entropies of vaporization (ΔS_{vap}) are observed. The ΔS_{vap} values range from 95.4 J/(mol·deg) for $CH_2{=}CHCH_2PH_2$ to 110.0 J/(mol·deg) for $HC{\equiv}CCH_2PH_2$. The higher value for $HC{\equiv}CCH_2PH_2$ might indicate a slightly higher degree of intermolecular association in the vapor phase for the $HC{\equiv}CCH_2PH_2$ than for the alkenyl derivatives (**1** or **2**).

Borane Coordination. The coordination properties of alkenyl- and alkynylphosphines toward B_2H_6 is of interest to compare with organophosphine–borane coordination chemistry observed previously.[25-27] Because of its relatively strong Lewis acidity toward "soft" donors, B_2H_6 generally reacts with phosphines to form BH_3 adducts. However, with the alkenyl- and alkynylphosphines the possiblity exists that coordination might occur also or preferentially at the $C{=}C$ or $C{\equiv}C$ bond sites, since BH_3 units are known to add efficiently across these bonds, e.g. as occurs in hydroboration.[28]

Reactions of $CH_2{=}CHCH_2PH_2$ and $HC{\equiv}CCH_2PH_2$ with excess B_2H_6 occur smoothly at −78 to −45 °C to form 1:1 phosphine:BH_3 adducts **4** and **5** as

$$RPH_2 + {}^{1}/_{2}B_2H_6 \rightarrow RPH_2{\cdot}BH_3 \qquad (4)$$
$$R = CH_2{=}CHCH_2\ (\mathbf{4}),\ HC{\equiv}CCH_2\ (\mathbf{5})$$

Only at longer reaction times and at higher temperatures does further reaction of B_2H_6 occur, presumably with reaction at the $C{=}C$ or $C{\equiv}C$ bonds in the adducts. Mass spectral data show that **4** and **5** remain associated in the gas phase; **4** and **5** exhibit parent ions at *m/e* 88 and 86, respectively. **4** also shows minor spectral peaks up to *m/e* 174, which likely arise either from traces of decomposition in the spectrometer inlet or from oligomerization of **4** in the gas phase.

That BH_3 coordination in **4** and **5** occurs at phosphorus and not at the $C{=}C$ or $C{\equiv}C$ bonds is clear from the NMR spectral data. The ^{11}B NMR spectra exhibit quartets (^{11}B–^{1}H coupling) of doublets (^{11}B–^{31}P coupling) at δ −42.4 and −41.3, respectively. Coupling of the ^{11}B nucleus to the PH_2 protons is small and not measurable. Chemical shifts and coupling constants agree closely with those reported previously for primary phosphine–boranes.[26,27] The ^{31}P NMR spectra consist of triplets [J(P–H)] at δ −48.2 and −41.9, in which each spectral member is strongly broadened as is expected for PH_2 groups coupled weakly to BH_3 groups. The ^{1}J(P–H) couplings in **4** and **5** are nearly twice what they are in **1** and **2**, again a situation reported earlier by Cowley and Damasco.[25] Also, borane coordination results in large downfield coordination shifts (84.4 ppm for **4**, 88.7 ppm for **5**) as is typically observed in borane or transition-metal complexes.[29]

The ^{1}H NMR spectra of **4** and **5** are assigned by using heteronuclear (^{11}B and ^{31}P) spin decoupling and by comparison of the spectra with those for **1** and **2**. Assignments are given in Table III, although proton coupling constants were not examined as extensively as in **1**. The $CH_2{=}$, $={CH}-$, and $-CH_2-$ protons of **4** and the $\equiv CH$ and $-CH_2-$ protons of **5** show little variance from their positions in **1** and **2**. The BH proton resonances, which undecoupled are quartets (with minor septets due to ^{10}B coupling) in the undecoupled spectra, collapse to doublets [^{2}J(H–P)] of triplets [^{3}J(H–H)] upon ^{11}B decoupling. The PH_2 protons are doublets of apparent sextets as a result of fortuitous peak overlap that results from coupling to the BH_3 and $-CH_2-$ protons. Since PH_2 proton coupling to the ^{11}B nucleus is small, it is only weakly evident. Assignment of the "sextet" peaks is substantiated by the absence of a ^{11}B-decoupling effect and by the $^{1}H\{^{31}P\}$ spectra, where the $-CH_2-$ resonances are single triplets [$^{3}J(H_d{-}H_f)$]. In **5**, a $^{4}J(H_a{-}H_f)$ of 3.0 Hz involving coupling of PH_2 protons to the H_a proton is also seen.

Complexes **4** and **5** are thermally unstable with respect to oligomerization/polymerization. Above 25 °C, **4** decomposes slowly to an oil that later becomes an intractable solid. **5** decomposes above 0 °C to form a resinous product along with some $HC{\equiv}CCH_2PH_2$ and $PH_3{\cdot}BH_3$.[30] Similar behavior has been reported for the complex $CH_2{=}CHCH_2PH(CH_3){\cdot}BH_3$.[31] Although details of these oligomerization/polymerization reactions are not known, they could be of sufficient interest to warrant further studies.

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Registry No. **1**, 81637-99-2; **2**, 114596-01-9; **3**, 114596-02-0; **4**, 114596-03-1; **5**, 114596-04-2; $CH_2{=}CHCH_2Cl$, 107-05-1; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}CHCH_2CH_2Br$, 5162-44-7; $HC{\equiv}CCH_2Br$, 106-96-7; $LiAl(PH_2)_4$, 25248-80-0; $CH_2{=}CHBr$, 593-60-2.

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Equilibrium Dissociation of Tetrakis(acetato)dichromium(II) in Acetic Acid/Water Media

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Chromium(II) acetate is predominantly dimeric in both water and acetic acid solutions, as shown by the red-brown color and similarity of absorption spectra[1] and by measurements of the dissociation constant in aqueous media.[2,3] Copper(II) acetate has the dimeric structure in the solid state and in nonpolar solvents, but in water it is fully dissociated into monomeric complexes.[4] In acetic acid solution, however, the dissociation constants of the copper dimer have been measured.[5] Evidently the copper–copper bond is weaker than the chromium–chromium bond, and we have attempted previously to quantify the difference, by estimating the copper dissociation constant in aqueous solution.[4] In order to provide a more direct comparison and to interpret more fully the kinetics of redox reactions in acetic acid media,[6] we have now determined the chromium dissociation constant in acetic acid media with varying water content. Care was taken to control the water activity and to allow for side oxidation of chromium(II) by analyzing the chromium(II) concentrations in situ.

Experimental Section

Chromium(II) acetate hydrate, $Cr_2(OAc)_4{\cdot}2H_2O$, was prepared as before[3a] and dried under flowing nitrogen. Acetic acid was dried by refluxing with $B(OAc)_3$[7] and redistilled. Water content of solutions was determined by the Karl Fischer method[8] using a visual or electrometric end point as appropriate. Stock solutions of chromium(II) acetate in acetic acid were mixed with further acetic acid, and with water, in glass spectrophotometric cells modified with a screw top and a PTFE–silicone rubber septum. All solutions were dispensed under nitrogen from the

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Table I. Data for $Cr_2(OAc)_4$ in $HOAc/H_2O$ Media[a]

$[H_2O]$, M	$\{H_2O\}$, M	$(K_D/4\epsilon)^{-1/2}$, 10^{-3} M $cm^{1/2}$	ϵ^{-1}, 10^{-3} M cm	ϵ, M^{-1} cm^{-1}	log (K_D/M)
8.32	27.5	0.033 ± 0.022[b]	5.95	168	−6.15 ± 0.3
8.88	28.4	0.025 ± 0.010	5.48	182	−6.4 ± 0.2
13.32	34.3	0.050 ± 0.026	5.84	171	−5.8 ± 0.25
14.98	36.1	0.073 ± 0.050	5.95	168	−5.45 ± 0.3
16.1	37.2	0.075 ± 0.035	5.59	178	−5.4 ± 0.2
20.3	40.9	0.110 ± 0.045	6.21	161	−5.1 ± 0.2
55.5	55.5				−4.35

[a] $T = 25$ °C, $\lambda = 470$ nm. [b] Limits of error are estimated as $(S/N)^{1/2}$ where S is the sum of squares of residuals in the least-squares fit of eq 4 and N is the number of data points.

storage vessels described previously,[3a] by using hypodermic syringes with glass needles. Concentrations were determined by weight, and chromium(II) concentrations were checked after measurement by titrating standard solutions of iodine in acetic acid, into the same cells, to a spectrophotometric end point.

Results

Writing the equilibrium in the generalized form

$$Cr^{II}{}_2 \underset{}{\overset{K_D}{\rightleftharpoons}} 2Cr^{II} \qquad (1)$$

where $Cr^{II}{}_2$ and Cr^{II} denote the aggregates of all binuclear and all mononuclear species and assuming that absorption by the monomer is negligible at the wavelength used, we obtain the absorbance A as

$$A = \epsilon l\,[Cr^{II}{}_2] \qquad (2)$$

where ϵ is the extinction coefficient per mole of dimer and l is the path length. Defining the total chromium(II) concentration by

$$C = [Cr^{II}] + 2[Cr^{II}{}_2] \qquad (3)$$

and using $K_D = [Cr^{II}]^2/[Cr^{II}{}_2]$ we obtain

$$\frac{C}{2A^{1/2}} = \frac{A^{1/2}}{\epsilon l} + \left(\frac{K_D}{4\epsilon l}\right)^{1/2} \qquad (4)$$

Values of A were measured at 470 nm, at concentrations in the range $C = 0.06$–1.6 mM. Data were fitted to eq 4 to yield the parameters listed in Table I.

Cheng and Howald[5] correlated their results for the copper(II) acetate system with the molar concentration of water in the solvent mixture and found a fourth-power dependence, log $K_D = -5.0 + 4.0$ log $[H_2O]$, though an empirical equation log $K_D = -4 + 0.29[H_2O]$ gave an almost equally good fit. It seems preferable, however, to take the water *activity* as the basis of a correlation. In Figure 1, values of log K_D for both the chromium and the copper systems are plotted against log $\{H_2O\}$, where $\{H_2O\}$ is the activity calculated by using the data of Hansen et al.[9] Over the range of $\{H_2O\}$ for which the two sets of data overlap, the trends are parallel within experimental error, and in the case of the chromium data, it is noteworthy that our previous value of K_D for the 100% aqueous medium falls in line with the new data for acetic-acid water mixtures. The slopes of the lines, by least-squares fitting, are 6.3 ± 0.5. This could be interpreted by expanding eq 1 into the form $Cr_2(OAc)_4(OH_2)_2 + 6H_2O \rightleftharpoons 2Cr(OAc)_2(OH_2)_4$, but this neglects the possibility of replacement of coordinated H_2O by HOAc as the water activity is reduced. The conclusion we regard as significant at present is that the difference log $K_D{}^{Cr}$ − log $K_D{}^{Cu}$ is ca. 5.5. This is similar to the value 6.4 suggested previously for aqueous media by using an estimated value of log $K_D{}^{Cu}$. It was argued previously that this difference is the result of two opposing effects: the greater stability of the Cr–Cr bond compared with the Cu–Cu bond is partly offset by greater strength of the Cu–acetate bond compared with the Cr–acetate bond. A calculation based on reported stability constants assessed the latter effect as being equivalent to 1.6 units in log K_D; hence, the difference in metal–metal bond strengths is approximately 5.5 + 1.6 = 7.1 units, corresponding to 40 kJ mol^{-1}.

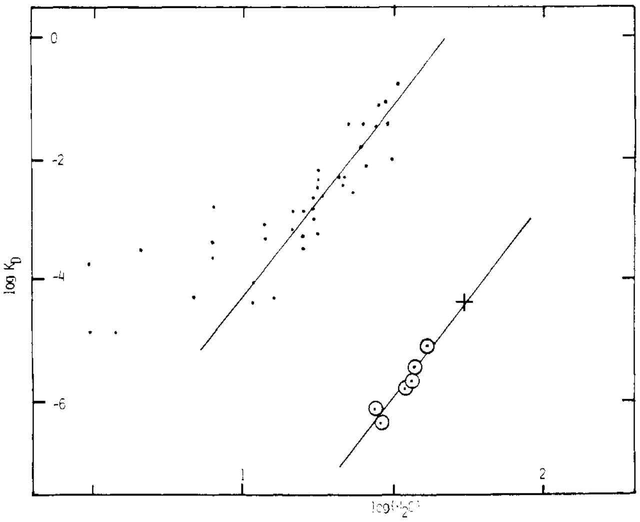

Figure 1. Plots of log K_D versus log $\{H_2O\}$ for the two reactions $M_2(OAc)_4 \rightleftharpoons 2M(OAc)_2$: upper line, M = Cu;[5] lower line, M = Cr; (⊙) this work; (+) ref 3. The lines are drawn by least-squares fitting (using data for log $\{H_2O\} > 1$ in the Cu case).

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Registry No. $Cr_2(OAc)_4(OH_2)_2$, 14404-41-2.

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Infrared Spectroscopic Studies of the Interaction of ClF and Cl_2 with H_2Se, $(CH_3)_2Se$, and AsH_3 in Argon Matrices

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Charge-transfer complexes of the molecular halogens have been known for many years; for example, the interpretation of the UV/vis spectrum of the benzene–I_2 complex occurred in the 1940s, leading to a surge of interest in CT complexes.[1-7] The primary focus of work in this area has been on complexes of the heavier, less reactive halogens I_2 and Br_2, such that they could be studied in solution at room temperature.[8-11] Recently, a series of complexes of ClF and Cl_2 have been studied by using the matrix-isolation technique,[12-15] which is well suited to the study of more

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