

- to glasses at low temperatures, rendering them unsuitable for study by X-ray methods.
- (8) The compound $[(\text{Me}_2\text{N})_3\text{P}]_2\text{Fe}(\text{CO})_3$ was prepared by the procedure of R. B. King, *Inorg. Chem.*, **2**, 936 (1963).
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 - (11) Conformation 3: C_3 symmetry; $r(\text{NP}) = 1.7468$, $r(\text{NH}) = 1.028$ Å (av); dihedral angle, $^{13}\phi = 88.0^\circ$; sum of bond angles around nitrogen, $S_N = 327.4^\circ$; total energy, $E = -501.627\ 006$ (STO 3G), $-501.731\ 487$ hartrees (STO 3G*). Conformation 4: C_s symmetry; $r(\text{NP}) = 1.738$ and 1.760 , $r(\text{NH}) = 1.026$ (av) and 1.030 Å; $\phi = 91.4$, 180° ; $S_N = 333.9$, 322.6° ; $E = -501.621\ 449$ (STO 3G), $-501.729\ 589$ hartrees (STO 3G*).
 - (12) There are no intermolecular contacts shorter than the sums of the respective van der Waals radii. The observed molecular geometry is therefore not affected appreciably by interactions between molecules. A complete discussion of inter- and intramolecular effects will appear in a full paper.
 - (13) The dihedral angle, ϕ , is taken to be the angle between the planes bisecting the X-N-X (X = C,H) and N-P-N bond angles viewed down the N-P bond.
 - (14) A. H. Cowley, M. W. Taylor, M.-H. Whangbo, and S. Wolfe, *J. Chem. Soc., Chem. Commun.*, 838 (1976).
 - (15) (a) R. D. Kroshefsky and J. G. Verkade, *Inorg. Chem.*, **14**, 3090 (1975); (b) J. G. Verkade, *Phosphorus Sulfur*, **2**, 251 (1976), and references therein.
 - (16) The molecular geometry of $\text{MeC}(\text{CH}_2\text{NMe})_3\text{P}$ has not been determined by X-ray crystallography; however, the corresponding phosphine oxide and phosphine-borane complexes have been characterized structurally and found to possess a local phosphorus geometry corresponding to 2. See J. C. Clardy, R. L. Kolpa, and J. G. Verkade, *Phosphorus*, **4**, 133 (1974). Owing to the constraints of the cage system it is safe to assume that the same conformation persists in the parent phosphine.
 - (17) (a) J. C. Slater and K. H. Johnson, *Phys. Rev.*, **B**, **5**, 844 (1972); (b) J. C. Slater, "Quantum Theory of Molecules and Solids", Vol. 4, McGraw-Hill, New York, 1974, p 583.
 - (18) NOTE ADDED IN PROOF. The X-ray crystal structure of $(\text{Me}_2\text{N})_3\text{PF}e(\text{CO})_4$ has now been determined and is undergoing refinement (present $R = 0.083$). The aminophosphine geometry in $(\text{Me}_2\text{N})_3\text{PF}e(\text{CO})_4$ is virtually identical with that of P-2 in $[(\text{Me}_2\text{N})_3\text{P}]_2\text{F}e(\text{CO})_3$ and may be described as approximately conformation 3 with two Me_2N groups nearly planar and twisted in the same direction ($\phi \approx 90$ – 100°), but with the third such group at $\phi \approx 180^\circ$ much more pyramidal. This lends further credence to our assertion¹² that the observed conformations and distortions from planarity of the Me_2N groups are not due to interactions between molecules. Structural details of both compounds will be discussed in a forthcoming paper.

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Anion-Radical Crystal Lattice Energies

Sir:

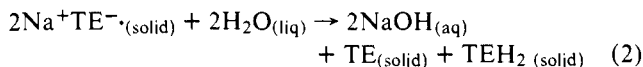
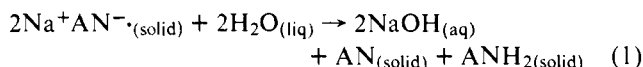
The factors that control the thermodynamic stability of organic anion radicals can be broken down into two major categories: those that are intramolecular and those that are intermolecular in nature. The major intramolecular consideration is the electron affinity of the neutral molecule, while the intermolecular factors for solvated anions include anion solvation and ion association with the cation. However, in the

solid phase the only intermolecular factor is the crystal lattice energy (U_0).

The classic work of Brauman and Blair¹ has demonstrated the vital importance of solvation in controlling the thermodynamic stability of solvated anions. However, there has been very little work concerning the crystal lattice energies of solid organic salt systems. Here we report the first crystal lattice energy measurements for anion-radical salts and show that this crystal lattice energy is much more important in controlling the thermodynamic stability of the salt than are the intramolecular effects.

Since it has been well established that the exclusive organic products resulting from the reactions of the anion radicals of anthracene (AN) and tetracene (TE) are 9,10-dihydroanthracene (ANH_2)² and 9,10-dihydro-tetracene (TEH_2),³ respectively, the enthalpy of this reaction was measured and used in a thermochemical cycle to obtain the heats of formation and the crystal lattice energies of the solid sodium anion-radical salts.

The anion radicals of AN and TE were generated under high vacuum in tetrahydrofuran (THF) via reduction with a diffi-cient amount of sodium metal. Once the entire sodium mirror had dissolved, the THF was evaporated from the solution under vacuum leaving the solid anion-radical salts. These solid salts were then left open to high vacuum for at least 48 h with two liquid nitrogen traps between the vacuum pump and the salt container to ensure complete removal of the solvent. The desolvated solid anion-radical salts were then placed into thin-walled evacuated glass bulbs, which were subsequently sealed off from the apparatus. The thin-walled bulbs were then placed into a Parr solution calorimeter and broken under 100 mL of deoxygenated water with a push rod. The change in the temperature of the calorimeter was due strictly to the reaction of the anion-radical salt with the water to produce the dihydro hydrocarbon and sodium hydroxide:



The only organic compounds remaining in the calorimeter after the reaction are the neutral hydrocarbon and the dihydro hydrocarbon. The possibility of the evolution of hydrogen gas from the reaction with water was eliminated by pumping any gaseous products into a calibrated gas buret with a Toepler pump as previously described.⁴ The fact that no gas-phase products could be detected means that at least 99.9% of the reaction leads to protonation of the anion radicals. Deuterated water was added to several samples of the anion-radical solid salts. Subsequent NMR analysis of these D_2O solutions showed no traces of THF, indicating that this solvent is not coordinated into the crystal lattice structure of the salt.

The calorimeter contents were titrated with standardized HCl solutions after each experiment. The number of millimoles of NaOH present in the water was considered to be equal to

Table I. Enthalpies of Reaction in Kilocalories/Mole

reaction	$\pi, \Delta H^\circ$		ref
	AN	TE	
$\frac{1}{2}\pi(\text{solid}) + \frac{1}{2}\pi(\text{solid}) + \text{NaOH}(\text{aq}) \rightarrow \text{Na}^+\pi^{\cdot-}(\text{solid}) + \text{H}_2\text{O}(\text{liq})$	+41.1	+33.4	this work
$\text{Na}^0(\text{solid}) + \text{H}_2\text{O}(\text{liq}) \rightarrow \text{NaOH}(\text{aq}) + \frac{1}{2}\text{H}_2(\text{g})$	-44.1	-44.1	8
$\frac{1}{2}\pi(\text{solid}) + \frac{1}{2}\text{H}_2(\text{g}) \rightarrow \frac{1}{2}\pi\text{H}_2(\text{solid})$	-8.5	-6.25	9, 13
$\pi(\text{g}) \rightarrow \pi(\text{solid})$	-23.5	-29.8	14, 12
$\text{Na}^0(\text{g}) \rightarrow \text{Na}^0(\text{solid})$	-25.9	-25.9	10
$\text{Na}^+(\text{g}) + e^-(\text{g}) \rightarrow \text{Na}^0(\text{g})$	-118.4	-118.4	11
$\pi^{\cdot-}(\text{g}) \rightarrow \pi(\text{g}) + e^-(\text{g})$	+12.7	+26.45	12
$\text{Na}^+(\text{g}) + \pi^{\cdot-}(\text{g}) \rightarrow \text{Na}^+\pi^{\cdot-}(\text{solid})$	-166.6	-164.6	

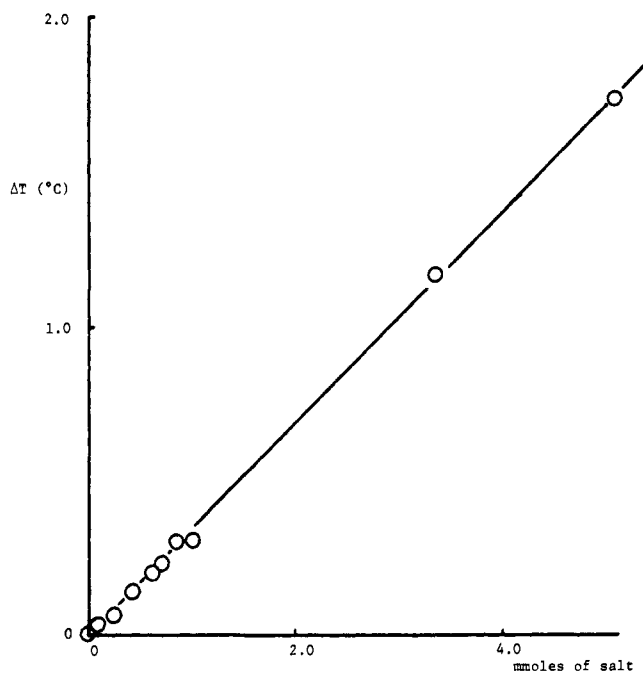


Figure 1. Plot of the change in the temperature of the calorimeter vs. the millimoles of solid Na^+AN^- sealed in the evacuated glass bulbs.

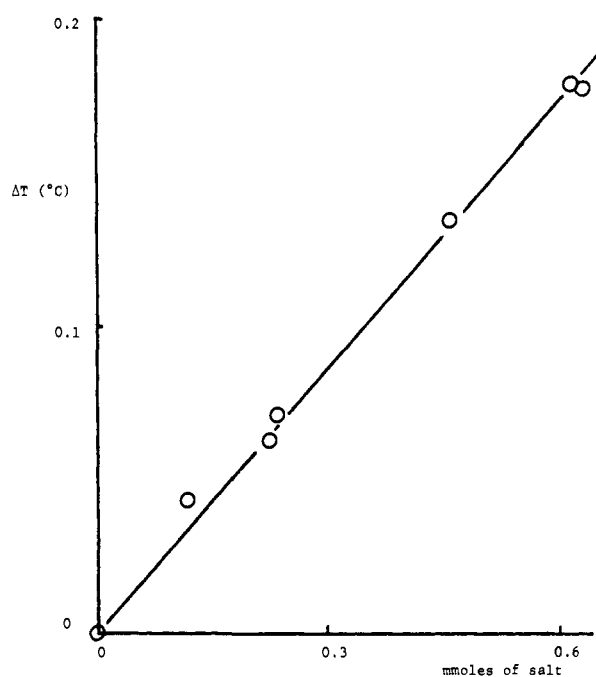


Figure 2. Plot of the change in the temperature of the calorimeter vs. the millimoles of solid Na^+TE^- sealed in the evacuated glass bulbs.

the initial amount of salt in the bulbs. Plots of the change in the temperature of the calorimeter vs. the number of millimoles of salt are linear (Figures 1 and 2) and the slopes of the lines are proportional to the enthalpy of the reactions depicted in eq 1 and 2. These enthalpies are -41.1 ± 0.3 and -33.4 ± 0.6 kcal/mol, respectively, for the anion radicals of anthracene and tetracene.⁵ If these enthalpies are combined with a series of well-known constants in a thermochemical cycle, the actual crystal lattice energies for Na^+AN^- and Na^+TE^- are found to be -166.6 ± 2 and -164.6 ± 3 kcal/mol, respectively (Table I). The negative of the enthalpy change for the reaction of the gas-phase sodium cation with the gas-phase anion radical to yield the solid anion radical salt represent the crystal lattice energy (U_0).⁶

From Table I there are two striking features. First, it is ob-

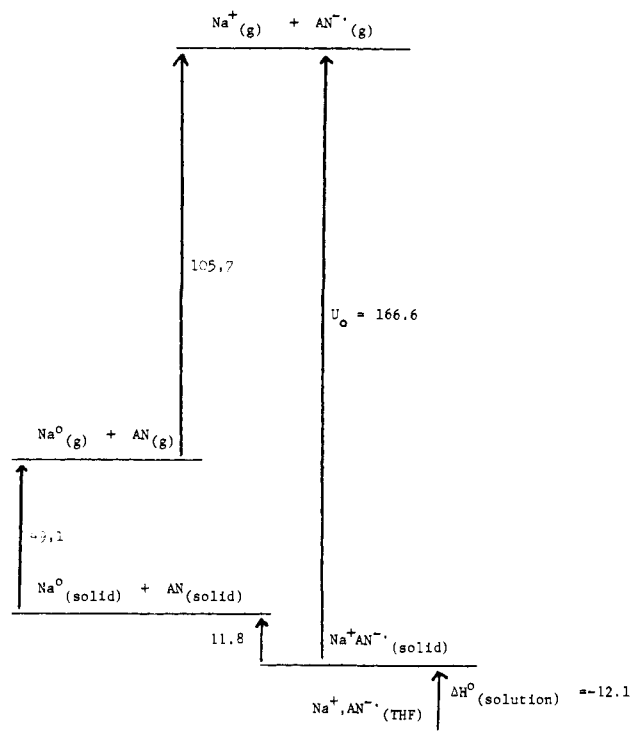


Figure 3. Energy diagram for the sodium anthracene system. The differences are in kilocalories/mole. The heat of solution of the solid salt was calculated from the data given in ref 15.

vious that the crystal lattice energies (the intermolecular factors) are very large and more important than any of the intramolecular factors in controlling the heat of formation of the salts. The second striking feature is the fact that the two crystal lattice energies are the same. This is in contrast to the fact that the electron affinity of TE⁻ is more than twice as great as that of AN.

The similarity of the two crystal lattice energies must be due to a counterbalancing effect by the Madelung constant (A) and the smallest anion-cation interatomic distance (R_0). For the larger anion (TE⁻) the charge is more delocalized, and there is a weaker coulombic attraction between the anion and the cation yielding a slightly larger value for R_0 . At the same time the larger anion radical may interact effectively with more neighboring cations, since the electron is delocalized over a larger area. This would result in the salt of TE⁻ having a larger A than would that of AN⁻.

Since for all crystals n lies in the neighborhood of 9,⁶ we can carry out a rough calculation of U_0 using 3 Å for R_0 and 1.7 for A . The Born-Landé equation (eq 3) yields a value for U_0 of 167 in agreement with the experimental result.⁷

$$U_0 = (ANZ^+Z^-e^2/R_0)[1 - (1/n)] \quad (3)$$

A summarization of the intramolecular and intermolecular energies controlling the thermodynamic stability of the sodium anthracene system is shown in Figure 3. Since the magnitude of the crystal lattice energy is close to that of the solvation energy, we might expect the chemistry of the solid anion systems to be very different from that in the gas phase. This has already proven to be the case for the solution state.¹

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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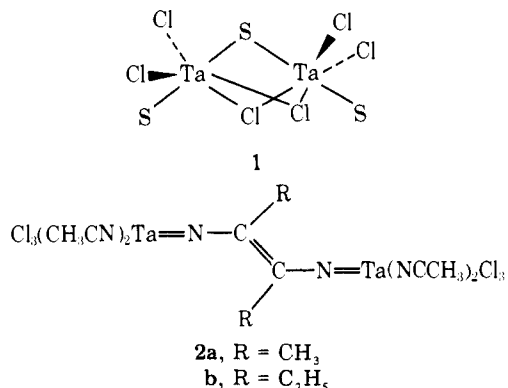
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Reactions of Tantalum(III) with Alkynes and Nitriles

Sir:

There has lately been an upsurge of interest in the chemistry of the early transition elements, especially with respect to organometallic reactions and possible catalytic applications thereof. Most of the work reported so far, however, deals with cyclopentadienyl derivatives, and the noncyclopentadienyl chemistry of tantalum and niobium in their intermediate oxidation states, e.g., III, is still practically unknown. This is particularly true of reactions with unsaturated organic molecules and the main reason appears to be a lack of convenient reactants. We report here that the compound $\text{Ta}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$, **1**,¹ serves as a convenient source of Ta(III) and we describe several interesting reactions that adumbrate a large and interesting chemistry of Ta (and, presumably, also Nb) with unsaturated organic compounds.

Compound **1** reacts with acetonitrile to form **2a**, the structure of which has been inferred from a crystallography study. The only previous synthesis of **2a** was by an indirect route which gave a poor yield. We have found that direct synthesis



from **1** proceeds quickly and in high yield and report a method that is applicable to alkyl cyanides in general. We have also found that **1** reacts with alkynes to give products of unusual properties.

Reaction of **1** with acetonitrile, propionitrile, or isobutyronitrile, gives a green product within a few minutes.³ The infrared spectrum of the MeCN product is identical with that of **2a**. IR, analysis, and chemical properties show that the compounds from EtCN (**2b**) and PrⁱCN are of the same type.

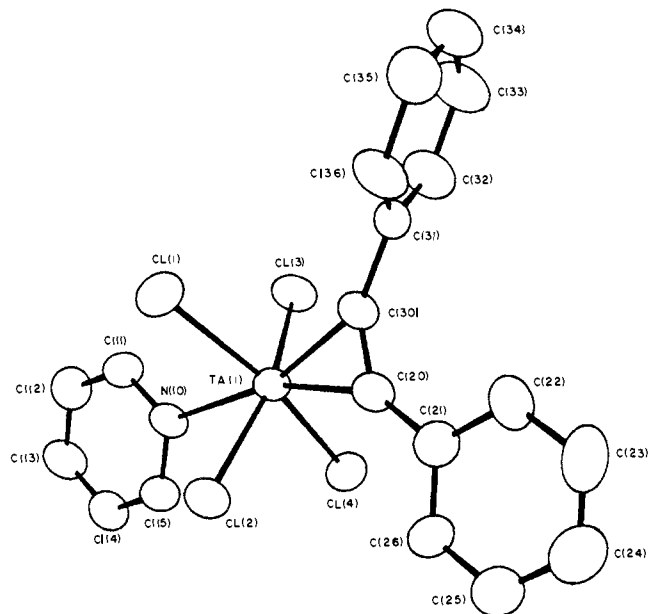
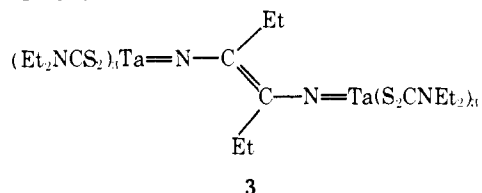


Figure 1. A computer-generated drawing of the $[\text{TaCl}_4(\text{py})(\text{PhCCPh})]^-$ anion.

Neither $(\text{CH}_3)_3\text{CCN}$ nor $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ reacts with **1** to give reductively coupled products.

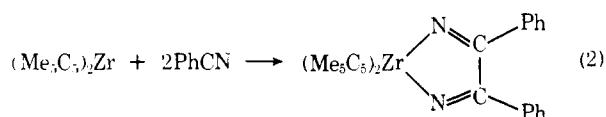
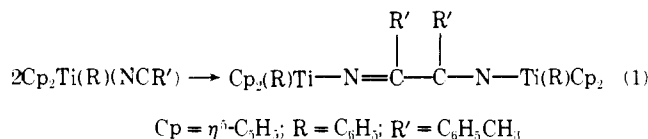
The tantalum(V)-nitrene complexes formed in these reactions are relatively resistant to protic attack. When an HCl/Et₂O solution was added to **2a**, no reaction was observed even after several hours. However, if, instead, acetone was added to **2a**, $\text{TaOCl}_3(\text{MeCN})_2$ was formed on standing overnight. We are attempting to learn what happens to the organic fragments. This sort of exchange of oxygen for nitrogen was suggested in the reaction of $[(\text{CH}_3)_2\text{N}]_3\text{Ta}=\text{NBu}^i$ and benzaldehyde.⁴

Compound **2b** reacts with the diethyl dithiocarbamate anion producing an air-stable crystalline compound shown by X-ray crystallography to be **3**, in which the Ta atoms are seven



coordinate. The details of this structure will be reported elsewhere, since they are not pertinent to the main thrust of this communication.

To our knowledge, this type of facile reductive coupling of nitriles (accompanied by oxidation of the metal atoms) is unprecedented. The closest related reactions we know of are eq 1 and 2, recently described by DeBoer and Teuben⁵ and by Bercaw.⁶



When a toluene or CH₂Cl₂ solution of **1** is mixed with 3-hexyne, hexaethylbenzene is formed in a rapid, exothermic reaction that is clearly catalytic at 25 °C. Such catalytic ac-