 mmol) was slowly added with stirring to a cold (−78 °C) slurry of tungsten(V) chloride (2.0 g, 5.5 mmol) in 20 mL of cold diethyl ether. The reaction mixture was gradually warmed to and maintained at −20 °C for 1 h. The resulting red-purple solution was cooled to −78 °C, quickly filtered, and then packed in dry ice for ca. 12 h. The red-purple crystals that deposited from the filtrate were recrystallized from cold diethyl ether to give approximately 1.0 g of product.

$Li_4W_2(CH_3)_{8-x}Cl_x{\cdot}4THF$. To a solution of ca. 1.0 g of $Li_4W_2(CH_3)_{8-x}Cl_x{\cdot}4Et_2O$ dissolved in 200 mL of diethyl ether at −20 °C was added 1.0 mL of carefully purified THF. The solution was packed in dry ice for 12–24 h. A near quantitative yield of red crystals was obtained.

Analyses of the Mixed Methyl–Chloro Compounds. Three samples, two containing THF, one containing Et_2O, were analyzed to establish the CH_3/W, Cl/W, and $(CH_3 + Cl)/W$ mole ratios. In each case, the sample was from a wholly different preparative reaction. The results obtained were as follows:

(1) $W/CH_3/Cl = 1{:}3.4{:}0.8$; $W/(CH_3 + Cl) = 1{:}4.2$

(2) $W/CH_3/Cl = 1{:}3.1{:}1.1$; $W/(CH_3 + Cl) = 1{:}4.2$

(3) $W/CH_3/Cl = 1{:}2.58{:}1.41$; $W/(CH_3 + Cl) = 1{:}3.99$

Sample 1 was the diethyl etherate, while samples 2 and 3 were tetrahydrofuranates. Relatively small samples (ca. 0.1 g) were used in the first two cases. Sample 3 was from the same batch as that used to grow crystals for the x-ray structure analysis and a much larger sample (ca. 0.4 g) was used to obtain greater accuracy.

A typical analysis (sample 2 above) was conducted as follows: The reaction of 1 mL of 1-butanol with ~0.13 g of $Li_4(CH_3)_{8-x}Cl_x{\cdot}4THF$ yielded 26 mL (1.1×10^{-3} mol) of CH_4 (T = 3 °C, P = 755 mm). The remaining solid was allowed to react with 15% HNO_3 for 2 h to yield WO_3 (0.080 g, 3.5×10^{-4} mol), which was recovered by filtration. To the filtrate was added 25 mL of 1 M $AgNO_3$; the resulting mixture was filtered and the weight of the AgCl (0.057 g, 4.0×10^{-4} mol) was determined. For this sample, the $W/CH_3/Cl$ ratio (W based upon WO_3) is calculated to be 1:3.1:1.1.

Electronic Spectra. These were measured at ca. 77 K on a Cary Model 14 spectrophotometer equipped with a quartz Dewar and a cylindrical quartz sample cell approximately 1 cm in diameter. The samples were dissolved in 2-methyltetrahydrofuran, which formed a glass when cooled rapidly to 77 K and retained the solute in homogeneous solution.

Results and Discussion

Preparation and Identification of Compounds. The reaction of either WCl_4 or WCl_5 with the methyllithium at low temperatures (<0 °C) leads to the formation of the red anion $W_2Me_8^{4-}$ if the MeLi/W ratio is sufficiently high and to $W_2Me_{8-x}Cl_x^{4-}$ anions, which have a red-purple color, if the MeLi/W ratio is lower. In the first experiments at Texas A&M only a slight excess of MeLi was used, namely, an overall 6.5:1 mole ratio for reaction with WCl_4. Thus, after allowing 2 mol of MeLi to serve simply to reduce W(IV) to W(II), we had only 4.5 mol of MeLi/mol of W, only about a 10% excess. Similarly, if WCl_5 is used and the $MeLi/WCl_5$ ratio is only about 7.5:1, there is again, after reduction of W(V) to W(II), only a 4.5:1 mole ratio of MeLi to W. Such ratios do not lead to the displacement of all Cl by CH_3 and thus afford the mixed methyl–chloro species, $W_2Me_{8-x}Cl_x^{4-}$. The formulation of all products as tetraetherates is based on the observation of 4THF in the crystal structure of $Li_4W_2Me_{8-x}Cl_x{\cdot}4THF$,[26] on the fact that the chromium, molybdenum, and rhenium analogues all contain one ether molecule per lithium ion, and on the approximate agreement of the relative intensities of the NMR signals with such an ether content.

When quantities of MeLi are used such that, after allowance for reduction, the MeLi/W ratios are in the range 5–6, crystalline products containing no detectable quantity of chlorine and corresponding analytically to the compositions $Li_4W_2Me_8{\cdot}4Et_2O$ are obtained. It is not only unnecessary but undesirable to go to still higher $MeLi/WCl_x$ ratios because the excess MeLi then becomes something of a nuisance during the low-temperature crystallizations.

It is ironic and not a little frustrating that, so far, only samples of the mixed methyl–chloro compound containing THF have afforded crystals of suitable quality and stability for x-ray crystallographic characterization. As reported elsewhere,[26] it has been possible to demonstrate the presence of the mixed anion, $W_2Me_{8-x}Cl_x^{4-}$, with the structure shown in Figure 1.

The crystal structure analysis of $Li_4W_2(CH_3)_{8-x}Cl_x{\cdot}4THF$ indicated a nonstoichiometric CH_3/Cl mole ratio of 1.5, i.e., $x \approx 3.2$. Chemical analysis of a sample from the same reaction mixture as the crystal used in the x-ray structure determination showed approximately the same CH_3Cl ratio, i.e., 1.8, equivalent to $x = 2.8$. By varying the reaction conditions, crystalline compounds with different CH_3/Cl ratios (2.7–4.6) were obtained with no apparent preference for any stoichiometric

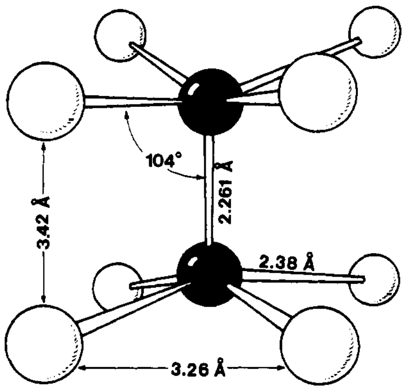

Figure 1. The anion occurring in $Li_4W_2Me_{8-x}Cl_x$·4THF according to x-ray crystallographic work described elsewhere.

CH_3/Cl ratio. In all cases the $(CH_3 + Cl)/W$ ratio was approximately 4. It may also be noted that the small discrepancy between crystallographically and analytically determined x values on the same preparative batch, viz., 3.2 vs. 2.8, may not be real in view of the possible errors in one or both measurements. On the other hand, even if real, it would not be surprising if that portion giving rise to the largest and best formed crystals might differ slightly from the bulk of the sample.

The important point about the crystal structure determination of the mixed methyl-chloro specimen (and it might as well be confessed that this was begun in the belief that the crystal was of the limiting, octamethyl compound) is that it proves the presence of a $W_2X_8^{4-}$ ion with virtual D_{4h} symmetry and an unbridged quadruple bond between tungsten atoms. We propose to extrapolate from $W_2Me_{8-x}Cl_x^{4-}$ where $x \approx 3$ to $x = 0$ and thus conclude that the octamethylditungsten(II) ion, $W_2Me_8^{4-}$, may be assigned the same sort of structure. Efforts are continuing to obtain a suitable crystal of a compound containing the $W_2Me_8^{4-}$ ion.

Chemical Properties of the Compounds. The all-methyl and mixed methyl-chloro compounds differ little in properties aside from the small but noticeable difference in color already mentioned. All the compounds are extremely sensitive to air and moisture. The mixed compounds seem to be thermally unstable above about −20 °C. While the all-methyl compounds may be somewhat more robust, they certainly decompose very slowly above 0 °C and more rapidly at room temperature. Benzene solutions appear to be stable for several days.

The compounds are readily soluble in ethers, somewhat soluble in benzene and toluene, but essentially insoluble in aliphatic hydrocarbons. The ether molecules are held very strongly in the solids and can only be removed by pumping at room temperature for several hours, but this leaves brown residues that are insoluble in ethers or hydrocarbons. Attempts to obtain thermally stable complexes from the mixed methyl-chloro compounds by reaction with various donors (pyridine, *n*-butyl ether, 2-methyltetrahydrofuran, dioxane, triethylamine) were not successful. However a bis(*N*,*N*′-dimethyl)ethylenediamine adduct was obtained as a red powder which was thermally stable at 20 °C for several days.

Reactions of the $Li_4W_2Me_8$·4THF with 4 equiv or more of CH_3COOH produced pale green powders soluble only in H_2O, CH_3OH, and not extractable into most organic solvents. Since the corresponding chromium[28] and molybdenum[29] complexes are known, the preparation of the phosphorus ylide derivatives, as shown in eq 1 and 2, has been attempted.

$$Li_4W_2(CH_3)_8 + 4[(CH_3)_4P]Cl \xrightarrow{THF} \underset{(I)}{W_2^{II}[(CH_2)_2P(CH_3)_2]_4} + 8CH_4 + 4LiCl \quad (1)$$

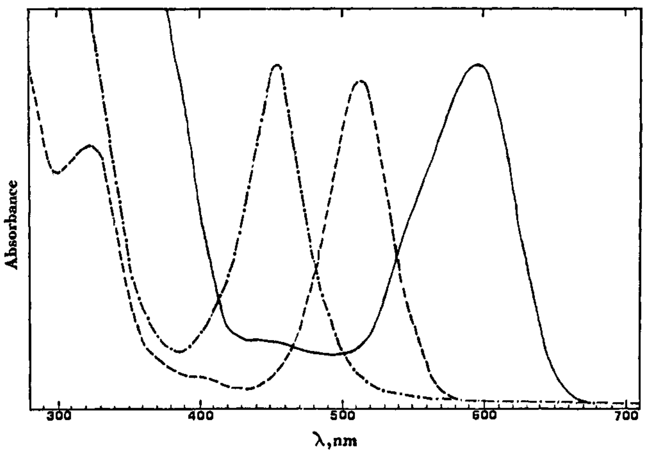

Figure 2. The visible spectrum of $W_2Me_8^{4-}$ (—) along with spectra of the congeneric $Mo_2Me_8^{4-}$ (- - -) and $Cr_2Me_8^{4-}$ (· · · · · ·) for comparison.

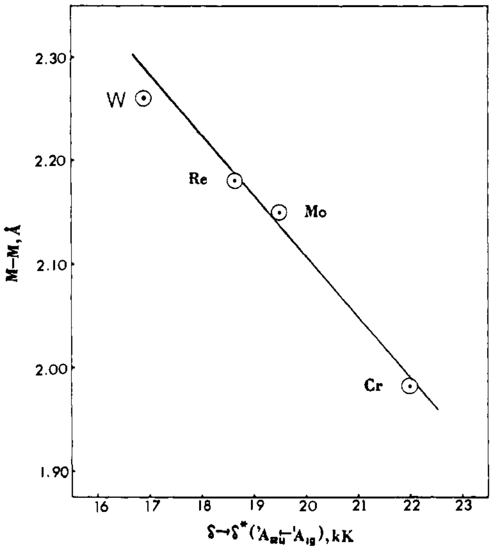

Figure 3. The energy at the band maximum for the $\delta \rightarrow \delta^*$ transitions of the four known $M_2Me_8^{n-}$ ions, with M = Cr, Mo, W, and Re.

$$WCl_5 + 8[Li(CH_2)_2P(CH_3)_2] \xrightarrow{Et_2O} I + \ldots \quad (2)$$

However reaction 1 did not produce I, but only a diamagnetic, olive-green oily product in very small yield which could not be purified and characterized.

Reaction 2 gives a yellow-brown, air and moisture sensitive, toluene-soluble complex whose spectroscopic properties (NMR, ^{31}P, mass spectrum) are consistent with I, but again the complex could not be purified, crystallized, or otherwise satisfactorily characterized.

Electronic Spectra. The spectra of solutions of the $W_2Me_8^{4-}$ and $W_2Me_{8-x}Cl_x^{4-}$ compounds in the visible region provide further evidence for the electronic and molecular structures of these species. It has already been shown by Sattelberger and Fackler[25] that the $M_2Me_8^{n-}$ species with M = Cr, Mo, and Re all have a band in the visible spectrum which can reasonably be assigned to the $\delta \rightarrow \delta^*$ transition arising in the metal-metal quadruple bond. We find that the $W_2Me_8^{4-}$ ion has a visible spectrum homologous to those of its Cr and Mo analogues, as shown in Figure 2. The spectra of the Cr and Mo compounds are taken from Sattelberger and Fackler.[25] The peak maximum is at 16.8 $cm^{-1} \times 10^3$ for $W_2Me_8^{4-}$. The spectrum of a solution of $Li_4W_2Me_{8-x}Cl_x$·4THF ($x \approx 3.2$) is nearly identical, but the peak maximum is shifted to 17.4 $cm^{-1} \times 10^3$.

If we assume that the W-W distance in $W_2Me_{8-x}Cl_x^{4-}$ (x

≈ 3.2) is essentially the same as that in $W_2Me_8^{4-}$, we can enter a point for the latter on Sattelberger and Fackler's plot of the $\delta \rightarrow \delta^*$ transition energy vs. M–M distance.[25] As shown in Figure 3, the new point lies very close to the straight line previously established using the Cr, Mo, and Re compounds.

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Methyl and Fluorine Substituent Effects on the Gas-Phase Lewis Acidities of Silanes by Ion Cyclotron Resonance Spectroscopy

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Abstract: Formation of gas-phase Lewis acid-base adducts $(CH_3)_nF_{4-n}SiF^-$ (n = 0–2) in reactions of SF_6^- and SF_5^- with neutral fluoromethylsilanes are examined using trapped-anion ion cyclotron resonance spectroscopy. Fluoride transfer reactions observed in binary mixtures of the silanes and of silanes with borane Lewis acids R_3B (R = CH_3, C_2H_5, i-C_3H_7, F), in the presence of trace amounts of SF_6 as the fluoride source, establish the Lewis acidity order $BF_3 > SiF_4 > (i\text{-}C_3H_7)_2FB > (i\text{-}C_3H_7)_3B > (C_2H_5)_2FB > (C_2H_5)_3B > (CH_3)_2FB > CH_3SiF_3 > (CH_3)_3B > (CH_3)_2SiF_2 > SF_4 > (CH_3)_3SiF$ in the gas phase for F^- as reference base. Quantitative estimates of adduct bond dissociation energies $D[(CH_3)_nF_{4-n}Si\text{–}F^-]$ (n = 0–2) and heats of formation of adducts $(CH_3)_nF_{4-n}SiF^-$ are derived. Variations in adduct bond strengths are discussed in terms of the effects of methyl and fluorine substitution on silicon. Analogies are drawn to similar substituent effects observed in the isoelectronic neutral fluoromethylphosphoranes.

Electron-pair dative bond formation between acceptor species A, which possess low-lying vacant orbitals, and donors B, which have accessible lone pairs (phenomena most generally described by the Lewis theory of acid-base interactions[2]), encompass chemical behavior common to much of the periodic table. Among the more familiar Lewis acids are the group 3b acceptors (compounds of B, Al, Ga, etc.) and many metal cations (from groups 1a, 2a, and compounds of the transition metals).[3,4] Studies of dissociation equilibria (eq 1) and displacement reactions (eq 2),

$$AB \rightleftharpoons A + B \quad \Delta H \equiv D[A\text{–}B] \tag{1}$$

$$A_1B + A_2 \rightleftharpoons A_1 + A_2B \tag{2}$$

employing a common reference base B, have provided information on adduct bond dissociation energies and insight into relationships between molecular structure and chemical reactivity for a wide variety of polyatomic Lewis acids, both in solution and in the gas phase.[3,4]

By comparison, much less is known about Lewis acid properties of neutral group 4b acceptors R_4M (M = C, Sn, Ge, etc.), where formation of acid-base adducts requires coordinative expansion of nominally closed-shell (electron octet) systems. Under the influence of higher effective nuclear charge and with the availability of lower energy vacant d orbitals, the tendency for dative bonding is increased for the heavier members of the group (e.g., Ge, Sn, Pb).[5] For carbon systems, Dougherty has reported several anionic halide adducts {CH_3XY^- (where X, Y = Cl, Br, I),[6] $H_nCl_{4-n}CCl^-$ (n = 0–3),[7] and $R_3CBr_2^-$ (where R = H, alkyl)[8]} in the gas phase using high-pressure mass spectrometry. Only in the case of CCl_5^-, however, is the involvement of pentacoordinate carbon