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. The aforementioned result promoted us to reexamine the complexes (5a and 5b) obtained from the reaction of \( \pi\)-C\(_4\)H\(_4\)Fe(CO)CH\(_2\)C\(_6\)H\(_4\)X-p \) (X = H or Cl) and C\(_6\)H\(_5\)NC, which we had identified as the "tris imino type complexes". We found that the resonances at \( \tau \) 3.27 (doublet) for X = H and at 3.38 (d) for X = Cl, assigned incorrectly as the benzylic methylene protons, respectively, disappear on treatment with D\(_2\)O, 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 \( \pi\)-C\(_4\)H\(_4\)Fe(CO)(CNC\(_6\)H\(_5\))CH\(_2\)C\(_6\)H\(_4\)X-p \) (X = H or Cl) with C\(_6\)H\(_5\)NC. It is of interest to note that \( \pi\)-C\(_4\)H\(_4\)Fe(CO)(CNC\(_6\)H\(_5\))CH\(_2\)C\(_6\)H\(_4\)Cl-p bearing no alkyl protons undergoes an expected multiple insertion to afford the tris imino type complex, 7, when treated with C\(_6\)H\(_5\)NC 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 isolcianides. Further studies are now in progress.

Detection of Rotational Isomerism in Diphosphines and Diarsines by Photoelectron Spectroscopy

Sir:

The stereochemistry of hydrazines\(^1\) and their heavier congeners\(^3\)\(^4\) has been a subject of interest for 4 decades. With few exceptions\(^4\) acyclic hydrazines prefer...
erentially adopt the gauche\(^5\) conformation. However, the stereochemistry of diphosphines\(^2\) and diarsines\(^3\) 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 A\(_2\)X\(_2\) molecules the interaction between the A lone pairs is anticipated to exhibit a dependence on the dihedral angle, \(\phi\), such that the lone pair splittings (\(\Delta\)) should be trans >> gauche.\(^6\)

![Diagram](image)

In \((\text{CH}_3)_2\text{P}_2\) (Figure 1a) peaks I\(_2\) and I\(_3\) can be assigned to the \(n^+\) and \(n^-\) phosphorus lone pair combinations. The remaining peak (I\(_1\)) 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 \(\sim 0.5\) eV with one component hidden under a trans peak.\(^7\) 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's of \((\text{CH}_3)_2\text{P}\) (Table I), an observation which is anticipated on the basis of the similarities of the electronegativities of the \((\text{CH}_3)_2\text{P}\) and H moieties.\(^8\) The fact that the mean lone pair IP for the trans rotamer is slightly less than that of the gauche rotamer is attributed to the net destabilizing effect of the trans lone pair interaction.

Analogous assignments can be made for the ionizations of \((\text{CH}_3)_2\text{As}_2\) (Figure 1b). Note that the trans lone pair splittings of \((\text{CH}_3)_2\text{P}\) and \((\text{CH}_3)_2\text{As}\) are similar. As with \((\text{CH}_3)_2\text{P}\) 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 \((\text{CH}_3)_2\text{AsH}\) (Table I).\(^9\)

The assignments for the trans and gauche rotamers of \((\text{CF}_3)_2\text{P}_2\) 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 \((\text{CF}_3)_2\text{P}\) (Table I). In the case of \((\text{CF}_3)_2\text{As}_2\) no gauche rotamer was detectable by PES; the assignments in Table I were made by analogy with those for \((\text{CF}_3)_2\text{P}\).

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

![Diagram](image)

**Table I.** PES Ionization Potential* Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>% abundance</th>
<th>Lone pair IP's</th>
<th>(\Delta)</th>
<th>Av lone pair IP</th>
<th>P-P or As-As</th>
<th>P-C or As-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>gauche ((\text{CH}_3)_2\text{P}_2)</td>
<td>16</td>
<td>8.79</td>
<td></td>
<td>8.79</td>
<td>10.33</td>
<td>11.22, 11.83</td>
</tr>
<tr>
<td>trans ((\text{CH}_3)_2\text{P}_2)</td>
<td>84</td>
<td>7.88, 9.54</td>
<td>1.66</td>
<td>8.71</td>
<td>10.33</td>
<td>11.22, 11.83</td>
</tr>
<tr>
<td>gauche ((\text{CH}_3)_2\text{As}_2)</td>
<td>12</td>
<td>8.85</td>
<td></td>
<td>8.85</td>
<td>9.82</td>
<td>10.60, 11.21</td>
</tr>
<tr>
<td>trans ((\text{CH}_3)_2\text{As}_2)</td>
<td>88</td>
<td>7.91, 9.50</td>
<td>1.59</td>
<td>8.70</td>
<td>9.82</td>
<td>10.60, 11.21</td>
</tr>
<tr>
<td>gauche ((\text{CF}_3)_2\text{P}_2)</td>
<td>10</td>
<td>11.57</td>
<td></td>
<td>11.57</td>
<td>13.09</td>
<td>13.49</td>
</tr>
<tr>
<td>trans ((\text{CF}_3)_2\text{P}_2)</td>
<td>10</td>
<td>10.71, 12.11</td>
<td>1.45</td>
<td>11.44</td>
<td>13.09</td>
<td>13.49</td>
</tr>
<tr>
<td>trans ((\text{CF}_3)_2\text{As}_2)</td>
<td>100</td>
<td>10.39, 11.94</td>
<td>1.55</td>
<td>11.17</td>
<td>12.07</td>
<td>12.58</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{PH})</td>
<td>100</td>
<td>9.13</td>
<td></td>
<td>9.13</td>
<td>11.75</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{AsH})</td>
<td>100</td>
<td>9.14</td>
<td></td>
<td>9.14</td>
<td>11.16, 11.54</td>
<td></td>
</tr>
<tr>
<td>((\text{CF}_3)_2\text{PH})</td>
<td>100</td>
<td>11.51</td>
<td></td>
<td>11.51</td>
<td>13.22</td>
<td></td>
</tr>
</tbody>
</table>

* Vertical ionization potentials in electron volts.

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(7) According to the interpretation of Nelsen, Buschek, and Hintz the mean of the gauche lone pair IP's would be \(\sim 1\) eV higher than that of the trans. It is difficult to see how this could be the case since the lone pair MO's, \(E_{\alpha}\) and \(E_{\beta}\), vary continuously with the dihedral angle, \(\phi\), e.g., at \(\phi = 0\) n- lies 1.45 eV above n+, and 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.

under a PES peak is proportional to the abundance of the rotamer.\(^\text{(11)}\)

While the actual per cent compositions in Table I differ from those estimated by vibrational spectroscopy\(^\text{(12)}\) for \((\text{CH}_3)_2\text{P}_2\text{A}_{\text{S}}\text{S}\) and \((\text{CF}_3)_2\text{P}_2\text{A}_{\text{S}}\text{S}\), the qualitative trends in the PES data substantiate the generalizations that have been made for \(\text{A}_2\text{X}\) species;\(^\text{(13)}\) \textit{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.\(^\text{(20)}\) Despite the steric bulk of the \(\text{C}_6\text{F}_5\) moiety, the fact that no gauche rotamer is detectable in \((\text{CF}_3)_2\text{A}_{\text{S}}\text{S}\) by PES or vibrational spectroscopy\(^\text{(26)}\) contrasts sharply with the claim\(^\text{(26)}\) that \((\text{C}_6\text{F}_5)_2\text{S}_2\) 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, \textit{J. Amer. Chem. Soc.}, \textbf{92}, 7241 (1970); W. Thiel, Ph.D. Dissertation, Philips-Universitat, 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.


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

\textbf{Sir:}

This report contains recent results which help clarify prior ambiguities about some aspects of Mn(III) coordination chemistry.\(^\text{(1)}\) These results clearly demonstrate the expected formation of distorted octahedral complexes of high-spin MnIII—a result contrary to some published structural work.\(^\text{(2)}\) This distortion, which frequently manifests itself in the form of a tetragonal elongation, is probably responsible for the ready incorporation of MnIII into porphyrins.\(^\text{(3)}\) 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.\(^\text{(4)}\)

A series of manganese(III) porphyrins having general formulas, \(\text{Mn(TPP)}(\text{X})\) and \(\text{Mn(TPP)}(\text{X})(\text{B})\), where TPP is the \(\alpha,\beta,\gamma,\delta\)-tetraphenylporphinato dianion, X is a mononuclear anionic ligand such as \(\text{N}_2^-, \text{NCS}^-, \text{Cl}^-\), and B is a neutral Lewis base such as pyridine or methanol, have been synthesized from the corresponding acetylacetonate (acac) complexes, \(\text{Mn(acac)}_2(\text{X})\) or \(\text{Mn(acac)}_2(\text{X})(\text{B})\).\(^\text{(5)}\) The results of single-crystal X-ray structural investigations for \(\text{Mn(TPP)}(\text{N}_2)(\text{CH}_3\text{OH})\) and its synthetic intermediate, \(\text{Mn(acac)}_2(\text{N}_2)\), as well as \(\gamma\text{-Mn(acac)}_2(\text{X})\), demonstrate several interesting facets of MnIII coordination chemistry and their effect in the biologically important manganese porphyrins.

Three-dimensional diffraction data on all compounds were collected on a computer-controlled four-circle Syntex P1 autodiffractometer using Nb-filtered Mo K\(\alpha\) radiation and \(\omega\) or \(\theta\)–2\(\theta\) scans. Except for the structure of \(\text{Mn(acac)}_2(\text{NCS})\) 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. \(\text{Mn(O}_2\text{C}_7\text{H}_7)(\text{N}_2)(\text{N})\) monoclinic; \(a = 11.527(4), b = 10.005(4), c = 11.263(3)\ \AA; \beta = 94.86(3)^\circ; D_{\text{calcd}} = 1.514, D_{\text{measd}} = 1.499 \text{g cm}^{-3}; Z = 4 \text{(molecular units)};\) space group \(C_2\text{i}; R = 0.042 \text{for 1908 independent reflections having } 2\theta_{\text{MOKA}} < 63.7^\circ \text{ and } I > 0\sigma(I);\) data-to-parameter ratio = 17.0 for ten anisotropic non-hydrogen atoms and seven isotropic hydrogen atoms. \(\text{Mn(O}_2\text{C}_7\text{H}_7)(\text{NCS})(\text{N})\) orthorhombic; \(a = 13.422(2), b = 14.519(3), c = 13.763(3)\ \AA; D_{\text{calcd}} = 1.541, D_{\text{measd}} = 1.540 \text{g cm}^{-2}; Z = 8 \text{(molecular units)};\) space group \(P_{\text{bc}}\text{i}; R = 0.057 \text{for 1917 independent reflections having } 2\theta_{\text{MOKA}} < 55^\circ \text{ and } I > 2\sigma(I);\) data-to-parameter ratio = 11.8 for 18 anisotropic non-hydrogen atoms. \(\gamma\text{-Mn(O}_2\text{C}_7\text{H}_7)(\text{N}_2)\text{N}_2\text{O}_2\text{H})\) monoclinic; \(a = 7.786(1), b = 27.975(4), c = 8.020(1)\ \AA; \beta = 100.34(1)^\circ; D_{\text{calcd}} = 1.361, D_{\text{measd}} = 1.366 \text{g cm}^{-2}; Z = 4;\) space group \(P_{\text{2}}\text{ni} \text{; } R = 0.062 \text{for 1696 independent reflections having } 2\theta_{\text{MOKA}} < 43.5^\circ \text{ and } I > 0\sigma(I);\) data-to-parameter ratio = 8.5 for 22 anisotropic non-hydrogen atoms (refinement is continuing with a data set twice as large). \(\text{Mn(N}_4\text{C}_4\text{H}_{28})(\text{CH}_3\text{OH})\cdot(\text{CH}_3\text{OH})\cdot\text{CH}_3\text{OH}\) monoclinic; \(a = 19.095(2), b = 9.790(2), c = 46.927(6)\ \AA; \beta = 106.35(1)^\circ; D_{\text{calcd}} = 1.221, D_{\text{measd}} = 1.282 \text{g cm}^{-2}; Z = 8;\) space group \(C_2\text{hi}; R = 0.096 \text{for 3569 independent reflections having } 2\theta_{\text{MOKA}} < 45.8^\circ \text{ and } I > 2\sigma(I);\) 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 \(\text{Mn(acac)}_2\text{N}_2\) and \(\text{Mn(acac)}_2(\text{NCS})\) have shown that, in both compounds, the mononuclear anionic ligand, X, bridges adjacent MnIII atoms in the three-dimensional lattice to form polymeric chains of six-coordinate (rather than five-coordinate) MnIII polyhedra. Both compounds exhibit a large tetragonal elongation of the octahedral lattice.\(^\text{(5)}\) See also ref. 6.

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