N-Phenyl-*P,P,P*-triarylphospha-λ^5-azenes, Triarylphosphines, and Triarylphosphine Oxides. Substituent Effects on ^{15}N, ^{31}P, and ^{13}C NMR Spectra

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The syntheses and ^{15}N, ^{31}P, and ^{13}C NMR spectra of a series of *N*-phenyl-*P,P,P*-triarylphospha-λ^5-azenes **4** and the ^{31}P and ^{13}C NMR spectra of the corresponding series of triarylphosphines **5** and triarylphosphine oxides **6** are reported. The substituent effects on the chemical shifts can be best accommodated and rationalized by use of a model for system **4** whereby the dipole of the aryl group and its pendant R group polarizes the rest of the molecule. This includes the P and N atoms and phenyl ring, where an electron-withdrawing R group increases the electron density on the P, N, and ipso C-1 while decreasing the electron density on C-3 and C-4 of the *N*-phenyl ring (Figure 3). A similar polarization pattern for the phosphine oxide series **6** is suggested. In the phosphine series **5**, the chemical shift data is consistent with the lone electron pair on the phosphorus atom delocalizing into the aryl rings. The coupling constant data, in particular $^1J_{PN}$ for series **4** and $^1J_{PC}$ for series **4–6**, were examined with use of the Hammett monosubstituent parameter (MSP) and the Taft dual-substituent parameter (DSP) approaches. For systems **4** and **6**, without a lone electron pair on the phosphorus atom, a better electron-donating substituent increases the one-bond P–C(Ar) coupling constant. On the contrary, in the phosphine series **5**, where there is a lone electron pair on the phosphorus, a better electron-withdrawing substituent increases the one-bond P–C(Ar) coupling constant. DSP treatment of $^1J_{PC}$, and comparing to the few related systems in the literature, shows three types of systems. One, which includes **4** and **6**, has an atom, phosphorus in these cases, that does not have a lone pair of electrons attached to the ring to which is attached an atom with a lone pair of electrons. Here, the resonance effect on $^1J_{PC}$ predominates. A second series, which includes phosphines **5**, has a lone pair on the atom attached to the aryl ring. In these cases, the resonance effect is ~50% greater than the inductive effect. Finally, the third series, exemplified by two examples from the literature, has a tetrahedral atom (without a lone pair) attached to the aryl ring and this in turn is attached to tetrahedral atoms without lone electron pairs. In these case, the resonance and inductive effects are fairly comparable.

Introduction

As part of our ongoing interest in the multinuclear NMR spectra of phospha-λ^5-azenes and their relationship to the electronic structure of these systems,[2-5] we have prepared and examined the ^{15}N, ^{31}P, and ^{13}C spectra of several series of substituted compounds. These have included *N*-aryl-*P,P,P*-triphenylphospha-λ^5-azenes **1**,[4,5] *N*-(arylsulfonyl)-*P,P,P*-triphenylphospha-λ^5-azenes **2**,[3] and *N*-aroyl-*P,P,P*-triphenylphospha-λ^5-azenes **3**.[2]

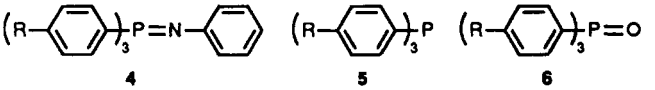
$Ph_3P{=}NC_6H_4R$ (**1**) $\quad Ph_3P{=}NSO_2C_6H_4R$ (**2**) $\quad Ph_3P{=}NCOC_6H_4R$ (**3**)

In system **1**, based on the ^{31}P, ^{15}N, and ^{13}C substituent effects on the NMR chemical shifts, we found considerable charge delocalization into the aryl ring as shown in resonance forms A, B, and C. With the strongly π-electron-withdrawing substituents *p*-NO_2 and *p*-CN, where it is possible to have direct resonance interaction between the lone pair of electrons on the nitrogen and the substituents, the chemical shift correlations were with the σ^- Hammett substituent constants rather than with σ.[4,5] Further, the changes in the one-bond coupling constants $^1J_{PN}$ and $^1J_{PC}$ were shown to be consistent with changes in the phosphorus–nitrogen double bonding, and PRDDO quantum mechanical calculations showed that the PN double bond is most likely composed of both pπ–dπ and pπ–σ^* components where the latter involves the antibonding P–C(phenyl) orbital.[4]

In series **2**, where an SO_2 group has been placed between the substituted aryl ring and the nitrogen atom, the substituent effects diminshed somewhat and now the observed effects on chemical shifts were with σ rather than σ^-.[3] The SO_2 group allows the transmission of inductive effects but is insulating with respect to resonance effects.[3] Again, changes in the one-bond coupling constants $^1J_{PC}$ and $^1J_{PN}$ were consistent with σ and π bonding effects, which include both pπ–dπ and pπ–σ^* multiple PN bonding.

Our most recent NMR study on *N*-aroyl-*P,P,P*-triarylphospha-λ^5-azenes **3**[2] showed, from the chemical shift data, that **3** can be viewed as being made up of three interacting subunits (see Figure 1). The response of the one-bond coupling constants $^1J_{PN}$ and $^1J_{PC}$ to changes in substituent is consistent with pπ–dπ and pπ–σ^* multiple bonding between the P and N atoms. An alternative explanation involving electrostatic interactions (Figure 1) could also explain the changes in these coupling constants.[3]

In this paper, we report on the ^{13}C, ^{15}N, and ^{31}P NMR spectra of the series of *N*-phenyl-*P,P,P*-triarylphospha-λ^5-azenes **4a–i** and compare the data with the ^{31}P and ^{13}C NMR spectra of a similar series of triarylphosphines **5a–i** and triarylphosphine oxides **6a–i**.



4: **a**: R = NMe_2; **b**: R = OMe; **c**: R = Me

5: **d**: R = H; **e**: R = F; **f**: R = Cl

6: **g**: R = CF_3; **h**: R = CO_2Me; **i**: R = CN

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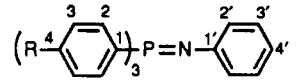
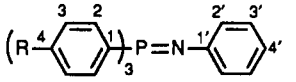
Table I. ^{13}C, ^{15}N, and ^{31}P NMR Chemical Shifts (δ) of *N*-Phenyl-*P*,*P*,*P*-triarylphospha-λ^5-azenes 4



		^{13}C									
compd	R	1	2	3	4	1′	2′	3′	4′	$^{15}N^a$	$^{31}P^b$
4a	NMe_2[c]	117.20	133.88	113.30	151.84	152.89	123.25	128.25	115.77		7.37
4b	OMe[d]	122.72	134.34	114.08	162.08	151.63	123.33	128.51	116.89	79.57	3.93
4c	Me[e]	128.03	132.59	129.23	141.86	151.51	123.37	128.47	116.92	78.24	4.23
4d	H[f]	130.98	132.61	128.56	131.63	150.91	123.43	128.57	117.39	77.34	3.73
4e	F	126.77	134.91	116.17	164.96	150.30	123.34	128.78	117.93	78.09	0.12
4f	Cl	128.93	133.77	129.17	138.71	149.91	123.35	128.81	118.14	77.06	−0.28
4g	CF_3[g]	134.34	132.93	125.84	134.13	149.11	123.43	129.01	118.81	76.03	−2.66
4h	COOMe[h]	135.05	132.54	129.74	133.42	149.53	123.46	128.86	118.46	76.26	−0.09
4i	CN[i]	134.68	132.86	132.55	116.44	148.14	123.34	129.12	119.38	75.91	−4.16

[a] Relative to $^{15}NH_3$. [b] Extrapolated to infinite dilution and relative to 85% H_3PO_4. [c] NCH_3: 39.97. [d] OCH_3: 55.30. [e] CH_3: 21.52. [f] The ^{13}C and ^{31}P chemical shifts are in reasonable agreement with those in refs 20 and 21. [g] CF_3: 123.39. [h] CO: 166.03. OCH_3: 52.53. [i] CN: 117.38.

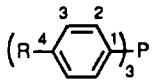
Table II. P–C, C–N, and P–N NMR Coupling Constants (Hz) of *N*-Phenyl-*P*,*P*,*P*-triarylphospha-λ^5-azenes 4



		J_{PC}								J_{CN}			
compd	R	1	2	3	4	1′	2′	3′	4′	1	1′	2′	J_{PN}^a
4a	NMe_2	108.8	10.7	12.5	3.4	3.0	18.6	1.6	*b*				
4b	OMe	105.4	10.9	12.9	2.8	2.8	18.0	1.5	*b*	3.7	6.8	4.2	33.9
4c	Me[c]	101.0	9.9	12.3	2.8	2.7	18.0	1.6	*b*	3.6	6.9	4.1	33.9
4d	H	99.0	9.6	11.9	2.9	2.6	17.5	1.4	0.6	3.6	7.1	4.1	33.5
4e	F[d]	103.1	11.2	13.2	3.3	2.4	17.4	1.1	0.7	*e*	7.0	4.0	32.8
4f	Cl	101.4	10.6	12.7	3.5	2.4	17.5	1.2	0.9	3.8	7.5	4.1	33.1
4g	CF_3[f]	98.2	10.1	12.3	3.0	2.1	17.2	1.0	1.0	*e*	7.8	4.0	32.5
4h	COOMe[g]	97.3	9.9	12.2	2.9	2.1	17.1	1.1	*b*	3.3	7.1	4.0	32.8
4i	CN[h]	97.6	10.0	12.2	3.2	1.7	16.8	0.8	1.0	3.7	7.5	3.9	31.5

[a] From ^{15}N spectra. [b] Too small to measure. [c] $^5J_{PC} = 1.4$. [d] $^1J_{FC\text{-}4} = 250.1$, $^2J_{FC\text{-}3} = 21.4$, $^3J_{FC\text{-}2} = 8.8$, $^4J_{FC\text{-}1} = 3.5$. [e] Broad peak (split by ^{19}F, ^{31}P and ^{15}N). [f] $^1J_{FC}(CF_3) = 272.9$, $^2J_{FC\text{-}4} = 33.0$, $^3J_{FC\text{-}3} = 3.7$, $^4J_{FC\text{-}2}$ is too small to measure, $^5J_{FC\text{-}1} = 1.5$. [g] $^5J_{PC}(CO) = 1.0$. [h] $^5J_{PC} = 1.7$.

Table III. ^{13}C and ^{31}P NMR Chemical Shifts (δ) of Triarylphosphines 5



		^{13}C				
compd	R	1	2	3	4	$^{31}P^a$
5a	NMe_2[b]	124.42	134.54	112.27	150.32	−10.21
5b	OMe[c]	128.47	134.99	114.24	160.39	−9.48[d]
5c	Me[e]	132.12	133.65	129.37	139.16	−7.26[d]
5d	H[f]	137.16	133.70	128.45	128.67	−4.73[d]
5e	F	132.46	135.43	115.90	163.42	−8.41[d]
5f	Cl	134.85	134.81	128.98	135.54	−7.84[d]
5g	CF_3[g]	140.30	134.00	125.67	131.59	−5.48[d]
5h	COOMe[h]	141.68	133.60	129.64	130.86	−4.63
5i	CN[i]	140.90	134.09	132.39	113.64	−3.43

[a] Extrapolated to infinite dilution and relative to 85% H_3PO_4. [b] NCH_3: 40.32. [c] OCH_3: 55.21. [d] The ^{31}P chemical shifts are in reasonable agreement with those in ref 22. [e] CH_3: 21.34. [f] The ^{13}C chemical shifts are in reasonable agreement with those in refs 23 and 24. [g] CF_3: 123.86. [h] CO: 166.59, OCH_3: 52.28. [i] CN: 118.01.

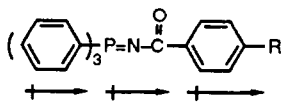
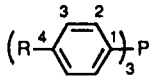


Figure 1. Dipoles induced in 3 when R becomes more electron withdrawing.

Table IV. P–C NMR Coupling Constants (Hz) of Triarylphosphines 5



		J_{PC}		
compd	R	1	2	3
5a	NMe_2	4.4	20.2	7.6
5b	OMe	5.6	20.1	8.2
5c	Me	10.3	18.8	7.7
5d	H	10.8[a]	19.5[a]	6.9[a]
5e	F[b]	10.9	21.2	7.7
5f	Cl	12.1	20.5	7.3
5g	CF_3[c]	13.9	19.8	7.3
5h	COOMe	13.7	20.7	7.0
5i	CN	16.1	20.2	7.0

[a] The J_{PC} values are in reasonable agreement with those in refs 23 and 24. [b] $^1J_{FC\text{-}4} = 249.6$, $^2J_{FC\text{-}3} = 21.0$, $^3J_{FC\text{-}2} = 8.0$, $^4J_{FC\text{-}1} = 3.5$, $^5J_{FP} = 4.5$. [c] $^1J_{FC}(CF_3) = 272.4$, $^2J_{FC\text{-}4} = 32.6$, $^3J_{FC\text{-}3} = 3.7$, $^4J_{FC\text{-}2}$ is too small to measure, $^5J_{FC\text{-}1} = 0.5$.

Results and Discussion

We have synthesized a series of nine *N*-phenyl-*P*,*P*,*P*-triarylphospha-λ^5-azenes 4 from the corresponding series of nine triarylphosphines 5, three of which were not commercially available and required synthesis,[6-8] and have also prepared the corresponding series of phosphine oxides 6.[6,9-13] The molecules of series 4 were made in one of three

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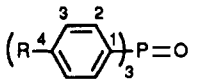
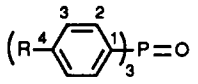
Table V. ^{13}C and ^{31}P NMR Chemical Shifts (δ) of Triarylphosphine Oxides 6



compd	R	^{13}C 1	2	3	4	$^{31}P^a$
6a	NMe_2[b]	119.54	133.37	111.29	152.32	30.66
6b	OMe[c]	124.55	133.84	113.95	162.28	29.30
6c	Me[d]	129.66	132.05	129.14	142.19	29.88
6d	H[e]	132.53	132.06	128.47	131.91	29.65
6e	F	128.14	134.48	116.14	165.21	27.33
6f	Cl	130.26	133.30	129.12	139.11	27.47
6g	CF_3[f]	135.29	132.50	125.83	134.60	26.17
6h	COOMe[g]	136.08	132.07	129.69	133.79	27.89
6i	CN[h]	135.37	132.46	132.54	116.90	25.24

[a] Extrapolated to infinite dilution and relative to 85% H_3PO_4. [b] NCH_3: 40.01. [c] OCH_3: 55.32. [d] CH_3: 21.57. [e] The ^{13}C chemical shifts are in reasonable agreement with those in refs 23 and 25. The ^{31}P chemical shift is in reasonable agreement with those in refs 25 and 26. [f] CF_3: 123.34. [g] CO: 166.96. OCH_3: 52.57. [h] CN: 117.29.

Table VI. P–C NMR Coupling Constants (Hz) of Triarylphosphine Oxide 6



compd	R	J_{PC} 1	2	3	4
6a	NMe_2	114.6	11.1	12.6	2.4
6b	OMe	110.9	11.3	13.1	2.8
6c	Me	106.5	10.2	12.5	2.7
6d	H	104.1[a]	9.9[a]	12.2[a]	2.9[a]
6e	F[b]	108.4	11.3	13.3	2.9
6f	Cl	106.4	10.8	12.9	3.4
6g	CF_3[c]	103.4	10.4	12.5	3.0
6h	COOMe	102.4	10.2	12.4	2.7
6i	CN	102.3	10.2	12.4	3.2

[a] The J_{Pc} values are in reasonable agreement with those in refs 22 and 23. [b] $^1J_{FC-4}$ = 254.4, $^2J_{FC-3}$ = 21.5, $^3J_{FC-2}$ = 8.9, $^4J_{FC-1}$ = 2.7. [c] $^1J_{FC}(CF_3)$ = 272.9, $^2J_{FC-4}$ = 33.0, $^3J_{FC-3}$ = 3.8, $^4J_{FC-2}$ is too small to measure, $^5J_{FC-1}$ = 1.0, $^5J_{PC}(CF_3)$ = 1.0.

ways, either from phenyl azide and the corresponding phosphines 5 by the Staudinger reaction[14,15] or by using one of two variations of the Kirsanov reaction, which involves reaction of the phosphine 5 with bromine to produce the triaryldibromophosphorane, which, in turn, is reacted with aniline and base to give the phospha-λ^5-azenes 4.[16,17] The phosphine oxides 6 were prepared from the triaryldibromophosphoranes by hydrolysis, using the methodology of Kroshefsky and Verkade.[18] The ^{15}N-labeled series 4, used for ^{15}N NMR spectroscopy (eight compounds), was prepared by the Kirsanov reaction using ^{15}N-labeled aniline.

Table VII. Linear Relationships between NMR Parameters of *N*-Phenyl-*P*,*P*,*P*-triarylphospha-λ^5-azenes 4 and Substituent Constants

Plot of Y vs X			correlation coeff	
Y	X	slope	(r)	no. of points
$\delta_{^{13}C-1'}$	σ_p	−3.42	0.991	9
$\delta_{^{13}C-3'}$	σ_p	0.645	0.976	9
$\delta_{^{13}C-4'}$	σ_p	2.62	0.990	9
$\delta_{^{15}N}$	σ_p	−2.95	0.963	8
$\delta_{^{31}P}$	σ_p	−8.41	0.960	9
$\delta_{^{13}C-1}$	σ_R^0	23.8	0.978	9
$^1J_{PN}$	σ_p	−2.15	0.923	8
$^1J_{PC-1}$	σ_R^{BA}	−11.0	0.992	9

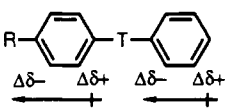


Figure 2. Polarization pattern of aryl/phenyl-substituted systems.

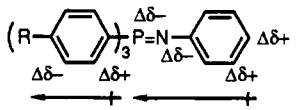


Figure 3. Polarization pattern induced in 4 when R becomes more electron withdrawing.

Tables I–VI show the measured ^{13}C, ^{15}N, and ^{31}P NMR spectra (chemical shifts and coupling constants) for the three series of compounds *N*-phenyl-*P*,*P*,*P*-triarylphospha-λ^5-azenes 4, triarylphosphines 5, and triarylphosphine oxides 6. The carbon numbering scheme is shown in the tables. The ^{15}N data were obtained by use of ^{15}N-labeled compounds. As was done previously,[2-5] the ^{31}P chemical shifts were measured at three different concentrations and extrapolated to infinite dilution. For ^{15}N spectra, the chemical shifts are reported relative to NH_3(l) and were obtained with use of an external $K^{15}NO_3$ (labeled-^{15}N) solution as reported earlier.[2-5,19] All the chemical shifts and coupling constants in 4, where there were significant substituent effects, were plotted against the Hammett σ-type constants. Table VII presents the slopes and the correlation coefficients of a number of these plots. All correlations shown are either excellent or satisfactory[27] except $^1J_{PN}$ vs σ_p, which is marginal but shows the trend.

Chemical Shifts. The plot of $\delta_{^{13}C-1'}$ vs σ_p in 4 gives a negative slope, whereas the corresponding plots of $\delta_{^{13}C-3'}$ and $\delta_{^{13}C-4'}$ vs σ_p give positive slopes. This is consistent with an argument on related systems involving π polarization of a distal phenyl ring by the aryl ring containing the substituent (Figure 2; T is CH=N, N=CH, CH=CHCO,

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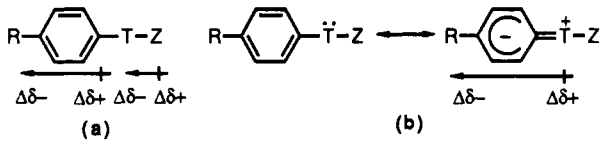

Figure 4. Polarization patterns of Ar–T–Z (a) without and (b) with a lone electron pair on T when R becomes more electron withdrawing.

COCH=CH, CH_2N=CH, CH=NCH_2 or C_6H_4).[28-31] In the case of the *N*-phenyl-*P,P,P*-triarylphospha-λ^5-azenes **4**, the slope of the plots of δ_{13_C} vs σ_p is negative for C-1′ and positive for both C-3′ and C-4′ supporting this type of induced polarization in the phenyl ring.

The ^{15}N-substituent chemical shift (SCS) in **4** also shows a good correlation with σ_p with a negative slope. Since a plot of $\delta_{13_{C\text{-}1'}}$ vs σ_p likewise gives a negative slope, a π-electron withdrawing substituent will cause the ^{15}N, as well as ^{13}C-1′, chemical shifts to move upfield. We have previously shown that in the *N*-aryl-*P,P,P*-triphenylphospha-λ^5-azenes **1** the corresponding ^{15}N and ^{13}C chemical shifts give positive slopes. Furthermore, the phosphorus SCS in both series **1** and **4** show the same sign as the nitrogen SCS, which means the phenyl, nitrogen, and phosphorus should be considered as a unit. In series **1**, the three phenyl rings on the phosphorus show the same π-polarization by the aryl ring on nitrogen, completely analogous to the phenyl polarization **4**.[4] Thus, the polarization pattern shown in Figure 3 for **4** when R is electron withdrawing can be drawn.

The phospha-λ^5-azene series **4** is an example of the general case RC_6H_4TZ. As long as there is not a free electron pair on T then an aryl group with an electron-withdrawing substituent will polarize the T–Z bond and the result will be shielding of nucleus T when it is NMR active. Figure 4a shows the polarization expected in this situation. Also shown in Figure 4b is the polarization expected when there is a lone pair of electrons on T. In this case, the major effect is the loss of the electron density around T due to delocalization of the lone pair into the aryl ring resulting in deshielding of nucleus T. Thus, the aryl ring and T must be considered as a unit.

The phosphine oxide series **6** is another example of the former (Figure 4a) polarization pattern. The tetracoordinate phosphorus atom without a lone pair of electrons effectively insulates the oxygen with its lone pairs from directly interacting by resonance with the aryl ring, as was also true for the phospha-λ^5-azene series **1** and **4**. Indeed, an electron-withdrawing R group will shield the phosphorus, and a plot of δ_{31_P} vs σ_p gives $\rho = -3.91$ ($r = 0.91$, $n = 9$). The relationship between series **4** and **6** is shown in Table VIII where plots of $\delta_{13_{C\text{-}1}}$, $\delta_{13_{C\text{-}2}}$, $\delta_{13_{C\text{-}3}}$, $\delta_{13_{C\text{-}4}}$, and δ_{31_P} for **6** vs **4** provide excellent straight lines.[27] The slopes for the carbon atom plots are very close to unity indicating rather similar SCS effects due to the substituent R. However, the ^{31}P SCS effect is twice as large in the phospha-λ^5-azene series **4** than in the oxide series **6**. This is undoubtedly due to the more extended conjugated system, NC_6H_5, in **4**. With electron-donating R groups, the electron density in **4** can interact with the benzene ring, resulting in a larger effect. In the phosphine oxide series **6**, however, the electrons can be pushed away no further than the oxygen atom so the electron density fluctuations around the phosphorus atom are smaller.

Table VIII. Linear Relationships of ^{13}C and ^{31}P Chemical Shifts between *N*-Phenyl-*P,P,P*-triarylphospha-λ^5-azenes 4 and Triarylphosphine Oxides 6 and between 4 and Triarylphosphines 5

δ or J	Plot of X vs 4: X	slope	correlation coeff (r)[a]
^{13}C-1 SCS	6	1.086	0.999
^{13}C-2 SCS	6	0.985	0.998
^{13}C-3 SCS	6	1.000	1.000
^{13}C-4 SCS	6	1.005	1.000
^{31}P SCS	6	2.006	0.986
$^1J_{PC\text{-}1}$	6	0.930	0.999
^{13}C-1 SCS	5	0.998	0.990
^{13}C-2 SCS	5	1.320	0.982
^{13}C-3 SCS	5	1.011	0.997
^{13}C-4 SCS	5	0.968	1.000
$^1J_{PC\text{-}1}$	5	−0.945	0.926

[a] Number of points is 9 in all cases.

There are a number of aryl-substituted systems in the literature where the atom next to the substituted aryl ring does not have a lone pair of electrons. In these systems, as in the case of **4** and **6**, electron-withdrawing substituents shield this nucleus (marked with an *). These include p-$RC_6H_4C^*OX$ (X = NH_2, F, OEt, OH, H, and CH_3),[32] p-$RC_6H_4N^*O_2$,[33] and p-$RC_6H_4P^*(BH_3)Me_2$.[34]

The chemical shift data for the triarylphosphines **5** (Table III) show that this series falls into the class of compounds shown in Figure 4b where electron-pair delocalization into the aryl ring is possible. Indeed, electron-withdrawing groups deshield the phosphorus nucleus and a plot of δ_{31_P} vs σ_R^0 gives a straight line, $\rho = 9.17$ ($r = 0.952$, $n = 9$). This effect, which is primarily a delocalization effect (best plotted vs σ_R^0) is similar to the deshielding effect exerted by electron-withdrawing substituents on other nuclei with a lone electron pair directly attached to an aryl ring. These series include (observed nuclei mark with an *) p-$RC_6H_4N^*H_2$,[35] p-$RC_6H_4O^*CH_3$,[36] and p-$RC_6H_4F^*$.[37]

There are linear correlations of the ^{13}C SCS for phospha-λ^5-azenes **4** vs those for the phosphines **5** (Table VIII). The major effect is due to the R group attached to the ring as shown by the near-unity slopes (Table VIII) for the C-1 and C-3 SCS. Superimposed on this effect, however, is the resonance effect that is seen at C-2 and C-4, the positions ortho and para to the substituent diphenylphosphino group.

Coupling Constants. In **4**, as shown in Figure 3, a polarized RC_6H_4 group can induce a polarization of the NC_6H_5 group through space. Therefore, a π-electron-withdrawing group will cause the electrons of the N–C-1′ bond to be closer to the nitrogen atom. The N atom uses an orbital with more s character to bond to C-1′, leaving an orbital with more p character to bond to the phosphorus atom. Since the P–N σ-bond orbital contains less s

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character, $|^1J_{PN}|$ will become smaller by decreasing the Fermi contact term. Thus, the plot of $^1J_{PN}$ vs σ_p gives $\rho = -2.15$ (r is marginal ($r = 0.923$, $n = 8$), but shows the trend, Table VII). This argument also agrees with the overall change in $^1J_{NC\text{-}1'}$ in **4** where the electron-withdrawing substituents increase $|^1J_{NC\text{-}1'}|$ but the effect is much smaller and so there is more scatter in the data.

By the same reasoning, we can rationalize the observation in the literature involving the aryldimethylphosphane boranes p-$RC_6H_4P(BH_3)Me_2$,[34] where electron-withdrawing substituents R decrease $|^1J_{PB}|$. A polarized RC_6H_4 group can induce the polarization of the BH_3 group (Figure 4a), which will cause the BH bonding electrons to move closer to B, giving these orbitals more s character. This will leave an orbital with less s character (more p character) available to bond to the phosphorus and so a decrease in $|^1J_{PB}|$ is observed with electron-withdrawing substituents.[34]

A plot of $|^1J_{PC\text{-}1}|$ in **4** vs σ_R^{BA} gave an excellent correlation with a negative slope (Table VII, $\rho = -11.0$, $r = 0.992$). An electron-donating substituent, for example NMe_2, can donate its electron density (by resonance) to C-1, which makes C-1 more negative (Table I). Meanwhile, as indicated previously, the NMe_2 group also makes the phosphorus atom more positive (Table I). The more negative C-1 atom and the more positive phoshorus atom will shorten the P–C-1 bond due to the electrostatic attraction. The shorter σ bond, which has more s character, will show an increase in $|^1J_{PC\text{-}1}|$.

A similar trend was also found in the case of the phosphine oxides **6**. A plot of $|^1J_{PC\text{-}1}|$ vs σ_R^{BA} gave $\rho = -11.8$ ($r = 0.990$) and an analogous argument can be made about the P–C-1 bonding.

Also, in the following compounds taken from the literature the situation is similar. In p-$RC_6H_4C^*H_3$, when R is NH_2, H, and NO_2, $|^1J_{CC^*}|$ is 45.91, and 43.45 Hz, respectively. The compound with the electron-donating substituent shows the largest $|^1J_{CC^*}|$.[38,39] When the $|^1J_{CC^*}|$ value of p-$RC_6H_4C^*OY$ (Y = OCH_3, CH_3, H)[40] was plotted against σ_R^0 the correlations shown below were obtained.

$$Y = OCH_3 \quad |^1J_{CC^*}| = -5.18\sigma_R^0 + 75.1 \quad r = 0.978$$

$$Y = H \quad |^1J_{CC^*}| = -5.60\sigma_R^0 + 52.8 \quad r = 0.973$$

$$Y = CH_3 \quad |^1J_{CC^*}| = -5.53\sigma_R^0 + 52.2 \quad r = 0.940$$

In p-$RC_6H_4SnMe_3$,[41] $|^1J_{SnC\text{-}1}|$ did not give a good correlation with any σ_R (σ_R^0, σ_R^{BA}, σ_R^-, and σ_R^+); however, it showed an excellent correlation with σ_p. In p-$RC_6H_4P(BH_3)Me_2$, an excellent correlation between $|^1J_{PC\text{-}1}|$ and σ_p^+ was also obtained as shown below. In these cases, where there is

$$|^1J_{SnC\text{-}1}| = -75.3\sigma_p + 473 \quad r = 0.997$$

$$|^1J_{PC\text{-}1}| = -5.47\sigma_p^+ + 55.3 \quad r = 0.999$$

no lone pair of electrons on the nuclei being observed (P in **4**, p-$RC_6H_4P(BH_3)Me_2$, and **6**, C* in p-$RC_6H_4C^*OY$, and Sn in p-$RC_6H_4SnMe_3$), the plots of $|^1J_{PC\text{-}1}|$, $|^1J_{CC^*}|$, and $|^1J_{SnC\text{-}1}|$ vs substituent constants all gave negative slopes. These are consistent with the previous explanation that an electron-donating substituent will shorten the P–C-1, C–C*, and Sn–C-1 bonds, respectively, and increase these coupling constants.

On the contrary, in the phosphine series **5** as well as the two series taken from the literature, $RC_6H_4NH_2$[42] and RC_6H_4F,[43] there are lone pairs of electrons on P, N, and F, which are available to π bond with C. An electron-withdrawing substituent causes the para carbon atom (relative to R) to become more positive, resulting in the lone pair of electrons on P, N, or F to donate back to this carbon atom, which increases the C–P, C–N, or C–F electron-overlap population. This increase should make $|^1J_{CP}|$, $|^1J_{CN}|$, and $|^1J_{CF}|$ larger. This explanation is consistent with the positive slopes of the plots of these coupling constants vs σ_p. For **5**, $\rho = 8.70$, $r = 0.967$, $n = 9$, for $RC_6H_4NH_2$, $\rho = 3.16$, $r = 0.983$, $n = 6$; and for RC_6H_4F, $\rho = 15.3$, $r = 0.968$, $n = 6$.

In summary, for the RC_6H_4TZ system, if the atom T attached to the para carbon atom (relative to R) has no lone pair of electrons, a better electron-donating substituent will increase $|^1J_{TC}|$ because the electrostatic attraction between C and T is enhanced. On the contrary, if the atom T has a lone pair of electrons, a better electron-withdrawing substituent will increase $|^1J_{TC}|$ because the T–C overlap population is enhanced (more double-bond character), resulting from the delocalization of the lone pair of electrons into the aryl ring. We will discuss this substituent effect further using the dual-substituent parameter (DSP) treatments.

DSP Treatments. As has frequently been done with disubstituted benzenes, the Taft DSP treatment (eq 1)[44] was applied to the SCS and coupling constant effects in **4** and to the coupling constant effects **5** and **6**. Table IX

$$\text{substit effect} = \sigma_I\rho_I + \sigma_R\rho_R \quad (1)$$

shows the DSP analyses of the SCS effects of various carbon atoms and the nitrogen and phosphorus atoms. The table gives the best-fit correlations (after trying the four resonance scales σ_R^0, σ_R^{BA}, σ_R^- and σ_R^+) on the basis of the Taft f parameter, $f = SD/rms$. All treatments involved subtracting the parameter for the parent compound (R = H) from that for the substituted material. All but one correlation was excellent ($f < 0.1$) and the other was good ($f < 0.2$). All chemical shifts, except for C-1, clearly depend on a combination of resonance and inductive effects with the ratio ρ_R/ρ_I varying between 2.3 and 0.45. In the case of the ipso carbon C-1 in the ring containing the

Table IX. Taft DSP Analyses of SCS in *N*-Phenyl-*P*,*P*,*P*-triarylphospha-λ^5-azenes 4

nucleus	ρ_I	ρ_R	scale[a]	f[b]	no. of points
^{13}C-1	4.28	23.4	σ_R^0	0.098	9
^{13}C-1′	−3.92	−4.11	σ_R^0	0.079	9
^{13}C-3′	0.862	0.699	σ_R^0	0.055	9
^{13}C-4′	2.97	3.17	σ_R^0	0.047	9
^{15}N	−1.99	−4.65	σ_R^0	0.171	8
^{31}P	−12.71	−5.75	σ_R^{BA}	0.095	9
^{31}P	−12.59	−8.21	σ_R^0	0.098	9

[a] The correlations were done for each of the four resonance scales (σ_R^0, σ_R^{BA}, σ_R^-, and σ_R^+), and the results for the one with the lowest f (best fit) are shown. [b] $f = SD/rms$.

Table X. Taft DSP Analyses of the One-Bond P–C Coupling Constants ($^1J_{PC}$) in 4, 5, and 6

series	ρ_I	ρ_R[a]	f[b,c]
4	−0.59	−11.2	0.10
5	6.9	9.0	0.19
6	−0.77	−12.1	0.10

[a] Using σ_R^{BA}. [b] $f = SD/rms$. [c] Number of points is 9 in all cases.

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Table XI. Taft DSP Analyses of One-Bond Coupling Constants Using Literature Data

compd	bond (coupled nuclei)	ρ_I	ρ_R	f^a	ref
RC_6H_4CHO	(O)C–C(Ar)	−0.57	−6.0[b]	0.04	40
$RC_6H_4C(O)CH_3$	(O)C–C(Ar)	−1.2	−6.1[b]	0.06	40
$RC_6H_4CO_2CH_3$	(O)C–C(Ar)	0.45	−5.5[b]	0.09	40
$RC_6H_4P(BH_3)Me_2$	P–C(Ar)	−6.5	−10.1[c]	0.02	34
$RC_6H_4SnMe_3$	Sn–C(Ar)	−72.9	−60.5[c]	0.12	41
$RC_6H_4NH_2$	N–C(Ar)	2.0	3.1[d]	0.15	42
RC_6H_4F	F–C(Ar)	11.2	17.6[c]	0.13	43

[a] f = SD/rms. [b] Using σ_R^0. [c] Using σ_R^{BA}. [d] Using σ_R^-.

substituent, values such as those observed here are quite typical and the resonance effect is 4–5 times more important than the inductive effect.[2,44]

DSP treatment of the one-bond P–C coupling constants (substraction of J for R = H from J for the other substituents) for series of **4**–**6** gave the results shown in Table X.

For the phospha-λ^5-azene **4** and phosphine oxide **6** series, the resonance effect is more important and ρ_R/ρ_I = 19.0 for **4** and 15.7 for **6**. To see if this was a typical situation or unique to the phosphorus systems we again used data from the literature.

Table XI gives the results for the data on ring-substituted benzaldehydes, acetophenones, and methyl benzoates.[40] When the values and ratio of ρ_R/ρ_I for these systems are compared with those for **4** and **6**, one sees that ρ_R is always negative and much larger than ρ_I. Also, ρ_I is a small negative number, except in one case where it is small but positive. Each of these systems has one atom with a lone pair of electrons (O or N) bonded to the carbon or phosphorus attached to the aromatic ring. The exception is the benzoate ester series, where there are two oxygen atoms bonded to the carbonyl carbon and this is the same system that gives the positive value for ρ_I.

There are two systems in the literature where neither the atom bound to the aryl ring nor the next atom has a lone electron pair. They are $RC_6H_4P(BH_3)Me_2$[34] and $RC_6H_4SnMe_3$,[41] and the DSP data for the P–C(Ar) and Sn–C(Ar) one-bond coupling constants are presented in Table XI. Both ρ_I and ρ_R are negative, and in both cases the ρ_R/ρ_I ratio (1.55 and 0.83, respectively) indicate that the resonance and inductive effects are both important.

Finally, there is a third series where the atom attached to the aryl ring contains a lone electron pair. These include the phosphines **5** (Table X) and the substituted anilines[42] and fluorobenzenes[43] (Table XI). In all three cases, ρ_I and ρ_R are positive with the resonance effect being ~50% more important than the inductive effect. That is ρ_R/ρ_I is 1.30, 1.55, and 1.57 for the previous systems, respectively.

Thus, on the basis of the limited data available, there are three types of one-bond T–C(Ar) coupling constants. The data are consistent with the previous discussion on these three types of systems using the MSP (monosubstituent parameter) treatment. Any further more detailed discussion, however, must await additional studies and more data.

Experimental Section

General Methods. Melting points are uncorrected. Elemental analyses were determined by Texas Analytical Laboratories, Tallahassee, FL or by use of the C, H, N analyzer in the Chemistry Department at The University of Texas at Arlington. Benzene and tetrahydrofuran (THF) were dried and distilled before use. Chromatographic separations were carried out by employing a Chromatotron, where the plates were 2-mm thick silica gel 60 PF254 containing gypsum, or by column chromatography with a 30 cm × 2 cm i.d. column on 60–200 mesh silica gel. The Statworks program (Cricket Software, Inc.) or a DSP program written by Prof. K. L. Brown (UTA) were used for MSP and DSP calculations. FT-IR spectroscopy was carried out with use of a diffuse reflectance accessory. The samples were 1.0 mg of **4** and 100 mg of KBr.

NMR spectra were recorded at 200.07, 50.31, 20.28, 188.24, and 80.99 MHz for ^1H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P, respectively. $CDCl_3$ was used as solvent, digital resolution was sufficient to give the accuracy shown in the tables, and no exponential line broadening was used. The ^{13}C, ^{31}P, and ^{15}N spectra were recorded as discussed earlier.[2] For ^{31}P, concentrations of 150, 100, and 50 mg in 3 mL were used and the reported chemical shifts were extrapolated to infinite dilution. ^{19}F spectra were recorded with use of an external C_6H_5F standard. (C_6H_5F δ 113.12 relative to $CFCl_3$).

Synthetic Procedures. Tris[*p*-(*N*,*N*-dimethylamino)phenyl]phosphine Oxide (6a). An excess of Br_2 (1.0 mmol) was added to a stirred solution of 200 mg (0.51 mmol) of tris[*p*-(*N*,*N*-dimethylamino)phenyl]phosphine (**5a**) in 8 mL of benzene over 5 min. The Br_2 and benzene were evaporated, and acetone was added to dissolve the residue. Water was then added, and the precipitate was filtered. The oxide was recrystallized from acetone/water to give 185 mg (89%) of tris[*p*-(*N*,*N*-dimethylamino)phenyl]phosphine oxide (**6a**); mp 278–283 °C (lit.[9] mp 275–280 °C).

Tris(*p*-methoxyphenyl)phosphine Oxide (6b). By use of the procedure for **6a**, 300 mg of tris(*p*-methoxyphenyl)phosphine (**5b**) gave 254 mg (81%) of tris(*p*-methoxyphenyl)phosphine oxide (**6b**); mp 142–144 °C (lit.[10] mp 143–144 °C).

Tris(*p*-methylphenyl)phosphine Oxide (6c). By use of the procedure for **6a**, 300 mg of tris(*p*-methylphenyl)phosphine (**5c**) gave 278 mg (88%) of tris(*p*-methylphenyl)phosphine oxide (**6c**); mp 139–142 °C (lit.[11] mp 145-146 °C).

Tris(*p*-fluorophenyl)phosphine Oxide (6e). By use of the procedure for **6a**, 300 mg of tris(*p*-fluorophenyl)phosphine (**5e**) gave 272 mg (86%) of tris(*p*-fluorophenyl)phosphine oxide (**6e**); mp 120–123 °C (lit.[12] mp 121–123 °C).

Tris(*p*-chlorophenyl)phosphine Oxide (6f). By use of the procedure for **6a**, 500 mg of tris(*p*-chlorophenyl)phosphine (**5f**) gave 446 mg (85%) of tris(*p*-chlorophenyl)phosphine oxide (**6f**); mp 176–178 °C (lit.[11] mp 177–178 °C).

Tris[*p*-(trifluoromethyl)phenyl]phosphine Oxide (6g). By use of the procedure for **6a**, 466 mg of tris[(*p*-trifluoromethyl)-phenyl]phosphine (**5g**) gave 417 mg (86%) of tris[*p*-(trifluoromethyl)phenyl]phosphine oxide (**6g**); mp 179–182 °C (lit.[13] mp 181–183 °C).

Tris[*p*-(methoxycarbonyl)phenyl]phosphine Oxide (6h). A solution of 5.00 g (16.4 mmol) of tris(*p*-methylphenyl)phosphine (**5c**) in 80 mL of pyridine and 40 mL of water was refluxed for 24 h under an air atmosphere to oxidize **5c** to **6c**. Then, 50 g of $KMnO_4$ was added and the mixture was refluxed an additional 48 h. The pyridine/water azeotrope was removed by distillation, the product was acidified with 6 N HCl, the precipitate was filtered and dried to give 4.54 g (11.1 mmol; 70.7%) of tris(*p*-carboxyphenyl)phosphine oxide. A solution of 2.00 g (4.87 mmol) of tris(*p*-carboxyphenyl)phosphine oxide in 40 mL of methanol and 3 mL of sulfuric acid was refluxed overnight, and then 50 mL of water was added. The mixture was extracted with three 50-mL portions of benzene, and the benzene was evaporated under reduced pressure to give 2.05 g (4.5 mmol; 92%) of crude product. Recrystallization from benzene gave 1.21 g (55%) of pure tris-[*p*-(methoxycarbonyl)phenyl]phosphine oxide (**6h**); mp 116–119 °C (lit.[6] mp 118–120 °C).

Tris(*p*-cyanophenyl)phosphine Oxide (6i). A solution of 2.50 g (6.09 mmol) of tris(*p*-carboxyphenyl)phosphine oxide in 35 mL of benzene and 25 mL of thionyl chloride was refluxed for 3 h, after which the benzene and thionyl chloride were removed under reduced pressure. Benzene (50 mL) was added, and the mixture was heated to dissolve the residue. This was slowly added to 30 mL of concd ammonia and then stirred overnight. The precipitate was filtered to give 2.15 g of crude tris(*p*-carbonylphenyl)phosphine oxide. This product in 45 mL of pyridine was cooled to 0 °C, and 3.26 mL (3.54 mmol) of $POCl_3$ was added slowly at 0 °C. The mixture was stirred for 1 h at this temperature, then 4 h at 80 °C, and finally cooled to room temperature, acidified with 3 N HCl, and then extracted twice with 80-mL portions of

benzene. The combined extract was evaporated under reduced pressure to give 0.92 g of crude tris(*p*-cyanophenyl)phosphine oxide (**6i**), which was purified by use of a Chromatotron ($CHCl_3$) to give 0.60 g (1.7 mmol; 28%) of pure tris(*p*-cyanophenyl)-phosphine oxide (**6i**); mp 212–215 °C (lit.[6] mp 215–217 °C).

Tris[*p*-(trifluoromethyl)phenyl]phosphine (5g). To a mixture of 1.35 g (55 g-atom) of Mg turnings, 50 mL of ethyl ether, and a small amount of I_2 was added slowly a solution of 12.25 g (55 mmol) of *p*-bromo(trifluoromethyl)benzene in 12.5 mL of ethyl ether while the mixture was refluxed under argon. When the reaction started, the heating was stopped and the mixture was cooled in ice. When the reaction had ceased, a solution of 2.52 g (18.4 mmol) of PCl_3 in 12.5 mL of ethyl ether was added slowly at 0 °C under argon, refluxed 1 h more, cooled to room temperature, and acidified with 6 N HCl. The ether layer was separated, the aqueous layer was extracted twice with 40 mL of ethyl ether, and the combined ether extract was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by sublimation at 70–72 °C (0.1 Torr) to give 1.20 g (2.58 mmol; 14.2%) of tris[*p*-(trifluoromethyl)phenyl]phosphine (**5g**); mp 67–71 °C (lit.[7] mp 68–70 °C).

Tris[*p*-(methoxycarbonyl)phenyl]phosphine (5h). To a solution of 1.76 g (3.9 mmol) of tris[*p*-(methoxycarbonyl)-phenyl]phosphine oxide (**6h**) in 30 mL of benzene was added 5 mL of trichlorosilane under argon at room temperature. After the mixture was refluxed for 24 h, it was cooled to 0 °C and excess precooled 2 N NaOH was added to destroy the excess trichlorosilane. The mixture was extracted twice with 25-mL portions of benzene and the combined extract was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$) to give 0.93 g (55%) of pure tris[*p*-(methoxycarbonyl)phenyl]phosphine (**5h**); mp 128–130 °C (lit.[8] mp 124–126 °C).

Tris(*p*-cyanophenyl)phosphine (5i). By use of the procedure for **5h**, 1.10 g (3.1 mmol) of tris(*p*-cyanophenyl)phosphine oxide (**6i**) and 5 mL of trichlorosilane in 60 mL of benzene gave 605 mg (58%) of tris(*p*-cyanophenyl)phosphine (**5i**); mp 180–183 °C (lit.[6] mp 186–189 °C).

***N*-Phenyl-*P*,*P*,*P*-triarylphospha-λ⁵-azenes 4.** Three different procedures were employed for the syntheses of the derivatives of **4**.

Procedure A. A solution of 1 mmol of dry triarylphosphine in 10 mL of dry THF was cooled in an ice–water bath; 1 mmol of phenyl azide[45] in 1 mL of THF was added slowly under argon with stirring over 4 h at room temperature. The THF was evaporated under reduced pressure, and the residue was purified by recrystallization or washing with a solvent.

Procedure B. A solution of 1 mmol of triarylphosphine in 5 mL of benzene was cooled to 6–8 °C; 1 mmol of Br_2 in 1 mL of benzene was added under argon with stirring over 20 min. Another solution of 1 mmol of aniline and 2 mmol of triethylamine in 2 mL of benzene was added to the mixture at room temperature under argon. After being stirred an additional 4 h, the reaction mixture was filtered, the benzene was evaporated under reduced pressure, and the residue was then purified by recrystallization.

Procedure C. A solution of 1 mmol of triarylphosphine in 5 mL of benzene was cooled to 6–8 °C; 1 mmol of Br_2 in 1 mL of benzene was added under argon with stirring over 20 min. Another solution of 1 mmol of aniline and 1 mmol of triethylamine in 2 mL of benzene was added at room temperature under argon, and the stirring was continued for 3 h. The precipitate was filtered and washed twice with 15 mL of water and twice with 15 mL of ethyl ether. The residue was mixed with 10 mL of ethyl ether and 1 g of KOH, stirred overnight, and filtered, and the ether was evaporated under reduced pressure. The crude product was purified with use of a Chromatotron ($CHCl_3$).

***N*-Phenyl-*P*,*P*,*P*-tris[*p*-(*N*,*N*-dimethylamino)phenyl]-phospha-λ⁵-azene (4a).** Procedure A was used. From 1.05 g (2.68 mmol) of tris[*p*-(*N*,*N*-dimethylamino)phenyl]phosphine (**5a**) and 414 mg (4.48 mmol) of phenyl azide was obtained, after the product was washed with methanol, 685 mg (53%) of *N*-phenyl-*P*,*P*,*P*-tris[*p*-(*N*,*N*-dimethylamino)phenyl]phospha-λ⁵-azene (**4a**); mp 253–257 °C. IR: 3050 (m), 2890 (s), 1597 (s), 1512 (s), 1485 (s), 1362 (s), 1327 (s), 1111 (s), 1034 (m), 945 (m) cm^{-1}. ^1H NMR: δ 6.5–7.7 (m, 17 H, ArH), 2.95 (s, 18 H, CH_3). Anal. Calcd for $C_{30}H_{35}N_4P$: C, 74.66; H, 7.31; N, 11.61. Found: C, 74.38; H, 7.31; N, 11.26.

***N*-Phenyl-*P*,*P*,*P*-tris(*p*-methoxyphenyl)phospha-λ⁵-azene (4b).** Procedure B was used. From 0.528 g (1.5 mmol) of tris(*p*-methoxyphenyl)phosphine (**5b**) was obtained after the product was recrystallized from methanol 0.328 g (49%) of *N*-phenyl-*P*,*P*,*P*-tris(*p*-methoxyphenyl)phospha-λ⁵-azene (**4b**); mp 159–161 °C. IR: 3067 (s), 3021 (s), 3001 (s), 2970 (s), 2940 (s), 2905 (s), 2839 (s), 1598 (s), 1501 (s), 1481 (s), 1331 (s), 1292 (s), 1254 (s), 1180 (s), 1119 (s), 1103 (s), 1038 (s), 1022 (s) cm^{-1}. ^1H NMR: δ 6.6–7.9 (m, 17 H, ArH), 3.82 (s, 9 H, CH_3). Anal. Calcd for $C_{27}H_{26}NO_3P$: C, 73.13; H, 5.91; N, 3.16. Found: C, 73.03; H, 5.93; N, 3.14.

***N*-Phenyl-*P*,*P*,*P*-tris(*p*-methylphenyl)phospha-λ⁵-azene (4c).** Procedure C was used. From 1.20 g (4 mmol) of tris(*p*-methylphenyl)phosphine (**5c**) was obtained 0.825 g (52%) of *N*-phenyl-*P*,*P*,*P*-tris(*p*-methylphenyl)phospha-λ⁵-azene (**4c**); mp 126–130 °C. IR: 3059 (m), 3019 (m), 2905 (m), 1586 (s), 1489 (s), 1335 (s), 1103 (s), 1041 (m), 1010 (m), 810 (s) cm^{-1}. ^1H NMR: δ 6.5–7.8 (m, 17 H, ArH), 2.37 (s, 9 H, CH_3). Anal. Calcd for $C_{27}H_{26}PN$: C, 82.00; H, 6.63; N, 3.54. Found: C, 81.95; H. 6.28; N, 3.52.

***N*-Phenyl-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (4d).** Procedure C was used. From 0.526 g (2 mmol) of triphenylphosphine was obtained 0.260 g (37%) of *N*-phenyl-*P*,*P*,*P*-triphenylphospha-λ⁵-azene; mp 127–130 °C (lit.[46] mp 128–130 °C).

***N*-Phenyl-*P*,*P*,*P*-tris(*p*-fluorophenyl)phospha-λ⁵-azene (4e).** Procedure C was used. From 0.316 g (1 mmol) of tris(*p*-fluorophenyl)phosphine (**5e**) was obtained 0.156 g (39%) of *N*-phenyl-*P*,*P*,*P*-tris(*p*-fluorophenyl)phospha-λ⁵-azene (**4e**); mp 106–108 °C. ^{19}F NMR: δ 6.60 relative to fluorobenzene (116.52 relative to $CFCl_3$; lit.[47] δ 6.75 relative to C_6H_5F).

***N*-Phenyl-*P*,*P*,*P*-tris(*p*-chlorophenyl)phospha-λ⁵-azene (4f).** Procedure C was used. From 0.730 g (2 mmol) of tris(*p*-chlorophenyl)phosphine (**5f**) was obtained 0.365 g (40%) of *N*-Phenyl-*P*,*P*,*P*-tris(*p*-chlorophenyl)phospha-λ⁵-azene (**4f**); mp 157–160 °C (lit.[48] mp 160–161 °C).

***N*-Phenyl-*P*,*P*,*P*-tris[*p*-(trifluoromethyl)phenyl]phospha-λ⁵-azene (4g).** Procedure B was used. From 0.700 g (1.5 mmol) of tris[*p*-(trifluoromethyl)phenyl]phosphine (**5g**) was obtained 0.230 g (28%) of tris[*p*-(trifluoromethyl)phenyl]phospha-λ⁵-azene (**4g**) after recrystallizing from cyclohexane; mp 136–139 °C (lit.[13] mp 138–139 °C).

***N*-Phenyl-*P*,*P*,*P*-tris[*p*-(methoxycarbonyl)phenyl]-phospha-λ⁵-azene (4h).** Procedure A was used. From 0.475 g (1 mmol) of tris[*p*-(methoxycarbonyl)phenyl]phosphine (**5h**) and 0.157 g (1.3 mmol) of phenyl azide was obtained 0.185 g (23%) of *N*-phenyl-*P*,*P*,*P*-tris[*p*-(methoxycarbonyl)phenyl]phospha-λ⁵-azene (**4h**) after recrystallizing from isopropyl alcohol; mp 95–98 °C. IR: 3055 (m), 3044 (m), 3021 (m), 2591 (s), 1732 (s), 1717 (s), 1589 (s), 1562 (m), 1481 (s), 1435 (s), 1393 (s), 1335 (s), 1277 (m), 1192 (m), 1096 (s), 1015 (s), 961 (m), 910 (m) cm^{-1}. ^1H NMR: δ 6.6–8.2 (m, 17 H, ArH), 3.94 (s, 9 H, CH_3). Anal. Calcd for $C_{30}H_{26}NO_6P$: C, 68.31; H, 4.97; N, 2.66. Found: C, 68.30; H, 5.01; N, 2.64.

***N*-Phenyl-*P*,*P*,*P*-tris(*p*-cyanophenyl)phospha-λ⁵-azene (4i).** Procedure A was used. From 0.450 g (1.33 mmol) of tris(*p*-cyanophenyl)phosphine (**5i**) and 0.210 g (1.77 mmol) of phenyl azide, 0.310 g (54%) of *N*-phenyl-*P*,*P*,*P*-tris(*p*-cyanophenyl)-phospha-λ⁵-azene (**4i**) was obtained after recrystallizing from THF/Et_2O; mp 268–272 °C. IR: 3071 (m), 3055 (m), 2230 (s), 1589 (s), 1489 (s), 1393 (s), 1339 (s), 1303 (m), 1308 (m), 1265 (m), 1099 (s), 1049 (m), 1015 (m) cm^{-1}. ^1H NMR: δ 6.6–8.0 (m, 17 H, ArH). Anal. Calcd for $C_{27}H_{17}N_4P$: C, 75.69; H, 4.00; N, 13.08. Found: C, 75.50; H, 4.05; N, 12.96.

^{15}N-Labeled *N*-phenyl-*P*,*P*,*P*-triarylphospha-λ⁵-azenes. ^{15}N-Labeled aniline (60%) was used. Procedure B was employed for the syntheses where the substituents, R, were OMe, CF_3, COOMe, and CN. Procedure C was employed for the syntheses where the substituents were Me, H, F, and Cl. From 0.528 g (1.50

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mmol) of tris(*p*-methoxyphenyl)phosphine (**5b**) was obtained 0.180 g (29%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris(*p*-methoxyphenyl)-phospha-λ^5-azene (**4b**) after recrystallizing from methanol. From 0.547 g (1.80 mmol) of tris(*p*-methylphenyl)phosphine (**5c**) was obtained 0.380 g (53%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris(*p*-methylphenyl)phospha-λ^5-azene (**4c**). From 0.526 g (2.00 mmol) of triphenylphosphine (**5d**) was obtained 0.202 g (29%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-triphenylphospha-λ^5-azene (**4d**). From 0.316 g (1.00 mmol) of tris(*p*-fluorophenyl)phosphine (**5e**) was obtained 0.154 g (38%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris(*p*-fluorophenyl)phospha-λ^5-azene (**4e**). From 0.604 g (1.80 mmol) of tris(*p*-chlorophenyl)phosphine (**5f**) was obtained 0.393 g (51%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris(*p*-chlorophenyl)phospha-λ^5-azene (**4f**). From 0.700 g (1.50 mmol) of tris[*p*-(trifluoromethyl)phenyl]phosphine (**5g**) was obtained 0.205 g (24.5%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris[*p*-(trifluoromethyl)phenyl]-phospha-λ^5-azene (**4g**) after recrystallizing from cyclohexane. From 0.500 g (1.05 mmol) of tris[*p*-(methoxycarbonyl)phenyl]-phosphine (**5h**) was obtained 0.126 g (23%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris[*p*-(methoxycarbonyl)phenyl]phospha-λ^5-azene (**4h**) after recrystallizing from isopropyl alcohol. From 0.460 g (1.36 mmol) of tris(*p*-cyanophenyl)phosphine (**5i**) was obtained 0.152 g (26%) of ^{15}N-labeled *N*-phenyl-*P,P,P*-tris(*p*-cyanophenyl)phospha-λ^5-azene (**4i**) after recrystallizing from ethyl ether.

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Stereocontrolled Epoxidations of Cycloheptene Derivatives in the Palladium-Catalyzed Route to Tropane Alkaloids. Total Syntheses of Scopine and Pseudoscopine

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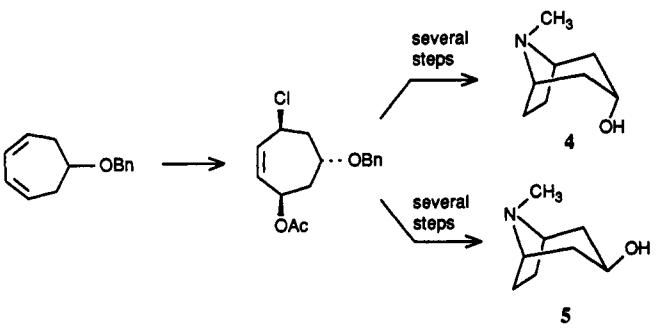
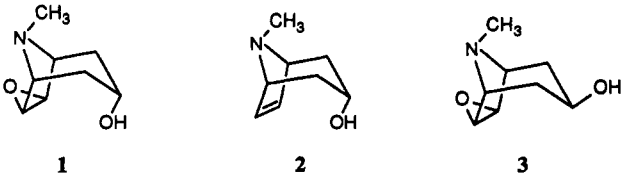
Stereoselective total syntheses of the tropane alkaloids scopine (1) and pseudoscopine (3) have been developed via the chloroacetoxylation approach. Palladium-catalyzed 1,4-chloroacetoxylation of diene **6** afforded the key intermediate **7**. Subsequent substitution of the allylic chloride by $TsNH^-$ with either retention (Pd(0) catalysis) or inversion (S_N2) of configuration gave **10** and **16**, respectively. The epoxy oxygen was introduced syn to the nitrogen function prior to cyclization by utilizing the syn-directive effect of the allylic sulfonamido group in the epoxidation. Cyclization of the epoxides **12** and **21**, followed by replacement of the tosyl group by a methyl group and subsequent debenzylation, afforded the title compounds 1 and 3, respectively.

Tropane alkaloids show an interesting and diverse pharmacological activity and they are still used in medicine, which makes them an important class of natural products.[1,2] Ever since Willstätter[2] and Robinson[3] published their classical tropinone syntheses, organic chemists have put much effort in to developing general methods to prepare the 8-azabicyclo[3.2.1]octane ring system, i.e. the tropane skeleton.[4] An important member of these alkaloids is scopine (1) with a unique epoxy bridge between C-6 and C-7. Although the Robinson method has wide generality for the preparation of many tropane alkaloids,[5] it cannot be used to synthesize scopine since it fails when epoxysuccinaldehyde is employed.[6] Instead, scopine has been prepared by epoxidation of 6,7-dehydrotropine (2), a reaction that takes 7 days without complete conversion.[7] Pseudoscopine (3), an isomer of scopine, is not as well studied since it is not a naturally occurring compound and synthetic approaches toward 3 are rare in the chemical literature.[8]

Scheme I





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