Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ligands Enhanced Ac≡Ac Triple Bond

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Table S1 EDA-NOCV results of $H_3PAcAcPH_3$ with four different sets of fragments with different charges and electronic states and the corresponding energy components (kcal/mol) at the PBE/TZ2P/TZP level.

Fragments	ΔE_{int}	ΔE_{pauli}	ΔE_{elstat}	ΔE_{orb}
$H_3PAc(^4A_1)+AcPH_3(^4A_1)$	-49.35	113.83	-78.15	-85.04
$H_3PAc^+(^3A_1)+AcPH_3^-(^3A_1)$	-140.49	162.80	-167.72	-135.58
$H_3PAc^{2+}(^2A_1)+AcPH_3^{2-}(^2A_1)$	-458.48	265.20	-443.08	-280.60
$H_3PAc^{3+}(^1A_1)+AcPH_3^{3-}(^1A_1)$	-979.25	188.57	-712.25	-455.58

Table S2 EDA-NOCV energies of the frontier electrons between Ac_2 unit of other compounds at the PBE/TZ2P/TZP level.

	$H_3AsAcAcAsH_3$	$H_3PAcAcPH_3$	OCAcAcCO	ONAcAcNO	$H_3NAcAcNH_3$
$\Delta E_{ord}^{\sigma-s}$	-9.55(10.5%)	-8.88(10.4%)	-12.37(16.7%)	-13.15(18.7%)	-5.79(9.4%)
$\Delta E_{ord}^{\sigma-d}$	0	0	0	0	0
$\Delta E_{ord}^{\pi-d}$	-76.58(84.1%)	-72.24(84.9%)	-57.08(76.9%)	-56.53(80.2%)	-53.37(86.5%)
ΔE_{ord}^{rest}	-4.91(5.4%)	-3.92(4.7%)	-4.80(6.5%)	-0.81(1.1%)	-2.54(4.1%)
ΔE_{ord}	-91.04	-85.04	-74.25	-70.49	-61.70

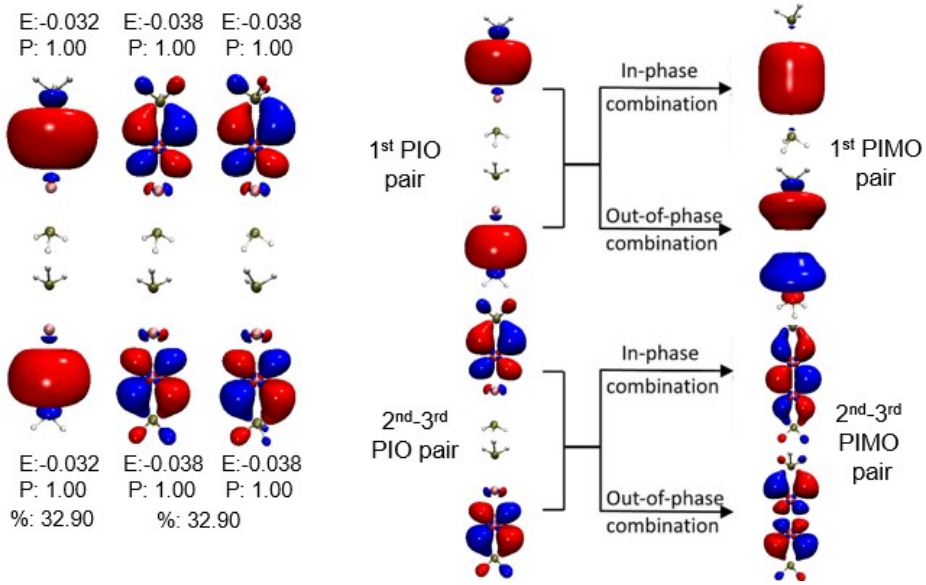

Fig. S1 The results of the PIO analysis for the equivalent fragments at the B3LYP/cc-pVTZ level. The main PIOs with the orbitals' energies, populations and the contributions of each pair to the total interactions are listed on the left. The main principal interacting molecular orbitals (PIMOs) are listed on the right.

Table S3 The electron densities (ρ), potential densities (V), energy densities (H) and the electron density Laplacian $\nabla^2\rho$ of the Ac-Ac bond critical point of the six calculated compounds and the corresponding Ac-Ac bond lengths at the B3LYP/cc-pVTZ level.

Compounds	Ac-Ac(Å)	ρ	V	H	$\nabla^2\rho$
$H_3AsAcAcAsH_3$	3.012	0.0298	-0.0253	-0.0028	0.0787
$H_3PAcAcPH_3$	3.025	0.0300	-0.0270	-0.0025	0.0877
OCAcAcCO	3.082	0.0288	-0.0318	0.0003	0.1373
HAcAcH	3.255	0.0259	-0.0243	-0.0011	0.0879
ONAcAcNO	3.565	0.0161	-0.0116	-0.0005	0.0424
$H_3NAcAcNH_3$	3.652	0.0130	-0.0058	-0.0018	0.0083
R^2		0.9851	0.8854	---	0.6797

Table S4 The energy and compositions of the frontier MOs of $H_3PAcAcPH_3$ and $H_3NAcAcNH_3$ based on the fragment analysis at the PBE/TZ2P/TZP level.

	E(eV)	Contribution (%)	MO	Energy (eV)	Fragments
$H_3PAcAcPH_3$	$1\sigma_g^2 1\pi_u^4$				
1^{σ_g}	-0.1166	80.50	HOMO-1	-0.127257	Ac_2
		16.10	LOMO+1	-0.07596	Ac_2
		2.47	LOMO	-0.017773	PH_3
1^{π_u}	-0.1031	86.97	HOMO	-0.091068	Ac_2
		12.06	LOMO+2	-0.012729	PH_3
$1^{\sigma_u^*}$	-0.0706	78.57	LOMO	-0.080585	Ac_2
		9.57	LOMO+1	-0.016410	PH_3
		7.94	LOMO+6	-0.015147	Ac_2
		2.22	LOMO+12	0.046528	Ac_2
		1.79	LOMO+5	0.087443	PH_3
$H_3NAcAcNH_3$	$1\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$				
1^{σ_g}	-0.1429	90.53	HOMO-2	-0.165938	Ac_2
		5.33	LOMO	-0.103737	Ac_2
		2.58	HOMO	-0.222067	NH_3
1^{π_u}	-0.1109	98.84	HOMO	-0.110883	Ac_2
$1^{\sigma_u^*}$	-0.1004	95.31	HOMO-1	-0.115767	Ac_2
		2.41	LOMO+1	-0.013788	NH_3
		1.82	LOMO+14	0.020089	Ac_2

Table S5 The change of electronic energy (ΔE) and Gibbs free energy (ΔG) for the reactions of Ac_2(g) + 2L(g) --> LAcAcL(g) (L = AsH_3, PH_3, CO, NO, NH_3) at the PBE/TZ2P/TZP level.

Compounds	ΔE	ΔG
$H_3AsAcAcAsH_3$	-31.24	44.07
$H_3PAcAcPH_3$	-55.75	22.46
OCAcAcCO	-177.53	-91.91

ONAcAcNO	-471.27	-383.35
$H_3NAcAcNH_3$	-94.39	-32.15

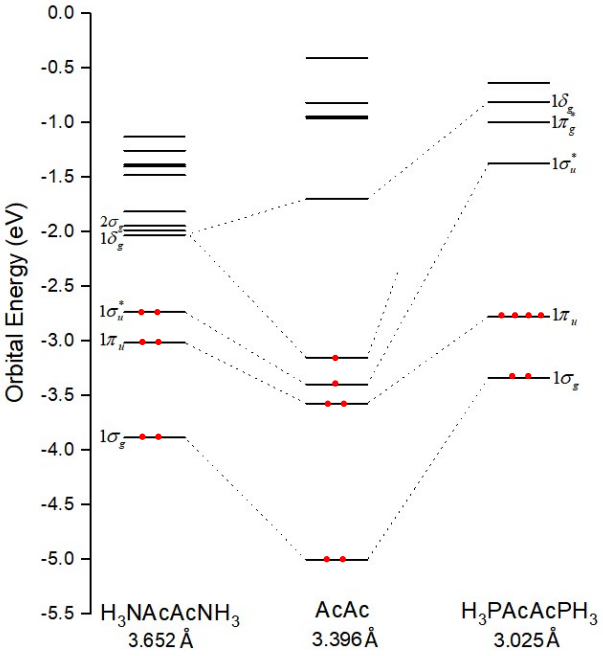

Fig. S2 The valence MO energy level diagrams of $H_3PAcAcPH_3$ and $H_3NAcAcNH_3$ and the corresponding Ac-Ac bond length at the PBE/TZ2P/TZP level.

The optimized geometry structure of all the compounds at the PBE/TZ2P/TZP level.

1, $H_3AsAcAcAsPH_3$

Ac	0.000000	0.000000	-1.509720
Ac	0.000000	0.000000	1.509720
H	1.076182	0.705416	-5.512527
H	0.072817	-1.284708	-5.512527
H	-1.148999	0.579293	-5.512527
H	0.072817	1.284708	5.512527
H	-1.148999	-0.579293	5.512527
H	1.076182	-0.705416	5.512527
As	0.000000	0.000000	4.668131
As	0.000000	0.000000	-4.668131

2, $H_3PAcAcPH_3$

Ac	0.000000	0.000000	-1.512331
Ac	0.000000	0.000000	1.512331
H	0.000000	1.214627	-5.342044
H	1.051898	-0.607313	-5.342044
H	-1.051898	-0.607313	-5.342044
H	0.000000	-1.214627	5.342044

H	1.051898	0.607313	5.342044
H	-1.051898	0.607313	5.342044
P	0.000000	0.000000	-4.567414
P	0.000000	0.000000	4.567414

3, OCAcAcCO

Ac	0.000000	0.000000	-1.540763
Ac	0.000000	0.000000	1.540763
C	0.000000	0.000000	-4.086576
C	0.000000	0.000000	4.086576
O	0.000000	0.000000	-5.252379
O	0.000000	0.000000	5.252379

4, HAcAcH

Ac	0.000000	0.000000	-1.627502
H	0.000000	0.000000	-3.813998
Ac	0.000000	0.000000	1.627502
H	0.000000	0.000000	3.813998

5, ONAcAcNO

Ac	0.000000	0.000000	-1.780295
Ac	0.000000	0.000000	1.780295
O	0.000000	0.000000	-5.253317
O	0.000000	0.000000	5.253317
N	0.000000	0.000000	-4.034137
N	0.000000	0.000000	4.034137

6, $H_3NAcAcNH_3$

Ac	-0.002633	0.000732	-1.826428
Ac	-0.002292	0.000090	1.826430
H	0.382594	0.878641	-4.932135
H	0.571287	-0.769643	-4.931904
H	-0.950563	-0.108905	-4.934771
H	-0.854724	0.431394	4.933378
H	0.054172	-0.956573	4.932905
H	0.801703	0.524572	4.932542
N	0.000350	-0.000021	-4.554682
N	0.000221	-0.000223	4.554674