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Halocyanophosphines, $P(CN)_yX_{3-y}$, and Related Cyanophosphine Derivatives

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Using pyridine and boron trifluoride as reference compounds and ^{31}P and ^{13}C NMR as reaction probes, we have shown that $P(CN)_3$ is acidic, $P(CN)_2(Ph)$ is essentially neutral, and $PCN(Ph)_2$ is slightly basic. It is known that $P(Ph)_3$ is a σ base. It was also possible to show that $P(CN)_2N(C_2H_5)_2$ is markedly basic; ^{13}C and ^{31}P parameters are given. Attempts to make $P(CN)_yCl_{3-y}$ by scrambling reactions, by replacement of $N(C_2H_5)_2$ with Cl by treatment of $P(CN)_2N(C_2H_5)_2$ with HCl, and by treating $P(CN)_3$ with HCl indicated that chlorocyanophosphines disproportionate at temperatures as low as −80 °C to give PCl_3 and $P(CN)_3$. This phenomenon is explained in terms of an intermolecular interaction which sets up the transition state for the scrambling process.

Introduction

Recent identification of dicoordinate phosphorus cations[1] and their use as ligands in organometallic compounds[2] prompted us to seek other types of phosphorus(III) compounds which might be converted to dicoordinate cations. The most stable noncyclic dicoordinate cation isolated so far has the general formula $[(R_2N)_2P]^+$. It has been postulated[1c] that the ion owes its stability, at least in part, to the pseudocarbene structure resulting from presumed $p\pi$–$p\pi$ bonding between nitrogen and phosphorus. In a search for simple groups other than $(CH_3)_2N$ to coordinate to phosphorus(III), the capacity of the group to form π bonds back to the open orbital on phosphorus seemed of paramount importance. The cyanide group seemed particularly attractive in this sense, and it offered the further possibility of generating a cation with two stable P–C multiple bonds. For this reason a study of the halocyanophosphines was initiated. The results were quite unexpected.

Although $P(CN)_3$ and PX_3, where X is a halogen, are well-known, the only known compound of general formula $P(CN)_yX_{3-y}$ is $P(CN)F_2$ made by Rudolph[3] in this laboratory in 1966. Although the compound undergoes significant disproportionation at −20 °C to give PF_3 and $P(CN)_3$, it has been unequivocally characterized. A number of other substituted cyanophosphines have been reported.[4] These include compounds of the general formula $P(CN)_2R$ where R can be an alkoxy, a dialkylamino, an alkyl, or an aryl group. In this paper we report attempts to prepare chlorocyanophosphines as well as studies on the acid–base reactions of $P(CN)_3$ and substituted cyanophosphines.

Attempted Preparation of $P(CN)_2Cl$. Three procedures have been used successfully in the preparation of mixed halophosphines; hence, their successful application with the pseudohalide CN^- was anticipated. The procedures are (1) scrambling reactions[5] of the form $2PX_3 + PY_3 \rightarrow 3PX_2Y$, (2) replacement reactions[6] where a dialkylamino group is replaced by a halogen in a process represented as $X_2PNR_2 + 2HY \rightarrow X_2PY + [NR_2H_2]Y$, and (3) a replacement reaction in which a weak acid such as HCN is eliminated through use of a strong acid. A typical equation would be $P(CN)_3 + HX \rightarrow P(CN)_2X + HCN$. In our experience $P(CN)_3$ and PCl_3 did not react in a scrambling reaction after 72 h at room temperature. Starting materials were recovered completely. The reaction of $P(CN)_2NR_2$ with HCl at room temperature for 0.5 h generated only PCl_3 and a trace of HCN as volatile products. No evidence could be found for $P(CN)_2Cl$. Finally, the reaction between $P(CN)_3$ and HCl at −80 °C for 10 min was carried out. The volatile materials which could be removed at −80 °C consisted of HCN, PCl_3, and HCl; the nonvolatile residue was $P(CN)_3$. These last results suggest quite clearly that $P(CN)_2Cl$ was generated at temperatures from −80 to 25 °C but underwent disproportionation to give PCl_3. Apparently $Cl_2P(CN)$ and $ClP(CN)_2$ are less stable than F_2PCN.[3]

Reactions of $P(CN)_3$. Reactions as a Lewis Base. Reactions of $P(CN)_3$ as a Lewis base would normally be anticipated. In 1968 Kirk and Smith[7] reported that a solid of composition $AlCl_3{\cdot}P(CN)_3{\cdot}0.8(C_2H_5)_2O$ was isolated when ether solutions of $AlCl_3$ and $P(CN)_3$ were mixed. A similar process was reported for $AlBr_3$. No structural data or further characterization of the products beyond analysis was given, but an acid–base reaction between acidic $AlCl_3$ and basic $P(CN)_3$ seemed reasonable. In 1972 Sabberwal and Burg[8] prepared $(CN)_3PCo(NO)(CO)_2$ and reported that the compound had some of the highest CO stretching frequencies yet observed. They drew the defensible conclusion that the $(CN)_3P$ molecule was "more effective than any previously studied ligands for attracting metal 3d electrons and so minimizing the interaction of such electrons with the CO antibonding orbitals". Evidence was presented to show that the coordination was through the phosphorus, and it was suggested that metal electrons would be delocalized through phosphorus into the antibonding orbitals of the CN group. Arguments of this type suggest that the lone pair of electrons in $P(CN)_3$, like those in PF_3, might have relatively little σ-bonding capacity. In such a case the π-acid capability of $P(CN)_3$ would be the dominant factor in its use as an organometallic ligand. Under these circumstances a relatively weak interaction of $P(CN)_3$ with acids such as BH_3 and $AlCl_3$ would be expected. In view of these arguments the reactions of $P(CN)_3$ with BH_3 and $AlCl_3$ were investigated by using NMR, IR, and possible product isolation as probes. All reactions were carried out in a vacuum system[9] with resublimed solids (i.e., $AlCl_3$ and $P(CN)_3$), very dry solvents, and purified B_2H_6. When reactions were run in solution, dry acetonitrile, nitromethane, and 2-nitropropane were most suitable as solvents for $P(CN)_3$. The material was not very soluble in dry diethyl ether. Two kinds of reaction procedures were used to determine the base strength of $P(CN)_3$. With

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(1) (a) S. S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972); (b) B. E. Maryanoff and R. O. Hutchins, *J. Org. Chem.*, **37**, 3475 (1972); (c) M. G. Thomas, C. W. Schultz, and R. W. Parry, *Inorg. Chem.*, **16**, 994 (1977).

(2) R. W. Montemayor, D. T. Sauer, S. S. Fleming, D. W. Bennett, M. G. Thomas, and R. W. Parry, *J. Am. Chem. Soc.*, **100**, 2231 (1978); D. W. Bennett and R. W. Parry, *ibid.*, **101**, 755 (1979).

(3) (a) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966); (b) G. G. Flaskerud, K. E. Pullen, and J. M. Shreeve, *Inorg. Chem.*, **8**, 728 (1969).

(4) C. E. Jones and K. Coskran, *Inorg. Chem.*, **10**, 1536 (1971).

(5) E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81**, 6363 (1959).

(6) R. G. Montemayor and R. W. Parry, *Inorg. Chem.*, **12**, 2482 (1973).

(7) P. G. Kirk and T. D. Smith, *Chem. Commun.*, 42 (1968).

(8) I. H. Sabberwal and A. B. Burg, *Inorg. Chem.*, **11**, 3138 (1972).

(9) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.

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Table I. Interaction of $P(CN)_3$ with σ-Type Lewis Acids and σ-Type Lewis Bases

A. NMR Data for Free $P(CN)_3$

solvent	$\delta\ {}^{31}P^{20}$	$\delta\ {}^{13}C$	J_{PC}, Hz	temp, °C
$NCCD_3$	−139.1	111.5	60.0	~25
$NCCD_3$	−139.2	112.5	60.8	~−38
H_3CNO_2	−132.8	109.5	54.1	~25
2-nitropropane	−133.1	110.3	58.9	25 (^{31}P) −77 (^{13}C)

B. NMR Data for $P(CN)_3$ with Acid ($AlCl_3$) and Bases (Pyridine, CN^-)

acid or base	solvent	$\delta\ {}^{31}P$	$\delta\ {}^{13}C$	J_{PC}, Hz	Δ-$\delta\ {}^{31}P$	Δ-$\delta\ {}^{13}C$
$AlCl_3$	$NCCD_3$	−139.2	111.6	61.2	0.1	0.1
pyridine	$NCCD_3$	−151.0	113.8	60.0	11.9	1.4
cyanide	$NCCD_3$	−192.7	*a*	*a*	53.6	*a*

[a] Peak for ^{13}C under solvent.

B_2H_6 the gas was frozen on top of solid $P(CN)_3$. The system was allowed to warm to room temperature and to stand for 18 h. At the end of that time 97% of the B_2H_6 could be recovered unchanged. Clearly $P(CN)_3$ is too weak as a σ base to give a BH_3 adduct which is stable at 25 °C.

The reaction between $AlCl_3$ and $P(CN)_3$ was studied in acetonitrile. After mixing equimolar quantities of $P(CN)_3$ and $AlCl_3$ in acetonitrile, we obtained the ^{31}P and ^{13}C NMR spectra. Data are shown in Table I. The essential identity of $\delta_{^{31}P}$, $\delta_{^{13}C}$, and J_{PC} for $P(CN)_3$ before and after adding $AlCl_3$ argues persuasively against any acid–base interaction between these reagents in acetronitrile and argues strongly *against* assigning significant σ-base character to $P(CN)_3$.[10]

Reactions of $P(CN)_3$ as a Lewis Acid. In 1969 Kirk and Smith,[11] following an earlier observation of Holmes and Wagner[12] on the addition reaction between PF_3 and $N(CH_3)_3$, showed that $P(CN)_3$ will add several bases such as pyridine, pyridine oxide, and triphenylphosphine oxide. They used ^1H NMR and IR spectroscopy as probes. We have now verified the pyridine–$P(CN)_3$ reaction by using ^{31}P and ^{13}C NMR techniques; we have obtained significant structural information and have established the existence of a new compound, $K[P(CN)_4]$.

The change in both ^{13}C and ^{31}P spectra when pyridine was added at room temperature to acetonitrile solutions of $P(CN)_3$ confirms the presence of reasonably strong interaction between $P(CN)_3$ and pyridine. Data are in Table IB. Since the shift in δ_P is large (12 ppm) compared to the shift in δ_C (1.4 ppm), it is quite clear that there is a direct P–py (py = pyridine) linkage. Since a change in δ_P can be correlated with changes in the CPC bond angle,[13] a five-coordinate trigonal bipyramid with two cyanide groups in the axial positions would be a logical structural choice, but rapid intramolecular exchange is indicated since only a single cyanide frequency is found in the ^{13}C spectrum. Since pure solid $P(CN)_3$ is known to belong to point group C_{3v} and to have a *nonlinear* P–CN linkage[14] and since Lee, Cohn, and Schwendeman[15] showed that gaseous PF_2CN has a *nonlinear* P–CN linkage, it would be expected that $P(CN)_3 \cdot py$ would belong to either point group C_s or C, depending on the geometry of the axial cyanides. In the infrared spectrum three almost equally intense C–N stretching frequencies were observed for the pyridine adduct. These appeared at 2170, 2050, and 2040 cm^{-1} and can be assigned to the equatorial C–N stretch (2040 cm^{-1}) and the asymmetric (2050 cm^{-1}) and symmetric axial C–N stretch (2170 cm^{-1}), in agreement with the trigonal-bipyramidal model proposed.[16] (The parent $P(CN)_3$ has ν_{CN} at 2206.) It is known that pure $P(CN)_3$ is associated in solution[17] and that in the solid state[14] nitrogen atoms are significantly closer to the phosphorus atoms than van der Waals distances. These facts suggest internal acid–base interactions, with phosphorus serving as the acid center and nitrogen as the base.[18]

As mentioned earlier, potassium cyanide will add to $P(CN)_3$ in acetonitrile solution to give $K[P(CN)_4]$. The cyanide carbon of $P(CN)_4^-$ was not observed in the ^{13}C NMR spectrum presumably because it was under the CN peak of the acetonitrile solvent. A downfield shift in the ^{13}C value would be expected for CN in $P(CN)_4^-$; hence, this position under the acetonitrile signal (~118 ppm) is reasonable. As seen in Table I, the phosphorus chemical shift value is 53.6 ppm more negative than that of the P in the original $P(CN)_3$. This shift is just opposite to that observed when the coordination around phosphorus changes from three chlorines in PCl_3 to four to give PCl_4^+. In that case the chemical shift changes to a more positive value. It should be remembered that in going from $P(CN)_3$ to $P(CN)_4^-$, symmetry changes from C_{3v} to C_s (time averaged), while in PCl_3 to PCl_4^+ the symmetry changes from C_{3v} to T_d. Charge changes are also opposite in sign; a cation is formed with PCl_3 and an anion with $P(CN)_3$.

The infrared spectrum of $K[P(CN)_4]$ shows peaks at 2195, 2160, 2097, and 2070 cm^{-1}, suggesting a distorted trigonal-bipyramidal structure. Assignments are 2195 (A_1, sym, ax), 2160 (A_1, sym, eq), 2097 (B_2, sym, ax), and 2070 cm^{-1} (B_1, sym, eq).[19]

Reactions of Substituted Cyanophosphines. Although compounds of the form $P(CN)Cl_2$ and $P(CN)_2Cl$ disproportionated rapidly, the compounds $P(CH)Ph_2$, $P(CN)_2Ph$, and $P(CN)_2[N(C_2H_5)_2]$ are known.[4] The acid–base character and NMR characteristics of these compounds were determined as a part of this study. Triphenylphosphine is known to be a Lewis base, forming complexes with BF_3[18a] and BH_3.[18b] Thus, substitution of cyanides by phenyls should give rise to an

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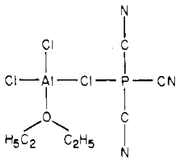
(10) The question of the nature of the solid of composition $AlCl_3 \cdot P(CN)_3 \cdot Et_2O$ reported in an earlier study remains unanswered by these data. It is possible, on the basis of the acidic character of $P(CN)_3$, that the product could be a bridge structure of the form



More data are needed. We feel quite confident, however, that the product is not a conventional Lewis acid–base adduct.

(11) P. G. Kirk and T. D. Smith, *J. Chem. Soc.* A, 2190 (1969).

(12) R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, 2, 384 (1963).

(13) D. Purdella, *J. Magn. Reson.*, **6**, 23 (1971).

(14) K. Emerson and D. Britton, *Acta Crystallogr.*, **17**, 1134 (1964).

(15) P. L. Lee, K. Cohn, and R. Schwendeman, *Inorg. Chem.*, **11**, 917 (1972).

(16) The assignment given is based on the trigonal-bipyramidal model with two axial CN groups, one equatorial CN, one equatorial pyridine, and one equatorial electron pair. This geometry is based on the assumption that the CN groups will occupy axial positions. For example, in $Ni(CN)_2L_3$, where L is $PPh(OET)_2$, the phosphorus ligands are equatorial while the cyanides are axial [J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084 (1969)]. The spectral assignments are based on modified metal carbonyl analogies. In $LFe(CO)_4$ there is less than maximum mixing of the two A_1 modes. The lower frequency of the A_1 bands corresponds principally to the vibration of the axial carbonyl: P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, New York, 1975. In the geometry assumed here, the equatorial ligand because of its short P–C distance is assumed to have the lowest frequency C–N mode, i. e., P=C=N. Thus the equatorial C–N is assigned at 2040 cm^{-1}. The asymmetric axial CO is assigned at 2050 cm^{-1}, and the symmetric axial is assigned at 2170 cm^{-1} by analogy to CO spectra where the symmetric mode is usually higher than the asymmetric mode.

(17) P. G. Kirk and T. D. Smith, *J. Inorg. Nucl. Chem.*, **30**, 892 (1968).

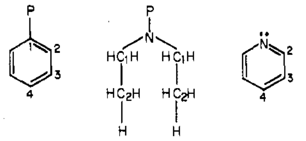
(18) D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963).

(19) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959); B. M. Graybill and J. K. Ruff, *J. Am. Chem. Soc.*, **84**, 1062 (1967).

Table II. NMR Data for Phenyl and Diethylamido Derivatives of Tricyanophosphine and Their Acid or Base Adducts[a]

	$(Ph)P(CN)_2$	$(Ph)P(CN)_2$ + py	$(Ph)P(CN)_2$ + BF_3	$(Ph)_2$-P(CN)	$(Ph)_2P(CN)$ + py	$(Ph)_2$-P(CN) + BF_3	$Et_2NP(CN)_2$	Et_2NP-$(CN)_2$ + py	Et_2NP-$(CN)_2$ + BF_3
δ_P	−75.5	−77.0	−75.2	−35.7	−35.8	−33.3	−13.5	−13.4	58.0
J_{P-C}	60.9	61.1	61.8	67.1	67.3	83.6	74.9		
$\delta_{C(CN)}$	113.7	114.1	113.7	121.0	121.0	122.2	116.5		
$\delta_{C_1}{}^d$	119.6	120.1[b]	120.2	129.8	129.8[b]	127.0	47.5		
J_{P-C_1}	60.9			5.2	5.1,[b]	5.1	17.3		
$\delta_{C_2}{}^d$	135.0	134.7,[b] 149.4[c]	135.3	133.2	133.2,[b] 149.7[c]	133.7	13.7		
J_{P-C_2}	26.2	26.1[b]	26.3	21.8		22.3	4.7		
$\delta_{C_3}{}^d$	130.3	130.1,[b] 123.6[c]	130.8	129.2	129.3,[b] 123.7[c]	129.8			
J_{P-C_3}	10.5	10.8[b]	10.3	8.4	7.9[b]	8.5			
$\delta_{C_4}{}^d$	133.6	133.3,[b] 135.9[c]	134.1	130.6	130.6,[b] 135.9[c]	131.7			

[a] Solvent was $CDCl_3$ and $T = 25$ °C. [b] Ph. [c] py. [d] Subscripts on carbons are as indicated below:



increase in base strength of the phosphine. As the data in Table II show, such a change from acidic character to basic character is seen. The NMR parameters for the compound $PhP(CN)_2$ in $CDCl_3$ (Table II, column 1) are essentially identical with those measured for the same compound in the presence of BF_3, (Table II, column 3); thus, there is essentially no basic character to $PhP(CN)_2$. Similarly, the parameters for the molecule in the presence of pyridine show only marginal change from those of the pure compound. Very slight acidic character is suggested, but the molecule has surprisingly little σ-bonding capability. On the other hand, the NMR parameters for the molecule Ph_2PCN (column 4) are quite markedly changed (note: $\Delta\delta_P$ 2.4 and $\Delta J_{P-C} = 16$) when BF_3 is added (column 6) to the system, and these parameters remain unchanged when pyridine is added (column 5); thus, $Ph_2P(CN)$ is clearly basic in character.

The molecule $(C_2H_5)_2NP(CN)_2$ is quite strongly basic (column 8) in comparison to $(Ph)_2P(CN)$. It shows no acidic properties (column 7). This fact can be rationalized in terms of the availability of the free electron pair on the NR_2 group and its propensity for a π interaction with the phosphorus, thus making the free electron pair on the phosphorus more available for σ bonding. The very low electron-donating ability of the cyanide group, despite the availability of π electrons, stands in dramatic contrast to the behavior of the NR_2 groups.

The NMR data show a fall in δ_P[20] (δ values in parentheses) in the series $P(Ph)_3$ (−5.9), $P(Ph)_2CN$ (−35.7), $P(Ph)(CN)_2$ (−75.5), and $P(CN)_2$ (−139.1). The shift is opposite in direction to that seen for the series $P(Ph)_3$ (−5.9), $P(Ph)_2Cl$ (+80), $P(Ph)Cl_2$ (+162), and PCl_3 (+215). In the $P(CN)_y$-$(Ph)_{3-y}$ series, changes in bond angles[21] are expected since $P(Ph)_3$ has a value of 102° and $P(CN)_3$ has an average angle in the solid of 93°. The chloride PCl_3 has almost the same angle (101°) as $P(Ph)_3$ (102°). The carbon shifts for the phenylcyano compounds may be compared with those for the phenylchloro compounds. The C_1 aryl carbon (bonded directly to P) shows a lower δ_C value as cyanides replace phenyls. The reverse is seen when chlorides replace phenyls. The C_2 carbons (ortho) show a similar but opposite trend, a higher δ_{C_2} as cyanides replace phenyls; chloride replacement makes δ_{C_2} lower.

The strong tendency for $P(CN)_2Cl$ and $P(CN)Cl_2$ to disproportionate was not anticipated, particularly since $P(CN)Ph_2$ and $P(CN)_2NR_2$ are known species. One possible explanation for the instability of $P(CN)_2Cl$ involves the external cyanide–phosphorus interaction comparable to that seen in $P(CN)_3$. Presumably, any constituent which withdraws electron density from the phosphorus reduces its basic character and increases its acidity. Despite its lone electron pair, PCl_3 (δ 2150)[20] is essentially ineffective as a Lewis base. Accepting this premise, one notes that replacing one CN group on $P(CN)_3$ by a chloride should increase the acidic character of the phosphorus and increase the intermolecular interaction with other cyanide groups. Such association would build the transition complex in which disproportionation can occur. The phenyl and diethylamido groups, which increase the basic character and reduce the acid character of the phosphorus, would not promote the formation of the transition complex. Isolation of the mixed species would be expected and was observed. The molecule $PF_2(CN)$ might owe its very limited stability to back-donation from fluorine to phosphorus in a way which retards somewhat the development of acid character on the phosphorus atom.

Experimental Section

General Methods. Standard vacuum-line procedures were used,[9] and all solvents were carefully dried. NMR spectra were obtained on a Varian XL-100 spectrometer operating at 25.2 MHz for carbon and 40.4 MHz for phosphorus. Spectra were obtained in the FT mode by using a pulse of 100–110 μs. Sample tubes were 12 mm in diameter and were rotated. Tetramethylsilane was used as the internal standard for carbon and 85% H_3PO_4 as an external standard for phosphorus. As recommended by IUPAC,[20] a chemical shift *downfield* of the standard is given a positive sign.

Infrared spectra were obtained on a Beckman IR-20 using a scale-expansion mode.

Sources of Materials. The following materials were prepared by literature methods: $P(CN)_3$,[4,22] $P(CN)_2(Ph)$,[4] $P(CN)(Ph)_2$,[4] $P(CN)_2N(C_2H_5)_2$.[4] All other materials, $(Ph)_2PCl$, $(Ph)_2PCl$, $(Ph)_3P$, PCl_3, $HN(C_2H_5)_2$, $AlCl_3$, BF_3, etc., were commercial products.

Attempted Preparation of $Cl_xP(CN)_{3-x}$. Three processes were tried. In the scrambling reaction 0.800 g of $P(CN)_3$ (7.34 mmol) and a

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(20) Assignments for $P(CN)_4^-$ are based on a modification of the spectrum of equatorial $LFe(CO)_4$. Frequencies given by D. Darensbourg, H. H. Nelson, III, and C. L. Hyde, *Inorg. Chem.*, **13**, 2135 (1974), for equatorial $LFe(CO)_4$ are A_1 (sym, eq), A_1 (sym, ax), B_2 (asym, eq), and B_1 (asym, ax). Because the axial distance in $P(CN)_4^-$ is assumed to be the longer while in $LFe(CO)_4$ the axial distance is known to be shorter, axial and equatorial assignments are reversed. We thus assume the following sequence for $P(CN)_4^-$ in order of decreasing energy: A_1 (sym, ax), A_1 (sym, eq), B_1 (asym, ax), B_2 (asym, eq).

(21) The newly recommended IUPAC convention for ^{31}P chemical shift is now used; a chemical shift downfield of the reference signal is positive: *IUPAC Inf. Bull.*, No. **38** (1974).

(22) J. R. Van Wazer, and J. H. Letcher in "Topics in Phosphorus Chemistry", Vol. 5, M. Grayson and E. J. Griffith. Eds., Wiley-Interscience, New York, 1967, Chapters 2 and 4.

(23) P. A. Stoats and H. W. Morgen, *Inorg. Synth.*, **6**, 84 (1960).

0.500-g sample of PCl_3 (3.65 mmol) were combined under vacuum and allowed to stand at 25 °C. After 72 h the materials were fractionated by trap-to-trap distillation. The more volatile fraction was 0.500 g of PCl_3. In a second experiment $P(CN)_3$ (~2 mmol) was combined with PCl_3 (~2 mmol) in 2.5 cm^3 of dry CD_3CN. The reaction was followed by ^{31}P NMR. Only signals for starting materials were ever detected.

In the second process the reaction between $(C_2H_5)_2NP(CN)_2$ and HCl was carried out on the vacuum line of a 100-mL flask. A 5.00-g sample of $P(CN)_2N(C_2H_5)_2$ (32.7 mmol) was frozen with a 65.4-mmol sample of HCl at −196 °C and then allowed to warm to 25 °C. After 0.5 h the volatiles were removed, fractionated, and identified by infrared spectroscopy. Only PCl_3 and a trace of HCN could be identified.

The third process involved the reaction of $P(CN)_3$ with HCl. In a 100-mL flask was frozen a 0.72-g sample of $P(CN)_3$ (6.6 mmol) (−196 °C) with a 7.3-mmol sample of HCl. The system was warmed to −78 °C, allowed to stand 10 min at −78 °C, and then fractionated through a trap at −196 °C to remove the volatiles. Trapped volatiles were identified by IR as PCl_3, HCl, and HCN. Finally, the nonvolatile residue was identified as $P(CN)_3$.

Reactions of $P(CN)_2N(C_2H_5)_2$ and $P(CN)_3$ with B_2H_6. A 0.18-g sample of $P(CN)_3$ (1.4 mmol) was frozen (−196 °C) with a 0.77-mmol sample of B_2H_6 on the vacuum line. The system was warmed to 25 °C, allowed to sit for 18 h, and then fractionated on the vacuum line. A 0.74-mm sample of B_2H_6 was recovered unchanged.

A 0.520-g sample of $P(CN)_2N(C_2H_5)_2$ (3.35 mmol) was frozen (−196 °C) on the vacuum line with a 1.83-mmol sample of B_2H_6. The system was warmed to 25 °C and allowed to stand for 18 h, and then the volatiles were removed. A 0.100-mmol sample of B_2H_6 was identified as the volatile component by IR. Thus, a 1.73-mmol sample of B_2H_6 had reacted with 3.35 mmol of $P(CN)_2N(C_2H_5)_2$.

Reactions of Cyanophosphines with Pyridine and BF_3. Approximately a 2.0-mmol sample of the desired cyanophosphine was dissolved in 2.5 mL of $CDCl_3$ in an NMR tube. In a separate tube a similar solution of the cyanophosphine in $CDCl_3$ was treated with either 2.0 mmol of pyridine or 2.0 mmol of BF_3. NMR spectra were then run on the samples.

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Registry No. $P(CN)_3$, 1116-01-4; $P(CN)_2(Ph)$, 2946-59-0; $P(CN)(Ph)_2$, 4791-48-4; $P(CN)_2N(C_2H_5)_2$, 33326-16-8; $K[P(CN)_4]$, 73104-89-9; pyridine, 110-86-1; BF_3, 7637-07-2; B_2H_6, 19287-45-7; $P(CN)_3$·py, 73104-90-2.

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Photoconversion of Norbornadiene to Quadricyclene in the Presence of a Copper(I) Carbonyl Compound[1]

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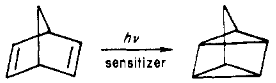
A detailed study of the thermal and photochemical behavior of $Cu[HB(pz)_3](CO)$ [$HB(pz)_3^-$ is hydrotris(1-pyrazolyl)borate] in the presence of norbornadiene (NBD) is reported. In solution NBD displaces CO from the coordination sphere of copper to produce a new complex formulated as $Cu[HB(pz)_3](NBD)$. This ground-state process is readily discernible by a shift in the absorption spectrum of the system to longer wavelengths. Irradiation of the complex with 313-nm light induces the valence isomerization of norbornadiene to quadricyclene with high quantum efficiency. The occurrence of this pathway is explicable in terms of the bonding changes that result from populating an excited state possessing Cu–NBD charge-transfer character.

Introduction

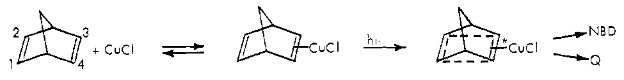


(1)

NBD Q

The photosensitized valence isomerization of norbornadiene, NBD, to quadricyclene, Q (eq 1), continues to be of interest as a model for photochemical energy storage.[2] Recently we reported that simple copper(I) salts, most notably cuprous chloride, function as effective sensitizers for this transformation.[3] Detailed spectral and mechanistic studies led us to assign a 1:1 ClCu–NBD complex as the key photoactive species in the system. As depicted in Scheme I, the immediate consequence of irradiating the intense metal–olefin charge-transfer band in the complex is to weaken the bonding between carbon atom pairs C_1–C_2 and C_3–C_4 while enhancing that between C_1–C_4 and C_2–C_3.[4] These photoinduced changes generate a reactive organic substrate which, upon relaxation, returns to NBD or completes the structural reorganization necessary to form Q.

Scheme I



In searching for new types of Cu(I) sensitizers for the NBD to Q conversion, we became intrigued by the reported properties of $Cu[HB(pz)_3](CO)$[5,6] [Figure 1; $HB(pz)_3^-$ is hydro-

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[1] Photobehavior of Copper(I) Compounds. 2. Part 1: Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1979**, *101*, 4228.

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[3] (a) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677. (b) In the present context, a sensitizer is a compound which enhances the rate of the photoconversion of NBD to Q, with at least one photon being required per product molecule formed. The detailed mechanism of sensitization will depend upon the nature of the sensitizer involved. Grutsch, P. A.; Kutal, C. *Adv. Chem. Ser.* **1979**, *No. 173*, 325.

[4] These bonding changes occur regardless of the direction (metal to olefin or olefin to metal) of charge transfer: (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1; (b) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719; (c) Jones, G.; Chiang, S.-H.; Xuan, P. T. *J. Photochem.* **1979**, *10*, 1.

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