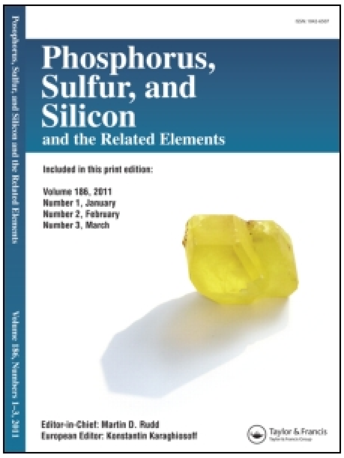

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The Triphosphenide $(^tBu_3Si)_2P_3Na$: ^{31}P NMR Shifts and Structures

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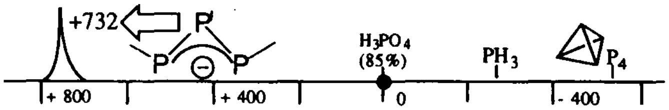
While allyl conjugation[1] is well known in organic chemistry inorganic analogs have only become available, recently (e.g. with $R^* = Si(^tBu)_3$ as buky substituent.[2] How can such compounds, which refute the 'double bond rule', be synthesized?

$3\,PCl_3$ --[+6 R^*Na ; - 4 R^*Cl ; - 5 NaCl; RT, THF] --> $P(P\text{-}R^*)_2$ Na •4THF (1)

The new substance has the backbone of the model HP-P-PH anion, **2**. In our *ab initio* calculations of models $(P(PR)_2^-$ with R= H, SiH_3) we find a Wiberg bond index of 1.5 for the P(terminal)-P'(central) bonds, supporting the allyl character of the P-P-P backbone. Compound 1 is characterized by high reactivity and probably the highest ^{31}P NMR chemical shift of a transition metal free molecule.[2,3] Can *ab initio* computations reproduce this unusual finding?

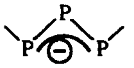


Theoretical studies on geometries and energies of some model allyl compounds comprising phosphorus are available (e.g. for the anions CH_2-CH-PH, PH-CH-PH, and PH-CH-NH).[4] Computation of possible structures of the R-PPP-R allyl indicates that silyl substituents tend to twist out of the P_3 plane.The table shows that *ab inito* calculated relative ^{31}P NMR chemical shifts, $\delta_{calc}{}^{31}P$, of the P_3H_2 anion, silylated derivatives and the corresponding salts. In $\delta_{calc}{}^{31}P$ for 'normal' molecules the systematic error of neglecting electron correlation is compensated (e.g. in H_3C-PH_2, H_2C=PH). In contrast, molecules with allylic conjugation appear to require refined theoretical treatment. While the GIAO-MP2[5] computations could only be done for very small molecules (**2** to **4** and references) the agreement with corresponding DFT results allows to extend the appropriate computations to silylated and even Me_3Si substituted models. This allows to estimate the primary, secundary, and tertiary substituent effects on the extraordinary deshielded central phosphorus of the anionic R-PPP-P system.

Table: Computed[a-d] ^{31}P NMR chemical shifts for molecules with R-PPP-R backbone and reference molecules based on MP2(fc)/6-31G* (6-31+G* for **2**) geometries.

	molecule		'central' Phosphorus			terminal Phosphorus		
		pg[e]	MP2[a,b]	DFT[a,c]	RHF[a,d]	MP2[a,b]	DFT[a,c]	RHF[a,d]
2	$P(PH)_2^-$	C_{2v}	606	594	994	159	168	218
3	$P(PH)_2$ Na	C_2	633	621	1098	133	136	193
4	$P(PH)_2$ Na	C_s	676	687	1103	154	159	209
5	$P(P\text{-}SiH_3)_2$ Na	C_2	---	677	1186	---	167	229
6	$P(P\text{-}SiH_3)_2$ Na	C_s	---	720	1205	---	176	233
	$H_3C\text{-}PH_2$	C_s	-162	-148	-172	---	---	---
	$H_2C{=}PH$	C_s	239	243	274	---	---	---
7	$HP(PH)_2$	C_{2v}	226	247	450	85	98	153
8	$HP(PH)_2$	C_{2v}	277	280	454	49	63	88

[a] Transformation of *ab initio* calculated, absolute magnetic shielding to chemical shifts with PH_3 as "theoretical reference": $\delta^{31}P(X) - \delta^{31}P(PH_3) = -(\sigma^{31}P(X) - \sigma^{31}P(PH_3))$ with $\delta^{31}P(PH_3) = -240$. [b] Explizit consideration of correlation effects, GIAO-MP2;[5] mixed basis set (P: tzp, H, Na: 6-31G*) with ACES II; $\sigma^{31}P(PH_3$, GIAO-MP2$)= 620$. [c] Implicit consideration of correlation effects, SOS-DFPT (Perdew-Wang'91 potential function) with DeMon-NMR;[6] $\sigma^{31}P(PH_3$,SOS-DFPT$)= 578$. [d] Neglect of correlation effects, GIAO-HF, also ACES II; $\sigma^{31}P(PH_3$, GIAO-HF$)= 586$. [e] pg = point group.



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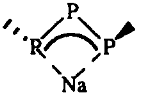

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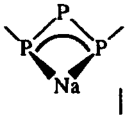

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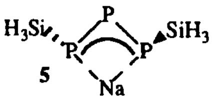

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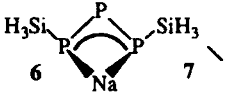

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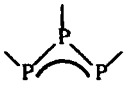

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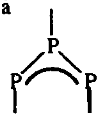

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