

Phospholes. Electronic Structure¹

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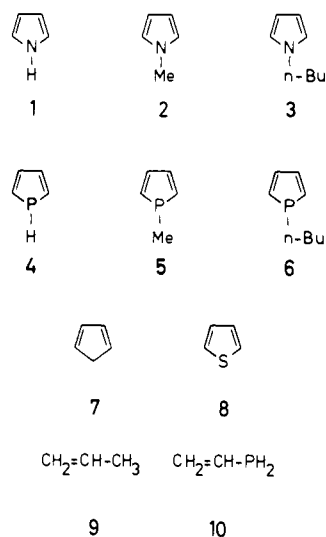
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Abstract: The phosphole system is investigated both theoretically and by uv photoelectron spectroscopy. The theoretical approach confirms that phospholes despite their pyramidal structure are "aromatic" systems. Their "aromatic" stabilization relative to the conjugatively interrupted subunits *cis*-butadiene and PR is gained from $n\pi^*$ conjugative and P-C/ π^* hyperconjugative interactions between both subunits. These interactions appear not to be accompanied by appreciable π -charge transfer (i.e., electron delocalization) from the PR unit to the π part mainly due to strong electron acceptance from the phosphorus d orbitals. In addition, the photoelectron spectroscopic results corroborate strong P-C/ π hyperconjugative but only weak n/π conjugative mixing. The results of the present study show that the n orbital energy is not a suitable means to deduce the "aromatic" nature of phospholes as a consequence of the combined $n\pi^*$ and $n\pi$ interactions. Moreover, the results constitute a first indication of the important role played by P-C hyperconjugation in these systems.

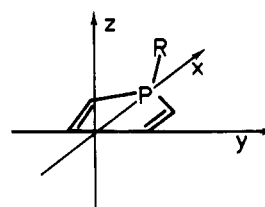
The nature and extent of interactions between orbitals of the *cis*-butadiene and PR units in phospholes have been unclear till present.³ In particular, the question as to whether such interactions are stabilizing (i.e., lead to an "aromatic" composite system) remains unsettled.³ Below we report on quantum chemical and photoelectron spectroscopic results that provide some answers to the aforementioned questions of topical importance regarding the electronic nature of phospholes.

Calculation and Discussion

To this end we apply a method used previously⁴⁻⁸ that allows one to decouple the conjugation between selected parts of a molecule. The method is used in conjunction with the extended CNDO/S⁹ and the MINDO/2¹⁰ procedures. The calculations extend to pyrrole (1), 1-methylpyrrole (2), 1-butylpyrrole (3), both planar and pyramidal phosphole (4), 1-methylphosphole (5), 1-butylphosphole (6), cyclopentadiene (7), thiophene (8), propene (9), and vinylphosphine (10). In all cases experimental geometries¹¹ (as for the



structural data of the phosphole ring, see ref 12 and 13) were used. The coordinate system chosen for the phospholes (both planar and pyramidal) is illustrated in 11. The calculations are done to provide information about the following points: (1) nature and extent of interactions between occupied orbitals of both units; (2) nature and extent of interactions between occupied and vacant orbitals of both units; (3) extent of stabilization ("aromaticity"), if at all, as a



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consequence of the latter interactions; and (4) as a further consequence of these interactions eventual π -charge transfer between the subunits. We first turn to the orbital interaction schemes. The subunit orbitals of relevance in connection with these problems are the butadiene $\pi(b_1)$ and $\pi^*(b_1)$ [$*$ designates empty orbitals] orbitals and the n orbital (lone pair orbital) on the planar nitrogen or phosphorus atom or the n orbital and one P-C orbital of the pyramidal phosphorus atom, respectively. These orbitals are illustrated as shown:

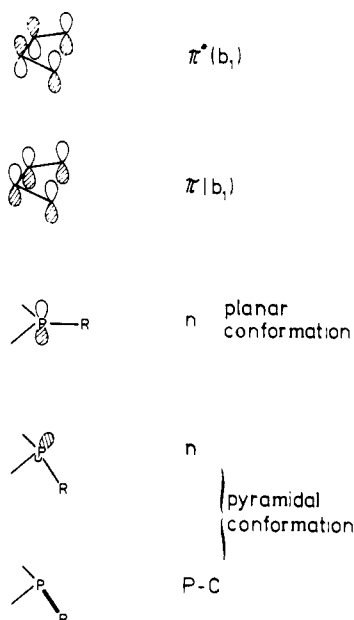


Figure 1 presents the evaluated orbital interaction diagram for the pyrroles 1 and 3.^{14a} As expected there is strong interaction between the n and $\pi(b_1)$ orbitals thereby considerably putting up the lone pair orbital energy (i.e., the $\pi(2b_1)$ orbital in the conjugatively coupled pyrroles). However, the

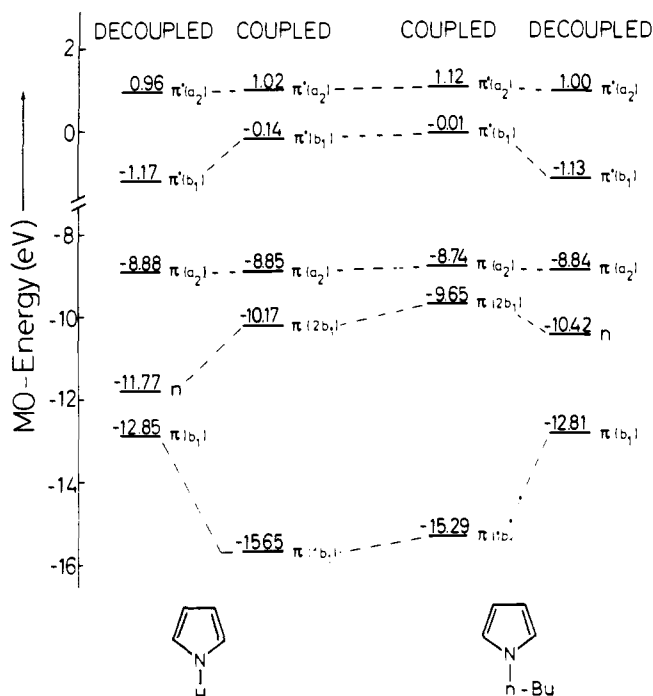


Figure 1. Interaction diagram of the respective orbitals of the *cis*-butadiene and NH or NBu units. The orbital (MO) energies prior to interaction (given under the heading "decoupled") are those obtained when the π conjugation between both units is interrupted. The orbital energies with π conjugation admitted are presented under the heading "coupled". The results are taken from CNDO/S calculations. The highest occupied and lowest unoccupied (*) orbitals are classified in terms of their respective nature (π or n) and, in addition, the π MO's in terms of the symmetry species of point group C_{2v} .

n orbital is less destabilized than the $\pi(b_1)$ orbital is stabilized due to the additional interaction with the vacant $\pi^*(b_1)$ orbital. From such interactions we have to expect "aromatic" stabilization for the pyrroles and considerable π -charge transfer from the NR to the butadiene subunit. These predictions are in accordance with the idea of an aromatic model for pyrroles.

Figure 2 shows the corresponding interaction diagram (evaluated in the *sp* and *spd* basis,^{14b} respectively) for 1-butylphosphole in its planar conformation. According to both calculations, the $\pi(b_1)/n/\pi^*(b_1)$ interactions are such that the n orbital (i.e., the $\pi(2b_1)$ orbital in the coupled system) remains at nearly the same energy when switching on conjugation between the subunit orbitals. Hence following the energy of this orbital by photoelectron spectroscopy would not constitute a suitable means to conclude about the importance of conjugative coupling of both moieties.^{14c} The destabilization found for the $\pi^*(b_1)$ orbital points at "aromatic" stabilization for **6** in the same sense as deduced above for the pyrroles.

In contrast to pyrroles, phospholes exist in a pyramidal conformation. Figure 3 displays the corresponding calculated orbital interaction diagram. In this case one P-C orbital is additionally involved in the interactions. As it is seen from the left-hand part of Figure 3 (results obtained by use of a *sp* basis), the dominant interaction between occupied orbitals is the hyperconjugative $\pi(b_1)/P-C$ one. The rise of n orbital energy, however, is comparatively small. But most interestingly, the $\pi^*(b_1)$ orbital is destabilized when admitting conjugative interactions between subunit orbitals which suggests that also the pyramidal phospholes should experience "aromatic" stabilization. Closer inspection of the $\pi^*(b_1)$ orbital of **6** (i.e., after coupling the subunits) shows that this orbital contains about equal contributions from the

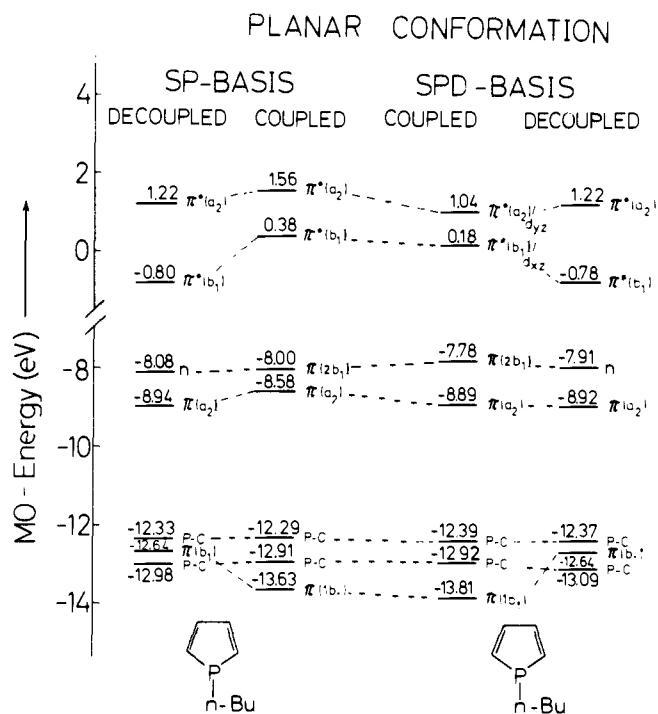


Figure 2. Interaction diagram of the respective orbitals of the *cis*-butadiene and PBU units for planar 1-butylphosphole. The results of two CNDO/S calculations are given, one performed using a *sp* basis and the other using a *spd* basis. For an explanation of the meaning of "decoupled" and "coupled" and of the labeling of levels, see caption to Figure 1. In addition to the levels presented there, two new ones, namely the high lying occupied P-C levels, occur in this diagram.

n and P-C orbitals (see Figure 4 where, for the sake of simplicity, the corresponding orbital of **5** is plotted¹⁵⁻²²). The $\pi(b_1)/P-C$ and n orbitals are additionally represented in Figures 5 and 6. In contradistinction to the planar **6**, the inclusion of *d* AO's drastically alters the energies of the empty coupled orbitals. While being itself raised in energy, the d_{xz} orbital lowers the $\pi^*(b_1)$ orbital energy. This evident mixing in of the d_{xz} orbital is further reflected in the calculated π -charge transfer (see below).

In brief, the orbital interaction diagram for 1-butylphosphole (**6**) (Figure 3) shows: (1) that the predominant interaction between occupied orbitals is hyperconjugative in nature [$\pi(b_1)/P-C$]; (2) that the vacant $\pi^*(b_1)$ interacts with both the n and the P-C orbitals. Therefore we would conclude that the "aromatic" stabilization of **6** is partly due to $n\pi^*$ conjugation and partly due to P-C/ π^* hyperconjugation; and (3) that an additional stabilization due to the d_{xz} orbital is to be expected. As far as we are aware, these results constitute the first indication of the possible role that P-C hyperconjugation may play in phospholes. The interac-

| | | |
|------|------|------|
| | | |
| 49.6 | 53.3 | 53.7 |
| 76.8 | 84.6 | 85.6 |
| 12 | 13 | 14 |
| | | |
| 34.1 | 34.4 | 34.5 |
| 61.4 | 61.2 | 61.0 |
| 15 | 16 | 17 |

PYRAMIDAL CONFORMATION

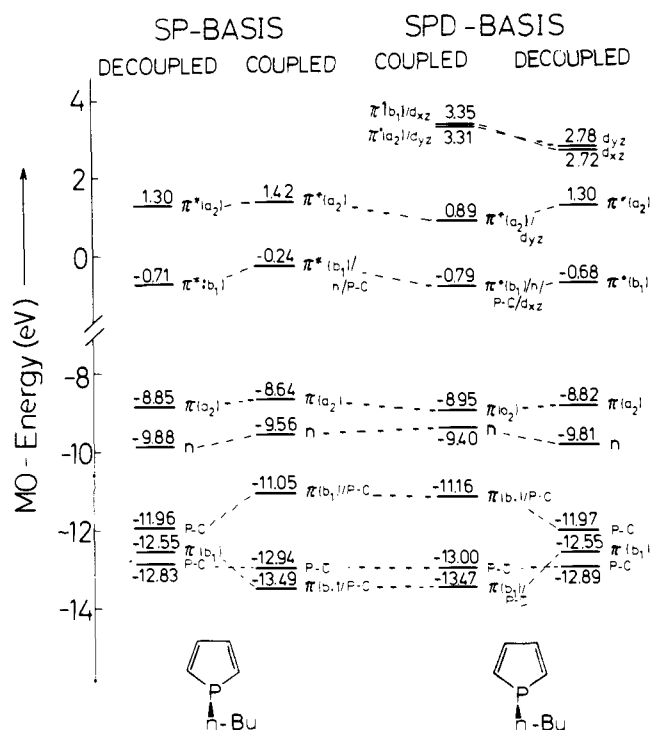


Figure 3. Interaction diagram of the respective orbitals of the *cis*-butadiene and P-Bu units for 1-butylphosphole in its pyramidal conformation. The results shown are taken from CNDO/S calculation (performed in a sp or spd basis, respectively). For an explanation of the meaning of "decoupled" and "coupled" and the symbols connected with the levels shown, see captions to Figures 1 and 2. Moreover, in the present diagram, dominant orbital mixing in the coupled cases is symbolized, e.g., as $\pi^*(b_1)/P-C$ or $\pi^*(b_1)/n/P-C$ and so on.

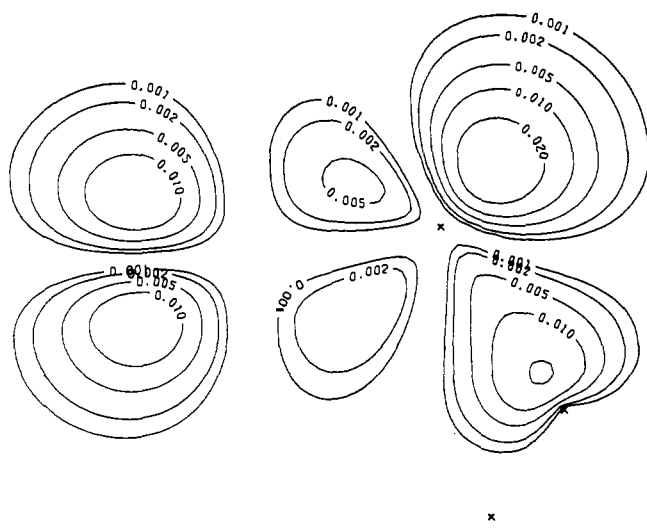


Figure 4. Computer plot²² of the $\pi^*(b_1)/n/P-C/d_{xz}$ orbital (for explanation of symbols, see caption to Figure 3) of 1-methylphosphole. Density contours are drawn in the plane of symmetry that is perpendicular to the molecular plane (C_{2v} symmetry assumed). The three crosses mark the positions of the phosphorus, the methyl carbon, and one of the methyl hydrogen atoms (meaning that the methyl group points to the bottom of the figure). In order to get a correct representation of orbital nodal properties²¹ the Löwdin transformed¹⁶ CNDO/S orbital (spd basis) was used to draw its density contours.

tion diagram leads us further to expect π -charge transfer from the PR unit to the butadiene part.

The stabilization energy for phospholes **4**, **5**, and **6** in their planar (P-R) and pyramidal (P-R) conformations

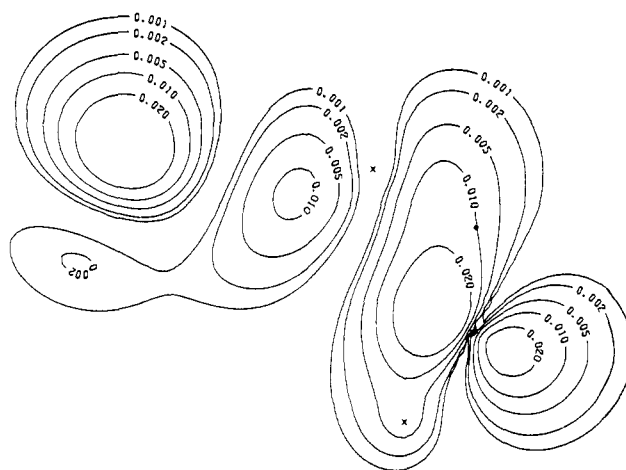


Figure 5. Computer plot of the antibonding $\pi(b_1)/P-C$ combination of 1-methylphosphole. For all explanations necessary to understand the presented orbital picture, see caption to Figure 4. The plot clearly shows the appreciable P-C admixture to the butadiene $\pi(b_1)$ orbital.

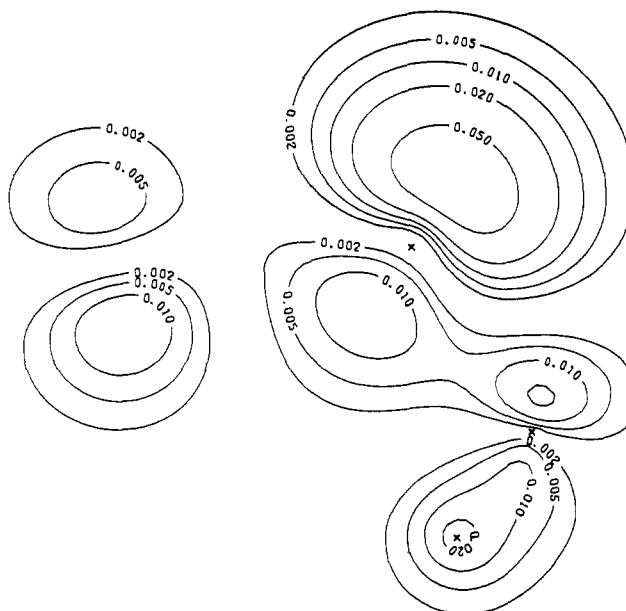
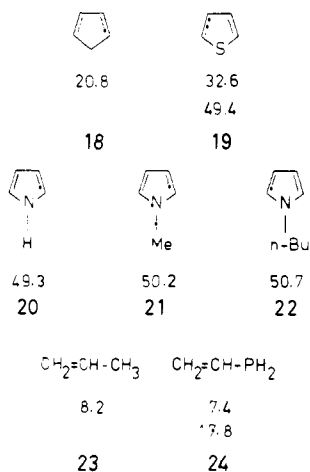
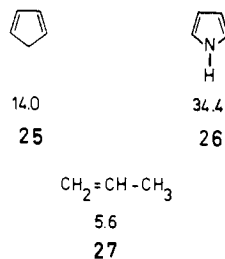


Figure 6. Computer plot of the n orbital of 1-methylphosphole. For all explanations necessary to understand the presented orbital picture, see caption to Figure 4. As expected by symmetry, the n orbital also contains contributions from the butadiene and methyl parts.

are shown (in **12-17**, values are given in kcal/mol and obtained from CNDO/S calculations; the upper values refer to a sp basis and the lower ones to a spd basis). The stabilization (conjugation) energy is defined here to be the difference in total energy between the coupled and decoupled cases. The point of interest is that the pyramidal phospholes (cf. **15** to **17**) still possess considerable conjugation energy. It still amounts to about 60-70% of the planar phospholes. The applied method further predicts appreciable extrastabilization due to the mixing in of d orbitals on the phosphorus atom. The calculated difference in conjugation energy between planar and pyramidal forms (for example, 19 to 23 kcal/mol for **5**) compares favorably with an experimental estimation (about 23 kcal/mol).²³ Some comparison values computed in the same manner for cyclopentadiene (**7**), thiophene (**8**), the pyrroles **1-3**, propene (**9**), and vinylphosphine (**10**) are summarized (see **18-24**, where again all values are in kcal/mol; the upper values of **19** and **24** refer to an sp basis and the lower ones to an spd basis). The stabilization energies listed for **23** and **24** refer to the coupling



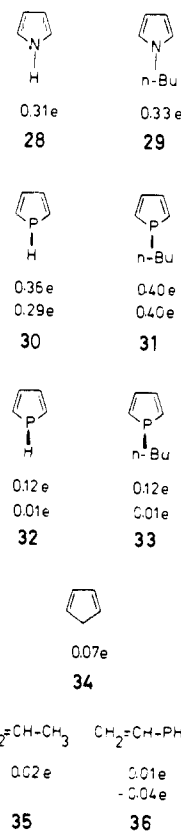
process between the vinyl group on the one hand and the CH_3 or PH_2 groups on the other. According to the calculations, the pyrroles 1–3 and the planar phospholes 4–6 (relating in both cases to the values produced by using the sp basis) dispose of the same conjugative stabilization. The result confirms early HMO calculations.²⁴ As it is well known, the parameterization of the CNDO/S method was achieved with the aim to reproduce electronic spectra.^{9,25,26} In contrast, the MINDO/2 parameters were chosen to describe correctly enthalpies of formation. In order to check the stabilization energies produced by the CNDO/S method, we also calculated these quantities, in some cases (1, 7, and 9), using the MINDO/2 method (values in kcal/mol summarized in 25–27). The comparison between these



values and the corresponding CNDO/S ones given in 18, 20, and 23 shows that the MINDO/2 conjugation energies constantly amount to about 70% of the CNDO/S ones. Accordingly, the CNDO/S values, though a little too high, are quite reasonable.

The evaluated π -charge transfer (values are given in electrons in 28–36) found after coupling both subunits is in full accord with the preceding results. In cases where two values are presented, the upper ones refer to sp and the lower ones to spd calculations. A positive sign means transfer from the heteroatom unit to the butadiene part, a negative sign in the opposite direction. The transfer is nearly the same in the pyrroles and planar phospholes. The amount of transferred π charge is, however, considerably reduced for the pyramidal phospholes. The role of the d_{xz} orbital on phosphorus shows up quite drastically in the pyramidal systems (cf. 32 and 33). The π -charge transfer from phosphorus to the butadiene system is nearly countermanded through the π -charge acceptance of the phosphorus d orbitals. Thus, we arrive at the conclusion that the phosphorus atom in phospholes (in their ground state conformation) probably loses little or no π charge to the unsaturated hydrocarbon part as a consequence of existing conjugative interactions.²⁷

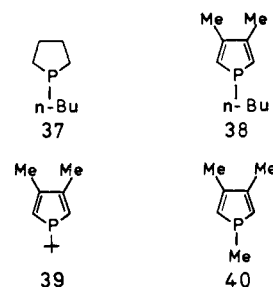
In conclusion, the main features of the present calculations regarding the electronic structure of phospholes are as follows. *Despite their pyramidal structure, phospholes are "aromatic" systems.* The conjugation energy of the pyramidal forms is about 60–70% of the planar ones. The "aromat-



ic" stabilization is due to stabilizing interactions between the $\pi^*(b_1)$ and the n and the external P–C orbitals, respectively. In consequence, the "aromaticity" of phospholes can be allotted both to the $n\pi^*$ conjugation (as has previously been done alone) and P–C/ π^* hyperconjugation. On the other hand, the predicted stabilization of pyramidal phospholes appears not to be accompanied by appreciable π -charge transfer from the P–R unit to the butadiene part (i.e., electron delocalization) mainly because of the strong electron acceptance of the d orbitals on the phosphorus atom. The calculations further revealed that the n orbital energy is not indicative of phosphole aromaticity in contradistinction to the pyrrole case.^{14c} However, rather strong P–C/ π hyperconjugation [P–C/ $\pi(b_1)$] is to be anticipated. To get insight into the nature and extent of these interactions, we measured and interpreted the photoelectron (PE) spectra of some simply substituted phospholes.

Photoelectron Spectra of 1-Butylphospholane (37), 1-Butylphosphole (6), 1-Butyl-3,4-dimethylphosphole (38), 1-tert-Butyl-3,4-dimethylphosphole (39), and 1,3,4-Trimethylphosphole (40) and Discussion

Figures 7 and 8 show the PE spectra of 1-butylphospholane (37), 1-butylphosphole (6), 1-butyl-3,4-dimethylphosphole (38), 1-tert-butyl-3,4-dimethylphosphole (39), and 1,3,4-trimethylphosphole (40), respectively.²⁸ The



spectrum of the phospholane 37 exhibits one band (①) and a clear-cut shoulder (②) on the onset of the σ continuum.

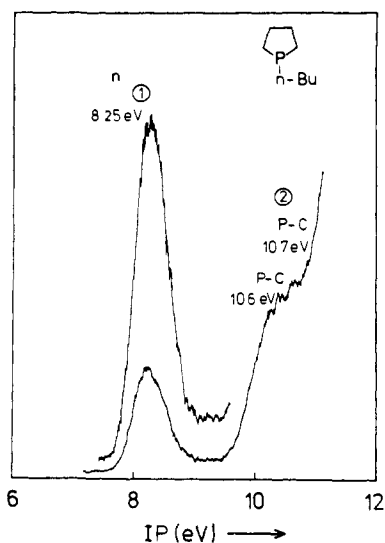


Figure 7. Photoelectron spectrum of 1-butylphospholane with assignments. The numbers associated with each band are vertical ionization potentials.

From previous experience with the PE spectra of other saturated phosphines, namely trimethylphosphine (41),^{29,30} dibutylmethylphosphine (42),³¹ tributylphosphine (43),³¹ and 1-phenylphospholane (44)³² (the corresponding ionization

| | |
|------------------|--------------------|
| PMe ₃ | MePBu ₂ |
| 8.60 eV(n) | 8.20 eV(n) |
| 11.34 eV(2P-C) | 10.48 eV(2P-C) |
| 41 | 42 |
| PBu ₃ | |
| 8.00(n) | 8.35(n) |
| 10.07 eV(2P-C) | |
| 43 | 44 |

potentials and assignments are given below), band ① must be assigned to ionization from the lone pair (n) orbital and band ② to ionization from the two P-C orbitals which, in 37 just as in 41-43, appear to be nearly degenerate. The spectra of the phospholes 6 and 37-40 consist of two bands. The relative intensity of both bands and the comparison of the phosphole spectra (mainly the spectrum of 6) with the phospholane spectrum (Figure 7) suggest that band ① is a composite band due to ionization from the n orbital and the highest occupied π orbital (i.e., from Figure 3 the $\pi(a_2)$ orbital), and band ② is attributable to one of the P-C orbitals somewhat raised in energy (mainly in 38-40) due to its mixing with the $\pi(b_1)$ orbital (i.e., P-C/ π hyperconjugation). The proposed assignment is fully corroborated by comparison of the measured (Figure 9) and calculated (Figures 10-12) ionic state correlation diagrams. Figures 10 and 11 show the Koopmans ion states³³ obtained in a sp and spd basis, respectively. Figure 12 presents ion states (obtained in the spd basis) improved by extensive configuration interaction (CI).^{34,35} All states are labeled according to the designation of orbitals which are vacated during the ionization process. These orbitals are illustrated (Chart I). The results clearly demonstrate that the sequence and spacing of orbital energies (i.e., the negative of the Koopmans state energies of Figures 10 and 11) and ionic state energies (Figure 12) agree. In consequence, the conclusions drawn throughout this paper are actually unaffected by invoking Koopmans' theorem.³³

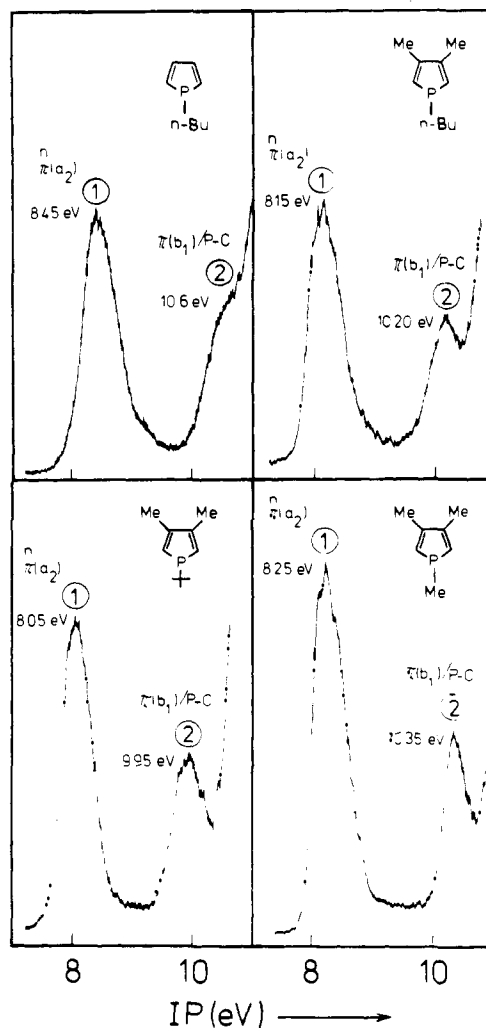
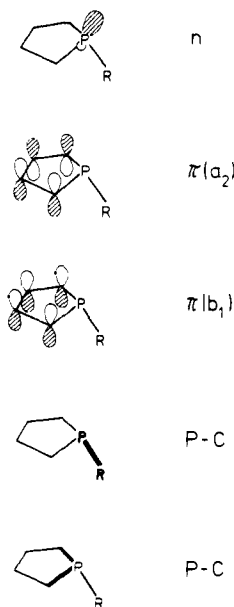


Figure 8. Photoelectron spectra of 1-butylphosphole, 1-butyl-3,4-dimethylphosphole, 1-*tert*-butyl-3,4-dimethylphosphole, and 1,3,4-trimethylphosphole with assignments. The numbers associated with each band are vertical ionization potentials.

Chart I



From these findings, we can show that both P-C/ $\pi(b_1)$ hyperconjugation and, to a smaller extent, n/ $\pi(b_1)$ conjugation are present in the phospholes. To this end we turn to the phosphole 6. In Figure 13, we compare its measured

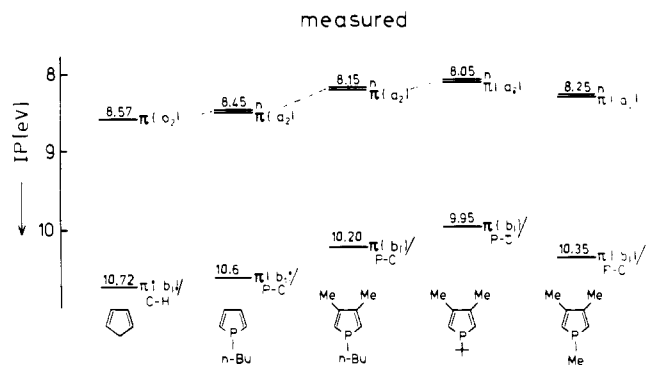


Figure 9. Measured correlation diagram for the lowest ion states of cyclopentadiene, 1-butylphosphole, 1-butyl-3,4-dimethylphosphole, 1-*tert*-butyl-3,4-dimethylphosphole, and 1,3,4-trimethylphosphole. The states are labeled according to the designation of orbitals from which they arise. The numbers shown above the levels are vertical ionization potentials (in eV). Since it is shown in the present work that Koopmans' theoretical description of the ion states considered is valid (see Figure 12), the present diagram can also be considered as an experimental orbital correlation diagram for the highest occupied orbitals of the respective molecules.

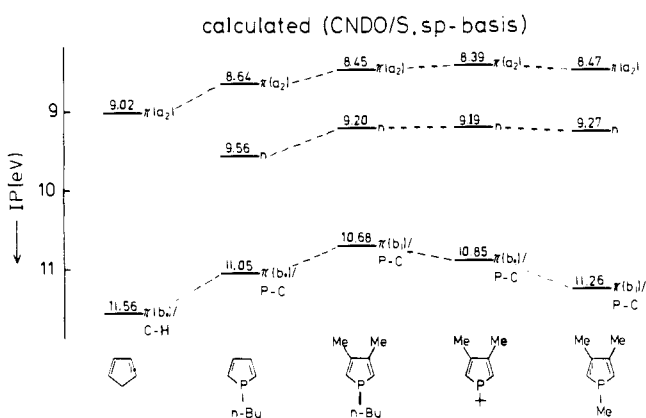


Figure 10. Calculated (using the CNDO/S method in conjunction with a *sp* basis) Koopmans' ionic state correlation diagram (identical with the orbital energy correlation diagram for the highest occupied orbitals) of cyclopentadiene, 1-butylphosphole, 1-butyl-3,4-dimethylphosphole, 1-*tert*-butyl-3,4-dimethylphosphole, and 1,3,4-trimethylphosphole. The numbers above the levels are vertical ionization potentials (or the negative of orbital energies) in eV.

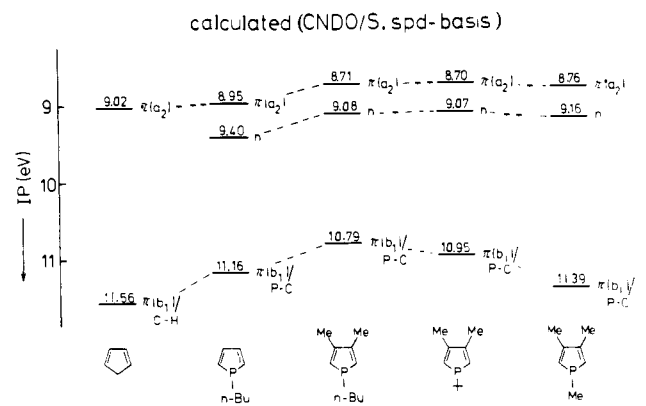


Figure 11. Calculated (using the CNDO/S method in conjunction with a *spd* basis) Koopmans' ionic state correlation diagram (identical with the orbital energy correlation diagram for the highest occupied orbitals) of cyclopentadiene, 1-butylphosphole, 1-butyl-3,4-dimethylphosphole, 1-*tert*-butyl-3,4-dimethylphosphole, and 1,3,4-trimethylphosphole. The numbers above the levels are vertical ionization potentials (or the negative of orbital energies) in eV.

ionization potentials with those of the phospholane **37** and cyclopentadiene (**7**). At first glance, no *P-C*/ $\pi(b_1)$ and *n*/

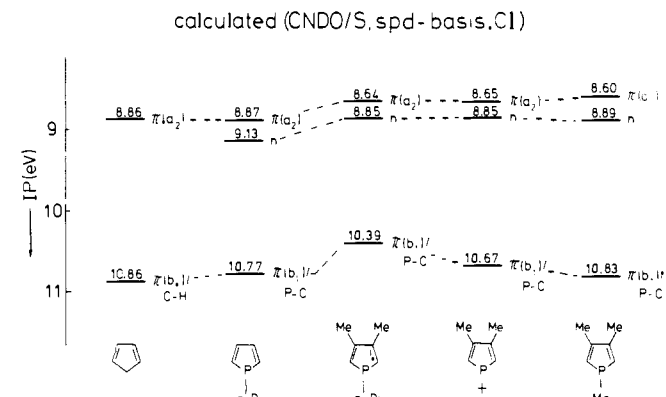


Figure 12. Calculated correlation diagram for the lowest ionic states of cyclopentadiene, 1-butylphosphole, 1-butyl-3,4-dimethylphosphole, 1-*tert*-butyl-3,4-dimethylphosphole, and 1,3,4-trimethylphosphole. The ionic states are evaluated on the base of the CNDO/S method (*spd* basis) and a recent CI approach.^{34,35} The ionizations are labeled according to the designation of orbitals from which they arise. The numbers above the levels are vertical ionization potentials in eV.

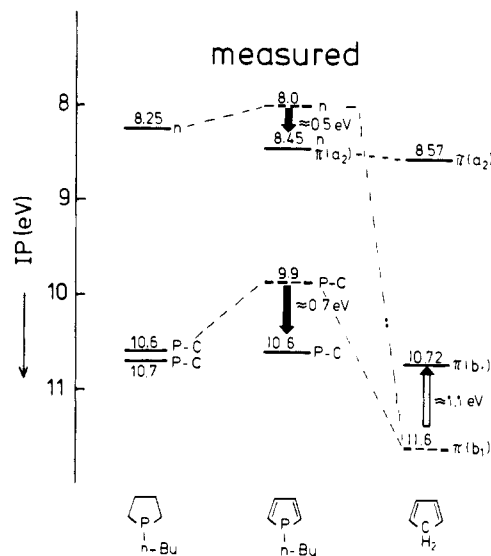


Figure 13. Experimentally derived interaction diagram for the respective orbitals (represented by their ionization potentials) of the *cis*-butadiene and PBu units. The white arrow and black arrows represent the conjugative effect of the CH_2 unit on the *cis*-butadiene $\pi(b_1)$ orbital and the inductive effects of the butadiene system on the *n* and *P-C* orbitals, respectively. For the quantitative derivation of these effects, see text.

$\pi(b_1)$ interactions would be inferred from the measured ion state energies of these compounds. But if account is taken of the facts that the $\pi(b_1)$ orbital of **7** is pushed up by about 1.1 eV³⁶ (\Rightarrow) as a consequence of *C-H*/ $\pi(b_1)$ hyperconjugation on the one hand and that the *P-C* and *n* orbitals of **6** are pulled down by about 0.5–0.7 eV (\Rightarrow) under the inductive influence of the π system, we arrive at the dotted levels of Figure 13. The corrected correlation diagram now confirms rather strong *P-C*/ $\pi(b_1)$ hyperconjugative and, as expected, weak *n*/ $\pi(b_1)$ conjugative interactions in **6**. What remains is for us to justify the applied inductive influence (0.5–0.7 eV). The 0.7 eV stems from the following three considerations. (1) The inductive effect of a *sp*² carbon atom on an adjacent ethylene π orbital has been estimated to be 0.35 eV.³⁷ Thus two *sp*² carbon atoms at α -position to the *n* and *P-C* orbitals may exert an inductive effect on these orbitals of about 0.7 eV. (2) Introduction of two double bonds into a saturated system shifts the σ ionization edge by about 0.7 eV³⁸ (for examples, see **45–47**) toward

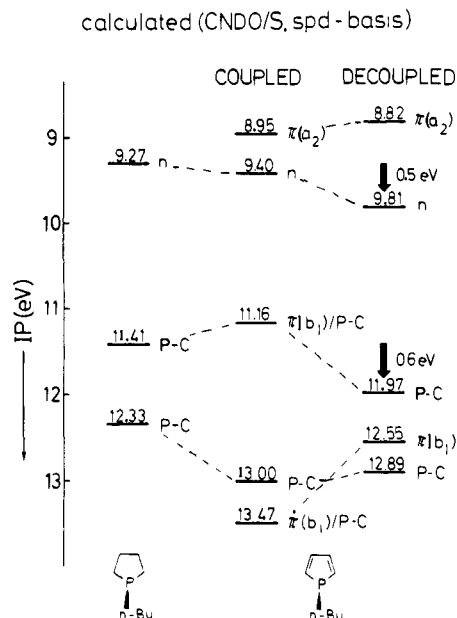


Figure 14. Comparison of calculated (using the CNDO/S method and the spd basis) orbital energies (represented by their ionization potentials) of 1-butylphospholane and coupled and decoupled 1-butylphosphole. The black arrows represent the theoretical inductive effects exerted by the π unit in phosphole on the n and P-C orbitals, respectively.

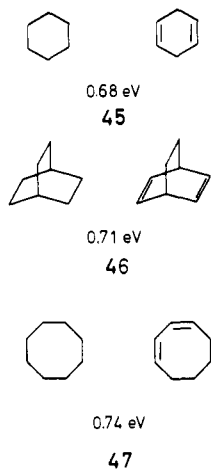
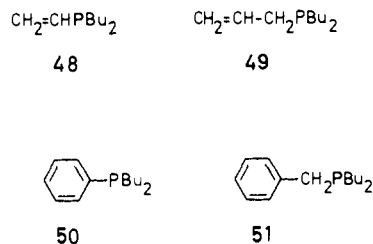


Figure 15. Calculated (on the base of the CNDO/S method in conjunction with the spd basis) $\pi(a_2)$ and $\pi(b_1)$ orbital energies of decoupled 1-butylphosphole, *cis*-butadiene (treated to have the same geometry as the π part of phospholes), and 2,3-dimethyl-*cis*-butadiene. The results demonstrate that the inductive effect of the P-Bu unit on the π orbitals is negligible and that the hyperconjugative effect of the methyl group on the $\pi(b_1)$ orbital is appreciable (represented by a white arrow).

regarding the n/ π conjugative and P-C/ π hyperconjugative interactions in dibutylvinylphosphine (**48**), allyldibutylphosphine (**49**), dibutylphenylphosphine (**50**), and benzyldibutylphosphine (**51**). In all these phosphines, n/ π interac-



tions are negligible or small and the P-C/ π interactions particularly strong. Moreover, the conformations (i.e., the stability) of **48**, **49**, and **51** are determined by P-C hyperconjugation.

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References and Notes

- (1) Part 60 of "Theory and Application of Photoelectron Spectroscopy"; part 59: G. Lauer, W. Schäfer, and A. Schweig, *Chem. Phys. Lett.*, **33**, 372 (1975).
- (2) (a) Universität Marburg/Lahn; (b) Institut National, Vert-le-Petit.
- (3) J. D. Andose, A. Rauk, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 6904 (1974), and references therein.
- (4) C. Müller, A. Schweig, and H. Vermeer, *Angew. Chem.*, **86**, 275 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 273 (1974).
- (5) W. Schäfer, A. Schweig, G. Maler, T. Sayrac, and K. J. Crandall, *Tetrahedron Lett.*, 1213 (1974).
- (6) W. Schäfer, H. Schmidt, A. Schweig, R. W. Hoffmann, and H. Kurz, *Tetrahedron Lett.*, 1953 (1974).
- (7) H. Schmidt, A. Schweig, and A. Krebs, *Tetrahedron Lett.*, 1471 (1974).
- (8) C. Müller, A. Schweig, and H. Vermeer, *J. Am. Chem. Soc.*, **97**, 982 (1975).
- (9) K. W. Schulte and A. Schweig, *Theor. Chim. Acta*, **33**, 19 (1974). All calculations are performed using the PSS1 parametrization scheme.
- (10) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.
- (11) L. E. Sutton, "Tables of Interatomic Distances", Chemical Society, London, 1968 and 1969.
- (12) Ph. Coggon, J. F. Engel, A. T. McPhall, and L. D. Quin, *J. Am. Chem. Soc.*, **92**, 5779 (1970).
- (13) W. P. Ozbirn, P. A. Jacobson, and J. C. Clardy, *Chem. Commun.*, 1062 (1971).

higher ionization potentials showing that the inductive effect of two double bonds on the highest occupied σ orbital amounts to about 0.7 eV. (3) In good agreement with these values, the calculations (Figure 14) predict inductive stabilizations for the P-C and n orbitals of about 0.6 and 0.5 eV, respectively, relative to the corresponding orbital energies of the phospholane **37**. Conversely as the calculations summarized in Figure 15 demonstrate, the inductive effect of the P-R unit on orbitals of the neighboring π system is negligible. In addition Figure 15 illustrates the influence of the methyl substituents on the butadiene π orbitals. As it is seen, the $\pi(b_1)$ orbital is appreciably shifted toward higher energies on substitution. Reconsidering Figure 9, this result helps us to explain the rather strong shifts of the $\pi(b_1)$ /P-C orbital in the series of molecules **6** and **37-40**. The $\pi(b_1)$ orbital of *cis*-2,3-dimethylbutadiene is closer in energy to the P-C orbital than is the corresponding orbital of butadiene and therefore can more effectively destabilize it.

Finally it is worthwhile to mention that the present results on the nature and extent of conjugative interactions between occupied orbitals of the π and P-R subunits of phospholes are in harmony with findings of a recent study³¹

- (14) (a) For the purpose of π -orbital classification, all molecules treated (1–8, planar as well as pyramidal forms) are regarded to have C_{2v} symmetry. (b) spd means here, as usual, inclusion of the five 3d orbitals on phosphorus in the atomic orbital basis set otherwise consisting only of the valence s and p orbitals of all atoms involved (i.e., the sp basis). In extending the CNDO/S procedure, explicit provision was made to avoid the over-emphasis of the importance of 3d orbitals known from the usual CNDO/2 method. For full details, see ref 9. (c) According to current ideas of conjugative effects in five-membered heterocycles as furane, thiophene, and pyrrole, the heteroatom lone pair (n) orbital energy is expected to be appreciably shifted in these systems relative to the corresponding n orbital energy in suitably chosen saturated reference compounds or in the respective conjugatively decoupled species as used here (for a confirmation of these ideas in the case of pyrrole, see Figure 1 of text). In addition, the idea that properties of the phosphorus lone pair (e.g., its energy) in the neighborhood of attached π systems are directly indicative of its involvement in π conjugation is very common in phosphorus chemistry. Against this backdrop, we interpreted—in a preceding preliminary (in sense that the calculations of the present paper were neither available nor possible) publication³²—our photoelectron spectroscopic observation that the n orbital energy in 1-phenylphospholes is not noticeably influenced by the attached *cis*-butadiene system as evidence for the “nonaromaticity” of phospholes. In view of the new theoretical insight into conjugated effects in phospholes gained in the present paper (it is essential in this context that the n orbital energy stays constant due to combined $n\pi$ and $n\pi^*$ effects), we may tentatively reinterpret the same experimental observation now as evidence for an “aromatic” nature of phospholes. As in this context, it must be stressed, however, that the present calculations do present the first clear-cut and direct theoretical evidence for an “aromatic” pyramidal phosphole ground state previously not available and, on the other hand, one should not forget that till now no clear experimental answer has become available to whether phospholes in their ground state conformation are “aromatic” or “nonaromatic” systems.
- (15) The orbital plots show the CNDO/S density after renormalization by the Löwdin transformation (including diatomic overlap).¹⁶ This ZDO orbital renormalization procedure was previously used on the CNDO/2 (INDO) level by several authors.^{17–20} As previously shown²¹ only the renormalized orbitals produce electron densities with correct nodal properties.
- (16) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).
- (17) C. Glesner-Prettre and A. Pullman, *Theor. Chim. Acta*, **11**, 159 (1968).
- (18) D. D. Shillady, F. P. Billingsley, and J. E. Bloor, *Theor. Chim. Acta*, **21**, 1 (1971).
- (19) D. B. Boyd, *J. Amer. Chem. Soc.*, **94**, 64 (1972).
- (20) J. W. McIver, P. Coppens, and D. Nowak, *Chem. Phys. Lett.*, **11**, 82 (1971).
- (21) H. L. Hase, H. Meyer, and A. Schweig, *Z. Naturforsch. A*, **29**, 361 (1974).
- (22) For the plot program used, see: (a) H. Hahn and J. Radloff, *Elektron. Reschenanl.*, **14**, 128 (1972); (b) H. L. Hase, A. Schweig, H. Hahn, and J. Radloff, *Tetrahedron*, **29**, 475 (1973); (c) *ibid.*, **29**, 469 (1973).
- (23) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **92**, 1442 (1970).
- (24) D. A. Brown, *J. Chem. Soc.*, 929 (1962).
- (25) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).
- (26) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 4050 (1968).
- (27) The role of d orbitals on phosphorus has also been recognized elsewhere: G. Kaufmann and F. Mathey, *Phosphorus*, **4**, 231 (1974).
- (28) For the synthesis of these compounds, see: (a) F. Mathey and R. Manowski-Faveller, *Bull. Soc. Chim. Fr.*, 4433 (1970); (b) *J. Org. Magn. Reson.*, **4**, 171 (1972); (c) F. Mathey, *Tetrahedron*, **28**, 4171 (1972).
- (29) J. H. Hillier and V. R. Saunders, *J. Chem. Soc., Faraday Trans. 2*, **66**, 2401 (1970).
- (30) S. Elbel, H. Bergmann, and W. Ensslin, *J. Chem. Soc., Faraday Trans. 2*, **70**, 555 (1974).
- (31) H. Schmidt, A. Schweig, F. Mathey, and G. Müller, *Tetrahedron*, **31**, 1287 (1975).
- (32) W. Schäfer, A. Schweig, G. Märkl, H. Hauptmann, and F. Mathey, *Angew. Chem.*, **85**, 140 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 145 (1973).
- (33) Ion states calculated on the base of Koopmans' theorem: T. Koopmans, *Physica*, **1**, 104 (1934).
- (34) G. Lauer, K. W. Schulte, and A. Schweig, *Chem. Phys. Lett.*, **32**, 163 (1975).
- (35) G. Lauer, W. Schäfer, and A. Schweig, *Chem. Phys. Lett.*, **33**, 312 (1975).
- (36) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971).
- (37) C. Batich, P. Bischoff, and Heilbronner, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 333 (1972–1973).
- (38) P. Bischoff, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

Mechanisms of Ligand Association in Complexes of the Type $RML_3^+X^-$ ($M = Ni, Pd, Pt$). I. Mechanistic Aspects of Nuclear Magnetic Resonance Line Shape Analysis for Intermolecular Exchange in Non-First-Order Multispin Systems

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Abstract: General computer programs applicable to intermolecular exchange in non-first-order spin systems have been developed. Their scope and application is illustrated with reference to the equilibrium $HPd[P(C_2H_5)_3]_3^+ + P(C_2H_5)_3 \rightleftharpoons HPd[P(C_2H_5)_3]_4^+$. In this case four separate rate processes can be considered, k_1 , k_{-1} , k_m (the rate of intramolecular rearrangement in HML_4^+), and k_m' (the rate of intramolecular rearrangement in HML_3^+). The computer programs can be applied to a wide range of combinations of simultaneously occurring intermolecular and intramolecular processes. Permutational analyses have been carried out for the intermolecular case which are an extension of those we have developed earlier for intramolecular rearrangement. The approach enables one to extract detailed mechanistic information concerning the mode of ligand attack and the site occupied by the attacking ligand in the five-coordinate intermediate. It also allows the generation of linear combinations of permutational sets, for use in the line shape calculations where competing rate processes are occurring at comparable rates. This can lead to a quantitative estimate of the ratio of the two rates, e.g., k_{-1}/k_m .

The application of detailed NMR line shape analyses to the determination of both rates and mechanisms for transition metal complexes undergoing intramolecular exchange is well established. In contrast, relatively little work of this type has been carried out for intermolecular exchange processes. General computer programs which can handle non-

first-order multispin systems undergoing intramolecular exchange have been available for some years.^{1–4} Most NMR line shape calculations for intermolecular exchange have been restricted to first-order systems where existing computer programs for nonmutual intermolecular exchange can be used directly or with slight modification. In some in-