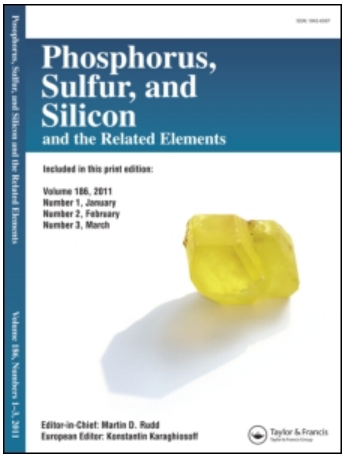

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Malito, John and Alyea, Elmer C.(1990) 'STERIC AND ELECTRONIC DESTABILIZATION OF THE P—Se BOND IN TRIARYLPHOSPHINE SELENIDE SYSTEMS', Phosphorus, Sulfur, and Silicon and the Related Elements, 54: 1, 95 — 99
To link to this Article: DOI: 10.1080/10426509008042125
URL: http://dx.doi.org/10.1080/10426509008042125

Phosphorus, Sulfur, and Silicon, 1990, Vol. 54, pp. 95–99
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STERIC AND ELECTRONIC DESTABILIZATION OF THE P—Se BOND IN TRIARYLPHOSPHINE SELENIDE SYSTEMS

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(Received February 12, 1990; in final form March 22, 1990)

Electronic and steric effects in $SeP(Ar)_3$ compounds are discussed with the assistance of $^1J(^{77}Se-^{31}P)$ correlations with d(P—Se) values and the pKa of the arylphosphines.

Key words: triarylphosphine selenides, steric and electronic effects, $^1J(^{77}Se-^{31}P)$ correlations

INTRODUCTION

While characterizing several bulky triarylphosphines, ($P(Ar)_3$) to complement ongoing studies of their transition metal chemistry,[1] we were surprised to find that neither trimesitylphosphine ($P(mes)_3$) nor tri*ortho*xylylphosphine ($P(o\text{-}oxylyl)_3$) form selenides despite the relative ease of formation and stability of the related oxides and sulphides. This prompted an investigation into the nature of the P—Se bond in $SeP(Ar)_3$ systems.

EXPERIMENTAL

Compounds (1)–(9) and (11) were prepared by direct reaction of the appropriate phosphine and selenium black (10% molar excess) in refluxing toluene (6h) under a dinitrogen atmosphere. Products were purified by recrystallization from ethanol followed by several ether washes. Yields were quantitative. This and other synthetic methods were attempted without success several times each for $P(mes)_3$ and $P(o\text{-}xylyl)_3$. As was detailed earlier for $P(mes)_3$[1(g)], the attempted methods included refluxing with KSeCN in acetonitrile, refluxing with a less basic triarylphosphine in toluene, and heating an intimate mixture of the phosphine and selenium to the melting point. The ^{31}P NMR spectra were recorded for 1M $CDCl_3$ solutions in 10.0 mm O.D. tubes on a Bruker WH-400 spectrometer operating in the pulsed FT mode at 161.98 MHz at 293 K. Chemical shifts downfield of the external reference, 80% aqueous H_3PO_4 (0.00 ppm), are positive. Chemical shifts and ^1J values are believed to be accurate to ± 0.01 ppm and ± 1.5 Hz respectively.

RESULTS AND DISCUSSION

The compounds considered in this investigation (see Table I) were all prepared in like manner. The ^{31}P NMR data were also acquired in a similar fashion, so as to maintain self-consistency in view of observable temperature and solvent effects on both ^1J and $\Delta\delta$ values. Data for (1), (3) and (11) are new. Compound (1) is the selenide of 1-phenyldibenzophosphole (DBP) which, strictly speaking, is not a triarylphosphine but is included for the purposes of discussion.

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TABLE I

Parameters for $SeP(Ar)_3$ Compounds

$P(Ar)_3$	pKa[a]	d(P—Se)(Å)	$^1J(^{77}Se\text{-}^{31}P)$(Hz)[b]	$\Delta\delta^{31}P$(ppm)[c]
(1) DBP	0.50	2.098(3)[d]	747(747)[i]	37.6
(2) $P(p\text{-}C_6H_4Cl)_3$	1.03	—	749(753)[j]	41.7
(3) $P(p\text{-}C_6H_4F)_3$	1.97	—	740(−)	41.4
(4) PPh_3	2.73	2.106(1)[e]	729(733)[k]	40.7
(5) $P(o\text{-tol})_3$	3.08	2.116(5)[f]	706(708,[j] 703)[l]	57.7
(6) $P(m\text{-tol})_3$	3.30	2.109(5)[g]	722(726)[j]	40.4
(7) $P(p\text{-tol})_3$	3.84	—	720(723,[j] 715)[l]	41.6
(8) $P(o\text{-}C_6H_4MeO)_3$	—	—	722(720)[l]	58.8
(9) $P(p\text{-}C_6H_4MeO)_3$	4.57	—	713(710)[l]	41.9
(10) $P(m\text{-}C_6H_4CF_3)_3$	—	2.094(2)[h]	(766)[l]	—
(11) $P(p\text{-}C_6H_4NMe_2)_3$	8.65	—	683(−)	41.6

[a] L. D. Quin, J. G. Bryson and C. G. Moreland, *J. Am. Chem. Soc.*, 1969, **91**, 3308 (value for (1)); T. Allman and R. G. Goel, *Can. J. Chem.*, 1982, **60**, 716 (values for (2)–(11)).

[b] Literature values are given in parentheses.

[c] $\Delta\delta = \delta SeP(Ar)_3 - \delta P(Ar)_3$ in ppm.

[d] Ref. 4.

[e] P. W. Codding and K. A. Kerr, *Acta Cryst.*, 1979, **B35**, 1261.

[f] T. S. Cameron and B. Dahlén, *J. Chem. Soc.*, Perkin II, 1975, 1737.

[g] T. S. Cameron, K. D. Howlett and K. Miller, *Acta Cryst.*, 1978, **B34**, 1639.

[h] Ref. 2.

[i] Ref. 6.

[j] R. P. Pinell, C. A. Megerle, S. L. Manatt and P. A. Kroon, *J. Am. Chem. Soc.*, 1973, **95**, 977.

[k] D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51.

[l] Ref. 13.

Comparisons of the coupling data with available P—Se bond distance and $P(Ar)_3$ pKa data lead to two very informative correlations. The first (Figure 1) represents a good inverse linear correlation of the $y = mx + b$ type (R_2 = 98.1% or 99.4% if the datum point for (1) is excluded) despite a previous suggestion[2] that differences in d(P—Se) values are not crystallographically significant.

Clearly, the P—Se interatomic distance decreases with increased phosphorus coupling to selenium-77. This implies, as expected, that the P—Se bond shortens (and presumably strengthens) with increasing s-orbital overlap between the two nuclei. The extent of this overlap must be affected by both the steric and electronic properties of the aryl substituents on phosphorus.

The parent phosphines of (4), (6) and (10) are of more or less equal size (i.e., $\Theta = 145°$)[3] whereas DBP must necessarily be smaller[4] and $P(o\text{-tol})_3$ is larger ($\Theta = 184°$).[3] Also, the rigidity of DBP should be a further steric factor[5] especially since C-P-C angle opening upon selenide formation is severely restricted relative to (4).[6] Nevertheless, (1) and (5) fit the correlation (Figure 1) very well.

The larger phosphines, $P(mes)_3$ and $P(o\text{-xylyl})_3$, ($\Theta = 212°$)[3] do not form selenides indicating that their size might be above the steric limit to P—Se bond formation inferred from linear extrapolation in Figure 1. In effect then, steric factors may have become so dominating for these two phosphines, that P—Se bond formation is thereby prevented, as found experimentally in several attempts[1(g)]. Electronic effects must also be considered however in explaining the phenomenon. The d(P—Se) values also increase with increasing pKa of the parent $P(Ar)_3$. Thus, the

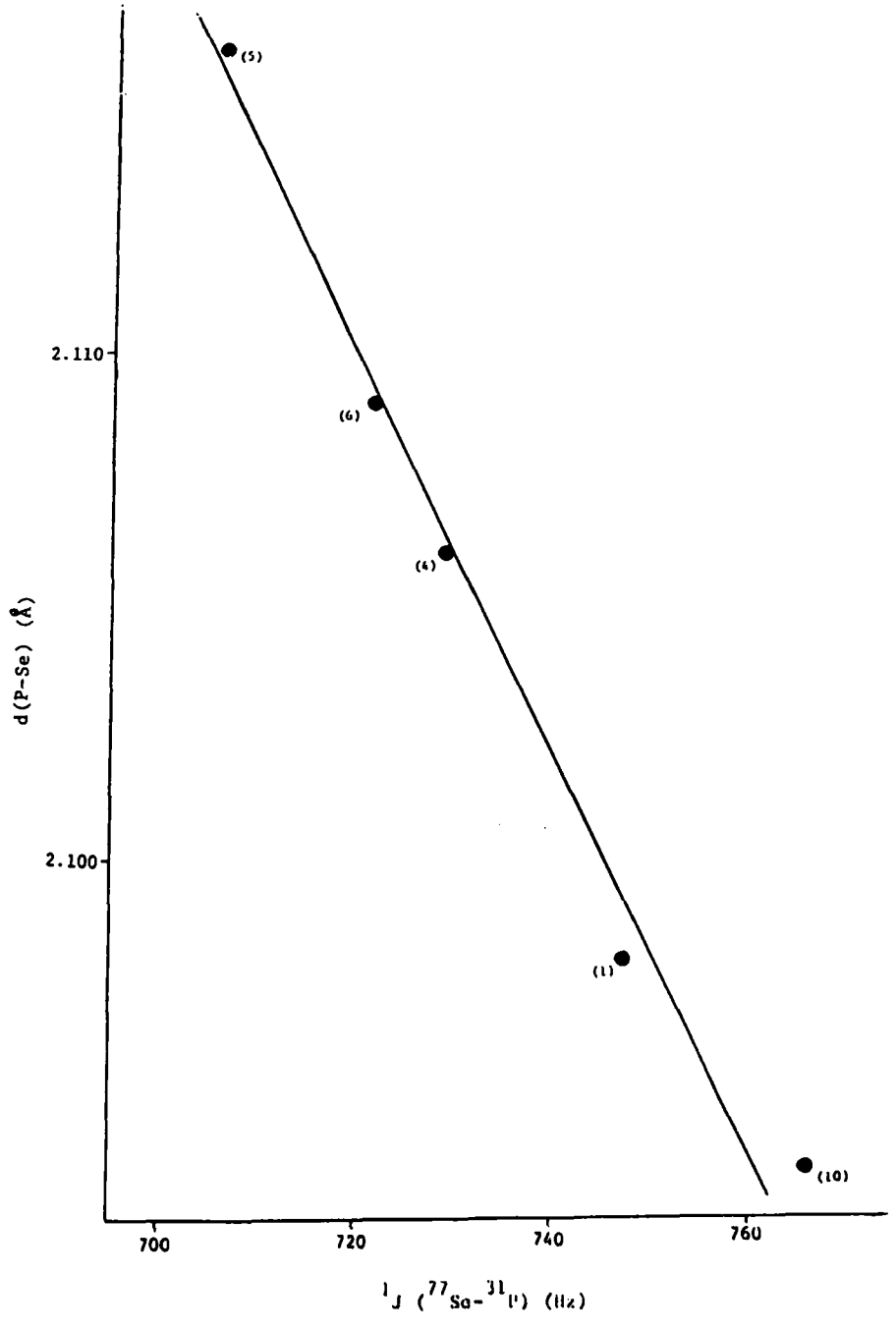


FIGURE 1 Correlation of P—Se internuclear bond distance with ^{31}P-^{77}Se coupling.

P—Se bond length is demonstrably sensitive to a combination of steric and electronic effects. Increases in either (or both) the size or basicity of $P(Ar)_3$ leads to relatively weaker P—Se bonds in $SeP(Ar)_3$.

Moreover, if strong P—Se bonds correspond to higher ^1J values (Figure 1), then the correlation in Figure 2 implies that d(P—Se) in the closely related series (1)–(11) is longest for (11). The ^1J value for this compound is perhaps the smallest hitherto reported for a tertiary phosphine selenide.[7] It should be noted however, that we have recently measured a value of 673 Hz for tricyclohexylphosphine selenide under almost similar conditions.[8]

Figure 2 is an attempt to restrict discussion to electronic effects only. Thus, it is not surprising that (1) and (5) do not fit this correlation in view of their very different steric properties. That (11) is "off the line" despite its "correct size" (i.e., $\Theta = 145°$) suggests a measurable electronic limit to P—Se bond formation. An X-ray crystal structure of (11) may lead to some physical meaning for the ordinate axis intercept in Figure 1. This value (2.379 ± 0.001 Å) is less than the van der Waals contact (3.75 Å)[9] but larger than either the sum of the covalent radii (2.27 Å) or the ionic radii (2.32 Å).[10] In any case, all the d(P—Se) values in Table I (2.09–2.12 Å) come close to what one might expect for a P=Se double bond (2.07 Å).[10]

This study is being pursued in more detail and with extension to trialkylphosphine

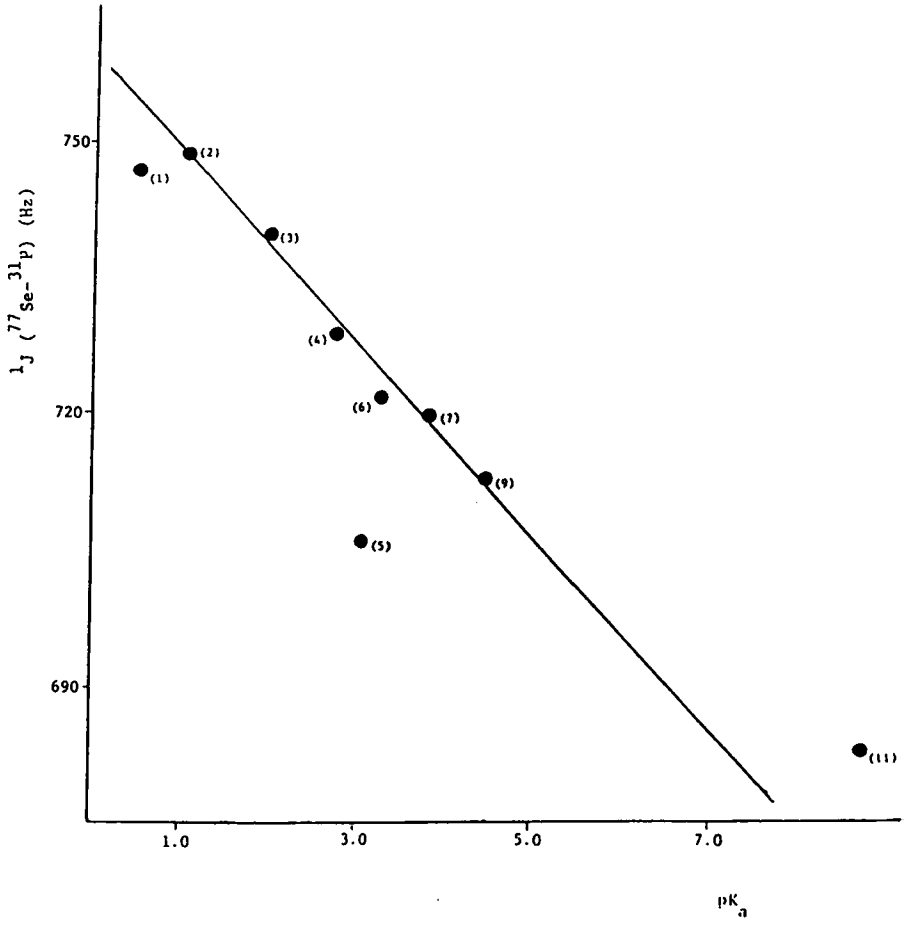
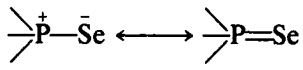


FIGURE 2 Correlations of ^{31}P-^{77}Se coupling with basicity (pKa) of the parent phosphine.

selenides in order to evaluate the relative importance and/or variability of the two suggested canonical forms of the resonance hybrid[11-13]



as contributors to P—Se bond formation and bond strength.

ACKNOWLEDGEMENTS

The authors wish to thank Imperial Oil Limited (Canada) for a University Research Grant (E. C. A. and J. M.) and the Government of Ontario for a Graduate Scholarship (J.M.).

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