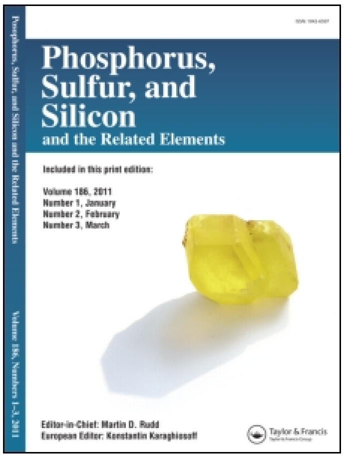

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Comparison of the Donor Properties of 5-Phenyldibenzophosphole and Triphenylphosphine in Tetrahedral Nickel(II) Complexes

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To cite this Article Allen, David W. and Hogarth, David(1977) 'A Comparison of the Donor Properties of 5-Phenyldibenzophosphole and Triphenylphosphine in Tetrahedral Nickel(II) Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 3: 3, 381 — 382

To link to this Article: DOI: 10.1080/03086647708079952

URL: http://dx.doi.org/10.1080/03086647708079952

Phosphorus and Sulfur
1977, Vol. 3, pp. 381-382

SHORT COMMUNICATION†

A Comparison of the Donor Properties of 5-Phenyldibenzophosphole and Triphenylphosphine in Tetrahedral Nickel(II) Complexes

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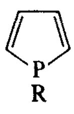
(*Received February 16, 1977*)

A comparison of the electronic spectra of tetrahedral nickel(II) complexes of 5-phenyldibenzophosphole and triphenylphosphine shows that the former is a better donor towards the metal ion.

The extent of delocalization of the lone pair at phosphorus in phosphole and its benzologues continues to be a matter of controversy and the somewhat conflicting literature relating to the phosphole "aromaticity problem" has been reviewed recently.[1] The most recent theoretical approaches, in conjunction with the results of photoelectron spectroscopy, view the phosphole system **1** as an "aromatic" species, and suggest that there is significant interaction of both the lone pair and the phosphorus *d* orbitals with the diene system.[2,3] There is clearly a need for further experimental work aimed at assessing the extent of lone pair availability in phosphole systems. We have recently reported[4] a comparison of the rates of quaternization of 5-phenyldibenzophosphole (5PhDBP, **2**, R = Ph) and triphenylphosphine (TPP, **3**, R = Ph), and now report a comparison of the donor properties of 5PhDBP and TPP in a series of tetrahedral complexes of nickel(II) halides by a consideration of the electronic spectra of the complexes.



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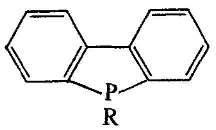

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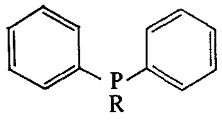

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The complexes, of composition $(phos)_2NiX_2$ (X = Cl, Br, I), have been described previously.[5-7] The TPP complexes have been shown to have a distorted tetrahedral structure[8,9] and a similar structure has been assumed for the 5-PhDBP complexes on the basis of magnetic susceptibility data.[7] Details of the solid state (diffuse reflectance) electronic spectra of the complexes of the above phosphines are given in Table.

Tetrahedral nickel(II) complexes exhibit an absorption band in the near IR at about 10-11,000 cm^{-1}, due to the $^3A_2 \leftarrow {}^3T_1$ transition. The position of this band reflects the ligand field strength of the ligands in the tetrahedral complex, the wavenumber increasing as the donor ability of the ligand increases. It has been shown that for the tetrahedral nickel(II) complexes of a series of p-substituted phenylphosphines that electron-withdrawing *para*-substituents cause the above absorption band to move to lower wavenumber.[10,11]

The overall similarity in the spectra of the two series of complexes is consistent with the previously assumed similarity in structure. It is apparent, however, from a consideration of the band positions, that in the above tetrahedral nickel(II) complexes, 5-PhDBP appears to be a *better* donor towards the metal ion than does TPP, since the absorption bands exhibited by the 5-PhDBP complexes are at higher energies than those of the TPP complexes. This is supported by calculation of the crystal field parameters, which show that the CFSE values for the 5-PhDBP complexes are consistently larger than for the TPP complexes, indicating a greater degree of interaction between the ligand and the metal.

This indication is of interest from a number of points of view. Firstly, it conflicts with the results of our earlier study of rates of quaternization in which we showed that 5-PhDBP undergoes quaternization with phenacyl bromide some five times more slowly than does TPP, suggesting that in the case of 5-PhDBP the lone pair at phosphorus is less available in the

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† No reprints available.

TABLE

Solid state (diffuse reflectance) spectra* of nickel(II) complexes of triphenylphosphine and 5-phenyldibenzophosphole

Complex	$\bar{\nu}_{max}$ cm^{-1}		Crystal field parameters†		
	$\nu_3(^3T_1(P) \leftarrow {}^3T_1)$	$\nu_2(^3A_2 \leftarrow {}^3T_1)$	10Dq cm^{-1}	B′ cm^{-1}	β
(5-PhDBP)$_2$NiCl$_2$	18,416	11,370	6133	938	0.90
(5-PhDBP)$_2$NiBr$_2$	18,083	11,370	6138	915	0.88
(5-PhDBP)$_2$NiI$_2$	14,285	11,025	5910	662	0.63
(TPP)$_2$NiCl$_2$	17,857	10,893	5596	928	0.89
(TPP)$_2$NiBr$_2$	16,949	10,893	5879	851	0.82
(TPP)$_2$NiI$_2$	13,986	9,970	5360	673	0.65

* Recorded on an SP700 spectrophotometer using MgO as reference (and diluent as necessary).

† Calculated as described by Lever.[14]

transition state of the quaternization reaction than is the case of TPP.[4] Secondly, it may have a bearing on certain apparent anomalies in the co-ordination chemistry of 5-substituted dibenzophospholes reported in recent years. In a study of the donor properties of 5-PhDBP towards rhodium, Hughes *et al.* have shown that the phosphole appears to have a donor character comparable to that of some trialkyl or arylalkylphosphines which are known to be better donors than TPP.[12,13] Thirdly, we have shown[7] that 5-alkyldibenzophospholes (2, R = Me, Et) have unusual donor properties towards d^8 metal ions in that they form series of five co-ordinate complexes of the type [(phos)$_3$MX$_2$] (M = Ni, Pd, Pt, X = halogen), whereas the corresponding acyclic alkyldiphenylphosphines (3, R = Me, Et) are only able to form four co-ordinate complexes of the type [(phos)$_2$MX$_2$] under the same conditions.

The above observations on dibenzophosphole-metal halide complexes, which may be consistent with the lone pair at phosphorus being *more* available (compared with TPP) for donation to the metal, are perhaps a consequence of the reduced steric bulk of the ligand compared with the acyclic phosphines, thus permitting the phosphole ligand to approach closer to the metal. Nevertheless, the donor properties of 5-PhDBP (and the corresponding 5-alkyldibenzophospholes) are certainly not in keeping with any significant degree of delocalization of the lone pair compared to the situation for TPP.

Our studies of the availability of the lone pair at phosphorus in phosphole systems are continuing.

REFERENCES

1. A. N. Hughes and D. Kleemola, *J. Heterocyclic Chem.* 13, 1 (1976).
2. W. Schäfer, A. Schweig and F. Mathey, *J. Amer. Chem. Soc.* 98, 407 (1976).
3. N. D. Epiotis and W. Cherry, *J. Amer. Chem. Soc.* 98, 4365 (1976).
4. D. W. Allen, J. R. Charlton and B. G. Hutley, *Phosphorus* 5, 9 (1974).
5. L. M. Venanzi, *J. Chem. Soc.* 719 (1958).
6. M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.* 4816 (1961).
7. D. W. Allen, F. G. Mann and I. T. Millar, *J. Chem. Soc. (A)* 1101 (1969).
8. G. Garton, D. E. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc.* 3625 (1963).
9. J. A. J. Jarvis, R. H. B. Mais and P. G. Owston, *J. Chem. Soc.* 1473 (1968).
10. L. H. Pignolet and W. De W. Horrocks Jr., *J. Amer. Chem. Soc.* 91, 3976 (1969).
11. L. H. Pignolet, W. De W. Horrocks Jr. and R. H. Holm, *J. Amer. Chem. Soc.* 92, 1855 (1970).
12. D. G. Holah, A. N. Hughes and B. C. Hui, *Can. J. Chem.* 50, 3714.
13. D. G. Holah, A. N. Hughes and K. Wright, *Coord. Chem. Reviews* 15, 239 (1975).
14. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, 1968; *J. Chem. Ed.* 45, 711 (1968).