Supporting information

optimized geometric structures, bonding distances, total energies and the number of imaginary frequencies and NICSs for P_5^- anion, [Ti (η^5–P_5)]$^-$ and [Ti (η^5–P_5)$_2$]$^{2-}$ were computed with other four methods : B3LYP/6-311++G(d, p), B3LYP/ 6-311++G(3df,3pd), HF/6-311++ G(d, p), and HF/gen (P:6-311+G(2d), Ti:6-311+G(2df)), the same results at different levels were obtained as at the B3LYP/gen(P:6-311+G(2d),Ti:6-311+G(2df)) .

Table 1 Bond distance or distance of atom for P_5^-, [Ti (η^5–P_5)$_2$]$^{2-}$, and [Ti (η^5–P_5)]$^-$ (Angstrom)

species	sym	B3LYP/ 6-311++G(d, p)		B3LYP/ 6-311++G(3df,3pd)		HF/ 6-311++G(d, p)		HF/gen	
		r(P–P)	r(Ti–P)	r(P–P)	r(Ti–P)	r(P–P)	r(Ti–P)	r(P–P)	r(Ti–P)
P_5^-	D_{5h}	2.126		2.108		2.094		2.094	
[Ti (P_5)$_2$]$^{2-}$	D_{5h}	2.181	2.597	2.162	2.597	2.149	2.588	2.149	2.602
[Ti (P_5)$_2$]$^{2-}$	D_{5d}	2.176	2.612	2.156	2.612	2.142	2.607	2.140	2.621
[Ti [P_5)]$^-$	C_{5v}	2.248	2.385	2.228	2.378	2.217	2.374	2.218	2.376

Table 2 Relative energies of [Ti (η^5–P_5)$_2$]$^{2-}$ (a.u)

species	sym	Energies and The Number of Imaginary frequencies(NIF)							
		B3LYP/ 6-311++G(d, p)		B3LYP/ 6-311++G(3df,3pd)		HF/ 6-311++G(d, p)		HF/ gen	
		E	NIF	E	NIF	E	NIF	E	NIF
P_5^-	D_{5h}	2556.497	0	2556.525	0	2552.121	0	2552.139	0
[Ti (P_5)$_2$]$^{2-}$	D_{5h}	0.000	0	0.000	0	0.000	0	0.000	0
[Ti (P_5)$_2$]$^{2-}$	D_{5d}	0.011	1	0.009	1	0.016	1	0.013	1
[Ti (P_5)]$^-$	C_{5v}	1707.036	0	1707.064	0	1703.793	0	1703.809	0

Table 3.Binding energies for P_5^-, $[Ti\ (\eta^5-P_5)_2]^{2-}$, and $[Ti\ (\eta^5-P_5)]^-$ according to imaginary reaction (kcal/mol) at B3LYP/6-311++G(d,p) level

species	sym	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5
P_5^-	D_{5h}		385.2			
$[Ti\ (P_5)_2]^{2-}$	D_{5h}	122.1	892.4	203.6	81.5	14.4
$[Ti\ (P_5)_2]^{2-}$	D_{5d}	115.3	885.7	192.8	77.5	7.6
$[Ti\ (P_5)]^-$	C_{5v}	107.7	492.9	118.7		

Table 4.The Total Nucleus Independent Chemical Shift (NICS) Values for P_5^-, $[Ti\ (\eta^5-P_5)_2]^{2-}$, and $[Ti\ (\eta^5-P_5)]^-$ (ppm)

Species	sym		B3LYP/ 6-311++G(d, p)		B3LYP/ 6-311++G(3df,3pd)		HF/ 6-311++G(d, p)		HF/ gen	
			NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)
P_5^-	D_{5h}		−16.6	−15.8 (-16.9)[c]	−16.0	−15.3	−16.3	−15.8	−15.3	−14.6
$[Ti\ (P_5)_2]^{2-}$	D_{5h}	a	−37.5	−21.9	−37.6	−21.8	−34.4	−22.1	−33.2	−21.2
		b		−46.5						
$[Ti\ (P_5)_2]^{2-}$	D_{5d}	a	−38.5	−22.5	−38.7	−22.3	−34.6	−23.8	−32.5	−22.1
		b		−51.2						
$[Ti\ (P_5)]^-$	C_{5v}	a	−70.6	−33.6	−73.8	−34.9	−71.1	−35.8	−73.9	−37.8
		b		-74.9						

a: outer plane, b: the most negative NICS in inner plane, r = 0.50Å (P_5^-),r = 0.75 Å ($[Ti\ (\eta^5-P_5)_2]^{2-}$) , r = 0.25 Å ($[Ti\ (\eta^5-P_5)]^-$) c: the most negative NICS outer plane, r = 0.50Å (P_5^-)

Table 5.The Nucleus Independent Chemical Shift (NICS) Values for P_5^-, eclipsed $[(\eta^5\text{–}P_5)\text{–}(\eta^5\text{–}P_5)]^{2-}$ (D_{5h}) and staggered $[(\eta^5\text{–}P_5)\text{–}(\eta^5\text{–}P_5)]^{2-}$ (D_{5d}) B3LYP/6-311++G(d, p)

Species	Sym		NICS(0)	NICS(1)	center
P_5^-	D_{5h}		–16.6	–15.8	
$[(\eta^5\text{–}P_5)\text{–}(\eta^5\text{–}P_5)]^{2-}$	D_{5h}	a	–9.6 [d]	–13.2 [d]	–6.3
			(–9.6) [c]	(–13.3) [c]	(–6.9) [c]
		b		–8.3 [d]	
				(–8.6) [c]	
$[(\eta^5\text{–}P_5)\text{–}(\eta^5\text{–}P_5)]^{2-}$	D_{5d}	a	–14.0 [e]	–13.0 [e]	–9.8
			(–11.4) [c]	(–14.6) [c]	(–9.7) [c]
		b		–12.1 [e]	
				(–11.3) [c]	

a: outer plane, b: inner plane, c: GIAO–HF/6-311++G(d, p)//B3LYP/6-311++G(d, p), d:computed at the geometric reference of eclipsed $[(\eta^5\text{–}P_5)\text{–}(\eta^5\text{–}P_5)]^{2-}$ (D_{5h}): r(P-P)=2.181Å, r(P_5–P_5)=3.634Å(at B3LYP/6-311++G(d, p). e: computed at the geometric reference of staggered $[(\eta^5\text{–}P_5)\text{–}(\eta^5\text{–}P_5)]^{2-}$ (D_{5d}): r(P-P)=2.176Å, r(P_5–P_5)=3.686Å(at B3LYP/6-311++G(d, p).