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R. H. Holm,* B. A. Averill, T. Herskovitz

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

R. B. Frankel

Francis Bitter National Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

H. B. Gray, O. Siiman, F. J. Grunthaler

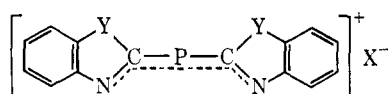
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California Institute of Technology
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The Bis(dimethylamido)phosphinium Cation with a $p_\pi-p_\pi$ Multiple Bond between Phosphorus and Nitrogen Atoms

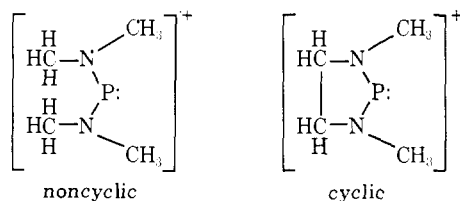
Sir:

In 1964 Dimroth and Hoffman¹ synthesized the first authentic compound containing a $p_\pi-p_\pi$ phosphorus-carbon double bond. This type of substance named as a phosphamethinecyanine, was represented as

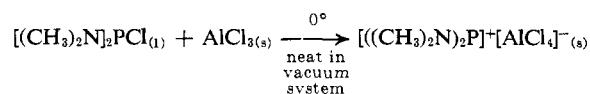


where $X^- = ClO_4^-$ and BF_4^- and Y is S or NR. Unstable tris(hydroxymethyl)phosphine and *N*-ethyl-2-chlorobenzothiazolium tetrafluoroborate served as starting materials.

We have found that the reaction between bis(dimethylamino)chlorophosphine and aluminum(III) chloride gives a one to one adduct which has an unexpected ionic structure $[(CH_3)_2N]_2P^+[AlCl_4]^-$. The compound also contains a two-coordinate phosphorus cation which shows unequivocal evidence for a multiple $p_\pi-p_\pi$ bond between phosphorus and nitrogen atoms. The corresponding $[(R_2N)_2P]^+[PF_6]^-$ and $[(R_2N)_2P]^+[B_2F_7]^-$ have also been prepared and characterized. An analogous cyclic cation was first reported in a definitive paper by Fleming, Lupton, and Jekot;² the cyclic and noncyclic structures represented below show marked formal similarities but rather striking differences in product properties.

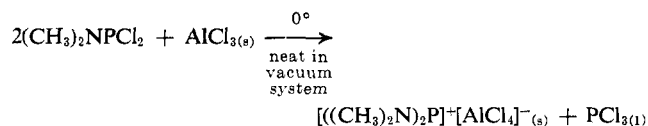


The noncyclic compound $[(CH_3)_2N]_2P^+[AlCl_4]^-$ can be prepared by either of the following reactions.



(1) K. Dimroth and P. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **3**, 384 (1964); R. A. Allman, *Angew. Chem.*, **77**, 134 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 150 (1965).

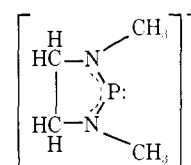
(2) S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972).



The product is a homogeneous white waxy solid which is extremely sensitive to attack by water at both the P-N and the Al-Cl bonds. The compound decomposes above 65° to give equiformal quantities of Cl_2PNR_2 and $(Cl_2AlNR_2)_n$ in a nonreversible reaction. Although some crystals of (this compound) have been obtained in a vacuum system, we have not yet been able to load a crystal for X-ray study. Even though the gross features of the structure are unambiguously established by the data noted below, an X-ray structure would still provide very significant details and is being pursued.

The adduct is soluble in CH_2Cl_2 . The conductivity of the adduct is approximately 50% of that of a similar solution of $[N(CH_3)_3]^+[AlCl_4]^-$ and more than 100 times greater than a CH_2Cl_2 solution of either $AlCl_3$ or $[(CH_3)_2N]_2PCl$. An ionic structure is clearly indicated. The ionic formulation is also indicated by the infrared spectrum. The N_2P-Cl stretching vibration (mostly P-Cl) is clearly apparent in a CH_2Cl_2 solution of $ClP[N(CH_3)_2]$ at 670 cm^{-1} . In a methylene chloride solution containing equimolar quantities of dissolved $[(CH_3)_2N]_2PCl$ and $AlCl_3$ the P-Cl stretching frequency at 670 cm^{-1} disappears and a strong frequency at 490 cm^{-1} , attributable to the nonsymmetric Al-Cl stretching frequency of $AlCl_4^-$ (ν_3), appears. Other details of the spectrum are also consistent with the ionic formulation.

The nmr spectra for 1H , ^{31}P , and ^{13}C (and ^{19}F for $[PF_6]^-$) are all consistent with the ionic structure and provide unequivocal evidence for restricted rotation about the P-N bond in the cation and thus for a delocalized electronic structure involving a clear $p_\pi-p_\pi$ P-N multiple bond. The free energy for rotation is 14.2 kcal based upon the variation of the 1H spectrum with temperature.³ The ΔH^\ddagger is about 10.3 kcal/mol. The ΔG^\ddagger and ΔH^\ddagger values are also confirmed by the variation of the ^{13}C spectrum with temperature. The proton spectrum at -50° consists of two equal area doublets at δ 2.13 (CH_2Cl_2) ($J_{PNCH} = 14.1$ Hz) and δ 1.97 ($J_{PNCH} = 5.0$ Hz). As the temperature is raised to 30° this becomes a single doublet at δ 2.06 ($J_{PNCH} = 9.6$ Hz). The carbon-13 spectrum shows two doublets at -20°, δ 52.46, ($J_{PNCH} = 6.25$ Hz) and δ 54.64, $J = 19.5$ Hz, that collapses to one doublet at 57°, δ 53, $J = 12.9$ Hz. The onset of rotation about the P-N bond is blocked in the cyclic cation



and the cyclic ion spectrum is not temperature dependent in the range -30° to +30°. It is significant that the cyclic cation shows a doublet for CH_2 at δ 2.10 ($J_{PNCH} = 11.0$ Hz) and a doublet for CH_3 at δ 1.37 ($J_{PNCH} = 5$ Hz). Both cyclic and noncyclic cations show a ^{31}P singlet at

(3) Max T. Rogers and James C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

ca. -264 (OPA) which is characteristic of the strongly deshielded ^{31}P atom in the cation.

The noncyclic cation may be compared in some sense to the allyl radical which has a bonding ($\alpha + 1.41\beta$), a nonbonding (α), and an antibonding π orbital ($\alpha - 1.41\beta$).

Applying the usual first-order corrections for energy differences in the p levels of N and P atoms one again obtains the expected bonding level

$$E = \alpha - \left(\frac{\lambda - \sqrt{\lambda^2 + 8}}{2} \right) \beta$$

nonbonding

$$E = \alpha$$

and the antibonding level

$$E = \alpha - \left(\frac{\lambda + \sqrt{\lambda^2 + 8}}{2} \right) \beta$$

where α = the Coulomb integral of the nitrogen atom, β = the $\text{N}_{2p}-\text{P}_{3p}$ overlap integral, and $(\alpha - \lambda\beta)$ is the Coulomb integral of the phosphorus atom. The bonding and nonbonding levels are filled. The photochemistry of the ion system is under investigation.

The cation is both a Lewis acid and a Lewis base. It has a rather rich chemistry which will be delineated in subsequent reports. For example, very small amounts of the noncyclic cation in a solution containing the PF_6^- ion will make the ^{31}P spectrum of the normally stable PF_6^- ion collapse to a broad single peak at room temperature. The cyclic cation does not bring about this labilization of fluorines on the PF_6^- ion. Other sharp differences associated with the onset of rotation around the P-N bond will be outlined.

M. G. Thomas, R. W. Kopp
C. W. Schultz, R. W. Parry*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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Novel Cyclic Carbene Complexes of Iron

Sir:

It is well known that isocyanides coordinate to a variety of transition metals.¹ One of the current interests in the coordination chemistry of isocyanides has been focused on the insertion reaction.^{2,3} Studies on this subject have been done in several laboratories.

During our extensive studies on the insertion reactions of alkyl iron complexes with isocyanides, we found new carbene complexes which resulted from unexpected insertion of isocyanide into the C-H bond of an alkyl group. In this communication we report the new finding and give the revised structure for "tris imino type complexes"⁴ obtained from dicarbonyl- π -cyclopentadienylbenzyliron and cyclohexyl isocyanide.

When the bis imino type complex **1**⁵ is treated with

(1) L. Malatesta and F. Bonati, "Isonitrile Complexes of Metals," Wiley, New York, N. Y., 1969.

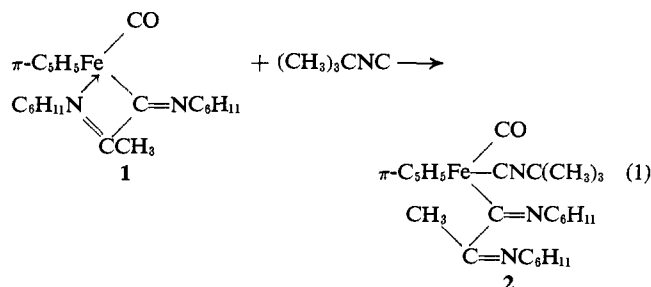
(2) Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, **8**, 225 (1972).

(3) P. M. Treichel, *Advan. Organometal. Chem.*, **11**, 21 (1973).

(4) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **11**, 211 (1972).

(5) Compound **1** can be prepared by two different methods: (1) the photochemical reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CNC}_6\text{H}_{11})\text{COCH}_3$ and

tert-butyl isocyanide in benzene at 40° for 8 hr, the reaction results in elimination of the coordinated nitrogen atom and coordination of an incoming isocyanide to the iron atom, giving **2**⁶ (eq 1). On treat-



ment of **2** in benzene at 70° for 38 hr, the reddish brown crystals, **3**, having the same empirical formula as that of **2** are formed and characterized by the absence of a coordinated isocyanide group in its infrared spectrum.

Crystals of **3** belong to the monoclinic space group $P2_1/c$. Unit cell data are $a = 11.732$, $b = 10.380$, $c = 22.831$ Å, $\beta = 112.97^\circ$, and $Z = 4$. A crystal of dimensions $0.1 \times 0.3 \times 0.7$ mm was mounted on the c axis, and the 3298 reflections having $F_o > 3\sigma(F_o)$ and $2\theta < 130^\circ$ were collected using Cu $K\alpha$ radiation and a four-circle diffractometer. The position of the Fe atom was determined by a Patterson method using the Harker line and sections, and the H, C, N, and O atoms appeared in successive electron-density maps. The final unweighted R value was 0.064. Distances and angles in the novel chelate system appear in Figure 1. The five-membered ring containing the iron atom is essentially planar with N(1), N(2), and N(3). The C(3)-C(4), C(2)-N(2), and C(4)-N(3) bond lengths are shorter than expected for normal single bonds, and the C(2)-C(3) bond length is longer than that found for the normal double bond, indicating the existence of a π system involving mainly the N(2)-C(2)-C(3)-C(4)-N(3) atoms. The complex is considered as a kind of carbene complex. The Fe-carbene carbon(4) distance of 1.926 (5) Å is similar to the Fe-C(1) σ -bonded length of 1.973 (5) Å and is relatively shorter than the Fe-C(carbene) distances of 2.02 and 2.03 Å reported for the carbene complex⁷ $[(\text{CH}_3\text{NC})_4\text{Fe}(\text{C}_2\text{N}_2)(\text{CH}_3)_3\text{H}_2] \cdot [\text{PF}_6]_2$.

The proton nmr spectrum of **3** is consistent with the X-ray structure determination and provides evidence for the location of protons. The spectrum consists of resonances at τ 8.57(singlet, $(\text{CH}_3)_3\text{C}$), 7.6-9.2(broad, C_6H_{10}), 6.4-7.2(b, C_6H), 5.67(s, C_3H_5), 4.15(s, CH), and 2.9-3.2(b, NH). The resonance due to two NH protons disappears on treatment with D_2O .

An apparent insertion of an incoming reagent into the C-H bond rather than into the Ru-C bond has been noted in the reaction of $\pi\text{-C}_5\text{H}_5\text{Ru}(\text{PPh}_3)_2[\text{C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$.⁸

It is less easy to rationalize the mechanism of formation of the carbene complex. Although there is no

(2) the photochemical reaction between $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CNC}_6\text{H}_{11})\text{COCH}_3$ and $\text{C}_6\text{H}_{11}\text{NC}$. The elemental analysis and the spectroscopic studies are in agreement with the proposed structure.

(6) The elemental analysis and the mass spectrum gave satisfactory results.

(7) J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **93**, 4613 (1971).

(8) T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Commun.*, 852 (1971).