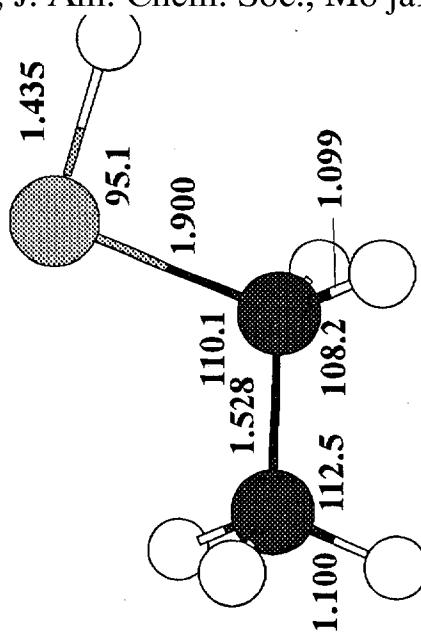


Supplementary material

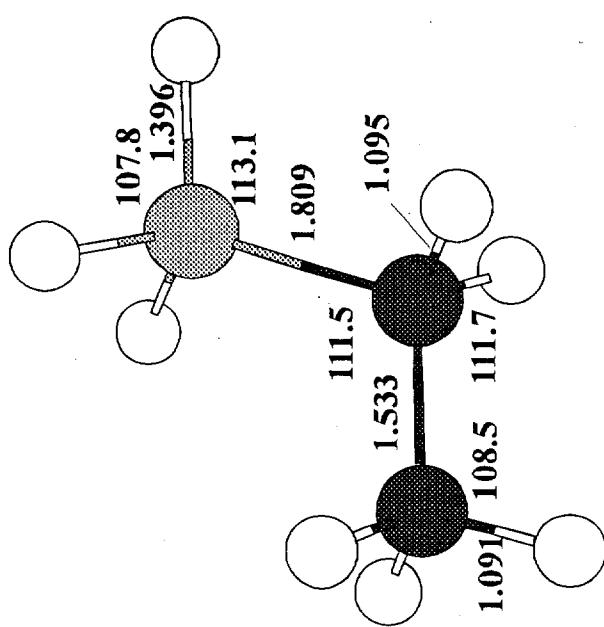
Fig. 1. MP2(full)/6-31G* optimized geometries for ethylphosphine (EtPH_2), vinylphosphine ($\text{H}_2\text{C}=\text{CHPH}_2$) and ethynylphosphine ($\text{HC}\equiv\text{CPH}_2$) and their protonated species. For the deprotonated structures a 6-31+G(d,p) basis set was used in the MP2(full) geometry optimizations. Bond length are in Å and bond angles in degrees.

Table 1. NBO Population Analysis of α , β -unsaturated amines, -phosphines and -arsines. For each bond the participation of each atomic hybrid is given. The *s* and *p* character of each hybrid orbital is indicated within parentheses. LP stands for lone-pair.

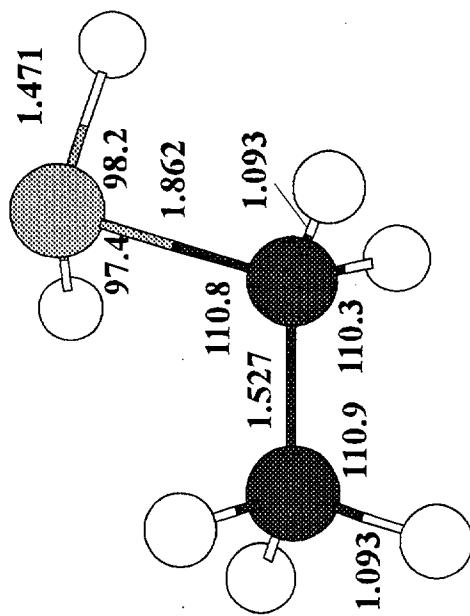
EtPH⁻

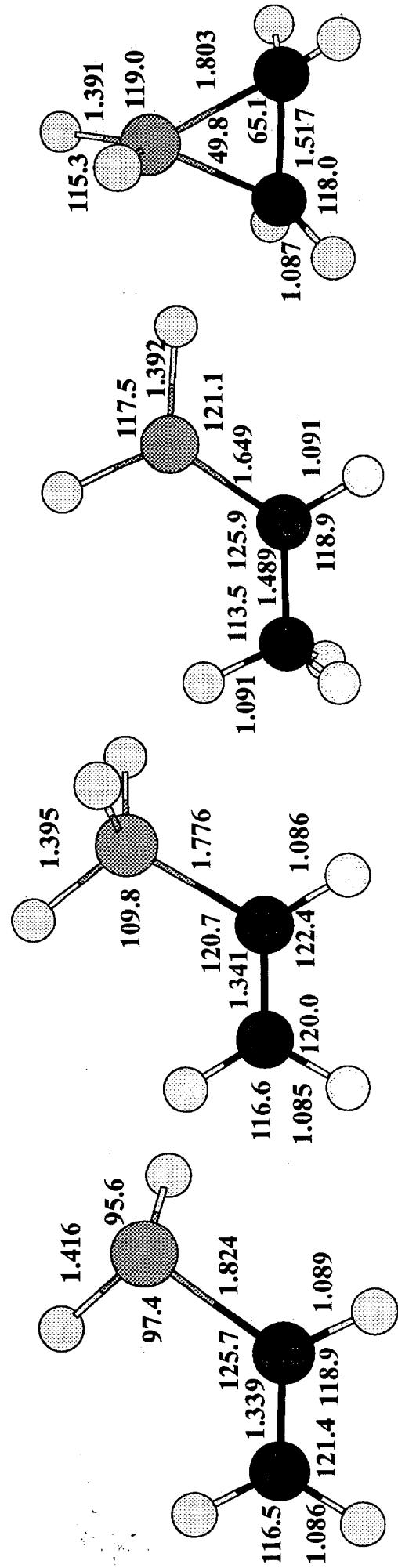


EtPH₃⁺



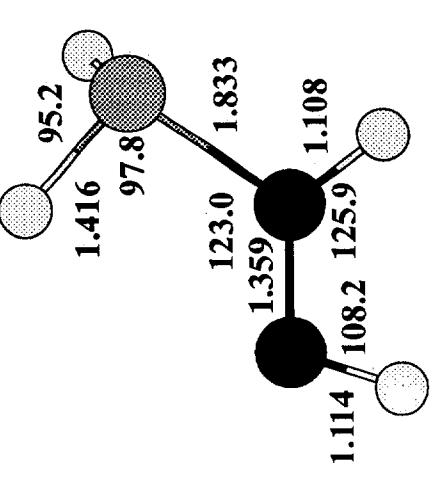
EtPH₂



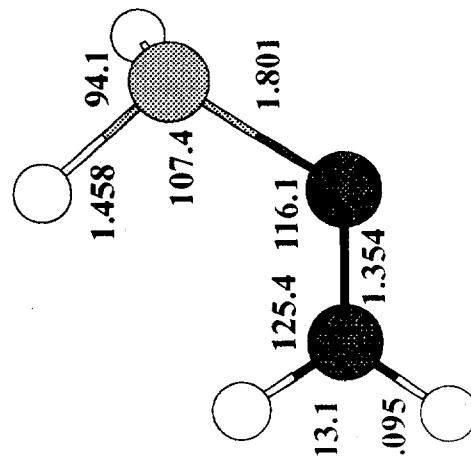


$\text{H}_2\text{C}=\text{CHPH}_3^+$

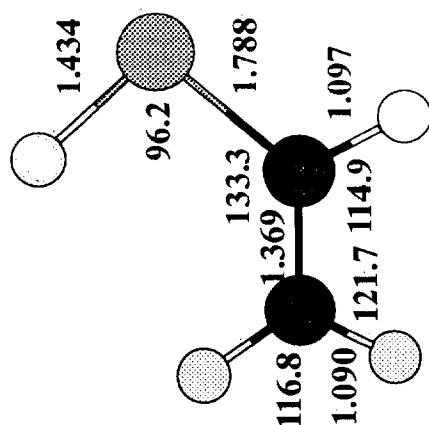
$(\text{CH}_2)_2\text{PH}_2^+$



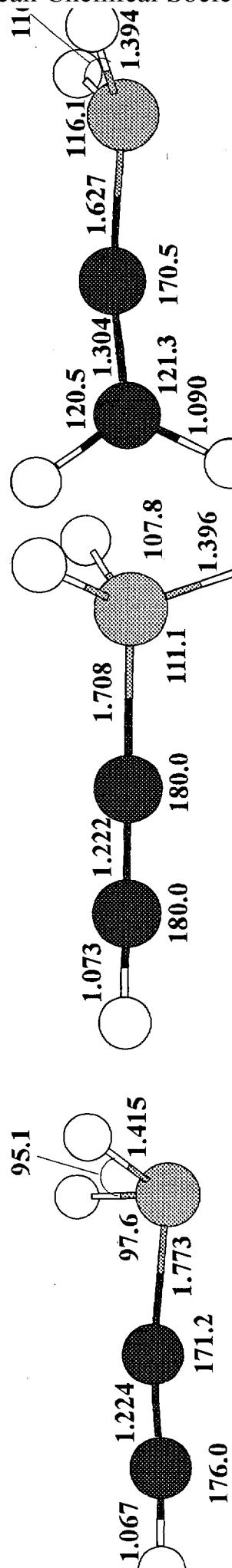
$\text{H}_2\text{C}=\text{C}\text{PH}_2^-$



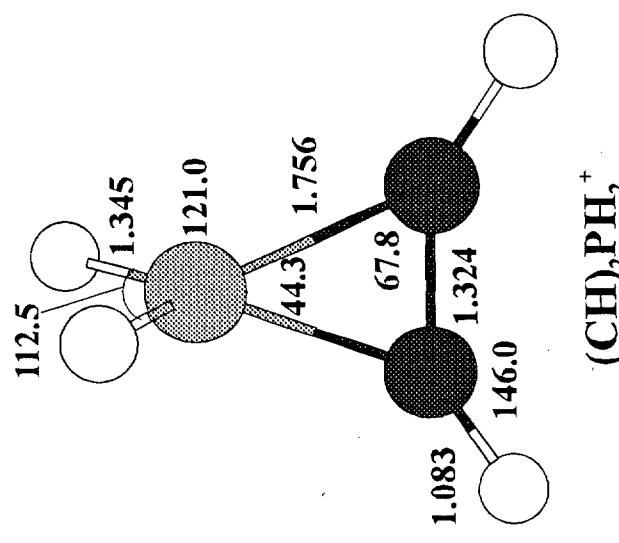
$\text{HC}=\text{C}\text{PH}_2^-$



$\text{H}_2\text{C}=\text{CHPH}_2^-$



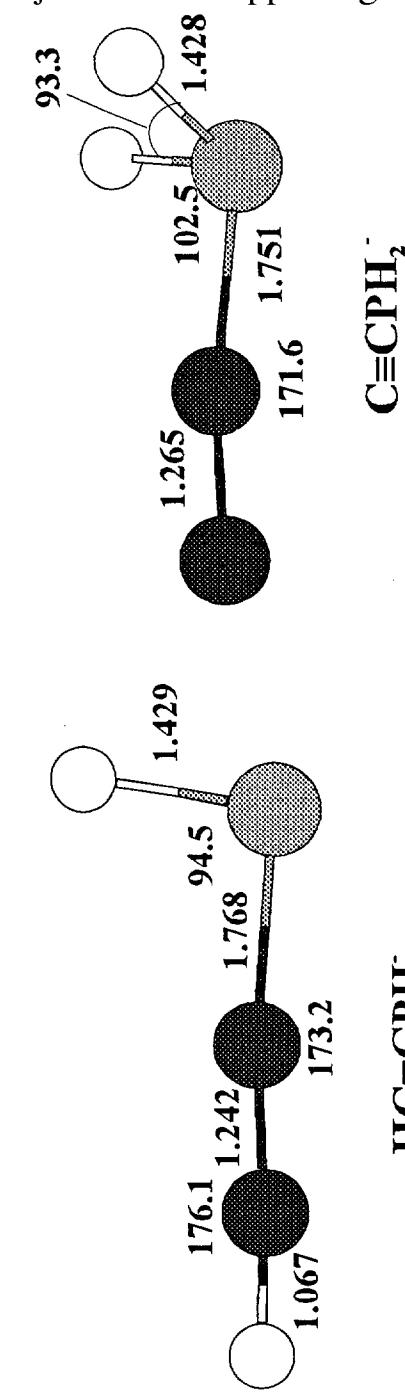
$\text{HC}\equiv\text{CPH}_2$



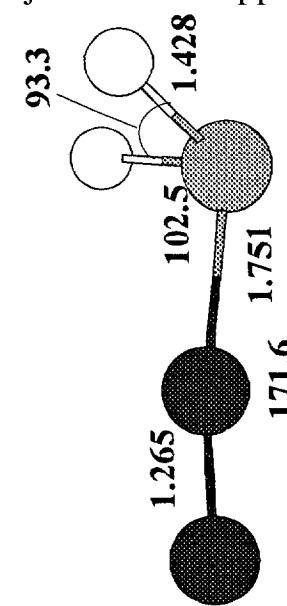
$(\text{CH})_2\text{PH}_2^+$



$\text{HC}\equiv\text{CPH}_3^+$



$\text{H}_2\text{C}\equiv\text{CPH}^+$



$\text{C}\equiv\text{CPH}_2^-$

System	$C_{\beta}-C_{\alpha}$	$C-X(N,P,As)$	$X(N,P,As)-H$	$LP-X(N,P,As)$
ethylamine	50 (34s + 66p) - 50 (33s + 67p)	42 (25s + 75p) - 58 (33s + 66p)	62 (17s + 83p) - 38 (100s)	(31s + 69p)
ethylphosphine	49 (30s + 70p) - 51 (30s + 70p)	60 (23s + 77p) - 40 (17s + 83p)	48 (14s + 86p) - 52 (100s)	(56s + 44p)
ethylarsine	50 (31s + 69p) - 50 (31s + 69p)	60 (21s + 79p) - 40 (13s + 87p)	48 (12s + 88p) - 52 (100s)	(62s + 37p)
vinyllamine	50 (33s + 67p) - 50 (34s + 66p)	40 (30s + 70p) - 60 (39s + 61p)	63 (22s + 78p) - 37 (100s)	(18s + 82p)
vinyolphosphine	54 (11s + 89p) - 46 (11s + 89p)	61 (30s + 70p) - 39 (19s + 81p)	48 (14s + 86p) - 52 (100s)	(54s + 46p)
vinyldarsine	50 (41s + 59p) - 50 (42s + 58p)	49 (100p) - 51 (100p)	48 (11s + 89p) - 52 (100s)	(63s + 37p)
ethynylamine	49 (100p) - 51 (100p)	61 (28s + 72p) - 39 (14s + 86p)	48 (11s + 89p) - 52 (100s)	(18s + 82p)
ethynylphosphine	50 (50s + 50p) - 50 (52s + 48p)	40 (42s + 58p) - 60 (38s + 62p)	63 (22s + 78p) - 37 (100s)	(55s + 45p)
ethynylarsine	54 (7s + 93p) - 46 (6s + 94p)	50 (100p) - 50 (100p)	49 (14s + 86p) - 51 (100s)	(64s + 36p)