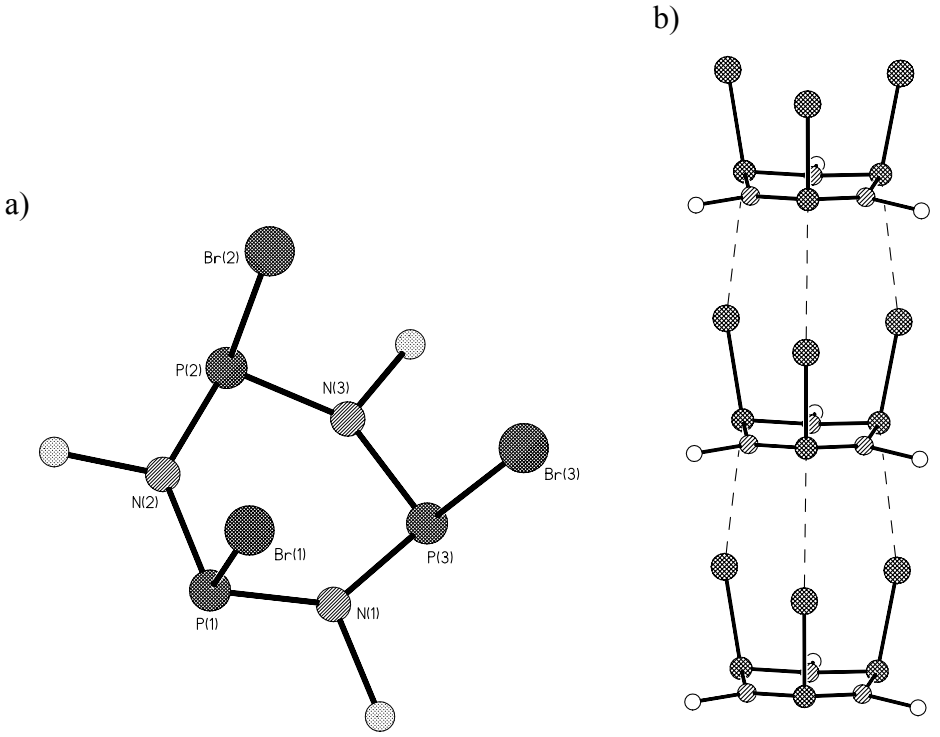


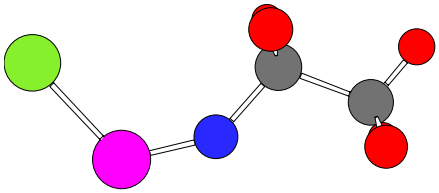

a) The structure of $[BrPNMe]_3$. b) Association of molecules of $[BrPNMe]_3$ along the crystallographic *a*-axis (Br···P range 3.42 – 3.45 Å, sum of Van Der Waals radii = 3.65 Å)

Crystal data: $C_3H_9Br_3N_3P_3$, $M = 419.77$, monoclinic, space group $P2(1)/c$, $Z = 4$, $a = 5.6856(11)$, $b = 13.590(3)$, $c = 16.245(3)$ Å, $\beta = 99.77(3)°$, $V = 1236.9(4)$ Å$^3$, $\mu$(Mo-K$\alpha$) = 10.131 mm$^{-1}$, $T = 180(2)$ K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 3385 reflections collected, 1122 were independent ($R_{int} = 0.1533$). The structure was solved by direct methods and refined by full-matrix least squares on $F^2$. Final $R1 = 0.122$ [$I > 2\sigma(I)$] and $wR2 = 0.329$ (all data). All H-atoms were modelled on idealised geometries and allowed to ride on their parent atoms.

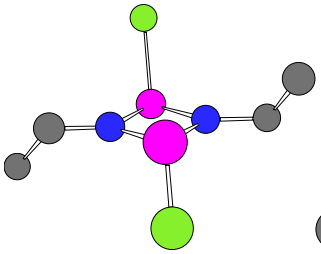
## Calculations of the Formation of $[ClP(\mu\text{-}N^tBu)]_3$

| Model | Calculational Level (kJ mol$^{-1}$) AM1 | MNDO | MNDO-d | PM3 |
|---|---|---|---|---|
| ***Monomer*** | -18.6 | -40.3 | -19.9 | 29.4 |
| ***Dimer*** | | | | |
| *cis* | -66.3 (29.1)* | -146.5 (65.9) | -72.5 (-32.7) | -122.3 (-63.5) |
| *trans* | -64.5 (27.3) | -145.0 (64.4) | -71.5 (-31.7) | -119.6 (-60.9) |
| ***Trimer*** | | | | |
| *cis* | -91.8 (-35.9) | -229.8 (-108.9) | -119.1 (-59.4) | -184.5(-96.3) |
| *trans* | -100.7 (-44.8) | -231.4 (-110.6) | -119.0 (-59.2) | -184.1 (-98.0) |

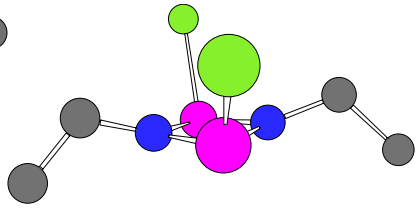
- values in parenthesis are ΔH values for the formation of each model from the monomer.



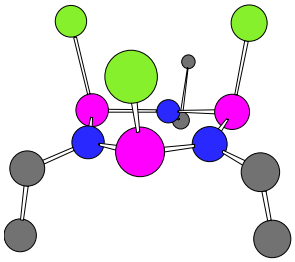
monomer



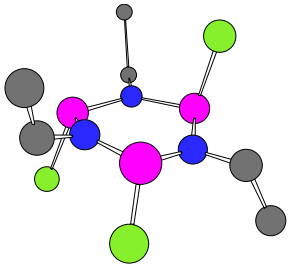
*trans* dimer



*cis* dimer



*cis* trimer



*trans* trimer

***2(MONOMER)*** ⟶ ***DIMER***

ΔH= − 29.1 to− 65.9 kJ mol$^{-1}$

***3(MONOMER)*** ⟶ ***TRIMER***

ΔH= − 44.8 to − 110.6 kJ mol$^{-1}$

***3(DIMER)*** ⟶ ***2(TRIMER)***

ΔH= − 2.1 to −23.4 kJ mol$^{-1}$

***MONOMER + DIMER*** ⟶ ***TRIMER***

ΔH= − 15.7 to− 44.6 kJ mol$^{-1}$

***2(DIMER)*** ⟶ ***TRIMER + MONOMER***

ΔH= +6.0 to +30.7 kJ mol$^{-1}$

The values in the above equations are those involving the most stable calculated models.

***Conclusions:***

(1) The trimer is always preferred to the dimer at all levels of theory, i.e., formation of the dimer from two monomers is less exothermic than formation of the trimer from three monomers and transformation of three dimers into two trimers is exothermic.

(2) Significantly, as regards the mechanism of the reaction, formation of the trimer from a monomer and a dimer is exothermic whereas the formation of a

trimer and monomer from two dimers in endothermic. The most likely mechanism therefore involves the intermediacy of monomers in the reaction.