Electronic Supplementary Material (ESI) for Dalton Transactions

Coulomb repulsion versus cycloaddition: Formation of anionic four-membered rings from sodium phosphaethynolate, Na(OCP)

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Supporting information

Table S1 Crystal data and structure refinement for **1**^{Tr*}

Empirical formula	$C_{54}H_{58}O_{10}P_2$
Formula weight	929.00
Temperature / K	100(2)
Crystal system	triclinic
Space group	P-1
a / Å	11.2018(6)
b / Å	11.2296(6)
c / Å	11.4596(6)
α / °	118.377(6)
β / °	107.308(5)
γ / °	93.323(4)
Volume / Å^3	1176.28(11)
Z	1
ρ_{calc} mg/mm^3	1.311
m / mm^{-1}	0.153
F(000)	492.0
Crystal size / mm^3	0.3 × 0.2 × 0.2
2Θ range for data collection	6.16 to 54.96°
Index ranges	−14 ≤ h ≤ 14, −14 ≤ k ≤ 14, −14 ≤ l ≤ 14
Reflections collected	12035
Independent reflections	5378[R(int) = 0.0253]
Data/restraints/parameters	5378/0/338
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0580, wR_2 = 0.1592
Final R indexes [all data]	R_1 = 0.0755, wR_2 = 0.1774
Largest diff. peak/hole / e Å^{-3}	0.66/−0.64

Table S2 Relative energies (kcal mol^{-1}) at different levels of theory, including solvent effects (SCRF).

Method	Basis set	**TS1**	**IM1**	**TS2**	**IM2**	**TS3**	**3**
B3LYP	6-31+G*	5.1	−11.6	5.8	−3.5	−0.9	−23.4
G(298 K)	6-31+G*	14.7	11.1	30.0	20.0	24.1	4.0
B3LYP	aug-cc-pVDZ	6.3	−9.0	7.8	−1.0	1.8	−19.8
ωB97XD	6-31+G*	6.3	−12.8	3.5	−7.2	−4.6	−31.2
M052X	6-31+G*	2.2	−18.0	−3.1	−13.2	−10.7	−37.1
CBS-QB3	–	8.6	−4.3	13.1	1.4	16.9	−21.2
G(298 K)	–	18.3	15.9	34.9	22.4	40.5	3.3

Table S3 Unscaled harmonic frequencies (f, cm^{-1}), reduced masses (μ, amu), force constants (k, mDyne $Å^{-1}$),IR intensities (I, km mol^{-1}), Raman scattering activities (A, $Å^4$ amu^{-1}) of dianion **3** with sodium counter ions, B3LYP/6-31+G*.

Nr.	Symmetry	f	μ	k	I	A
1	A''	54.69	17.54	0.03	0.78	1.40
2	A'	63.89	20.37	0.05	49.09	0.33
3	A'	91.26	21.53	0.11	1.13	5.80
4	A''	104.59	17.48	0.11	2.33	0.16
5	A''	132.90	18.14	0.19	36.95	0.69
6	A'	144.44	18.86	0.23	19.49	0.84
7	A'	241.00	20.82	0.71	34.32	3.74
8	A'	244.27	22.10	0.78	6.21	1.88
9	A''	256.03	18.78	0.73	6.04	4.73
10	A''	306.66	16.76	0.93	12.67	1.34
11	A''	356.91	18.03	1.35	63.14	0.13
12	A'	360.81	18.68	1.43	0.77	20.86
13	A'	370.85	17.91	1.45	21.37	9.35
14	A''	429.95	20.50	2.23	1.59	6.24
15	A'	468.85	22.10	2.86	8.44	5.55
16	A''	532.72	17.44	2.92	5.00	0.32
17	A'	538.62	15.12	2.58	1.84	4.59
18	A'	577.71	14.92	2.93	3.00	17.15
19	A''	603.66	13.42	2.88	15.58	3.14
20	A'	687.92	13.10	3.65	10.35	2.89
21	A''	745.19	12.76	4.17	4.35	7.39
22	A'	793.78	14.51	5.39	108.43	22.10
23	A'	909.54	13.60	6.63	55.40	27.18
24	A'	1322.06	14.03	14.45	489.42	12.59
25	A''	1547.71	13.37	18.87	877.22	8.21
26	A'	1639.72	13.17	20.87	27.46	105.54
27	A''	1657.85	13.04	21.11	979.93	15.31

Total energies (in hartree) and coordinates (in Å) of the calculated species at the B3LYP/6-31+G*(THF) level of theory

CO_2
HF = −188.592751

O	0.019806	0.000000	0.000000
C	1.189000	0.000000	0.000000
O	2.358194	0.000000	0.000000

Na(OCP)
HF = −617.052175

C	0.110377	0.000000	−0.059898
P	−0.010141	0.000000	1.570512
O	0.219619	0.000000	−1.255016
Na	−2.847459	0.000000	1.096864

TS1
HF = −805.636765

C	0.031873	−0.001207	−0.202165
O	−0.185066	0.001025	0.975872
P	0.173143	−0.004050	−1.828780
C	−2.239814	0.000274	−1.960511
O	−2.746028	0.002002	−0.859704
O	−2.442702	−0.000269	−3.142231
Na	−2.529525	0.003867	1.423793

IM1
HF = −805.638355

C	0.276642	0.002960	−0.181413
O	0.252698	0.003606	0.996105
P	0.224779	0.002284	−1.845223
C	−1.829249	−0.001641	−1.886978
O	−2.441466	−0.002103	−0.802618
O	−2.199319	−0.002924	−3.059180
Na	−2.636744	−0.000845	1.400790

TS2
HF = −1422.687788

C	0.072725	0.094801	0.092057
P	−0.146007	−0.013634	1.787154
C	1.777453	−0.043278	2.170130
O	2.588895	0.728766	1.610073
P	−2.132944	−1.158699	−0.814140
C	−1.433734	−2.406068	−0.031898
O	−0.888853	−3.287836	0.579626
O	0.682458	0.381799	−0.888939
O	2.011006	−0.949382	3.013321
Na	2.707891	1.698343	−0.392296
Na	0.629834	−2.837015	2.488723

IM2

HF = −1422.702633

C	−0.068262	−0.074903	0.091082
P	0.256079	−0.702360	1.713958
C	2.011742	−0.126960	2.156892
O	2.699371	0.678149	1.472099
P	−1.925648	−0.598610	−0.541405
C	−1.591849	−2.231711	−0.596852
O	−1.420108	−3.393294	−0.678580
O	0.530913	0.649489	−0.711417
O	2.395695	−0.659378	3.249961
Na	2.540178	1.667956	−0.489863
Na	1.633603	−2.289726	4.514012

TS3

C	−1.222740	0.749129	0.206152
P	0.135270	−0.337206	0.688647
C	1.741780	0.439195	0.049061
O	1.855801	1.670544	−0.203790
P	−2.834640	−0.262915	0.118991
C	−1.969160	−1.696329	−0.257058
O	−1.798842	−2.801776	−0.631293
O	−1.266221	1.961508	−0.075873
O	2.680966	−0.413295	−0.062976
Na	2.930819	−2.591266	−0.067342
Na	0.470785	3.383449	−0.324662

3

HF = −1422.734378

P	−0.012409	0.000000	−0.003182
P	0.019112	0.000000	2.853357
C	1.774492	0.000000	3.609461
O	2.273043	−1.130512	3.849883
O	2.273043	1.130512	3.849883
Na	1.762028	−3.197425	3.072673
Na	1.762028	3.197425	3.072673
C	0.171218	−1.179982	1.371022
C	0.171218	1.179982	1.371022
O	0.372307	2.402202	1.396138
O	0.372307	−2.402202	1.396138

Fig. S1. Bond parameters (bond lengths in Å and Wiberg bond indices in parenthesis) of $\mathbf{4}^{\mathbf{Me}}$ with Na^+ counter ion.