crystal orientation and stability. In all cases, the standard reflections were used to rescale the data automatically to correct the drift during data collection. Drift corrections were random and long term and are indicated in Table III. The total number of unique reflections measured, and their numbers with respect to the standard deviation in intensity, $\sigma(I)$, are given in Table III for each compound, with the criterion for observation being $I > 2\sigma(I)$. The integrated intensity, I, was calculated according to the expression[56] $I = [SC - 2(B_1 + B_2)]T_R$, where SC is the scan count, B_1 and B_2 are the background counts at each end of the scan, and T_R is the 2θ scan rate in degrees per minute. The unique, normalized, integrated intensity set was processed to give F and E values. Lorentz and polarization corrections[55] were applied in the determination of the structure factor amplitudes. Linear absorption coefficients (μ, cm^{-1}) for Mo Kα radiation are given in Table III. The values were sufficiently small that no absorption corrections were applied.

Structure Solution and Refinement. The positions of the metal atoms in each case were established from a sharpened, origin-removed Patterson map and were confirmed by a direct method solution. The remaining non-hydrogen atoms were located with one or two additional Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The number of parameters, including overall scale factor, positional parameters, and anisotropic thermal parameters,[26] varied in each case and are listed in Table III. Hydrogen atoms for compounds **5–7** were located at their calculated positions. All hydrogen atoms were assigned fixed isotropic temperature parameters[57] of $B = 5.0$ Å^2. None of the parameters for the hydrogen atoms were varied. Neutral-atom scattering factors were those by Cromer and Mann[58] and by Stewart et al.[59] for non-hydrogen atoms and hydrogen atoms, respectively. Real and imaginary anomalous dispersion corrections to the atomic scattering factors were included.[60] In the last cycle of least-squares refinement the maximum parameter shift was less than 0.33 of a standard deviation. The final R values[61] are listed in Table III. Final difference Fourier maps showed the residual electron density (e Å^{-3}) for each structure, as indicated in Table III.

Acknowledgment. We thank the U.S. Army Research Office for the support of this work. We also thank L. G. Lang for the Mössbauer data: The Mössbauer work was supported by the National Institutes of Health through Grant no. HL-16860. The NMR data were obtained by R. A. Nissan and J. L. Desorcie.

Registry No. **2**, 83437-98-3; **4**, 94042-46-3; **5**, 94042-47-4; **6**, 94042-48-5; **7**, 94042-49-6; $Co_2(CO)_8$, 10210-68-1; $CoCp(CO)_2$, 12078-25-0; $RhCp(CO)_2$, 12192-97-1; $[RhCl(CO)_2]_2$, 14523-22-9.

Supplementary Material Available: Listing of thermal parameters, root-mean-square displacements, and observed and calculated structure factors for compounds **4**, **5**, **6**, and **7** (54 pages). Ordering information is given on any current masthead page.

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Proton Affinities of Pyridine, Phosphabenzene, and Arsabenzene[†]

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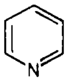
The proton affinities of phosphabenzene and arsabenzene are determined by ion cyclotron resonance techniques to be 195.8 and 189.3 kcal/mol, respectively, relative to PA(NH_3) = 203.6 kcal/mol. These values are compared to those of pyridine, 219.4 kcal/mol, and other group 5 compounds. Deuterium labeling experiments demonstrate that phosphabenzene is protonated on the phosphorus atom, and arsabenzene is protonated on carbon.

Introduction

The group 5 heterobenzenes, pyridine **1**, phosphabenzene **2**,[2,3] arsabenzene **3**,[2–4] stibabenzene **4**,[3–6] and bismabenzene **5**,[3,4,6,7] form a unique series in which elements from an entire column of the periodic table have been incorporated into aromatic rings. Spectroscopic studies have indicated that there are great similarities in aromatic character of the entire series.[3,4] However, chemical studies have shown a marked divergence of the heavier heterobenzenes from pyridine.[3,4]



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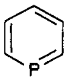

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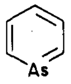

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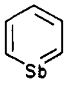

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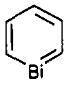

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In particular, the chemistry of pyridine is dominated by the basicity of the nitrogen atom. However, the heteroatoms of phosphabenzene and arsabenzene do not show basic properties in solution ($2 \not\rightarrow 6$)[8] nor are they quater-

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[†] Contribution No. 5680.

[1] (a) California Institute of Technology. (b) The University of Michigan. (c) N.S.F. Graduate Fellow (1973–1976).

[2] Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 3293.

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[4] Ashe, A. J., III *Top. Curr. Chem.* **1982**, *105*, 125.

[5] Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 6690.

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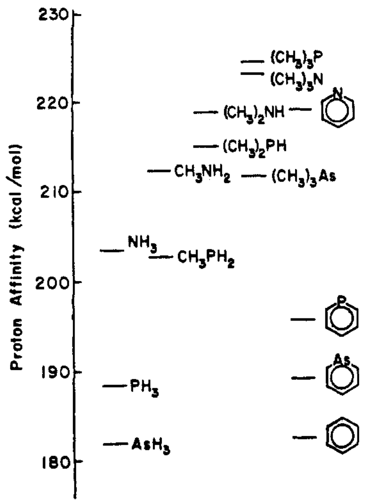
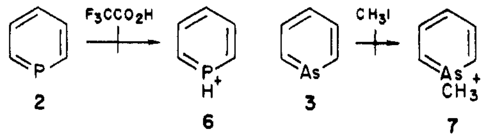


Figure 1. Proton affinities of group 5 bases. Data from Table I.

nized by strong alkylating agents ($3 \nrightarrow 7$).[9] This lack of observable solution phase basicity has led us to examine their gas phase basicity.



Gas-phase proton affinities provide a quantitative measure of base strength in the absence of solvent effects. The proton affinity of a base B is defined as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+ (reaction 1). The homolytic bond dissociation energy of the conjugate acid is defined as the standard enthalpy change for reaction 2. These two bond energies are related by the adiabatic ionization potentials of B and H according to eq 3. Comparisons of the proton affinities, ionization potentials, and homolytic bond dissociation energies of related compounds permit evaluations of the effects of changes in molecular and electronic structures on these quantities.[10,11]

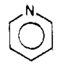
$$BH^+ \rightarrow B + H^+ \quad PA(B) = \Delta H° \tag{1}$$

$$BH^+ \rightarrow B^+ + H \quad D(B^+\text{-}H) = \Delta H° \tag{2}$$

$$D(B^+\text{-}H) = PA(B) + IP(B) - IP(H) \tag{3}$$

The proton affinities of a large number of amines,[10-16] including substituted pyridines,[12,14,16,17] are now known. The proton affinities of phosphine,[10] the methylphosphines,[18] arsine,[2] and trimethylarsine[19] are available

Table I. Proton Affinities, Adiabatic Ionization Potentials, and D(B^+-H) Homolytic Bond Dissociation Energies of Group 5 Bases[a,b]

molecule	PA[a]	IP[c,d]	D(B^+-H)[c,e]
	219.4[f]	210[g]	115.7
	195.8[h]	208 (217)[g]	90.1 (99.1)
	189.3[h,i]	199 (214)[g]	74.6 (<89.6)[i]
	182.7	213.1[j]	82.1
NH_3	203.6	234.3	124.2
CH_3NH_2	212.6	206.8	105.7
$(CH_3)_2NH$	219.2	190.0	95.5
$(CH_3)_3N$	223.4	181.5	91.2
PH_3	188.7	229.6	104.6
CH_3PH_2	203.1	210.2	99.6
$(CH_3)_2PH$	215.3	195.3	97.9
$(CH_3)_3P$	224.8	184.7	95.8
$(CH_2)_2PH$	193.2[k]	216	95.5
$(CH_2)_2NH$	214.1[k]	213	113.4
AsH_3	182.2	228	96.5
$(CH_3)_3As$	212.0	182	80.3

[a] All data are relative to PA(NH_3) = 203.6 kcal/mol. See ref 20 and 21. [b] Except as noted, data are from ref 10. [c] In kcal/mol. [d] Values in parentheses are lone-pair adiabatic ionization potentials, where these are not the first ionization potentials. [e] Values in parentheses are the corrected homolytic bond dissociation energies (see discussion in text). [f] Reference 25. [g] Estimated from the photoelectron spectrum published in ref 39. [h] Present work. [i] Arsabenzene protonates on carbon rather than the heteroatom. Thus the measured proton affinity is an upper limit to the heteroatom base strength and similarly the correlated homolytic bond energy is an upper limit to the true value for protonation on arsenic. [j] Abrink, L.; Lindholm, E.; Edqvist, O. *Chem. Phys. Lett.* 1970, *5*, 609. [k] Reference 46.

for comparison with the analogous amines (Figure 1 and Table I).[20,21] In general, the proton affinities of compounds with identical substitution decrease in the order N > P > As. An exception occurs in the trimethyl series, where PA[$(CH_3)_3P$] > PA[$(CH_3)_3N$]. The differences in proton affinity between the amines and the phosphines have been explained by considering the character of the lone pair to which the proton binds.[18] Protonation of the phosphine requires a rehybridization of the phosphorus lone pair from largely s (<H-P-H = 93° in PH_3)[22] to sp^3 character. Ammonia, which is sp^3 hybridized (<H-N-H = 107°),[23] requires little rehybridization energy upon protonation and is 14.9 kcal/mol more basic than phosphine.[24]

The phosphorus and arsenic compounds studied to date are similar, in that the heteroatom forms σ bonds to three substituents. This paper reports ion cyclotron resonance (ICR) investigations of the energetics and site specificity of the protonation of phosphabenzene and arsabenzene, compounds in which the heteroatom is involved in π bonding. The proton affinity of pyridine has been pre-

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(21) The problem of proper reference compound for the scale of gas-phase proton affinities has been discussed in detail by: Lias, S. G.; Liebman, J. F.; Lever, R. D. *J. Phys. Chem. Ref. Data*, in press.

(22) Sirvetz, M. H.; Weston, R. E., Jr. *J. Chem. Phys.* **1953**, *21*, 898.

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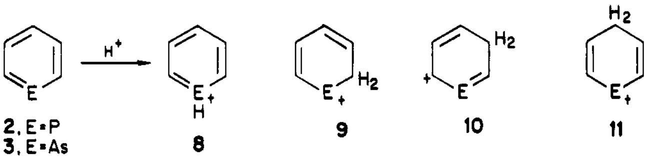
(24) For a discussion of rehybridization effects see: Gibbs, J. H. *J. Chem. Phys.* **1954**, *22*, 1460.

Table II. Proton-Transfer Equilibrium Constants, Free Energies, and Enthalpies

$C_5H_5EH^+ + B \rightleftharpoons BH^+ + C_5H_5E$	K^a	ΔG^b	ΔH^b	$PA(B)^{c,d}$	$PA(C_5H_5E)^d$
$(C_5H_5P)H^+ + (CH_3)_2CO \rightleftharpoons (CH_3)_2COH^+ + C_5H_5P$	0.7	0.2	0.6	195.2	195.8
$(C_5H_5P)H^+ + CH_3CO_2CH_3 \rightleftharpoons (CH_3CO_2CH_3)H^+ + C_5H_5P$	4.0	−0.8	−0.8	196.7	195.9
$(C_5H_5As)H^+ + HCO_2CH_3 \rightleftharpoons (HCO_2CH_3)H^+ + C_5H_5As$	0.6	0.3	0.3	189.0	189.3
$(C_5H_5As)H^+ + CH_3CN \rightleftharpoons CH_3CNH^+ + C_5H_5As$	0.2	0.9	0.9	188.3	189.2

[a] Average of three independent determinations. [b] In kcal/mol. [c] Reference 10. [d] Proton affinity in kcal/mol. All data relative to $PA(NH_3) = 203.6$ kcal/mol. References 20 and 21.

viously determined to be 219.4 kcal/mol.[25] Although it has not been demonstrated experimentally, protonation undoubtedly occurs at the nitrogen atom. Protonation of phosphabenzene and arsabenzene could conceivably occur at the heteroatom to give structure **8** or at a ring carbon to give **9** (α-protonation), **10** (β-protonation), or **11** (γ-protonation).



Experimental Section

Phosphabenzene and arsabenzene were prepared by the reaction of 1,1-dibutylstannacyclohexa-2,5-diene with phosphorus tribromide or arsenic trichloride, respectively.[2] The ICR mass spectra of these materials match the reported spectra.

The general features of ICR instrumentation and its operation in trapped-ion experiments have been previously described.[26,27] All experiments were performed at room temperature.

Pressure measurements were made by using a Schulz-Phelps gauge located adjacent to the ICR cell. This gauge is calibrated for each gas for a given emission current (5 μA) and magnetic field (6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer in the region 10^{-5}–10^{-3} Torr, where linear variation of gauge current with pressure is observed. Pressures in the trapped ion experiments were in the range 10^{-7}–10^{-5} torr.

Results

Phosphabenzene. Ion Chemistry. ICR trapped ion studies of phosphabenzene alone were performed at 14 eV. At this electron energy only the parent ion, *m/e* 96, is present. The parent ion clusters with the neutral (reaction 4) but is otherwise unreactive. In particular, the conjugate

$$C_5H_5P^+ + C_5H_5P \rightarrow (C_5H_5P)_2^+ \qquad (4)$$

acid, protonated phosphabenzene, *m/e* 97, is not observed. The variation of ion abundance with time is shown in Figure 2. The parent ion is initially unreactive. It may be formed with excess internal energy and then be collisionally deactivated. The rates of association reactions such as reaction 4 decrease as a function of the internal energy of the reactants.[28] The bimolecular rate constant for reaction 4 is 2.0×10^{-10} cm^3 mol^{-1} s^{-1}.[29] This value is constant to within ±20% over a pressure range of 1.8×10^{-6} to 4.0×10^{-6} torr. Bimolecular ion–molecule clustering at low pressure (10^{-6} torr) has also been observed to occur with ions in the fluoromethylsilanes.[30]

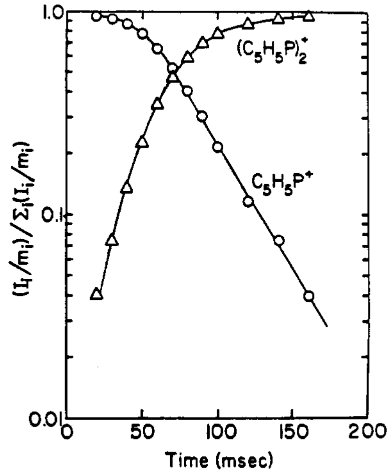


Figure 2. Temporal variation of ion concentrations in phosphabenzene at 4×10^{-6} torr pressure and 14-eV electron energy.

Proton Affinity. In mixtures of phosphabenzene and acetone or methyl acetate, the ratio of the protonated parent ion abundances reached a constant value. Double-resonance experiments established that proton transfer was occurring in both directions, thus demonstrating that proton transfer equilibria had been achieved. The free energies obtained from the equilibrium constants are listed in Table II. The enthalpies are calculated from the free energies with the assumption that entropy effects are small and are limited to changes in rotational symmetry numbers.[10,31,32] These data yield a proton affinity of 195.8 ± 0.1 kcal/mol for phosphabenzene.

Site of Protonation. In a mixture of CD_3CDO, phosphabenzene, and 2-pentanone, both protonated and deuterated phosphabenzene and ketone was observed. Double-resonance experiments demonstrated that deuterated phosphabenzene reacts to give deuterated, but *not* protonated ketone. The deuterium is, therefore, not equivalent to the ring hydrogens and must be located on the phosphorus atom.

Arsabenzene. Ion Chemistry. The reactivity of arsabenzene molecular ion is identical with that observed for phosphabenzene. Clustering with the parent neutral is the only observed process (reaction 5).

$$C_5H_5As^+ + C_5H_5As \rightarrow (C_5H_5As)_2^+ \qquad (5)$$

Proton Affinity. Proton transfer equilibria were achieved in mixtures of arsabenzene with methyl formate and with acetonitrile. The data from these experiments are listed in Table II. The proton affinity of arsabenzene is 189.3 ± 0.1 kcal/mol.

Site of Protonation. In a mixture of CD_3CDO, diethyl-d_{10}, ether, and arsabenzene, both protonated and deuterated arsabenzene and diethyl-d_{10} ether were observed. Double-resonance experiments indicated that deuterated arsabenzene reacts to give *both* protonated and

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(25) From a compilation of data by R. W. Taft. The experimental methods are the same as those in ref 11 and 12. This value differs slightly from that reported in ref 12 and 16.

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deuterated diethyl-d_{10} ether, in a ratio of ~1:1. This result indicates that arsabenzene is protonated at carbon rather than at the arsenic atom.

Discussion

The proton affinities, ionization potentials, and homolytic bond dissociation energies of the heterobenzenes and several other group 5 bases are listed in Table I. The first adiabatic ionization potentials of the bases are used to calculate the homolytic bond dissociation energies as strictly defined according to eq 3.[33] However, for the purpose of comparing the homolytic bond dissociation energies of compounds in a homologous series, the adiabatic ionization potential of the orbital which correlates with the bonding orbital in the conjugate acid should be used in eq 3.[33] The term correlated homolytic bond dissociation energy is suggested for this quantity. In the case of the heterobenzenes the appropriate orbital is the heteroatom lone-pair orbital. Calculations suggest that the preferred approach of the proton to pyridine or phosphabenzene is the σ plane along the symmetry axis of the heteroatom.[34-36] Although theoretical studies of the structure of protonated arsabenzene are lacking, calculations on arsaethene suggest a close balance between C and As basicity.[37] As noted above, protonation–deprotonation experiments provide evidence that arsabenzene preferentially protonates on a carbon position. In solution, arsabenzene undergoes deuterium exchange in trifluoroacetic acid-d_1, primarily at the α-position.[38] These combined results suggest that 7 is the most stable form of the conjugate acid. In addition, it may be inferred for arsabenzene that for protonation on the heteroatom, PA(C_5H_5As) $\leq$ 189.3 kcal/mol.

The photoelectron spectra of the heterobenzenes have been assigned.[39] The lone pair and $a_2(\pi)$ orbitals of pyridine have almost the same energy and are the highest occupied orbitals. However, in phosphabenzene and arsabenzene, the lowest energy ionization occurs from the $b_1(\pi)$ orbital. Ionization from the lone-pair orbitals corresponds to the third band in the photoelectron spectra. The estimated adiabatic ionization potentials of the lone pairs in phosphabenzene and arsabenzene and the correlated homolytic bond dissociation energies calculated from these values are given in parentheses in Table I.

The lone-pair ionization potentials of the heterobenzenes are relatively constant in this series. Thus, the homolytic bond dissociation energies follow the trend $C_5H_5N > C_5H_5P > C_5H_5As$. In the case of arsabenzene, the homolytic bond energy, $D(B^+-H)$ = 75 kcal/mol, refers to the C–H bond energy and can be compared to the value of 82 kcal/mol for benzene. The 7 kcal/mol difference can be ascribed to a stabilization of the radical cation due to the presence of the heteroatom.

The reactivity of the parent ions of the heterobenzenes is determined by the $D(B^+-H)$ homolytic bond dissociation energy. The homolytic bond dissociation energy for pyridine, 116 kcal/mol, is higher than the C–H bond energy of pyridine, if a value equal to the C–H bond energy of benzene, $D(C_6H_5-H)$ = 110 kcal/mol, is assumed.[40] Reaction 6 is, therefore, exothermic for pyridine and is observed.[41] The homolytic bond dissociation energies for phosphabenzene and arsabenzene, however, are considerably below 110 kcal/mol, and reaction 6 is endothermic for E = P or As. Clustering is the only reaction of parent ions of these molecules.

$$C_5H_5E^+ + C_5H_5E \rightarrow C_5H_5EH^+ + C_5H_4E \qquad (6)$$

The proton affinities (for heteroatom protonation) of the heterobenzenes decrease in the order $C_5H_5N > C_5H_5P > C_5H_5As$ in parallel to the order $NH_3 > PH_3 > AsH_3$. However, a comparison of the ordering of the proton affinities between series shows the relative position of the heterobenzenes to be quite different in the amine series than the phosphine and arsine series. For the amine series, the order of increasing PA is $NH_3 < MeNH_2 < Me_2NH < C_5H_5N < Me_3N$, while in the phosphine series the order is $PH_3 < C_5H_5P < MePH_2 < Me_2PH < Me_3P$. Although fewer arsenic compounds have been studied, the arsine series seem similar to the phosphine one.

In quantitative terms the proton affinity of pyridine (219.4 kcal/mol)[25] is only slightly less than that of trimethylamine (223.4 kcal/mol)[10] but considerably greater than ammonia (203.6 kcal/mol).[20] In contrast, phosphabenzene has a proton affinity nearly 30 kcal/mol less than trimethylphosphine while arsabenzene has a proton affinity at arsenic of at least 23 kcal/mol less than trimethylarsine. Extrapolation from the amine series suggests that the PA of phosphabenzene and arsabenzene are about 20 kcal/mol lower than expected.

We have previously suggested that the cause of the anomalously low basicity of the heavier heterobenzenes was due to a hybridization–geometric effect.[3,4,42] The CPC bond angle of phosphabenzene (101°)[43] and the CAsC bond angle of arsabenzene (99°)[44] imply a bond hybridization approaching p^3. The lone pair must be largely s hybridized. On protonation the lone pair must gain p character to take part in effective bonding. While acyclic phosphines and arsines are able to geometrically rearrange on protonation, the rigidity of the rings of phosphabenzene and arsabenzene may prevent large changes in CPC(CAsC) bond angles and may prevent rehybridization. Thus a strong PH(AsH) bond cannot form. In the case of pyridine, the CNC bond angle is 116°.[45] Since the lone-pair orbital is approximately sp^2 hybridized, little rehybridization energy is needed to form the sp^2-hybridized conjugate acid. Thus the proton affinity of pyridine is close to that of its acyclic relatives.

Although a similar argument has been used to explain the anomalous low basicity of phosphirane (where the bond angle constraints are very large),[46] application of this geometric argument to phosphabenzene has been controversial.[47] A recent theoretical study of the proton affinities

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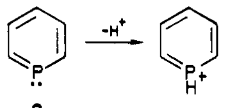
of molecules containing phosphorus-carbon multiple bonds has indicated that acyclic phosphaalkenes have low PA values similar to that of C_5H_5P.[36] These calculations suggest that the low basicity of the heterobenzenes may be due to the particular electronic character of carbon-phosphorus or (C-As) multiple bonds rather than a consequence of geometrical constraints. Since phosphaalkenes are now readily available,[48] an experimental determination of their PA is feasible and should answer this question.

Finally, it is interesting to speculate on the relation of phosphabenzene and its conjugate acid to the isoelectronic silicon compounds. Unlike phosphabenzene, silabenzene 12 is an extremely labile compound.[49,50] The observed low basicity of phosphabenzene suggests that silabenzene may be a strong acid. Perhaps the conjugate base of silabenzene 13 may even possess a kinetic stability that silabenzene does not have.



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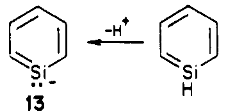

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Addition of Di-*p*-tolylcarbodiimide to Ditungsten Hexa-*tert*-butoxide. Preparation and Structure of $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$

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Ditungsten hexa-*tert*-butoxide reacts readily with di-*p*-tolylcarbodiimide, $CH_3C_6H_4NCNC_6H_4CH_3$, in toluene at 25 °C to afford in about 80% yield the moderately air-sensitive red-black adduct $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$. This product has been identified and characterized by NMR and X-ray crystallography. The molecule has the carbodiimide group bridging the W-W bond (2.482 (1) Å) and three $OCMe_3$ groups on each W atom, with effective symmetry C_2. The ^{13}C NMR indicates that in solution the molecule is either actually or effectively more symmetrical since the $OCMe_3$ groups form only two sets in 4:2 ratio. The crystalline compound belongs to space group *Pbca* with unit-cell dimensions a = 18.693 (4) Å, b = 17.739 (7) Å, c = 26.685 (8) Å, V = 8849 (3) Å^3, and Z = 8. The structure was refined to R = 0.045 and R_w = 0.058. The bonding of the carbodiimide molecule to the W-W unit is discussed, and a simple formulation that leaves a W-W double bond is proposed.

Introduction

We have been pursuing studies on the reactions between compounds containing metal-metal triple bonds (specifically $W_2(OCMe_3)_6$) and heterocumulenes (a-f) and allenes (g) in order to understand how these metallic and non-

$$\underset{a}{O{=}C{=}O} \qquad \underset{b}{O{=}C{=}NR} \qquad \underset{c}{RN{=}C{=}NR} \qquad \underset{d}{S{=}C{=}S}$$

$$\underset{e}{S{=}C{=}O} \qquad \underset{f}{S{=}C{=}NR} \qquad \underset{g}{R_2C{=}C{=}CR_2}$$

metallic unsaturated compounds interact. Cotton, Chisholm, and co-workers[1] have reported that allenes oxidatively add to $Cp_2M_2(CO)_4$ (M = Mo, W), and they also reported that the order of addition is as follows: $CH_2{=}C{=}CH_2 > MeCH{=}C{=}CH_2 > MeCH{=}C{=}CHMe$, but when $Me_2C{=}C{=}CH_2$ was used, no addition was observed across the M-M triple bond. Cotton, Chisholm, and coworkers also reported that CO_2 could insert into M-OR (M = W, Mo)[2] and W-NR_2[3] bonds to form either carbonato or carbamato bridging bidentate ligands, respectively. In our most recent work[4] we have reported that organic isocyanates insert into a M-OR (M = W, Mo) bond.

We now report on the reaction of a heterocumulene of type c, *p*-tolylcarbodiimide, with $W_2(OCMe_3)_6$.

Experimental Section

Ditungsten hexa-*tert*-butoxide was prepared[5] by Na/Hg reduction of WCl_4 in THF at -10 °C in the presence of $LiOCMe_3$, followed by recrystallization from hexane at -10 °C. Di-*p*-

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