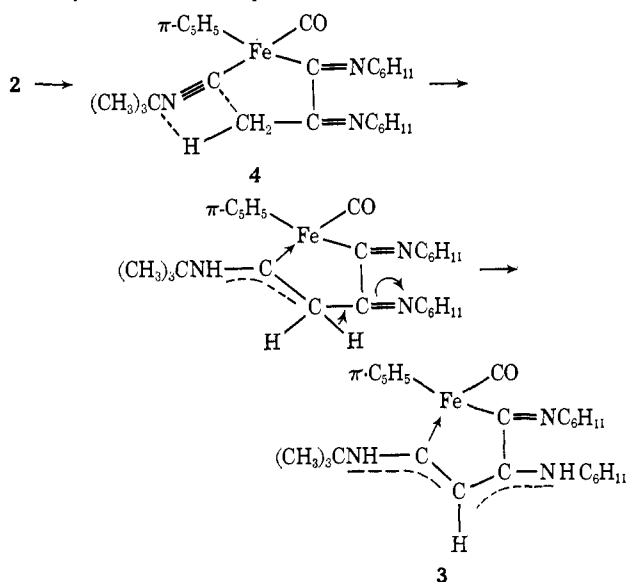


Figure 1. Distances and angles within the chelate ring of the compound **3**: (○) Fe; (○) C; (●) N; () O; () C₆H₅; () C₆H₁₁; () (CH₃)₃C. H atoms are not shown.

direct evidence for this type of reaction, the reaction involves a nucleophilic attack of an acidic C-H group of the methyl group on slightly polarizably coordinated isocyanide. The reaction presumably proceeds through a concerted mechanism with formation of a four-centered intermediate, **4**, and is followed by transfer of a proton onto the imino nitrogen atom (Scheme I).

Scheme I. Proposed Mechanism for Formation of the Cyclic Carbene Complex.



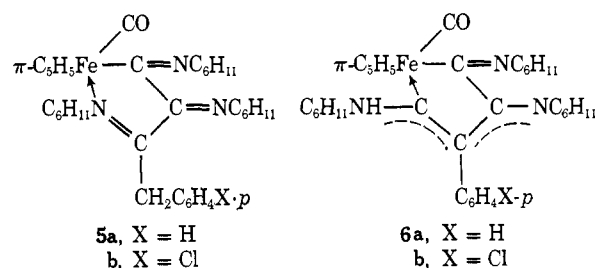
It has already been demonstrated that the addition of protonic substances to the coordinated isocyanide in metal-isocyanide complexes gives the carbene complexes.^{9,10}

The aforementioned result promoted us to reexamine the complexes (**5a** and **5b**) obtained from the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_4\text{X}-p$ (X = H or Cl) and C₆H₁₁NC, which we had identified as the "tris imino type complexes".⁴ We found that the resonances at τ 3.27 (doublet) for X = H and at 3.38 (d) for X = Cl,

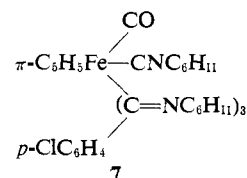
(9) (a) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 345 (1972); (b) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972).

(10) B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, *Inorg. Chem.*, **11**, 1292 (1972).

assigned incorrectly as the benzylic methylene protons, respectively, disappear on treatment with D₂O, attributable to the N-H group. We revise the structure of the compounds (**5a** and **5b**) as **6a** and **6b**.



The compounds (**6a** and **6b**) can be prepared from the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{CH}_2\text{C}_6\text{H}_4\text{X}-p$ (X = H or Cl)¹¹ with C₆H₁₁NC. It is of interest to note that $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{C}_6\text{H}_4\text{Cl}-p$ ¹² bearing no alkyl protons undergoes an expected multiple insertion to afford the tris imino type complex, **7**, when treated



with C₆H₁₁NC in benzene at 70°. Formation of the cyclic carbene complexes appears to be generalized in the reactions of the compound bearing the alkyl protons with isocyanides. Further studies are now in progress.

(11) This compound can be prepared from the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{I}$ with the corresponding Grignard reagent.

(12) This compound is obtained by the photoassisted decarbonylation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{COC}_6\text{H}_4\text{Cl}-p$.

Yasuhiro Yamamoto,* Katsuyuki Aoki, Hiroshi Yamazaki
The Institute of Physical and Chemical Research
Wako-shi, Saitama, Japan
Received October 27, 1973

Detection of Rotational Isomerism in Diphosphines and Diarsines by Photoelectron Spectroscopy

Sir:

The stereochemistry of hydrazines¹ and their heavier congeners^{2,3} has been a subject of interest for 4 decades. With few exceptions⁴ acyclic hydrazines pref-

(1) For some representative articles see (a) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934); (b) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973); (c) S. F. Nelsen, J. M. Buschek, and P. J. Hintz, *ibid.*, **95**, 2013 (1973); (d) M. J. S. Dewar and W. B. Jennings, *ibid.*, **91**, 3655 (1969).

(2) See, for example, (a) J. R. Durig and J. S. DiYorio, *Inorg. Chem.*, **8**, 2796 (1969); (b) J. D. Witt, J. W. Thompson, and J. R. Durig, *ibid.*, **12**, 811 (1973); (c) A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.*, **66**, 2732 (1970); (d) J. R. Durig, and R. W. MacNamee, *J. Mol. Struct.*, **17**, 426 (1973).

(3) (a) M. Green and D. Kirkpatrick, *Chem. Commun.*, **57** (1967); (b) J. R. Durig and J. M. Casper, *J. Chem. Phys.*, **55**, 198 (1971); (c) J. W. Thompson, J. D. Witt, and J. R. Durig, *Inorg. Chem.*, **12**, 2124 (1973).

(4) (a) P. Rademacher, *Angew. Chem., Int. Ed. Engl.*, **12**, 408 (1973); (b) C. B. Colburn, F. A. Johnson, and C. Hanvey, *J. Chem. Phys.*, **43**, 4526 (1965); (c) J. R. Durig and J. W. Clark, *ibid.*, **48**, 3216 (1968); (d) D. F. Koster and F. A. Müller, *Spectrochim. Acta, Part A*, **24**, 1487 (1968); (e) M. J. Cardillo and S. H. Bauer, *Inorg. Chem.*, **8**, 2086 (1969).

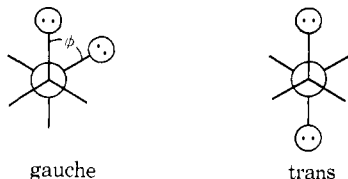
Table I. PES Ionization Potential^a Data

Compound	% abundance	Lone pair IP's	Δ	Av lone pair IP	P-P or As-As	P-C or As-C
gauche (CH ₃) ₄ P ₂	16	8.79		8.79	10.33	11.22, 11.83
trans (CH ₃) ₄ P ₂	84	7.88, 9.54	1.66	8.71	10.33	11.22, 11.83
gauche (CH ₃) ₄ As ₂	12	8.85		8.85	9.82	10.60, 11.21
trans (CH ₃) ₄ As ₂	88	7.91, 9.50	1.59	8.70	9.82	10.60, 11.21
gauche (CF ₃) ₄ P ₂	10	11.57		11.57	13.09	13.49
trans (CF ₃) ₄ P ₂	90	10.71, 12.11	1.45	11.44	13.09	13.49
trans (CF ₃) ₄ As ₂	100	10.39, 11.94	1.55	11.17	12.07	12.58
(CH ₃) ₂ PH	100	9.13		9.13		11.75
(CH ₃) ₂ AsH	100	9.14		9.14		11.16, 11.54
(CF ₃) ₂ PH	100	11.51		11.51		13.22

^a Vertical ionization potentials in electron volts.

erentially adopt the gauche⁵ conformation. However, the stereochemistry of diphosphines² and diarsines³ is of particular interest since the gauche and trans rotamers appear to be of comparable energy. The purpose of the present communication is to report the detection of rotational isomers in P-P and As-As compounds by means of photoelectron spectroscopy (PES). It is felt that PES offers a great promise as a tool for the rapid assay of rotational isomerism in acyclic species containing adjacent electron pairs.

In A₂X₄ molecules the interaction between the A lone pairs is anticipated to exhibit a dependence on the dihedral angle, ϕ , such that the lone pair splittings (Δ) should be trans \gg gauche.⁶



In (CH₃)₄P₂ (Figure 1a) peaks I₁ and I₃ can be assigned to the n₊ and n₋ phosphorus lone pair combinations. The remaining peak (I₂) in the lone pair region is therefore ascribed to the gauche rotamer. Note that this interpretation differs from that presented for certain cyclic hydrazines where the gauche splitting is ~ 0.5 eV with one component hidden under a trans peak.^{7,8} Note further that the present interpretation is internally self-consistent in the sense that the lone pair ionization potential (IP) for the gauche rotamer and the mean of the lone pair IP's for the trans rotamer are very similar. In turn these values are close to the lone pair IP of (CH₃)₂PH (Table I), an observation which is anticipated on the basis of the similarities of the electronegativities of the (CH₃)₂P and H moieties.⁹ The fact that the mean lone pair IP for the trans rotamer is slightly less than that of the gauche rotamer is attributed

(5) For an excellent discussion of the "gauche effect" see S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

(6) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3345 (1952).

(7) According to the interpretation of Nelsen, Buschek, and Hintz¹⁰ the mean of the gauche lone pair IP's would be ~ 1 eV higher than that of the trans. It is difficult to see how this could be the case since the mean lone pair IP's for the gauche and trans rotamers are expected to be nearly the same.

(8) MINDO/2 calculations (N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970) and ref 4a) indicate that in hydrazine the energies of the two nitrogen lone pair MO's, E_{n+} and E_{n-}, vary continuously with the dihedral angle, ϕ , e.g., at $\phi = 0^\circ$ n₋ lies 1.45 eV above n₊ and at $\phi = 80^\circ$ n₊ and n₋ have the same energy while at $\phi = 180^\circ$ n₋ lies 2.41 eV below n₊. Presumably the n₊ and n₋ lone pair combinations are very close in energy in the gauche conformations of the diphosphines and diarsines studied here.

(9) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

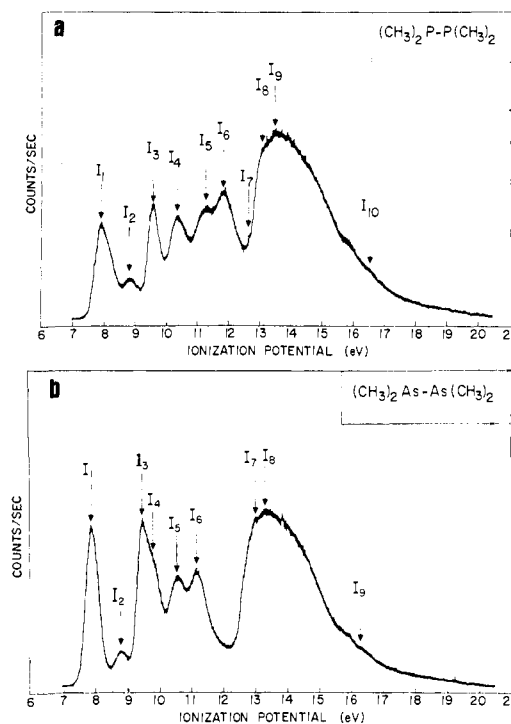


Figure 1. Photoelectron spectra of (a) (CH₃)₄P₂ and (b) (CH₃)₄As₂.

to the net destabilizing effect of the trans lone pair interaction.

Analogous assignments can be made for the ionizations of (CH₃)₄As₂ (Figure 1b). Note that the trans lone pair splittings of (CH₃)₄P₂ and (CH₃)₄As₂ are similar. As with (CH₃)₄P₂ the mean lone pair IP for the trans and the lone pair IP for the gauche rotamer agree with each other and are comparable to that of (CH₃)₂AsH (Table I).¹⁰

The assignments for the trans and gauche rotamers of (CF₃)₄P₂ follow from the foregoing arguments. Similar comments apply to the average of the trans lone pair IP's, the gauche lone pair IP, and the lone pair IP of (CF₃)₂PH (Table I). In the case of (CF₃)₄As₂ no gauche rotamer was detectable by PES; the assignments in Table I were made by analogy with those for (CF₃)₄P₂.

The per cent compositions of the rotameric mixtures (Table I) were computed from the relative peak areas. This approach is based on (a) the validity of our assignments (*vide supra*) and (b) the assumption that the area

(10) The close correspondence of the lone pair IP's of the P and As compounds in Table I is consistent with the PES data for PH₃ and AsH₃. See G. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **5**, 1 (1970).

under a PES peak is proportional to the abundance of the rotamer.¹¹

While the actual per cent compositions in Table I differ from those estimated by vibrational spectroscopy¹² for $(\text{CH}_3)_4\text{P}_2$,^{2a,d} $(\text{CF}_3)_4\text{P}_2$,^{2b} and $(\text{CH}_3)_4\text{As}_2$,^{3b} the qualitative trends in the PES data substantiate the generalizations that have been made for A_2X_4 species;¹³ *viz.*, the trans conformer is favored by (a) increasing the A-A bond distance and (b) increasing the electronegativity of X. The PES results, however, are not in accord with the electron diffraction study of $(\text{CH}_3)_4\text{P}_2$ which indicated that this molecule exists exclusively in the trans conformation.^{2c} Despite the steric bulk of the C_6F_5 moiety, the fact that no gauche rotamer is detectable in $(\text{CF}_3)_4\text{As}_2$ (by PES or vibrational spectroscopy^{3c}) contrasts sharply with the claim^{3a} that $(\text{C}_6\text{F}_5)_4\text{As}_2$ can be separated into gauche and trans rotamers.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 38027X), the U. S. Air Force Office of Scientific Research (Contract F44620-71-C-0119), and the Robert A. Welch Foundation for generous financial support.

(11) Such an assumption may not be generally valid since photoionization cross sections are dependent upon several factors such as the symmetry and orbital character of the MO from which the electron is removed and the relative energies of the light source and the MO in question. See, for example, L. L. Lohr, Jr., and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 7241 (1970); W. Thiel, Ph.D. Dissertation, Philipps Universität, Marburg/Lahn, West Germany, 1973. However, in the case of the ionization of the lone pair MO's of the trans and gauche rotamers of hydrazine-like molecules, this assumption is reasonable because the orbitals are close in energy and similar in character.

(12) This approach is based on the assumption that Raman peak intensities are proportional to the abundances of the rotamers. This assumption is clearly questionable since the dipole moments of the two rotamers must differ and their derivatives should differ likewise.

(13) For a review see J. R. Durig, B. M. Gimarc, and J. D. Odom in "Vibrational Spectra and Structure," Vol. 2, J. R. Durig, Ed., Marcel Dekker, New York, N. Y., 1973.

A. H. Cowley,* M. J. S. Dewar*
D. W. Goodman, M. C. Padolina

Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

Received October 29, 1973

Coordination Geometries of High-Spin Manganese(III) Porphyrins and Their Synthetic Intermediates

Sir:

This report contains recent results which help clarify previous ambiguities about some aspects of Mn(III) coordination chemistry.¹ These results clearly demonstrate the expected formation of distorted octahedral complexes of high-spin Mn(III)—a result contrary to some published structural work.² This distortion, which frequently manifests itself in the form of a tetragonal elongation, is probably responsible for the ready incorporation of Mn(III) into porphyrins.^{3,4} The results reported herein also tend to contradict to some extent those which report high-spin octahedral manganese(III) porphyrins containing a very tightly co-

ordinated axial neutral Lewis base which cannot be removed even under rather severe conditions.⁵

A series of manganese(III) porphyrins having general formulas, $\text{Mn}(\text{TPP})(\text{X})$ and $\text{Mn}(\text{TPP})(\text{X})(\text{B})$, where TPP is the $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato dianion, X is a mononegative anionic ligand such as N_3^- , NCS^- , or Cl^- , and B is a neutral Lewis base such as pyridine or methanol, have been synthesized from the corresponding acetylacetonate (acac) complexes, $\text{Mn}(\text{acac})_2(\text{X})$ or $\text{Mn}(\text{acac})_2(\text{X})(\text{B})$.⁴ The results of single-crystal X-ray structural investigations for $\text{Mn}(\text{TPP})(\text{N}_3)(\text{CH}_3\text{OH})\cdot\text{CH}_3\text{OH}$ and its synthetic intermediate, $\text{Mn}(\text{acac})_2(\text{N}_3)$, as well as $\text{Mn}(\text{acac})_2(\text{NCS})$ and $\gamma\text{-Mn}(\text{acac})_3$, demonstrate several interesting facets of Mn(III) coordination chemistry and their effect in the biologically important manganese porphyrins.⁶

Three-dimensional diffraction data on all compounds were collected on a computer-controlled four-circle Syntex P_1 autodiffractometer using Nb-filtered $\text{Mo K}\alpha$ radiation and ω or θ - 2θ scans. Except for the structure of $\text{Mn}(\text{acac})_2(\text{NCS})$ which required the use of "direct" methods, all structures were solved using the heavy-atom technique. The structural parameters for each compound have been refined to convergence in cycles of unit-weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for all non-hydrogen atoms.

Crystal data and refinement results are as follows. $\text{Mn}(\text{O}_2\text{C}_5\text{H}_7)_2(\text{N}_3)$ monoclinic; $a = 11.527$ (4), $b = 10.005$ (4), $c = 11.263$ (3) Å; $\beta = 94.86$ (3)°; $D_{\text{calcd}} = 1.514$, $D_{\text{measd}} = 1.499$ g cm⁻³; $Z = 4$ (molecular units); space group $\text{C}_{2/c}$; $R = 0.042$ for 1908 independent reflections having $2\theta_{\text{MoK}\alpha} < 63.7^\circ$ and $I > \sigma(I)$; data-to-parameter ratio = 17.0 for ten anisotropic non-hydrogen atoms and seven isotropic hydrogen atoms. $\text{Mn}(\text{O}_2\text{C}_5\text{H}_7)_2(\text{NCS})$ orthorhombic; $a = 13.422$ (2), $b = 14.519$ (3), $c = 13.763$ (3) Å; $D_{\text{calcd}} = 1.541$, $D_{\text{measd}} = 1.540$ g cm⁻³; $Z = 8$ (molecular units); space group P_{bca} ; $R = 0.057$ for 1917 independent reflections having $2\theta_{\text{MoK}\alpha} < 55^\circ$ and $I > 2\sigma(I)$; data-to-parameter ratio = 11.8 for 18 anisotropic nonhydrogen atoms. $\gamma\text{-Mn}(\text{O}_2\text{C}_5\text{H}_7)_3$ monoclinic; $a = 7.786$ (1), $b = 27.975$ (4), $c = 8.020$ (1) Å; $\beta = 100.34$ (1)°; $D_{\text{calcd}} = 1.361$, $D_{\text{measd}} = 1.366$ g cm⁻³; $Z = 4$; space group $\text{P}_{2_1/n}$; $R = 0.062$ for 1696 independent reflections having $2\theta_{\text{MoK}\alpha} < 43^\circ$ and $I > \sigma(I)$; data-to-parameter ratio = 8.5 for 22 anisotropic nonhydrogen atoms (refinement is continuing with a data set twice as large). $\text{Mn}(\text{N}_4\text{C}_{44}\text{H}_{28})(\text{N}_3)(\text{CH}_3\text{OH})\cdot\text{CH}_3\text{OH}$ monoclinic; $a = 19.095$ (2), $b = 9.790$ (2), $c = 46.927$ (6) Å; $\beta = 106.35$ (1)°; $D_{\text{calcd}} = 1.221$, $D_{\text{measd}} = 1.282$ g cm⁻³; $Z = 8$; space group $\text{C}_{2/c}$; $R = 0.096$ for 3569 independent reflections having $2\theta_{\text{MoK}\alpha} < 45.8^\circ$ and $I > 2\sigma(I)$; data-to-parameter ratio = 7.1 for 56 anisotropic nonhydrogen atoms (refinement is continuing with a data set twice as large).

The crystallographic studies for $\text{Mn}(\text{acac})_2\text{N}_3$ and $\text{Mn}(\text{acac})_2(\text{NCS})$ have shown that, in both compounds, the mononegative anionic ligand, X, bridges adjacent Mn(III) atoms in the three-dimensional lattice to form polymeric chains of six-coordinate (rather than five-coordinate) Mn(III) polyhedra. Both compounds exhibit a large tetragonal elongation of the octahedral

(1) See, for instance, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 851.

(2) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, **17**, 705 (1964).

(3) R. Khosropour and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).

(4) B. R. Stults, V. W. Day, E. L. Tasset, and R. S. Marianelli, *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).

(5) L. J. Boucher, *J. Amer. Chem. Soc.*, **90**, 6640 (1968). See also ref 6.

(6) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972), and references cited therein.