

Supporting Information

Table S1 Statistical data for bond lengths in P(OMe)₃ and PEt₃ data sets/Å

	Parameter	Original Dataset			After Removal of Outliers		
		<i>d</i> ₁₋₃	<i>d</i> ₄₋₆	<i>a</i> ₁₋₃	<i>d</i> ₁₋₃	<i>d</i> ₄₋₆	<i>a</i> ₁₋₃
P(OMe) ₃	Maximum	1.958	1.662	115.743	1.668	1.593	114.349
	Minimum	1.389	1.000	70.151	1.499	1.252	87.173
	Mean	1.585	1.422	101.671	1.586	1.430	101.682
	s	0.029	0.057	4.262	0.023	0.041	4.121
PMe ₃	Maximum	2.303	1.899	151.000	1.961	1.725	114.503
	Minimum	1.477	0.849	63.115	1.710	1.289	91.941
	Mean	1.833	1.507	103.343	1.832	1.516	103.393
	s	0.043	0.073	3.842	0.026	0.043	2.571

Table S2 Percentage of conformers in broad ($\pm 60^\circ$), medium ($\pm 40^\circ$) and narrow ($\pm 20^\circ$) ranges of ideal conformers.

Conformer	P(OMe) ₃				PEt ₃			
	No	%Broad	%Medium	%Narrow	No.	%Broad	%Medium	%Narrow
A	4	100.0	25.0	0.0	3	100.0	100.0	0.0
B	1	100.0	0.0	0.0	49	100.0	89.8	73.5
C	324	100.0	82.1	51.2	508	100.0	98.2	83.1
D	283	100.0	71.4	23.3	100	100.0	80.0	20.0
E	21	100.0	61.9	9.5	17	100.0	94.1	82.4
F	102	100.0	92.2	75.5	1263	100.0	99.8	97.8
G	0	-	-	-	32	100.0	98.0	88.3
All	735	100.0	78.4	42.3	1972	100.0	98.0	88.3