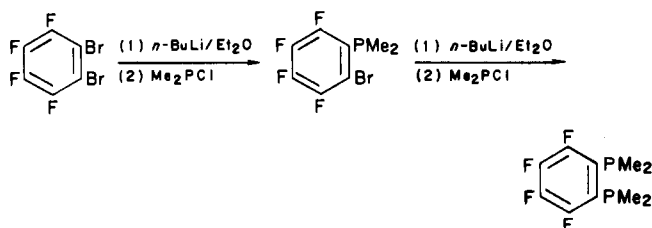


Table I. Redox Potentials^a

	Ni(II) → Ni(III)	Ni(III) → Ni(IV)	Fe(II) → Fe(III)	Fe(III) → Fe(IV)
[Ni(diphos) ₂ Cl ₂] ⁿ⁺	+0.36	+1.18	+0.045	+1.43
[Ni(F-diphos) ₂ Cl ₂] ⁿ⁺	+0.47	+1.40	+0.345	+1.69

^a ±0.01 V in MeCN with 0.1 M *n*-Bu₄NBF₄ as supporting electrolyte; carbon electrodes vs. standard calomel electrode.

Scheme I



Results and Discussion

The ligands *o*-C₆H₄(EMe₂)(E'Me₂) are made by reaction of EMe₂⁻ nucleophiles with *o*-C₆H₄Cl₂ (E = E') or *o*-C₆H₄Br (E'Me₂),¹¹ but an analogous route cannot be used for the title ligand since the C-F bonds are attacked.¹² F-diphos was obtained as in Scheme I in ca. 43% yield, as a colorless oil that is less air sensitive than *o*-C₆H₄(PMe₂)₂.

The ³¹P NMR resonance in F-diphos (-39.9 ppm) is shifted ca. 16 ppm to high frequency from that in diphos (-56 ppm),¹¹ and since the bond angles at P are assumed to be very similar, this indicates significant electron density changes at the phosphorus.

The Ni(II), Co(III), and Fe(III) complexes of F-diphos (Experimental Section) are generally similar to their diphos analogues, the most notable difference being that while diphos only gives the planar solid Ni(diphos)₂Cl₂,² Ni(F-diphos)₂Cl₂ can be obtained as both brown-planar (P₄) and green pseudooctahedral (P₄Cl₂) forms. Both dissolve in polar solvents to give a mixture of [Ni(F-diphos)₂]²⁺ and [Ni(F-diphos)₂Cl]⁺. Moreover, the ready synthesis of relatively stable [Pd^{IV}(F-diphos)₂Cl₂](ClO₄)₂ and [Ni^{III}(F-diphos)₂X₂](ClO₄)₂⁴ shows the ability of the ligand to stabilize high oxidation states. In order to probe differences between F-diphos and diphos complexes we have used cyclic voltammetry.¹³ As shown in Table I the F-diphos complexes of Ni(III) and Fe(III) are much less readily oxidized to the M(IV) states than those of diphos, while the oxidation of Fe(II) → Fe(III) is considerably harder with F-diphos. The Ni(II) → Ni(III) potentials are less strictly comparable; unlike the other systems they are not electrochemically reversible, as they involve a change in coordination number (4 or 5 in Ni(II), 6 in Ni(III)). Similar trends are present in the corresponding bromide complexes.⁵ It is notable that the redox potential differences between corresponding F-diphos and diphos complexes are much greater than between those of diphos and *o*-C₆H₄(AsMe₂)₂.^{2,5}

Conclusions

The electrochemical data demonstrate that diphos and F-diphos have significantly different abilities to stabilize high oxidation states, reflecting different *electronic* properties. Since both have excellent coordinating abilities toward transition-metal ions, they offer a means of probing (or modifying) the electronic effects, while steric changes are minimized, and hence should be valuable

in a wide range of coordination/organometallic systems.

Acknowledgment. We thank the SERC for financial support and Dr. D. Pletcher and D. J. Pearce for assistance with the electrochemical measurements.

Registry No. *o*-C₆F₄(PMe₂)₂, 95045-52-6; *o*-C₆F₄(Br)₂, 827-08-7; Me₂PCl, 811-62-1; *o*-C₆F₄(PMe₂)₂ methiodide, 95045-53-7; [Ni(*o*-C₆F₄(PMe₂)₂)₂Cl₂], 95045-54-8; [Ni(*o*-C₆F₄(PMe₂)₂)₂Cl₂], 95045-68-4; [Ni(*o*-C₆F₄(PMe₂)₂)₂Br₂], 95045-55-9; [Ni(*o*-C₆F₄(PMe₂)₂)₂](ClO₄)₂, 95045-57-1; [Ni(*o*-C₆F₄(PMe₂)₂)₂Cl₂](ClO₄)₂, 95045-59-3; [Ni(*o*-C₆F₄(PMe₂)₂)₂Br₂](ClO₄)₂, 95045-61-7; [Pd(*o*-C₆F₄(PMe₂)₂)₂Cl₂], 95045-62-8; [Pd(*o*-C₆F₄(PMe₂)₂)₂Cl₂](ClO₄)₂, 95045-64-0; [Co(*o*-C₆F₄(PMe₂)₂)₂Cl₂], 95045-65-1; [Fe(*o*-C₆F₄(PMe₂)₂)₂Cl₂](BF₄), 95045-67-3; [Fe(*o*-C₆F₄(PMe₂)₂)₂Cl₂], 95045-69-5; [Fe(*o*-C₆F₄(PMe₂)₂)₂Cl₂]²⁺, 95045-70-8; [Ni(*o*-C₆F₄(PMe₂)₂)₂Cl₂]²⁺, 95045-71-9.

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Synthesis of (Trimethylsilyl)- and (Trimethylgermyl)allylphosphine

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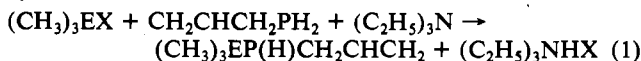
Received August 22, 1984

Trialkylsilyl-substituted phosphines [e.g. [(CH₃)₃-Si]_{3-m+n}P(H)_mR_n; *m* + *n* = 1, 2; R = phenyl or an organo moiety] are valuable synthons for the preparation of new organophosphorus and organophosphorus-metal compounds. Recent examples include the syntheses of novel nickel- and cobalt-phosphorus cluster complexes¹ and primary and secondary organophosphines^{2,3} such as [Co₄(μ₃-PC₆H₅)₄][P(C₆H₅)₃]₄ and [(C₆H₅)₂PCH₂CH₂]₂PH, respectively. In the former case, advantage is taken of facile Si-P bond cleavage in [(CH₃)₃Si]₂PC₆H₅ by metal halides. In the latter case, since Si-P bonds resist radical reaction, a two-step synthesis involving initial addition of (CH₃)₃SiPH₂ to the olefin followed by hydrolytic removal of (CH₃)₃Si groups can be exploited.

Previous syntheses of (CH₃)₃Si-substituted organophosphines have been limited to cases where R = alkyl and aryl; only recently have four-carbon or greater alkenyl-substituted compounds been prepared.^{2,3} Lower homologues, e.g. (CH₃)₃SiP(H)CH₂CHCH₂, could not be prepared. We have now investigated alternate syntheses of these and find that (CH₃)₃SiI or (CH₃)₃GeBr with CH₂CHCH₂PH₂ in the presence of (C₂H₅)₃N yield the new (trimethylsilyl)- and (trimethylgermyl)allylphosphines. This work is described below.

Results and Discussion

Trimethyliodosilane and (CH₃)₃GeBr react with CH₂CHCH₂PH₂ in CH₂Cl₂ in the presence of (C₂H₅)₃N to afford the unsymmetrically substituted (silyl)- and (germyl)allylphosphines, (CH₃)₃SiP(H)CH₂CHCH₂ (1) and (CH₃)₃GeP(H)CH₂CHCH₂ (3), respectively (eq 1). Reactions involve initial adduct formation



E, X = Si, I; Ge, Br

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(13) Analysis of the electronic spectra is precluded since an insufficient number of metal-centered transitions (d-d bands) are resolved, due to the presence of charge-transfer transitions at low energy in the high oxidation state complexes.

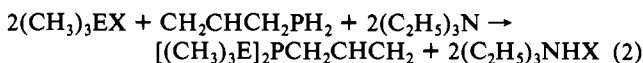
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between the silyl or germlyl halide and $(C_2H_5)_3N$. These rapidly formed gelatinous precipitates are subsequently replaced by finely divided insoluble $(C_2H_5)_3NHX$ ($X = Br, I$) as the adducts slowly react with $CH_2CHCH_2PH_2$. Formation of Si-P bonds by amine-promoted removal of HX between a halosilane and a phosphine has not been reported previously; however, other group 14¹⁴ elements (Ge, Sn, Pb) phosphorus bond formation reactions are well documented.⁴⁻⁷ Only $(CH_3)_3SiI$ is sufficiently reactive to be used; $(CH_3)_3SiCl$ and $(CH_3)_3SiBr$ did not react.

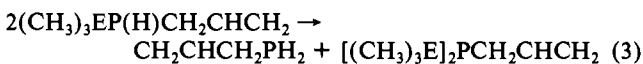
The formation of significant quantities of symmetrically substituted, tertiary phosphines $[(CH_3)_3Si]_2PCH_2CHCH_2$ (**2**) and $[(CH_3)_3Ge]_2PCH_2CHCH_2$ (**4**) (ca. 20–30 mol %) accompanies reactions in eq 1. With 2-fold excesses of silyl or germlyl halide and $(C_2H_5)_3N$, **2** or **4** are obtained quantitatively as



E, X = Si, I; Ge, Br

When $CH_2CHCH_2PH_2$ in 10-fold excess was premixed with the silyl or germlyl halide in CH_2Cl_2 prior to addition of $(C_2H_5)_3N$, the yield of **2** or **4** was reduced to ca. 10% w/w; however, these products were never eliminated completely.

The phosphines **1** and **3** are unstable, undergoing redistribution to $CH_2CHCH_2PH_2$ and the corresponding symmetrically substituted phosphines as in (3). Neat **1** is thermally stable at 25



E = Si, Ge

°C; however, redistribution to $CH_2CHCH_2PH_2$ and **2** occurs upon dissolution in dry and degassed benzene or toluene. In contrast, neat **3** redistributes slowly. Benzene or toluene solutions of **3** showed only minor reaction after periods of 3–4 days, with the rate of decomposition depending on concentration. These observations suggest that $(CH_3)_3SiP(H)CH_2CHCH_2$ redistribution may be catalyzed by traces of yet uncharacterized impurities. An apparently analogous thermal instability is reported for $CH_3P(H)CH_2CHCH_2$,⁸ however, the reason for the high reactivity of these unsymmetrically substituted secondary phosphines is not understood. This phenomenon is being studied further.

AIBN-initiated decomposition of $(CH_3)_3GeP(H)CH_2CHCH_2$ (**3**) produces $[(CH_3)_3Ge]_2PH$ in 40% yield along with complex, phosphorus-containing, apparently oligomeric materials. No $[(CH_3)_3Ge]_3P^{4,7}$ was observed. The stoichiometry and/or mechanism of this reaction is unclear; however, it may involve loss of the allyl functionality from phosphorus by radical displacement, accompanied by the redistribution of P-H and P-Ge bonds as observed in the redistribution reactions described above (e.g. eq 3). The $[(CH_3)_3Ge]_2PH$ formed is stable to repeated addition of the AIBN radical initiator. It is noteworthy that no evidence for phosphacylobutanes, i.e. $(CH_3)_3GePCH_2CH_2CH_2$, is obtained. Owing to the thermal instability of **1**, analogous AIBN-promoted reactions of **1** were not attempted.

The new phosphines prepared herein (**1–5**) were purified by standard vacuum line techniques and characterized by a combination of elemental analytical, chemical reaction, and ¹H and ³¹P NMR, IR, and mass spectral data. Mass spectral parent ions and readily attributable fragmentation patterns were observed in every case. All compounds exhibited ³¹P NMR resonances of the expected multiplicity and at characteristic chemical shifts.^{9,10} In every case, characteristic ³J_{HP} coupling (4.0–4.5 Hz) of $(CH_3)_3E$

(E = Si, Ge) protons to phosphorus⁹ and $-CH_2CHCH_2$ ABX coupling patterns¹¹ are seen in the ¹H NMR spectra. Hydrolysis of **1–4** or **5** quantitatively yields $[(CH_3)_3E]_2O$ (E = Si, Ge) and $CH_2CHCH_2PH_2$ or $[(CH_3)_3Ge]_2O$ and PH_3 , respectively.

The new (silyl)- and (germyl)allylphosphines **1–4** are multifunctional reagents with the potential to undergo a myriad of further synthetically useful reactions. Because the $(CH_3)_3SiP$ or $(CH_3)_3GeP$ units might remain intact through selected reactions involving the allyl groups, intermediate compounds that are later converted to new phosphines can be envisaged. The $(CH_3)_3Si-$ and $(CH_3)_3Ge-$ groups can be viewed as "protecting" groups at the phosphorus center. Synthetic applications for these silyl- and germlylphosphines are under study currently.

Experimental Section

Apparatus and Materials. All manipulations were carried out in N₂-flushed glovebags or standard high-vacuum apparatus.¹² Infrared spectra (4000–400 cm⁻¹) were obtained on Perkin-Elmer Model 467 and IR-4250 grating spectrophotometers. Mass spectra were obtained at 70 eV with a Varian MAT CH5 spectrometer. ¹H NMR spectra were obtained at 90.0 and 250 MHz with Varian EM-390 and Bruker WM-250 spectrometers. ³¹P NMR spectra were obtained at 40.5 MHz on a JEOL PFT-100 spectrometer. ¹³C NMR spectra were obtained at 25.1 and 62.9 MHz on JEOL PFT-100 and Bruker WM-250 spectrometers, respectively. ¹H, ³¹P, and ¹³C NMR spectra were measured relative to $(CH_3)_4Si$, H₃PO₄, and $(CH_3)_4Si$, respectively; chemical shifts downfield from the standards are assigned positive (+δ), values. $(CH_3)_3GeBr$ (Alfa Inorganics) and $(CH_3)_3SiI$ (Alfa Inorganics) were purified by fractional condensation. AIBN [2,2'-azobis(isobutyronitrile)] (Aldrich Chemical Co.) was used as obtained. Allylphosphine was prepared as described previously.¹³ Methylene chloride was distilled from P₄O₁₀ prior to use. Elemental analyses were performed by Huffman Laboratories, Wheatridge, CO.

$(CH_3)_3SiP(H)CH_2CHCH_2$ (**1**) and $[(CH_3)_3Si]_2PCH_2CHCH_2$ (**2**). Allylphosphine (9.3 mmol), $(CH_3)_3SiI$ (9.1 mmol), and CH_2Cl_2 (75 mmol) were condensed into a reaction vessel and mixed. $(C_2H_5)_3N$ (9.2 mmol) was added, and the reaction was warmed to room temperature and stirred. After 12 h, volatile reaction materials were removed in vacuo and passed through traps at 0 and –63 °C. The CH_2Cl_2 passed –63 °C; a white solid presumed to be $(C_2H_5)_3NHI$ remained in the reactor. The –63 and 0 °C traps contained $(CH_3)_3SiP(H)CH_2CHCH_2$ (**1**) and $[(CH_3)_3Si]_2PCH_2CHCH_2$ (**2**), respectively.

Characterization of 1. Anal. Calcd for C₆H₁₅PSi: C, 49.27; H, 10.36; P, 21.17. Found: C, 49.35; H, 10.27; P, 20.84. ¹H NMR (neat) δ 0.2 [d, J = 4.5 Hz, area 9; $(CH_3)_3Si$], 1.98 (d of t, J = 189 Hz, ³J_{HH} = 7 Hz, area 1; PH), 2.1–2.6 (complex, area 2; CH₂), 4.8–6.2 (ABX, area 3; CH₂CH); ³¹P NMR (20% in C₆D₆) δ –147.5 (d, J = 189.0 Hz); mass spectrum, parent at m/e 146 [C₆H₁₅²⁸SiP⁺]; IR (KBr) 3100 (m), 3085 (m), 2965 (vs), 2915 (vs), 2813 (s), 2306 (s), 1648 (m), 1637 (m), 1479 (m), 1435 (s), 1387 (s), 1270 (vs), 1214 (s), 1079 (s), 875 (vs), 698 (vs), 572 (w), 483 (m) cm⁻¹.}

Characterization of 2. ¹H NMR spectrum (10% in C₆D₆) δ 0.2 [d, J = 4.5 Hz, area 9; $(CH_3)_3Si$], 2.3 (d, ³J_{HH} = 9 Hz; CH₂), 4.8–6.2 (ABX, area 3; CH₂CH); ³¹P NMR (20% in C₆D₆) δ –168.1 (s); mass spectrum, parent at m/e 218 [C₆H₁₅²⁸Si₂P⁺]; IR (KBr) 3099 (m), 2972 (vs), 2911 (s), 2819 (s), 1848 (m), 1647 (m), 1482 (m), 1422 (vs), 1391 (s), 1292 (s), 1082 (s), 955 (m), 912 (m), 870 (vs), 798 (m), 700 (vs), 579 (m), 487 (m) cm⁻¹.}

Trimethylchlorosilane and $(CH_3)_3SiBr$ with allylphosphine did not react under the above conditions.

$(CH_3)_3GeP(H)CH_2CHCH_2$ (**3**) and $[(CH_3)_3Ge]_2PCH_2CHCH_2$ (**4**). Typically, $CH_2CHCH_2PH_2$ (6.0 mmol), $(CH_3)_3GeBr$ (5.1 mmol), and CH_2Cl_2 were condensed into a reaction vessel and mixed. $(C_2H_5)_3N$ (5.1 mmol) was condensed onto the mixture, and the reaction was warmed to room temperature. After 24 h, volatile materials were removed and passed through 0 and –45 °C traps. White solid, presumed to be $(C_2H_5)_3NHB$, remained in the reactor. Excess $CH_2CHCH_2PH_2$ and CH_2Cl_2 passed –45 °C. The –45 °C trap contained $(CH_3)_3GeP(H)C-$

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- (14) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

H_2CHCH_2 (3) along with a trace of $[(\text{CH}_3)_3\text{Ge}]_2\text{PCH}_2\text{CHCH}_2$ (4); 4 condensed at 0 °C. Repeated fractionation yielded pure 3 and 4.

Characterization of 3. ^1H NMR (40% in C_6D_6) δ 2.25 (d of t, $J = 186.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, area 1; PH) 0.3 [d, $^3J = 4.0$ Hz, area 9; $(\text{CH}_3)_3\text{Ge}$], 2.0–2.6 (complex, area 2; CH_2), 4.7–6.1 (ABX, area 3; CH_2CH); ^{31}P NMR (40% in C_6D_6) δ -139.7 (d, $J = 186$ Hz); mass spectral, IR, and elemental analyses not obtained, owing to rapid sample thermal decomposition.

Characterization of 4. Anal. Calcd for $\text{C}_9\text{H}_{15}\text{PGe}$: C, 35.16; H, 7.54. Found: C, 34.22; H, 7.37. ^1H NMR (10% in C_6D_6) δ 0.3 [d, $J = 4.0$ Hz, area 9; $(\text{CH}_3)_3\text{Ge}$], 2.45 (d, $J = 9$ Hz, area 1; CH), 4.7–6.1 (ABX, area 3; CH_2CH); ^{31}P NMR (20% in C_6D_6) δ -149.6 (s); mass spectrum, parent at m/e 308 [$\text{C}_9\text{H}_{23}^{76}\text{Ge}_2\text{P}^+$]; IR 3081 (s), 2978 (vs), 2913 (vs), 2801 (m), 1818 (m), 1637 (s), 1428 (m), 1410 (s), 1238 (vs), 1199 (m), 1059 (s), 990 (s), 909 (vs), 754 (s), 592 (vs), 512 (s), 406 (m) cm^{-1} .

Reaction of 1 and 3. Compounds 1 and 3 in C_6D_6 in NMR tubes in separate experiments were allowed to warm to 25 °C, while being monitored periodically by ^{31}P NMR spectral analysis. 1 reacts rapidly, yielding only resonances due to 2 (δ -168.1) and $\text{CH}_2\text{CHCH}_2\text{PH}_2$ (δ -132.6). 3 after 100 h at 25 °C underwent redistribution, exhibiting resonances attributed to 3, 4, and $\text{CH}_2\text{CHCH}_2\text{PH}_2$ in a ratio of 1.0:2.4:2.4.

Radical reactions of 3 were carried out in NMR tubes, typically by heating 3 (1.5 mmol) with ca. 8 mg of AIBN in C_6D_6 (5.0 mmol). After 3 h at 75 °C, the ^{31}P NMR spectrum showed a major doublet resonance at δ -228.1 [$J = 182.0$ Hz, singlet in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum] and a collection of very small peaks between δ -30 and δ -100. No 3 remained, and no 4 or $\text{CH}_2\text{CHCH}_2\text{PH}_2$ formed. Volatile material was removed in vacuo, separated by fractional condensation, and characterized as $[(\text{CH}_3)_3\text{Ge}]_2\text{PH}$ (5). Anal. Calcd for $\text{C}_6\text{H}_{19}\text{Ge}_2\text{P}$: C, 26.96; H, 7.16; P, 11.58. Found: C, 27.10; H, 7.21; P, 11.39. ^{31}P NMR δ -228.0; ^1H NMR δ 0.4 [d, $J = 4.5$ Hz, area 18; $(\text{CH}_3)_3\text{Ge}$], 1.0 (d, $J = 174$ Hz, area 1; PH); mass spectrum, parent at m/e 268 [$^{12}\text{C}_6\text{H}_{19}^{76}\text{Ge}_2\text{P}^+$]; IR (neat film) 2977 (s), 2896 (vs), 2291 (vs), 406 cm^{-1} .

Involatile reaction materials were partially soluble in C_6H_6 . ^{31}P NMR spectra of this material exhibited complex resonances in the δ -30 and δ -100 regions; however, the material was not characterized further. The rapid thermal decomposition of 1 in solution precluded studying its AIBN-promoted radical reactions.

Hydrolysis of 1 and 2 yields $\text{CH}_2\text{CHCH}_2\text{PH}_2$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ rapidly; 3 and 4 react slowly with H_2O to form $[(\text{CH}_3)_3\text{Ge}]_2\text{O}$ and $\text{CH}_2\text{CHCH}_2\text{PH}_2$.

Acknowledgment. Support for this work from the National Science Foundation (Grant CHE-7909497) and the Department of Energy (Grant DE-FG602-80C583112) is gratefully acknowledged.

Registry No. 1, 94570-42-0; 2, 94570-46-4; 3, 94570-43-1; 4, 94570-44-2; 5, 94570-45-3; $\text{CH}_2\text{CHCH}_2\text{PH}_2$, 81637-99-2; $(\text{CH}_3)_3\text{Si}$, 16029-98-4; $(\text{CH}_3)_3\text{GeBr}$, 1066-37-1; $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, 107-46-0; $[(\text{C}_6\text{H}_5)_3\text{Ge}]_2\text{O}$, 2237-93-6.

Contribution from the Inorganic Chemistry Laboratory, Oxford University, Oxford OX1 3QR, England

Estimation of the Effective On-Site One-Center Coulomb Repulsion Energy U in Mixed-Valence Cs_2SbCl_6

Kosmas Prassides and Peter Day*

Received May 11, 1984

Mixed valency¹ is a widespread phenomenon in the periodic table. In the groups 11–17,¹⁵ particularly for post-4d and -5d elements, the oxidation state $N - 2$, where N is the group oxidation state, is frequently stabilized. Thus, the usual combination of oxidation states when mixed-valency compounds are formed by these elements is $(N - 2, N)$. Other examples of mixed valency with a difference of 2 in oxidation state are provided by the later 4d and 5d transition elements, where compounds with electron configurations d^6 , d^8 (e.g., $\text{Pt}(\text{NH}_3)_2\text{Cl}_3$) and d^8 , d^{10} (e.g., CsAuCl_3) are found.

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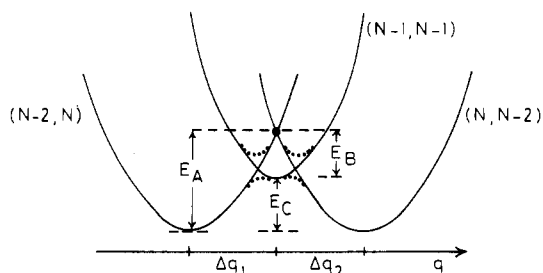
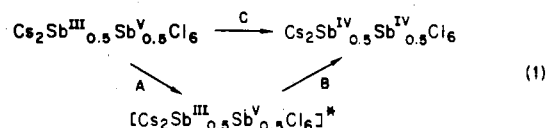


Figure 1. Potential energy surfaces for two-electron-difference mixed-valency systems. E_A , E_B , and E_C refer to (1).

In such crystals, a charge-ordered class II^1 ground state results from the localization of electron pairs on alternate metal ion sites and charge density alternation between neighboring sites. An alternative way of viewing $(N - 2, N)$ mixed-valency compounds is to say that disproportionation of the type $e^1 + e^1 \rightarrow e^2 + e^0$ has taken place. These two-electron-difference mixed-valency systems are then examples of what solid-state physicists² have called the "negative U " effect;² i.e., in the Hubbard³ model the Hamiltonian of the system includes a single-center Coulomb repulsion parameter U_{eff} that appears to be negative. Physically this means that the repulsion U of two electrons occupying the same orbital is outweighed by the gain in lattice Coulomb energy and the gain in elastic energy associated with strong electron-phonon coupling.

In the gas phase the energy U required to accomplish the disproportionation $5s^1 + 5s^1 \rightarrow 5s^2 + 5s^0$ for isolated ions is simply the difference between the N th and the $(N - 1)$ th ionization potentials of the elements involved: Cd, $I_2 - I_1 = 7.9$ eV; In, $I_3 - I_2 = 9.2$ eV; Sn, $I_4 - I_3 = 10.2$ eV; Sb, $I_5 - I_4 = 11.9$ eV. In a solid, $U_{\text{eff}} < U$ as a result of increasing effects, reduced ionicity, and electron correlation.

Considering the Sb(III, V) salt Cs_2SbCl_6 as an example, recent experiments in this laboratory have accumulated enough information to place an upper limit on U_{eff} for the above disproportionation reaction. We have determined the crystal structure of Cs_2SbCl_6 ⁵ and identified the superlattice ordering of Sb(III) and Sb(V) , including the bond lengths and angles of the constituent SbCl_6^{3-} and SbCl_6^- . Further, a set of force constants and ionic charges for this lattice is available from a rigid-ion^{6,7} lattice dynamical calculation⁸ fitted to published⁹ infrared and Raman data, which also gives a good account of the complete phonon density-of-states up to 400 cm^{-1} measured by incoherent inelastic neutron scattering.⁸ Consider the following thermochemical cycle:



$\text{Cs}_2\text{Sb}^{\text{III}}_{0.5}\text{Sb}^{\text{V}}_{0.5}\text{Cl}_6$ refers to the equilibrium state of the (III, V) mixed-valency salt. In step A, we produce an excited state $[\text{Cs}_2\text{Sb}^{\text{III}}_{0.5}\text{Sb}^{\text{V}}_{0.5}\text{Cl}_6]^*$ by contracting the $\text{Sb}^{\text{III}}\text{-Cl}$ and extending the $\text{Sb}^{\text{V}}\text{-Cl}$ bond lengths to the $\text{Sb}^{\text{IV}}\text{-Cl}$ equilibrium bond lengths. In step B, electron transfer between the Sb^{III} and Sb^{V} sites results in the relaxed $\text{Cs}_2\text{Sb}^{\text{IV}}_{0.5}\text{Sb}^{\text{IV}}_{0.5}\text{Cl}_6$ state.

The chemical fact of the nonexistence of $\text{Cs}_2\text{Sb}^{\text{IV}}\text{Cl}_6$ indicates that the overall reaction in (1) is endothermic. In step A, there

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