ELECTRONIC SUPPLEMENTARY INFORMATION

P–C Dichotomy: Divergent Iron(-I)-Mediated Alkyne and Phosphaalkyne Cycloligomerisations

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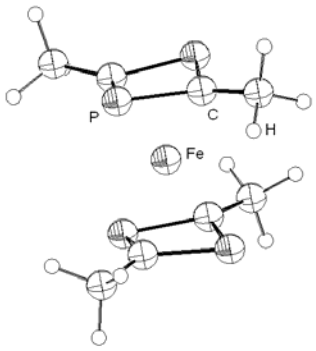
1. Details of the density functional calculations:

1.1. Theoretical methods

The Gaussian03 suite of programs[S1] was used for computations of the relevant isomers **1C**, **1P**, **2C, 2P**, metal-ligand binding energies and the oligomerisation energies. The exchange correlation functional OPBE[S2] with the SDD basis[S3] set for iron and 6-311+G(d,p) basis set for the other elements were used to compute the geometries and the normal mode vibrational frequencies. All stationary points were verified as minima by frequency analyses. In the text, E(0 K) energies are discussed, which contain zero-point corrections.

1.2. Spin state, energies (au), point groups and cartesian coordinates for the optimised structures

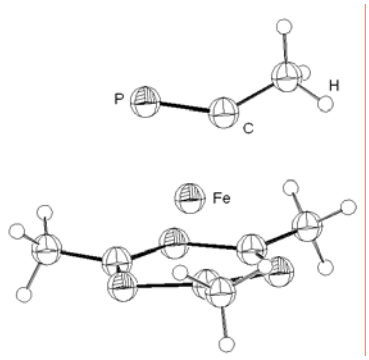


1P

$[Fe(\eta^4\text{-}P_2C_2Me_2)_2]^-$

S=1/2, E = -1801.450043, D_{2d}

C	-0.910928	1.823945	-0.527598
P	-0.914454	1.816400	1.283108
C	0.868937	1.823945	0.969764
P	0.857232	2.079227	-0.822837
Fe	0.082499	0.140585	0.098063
C	0.931283	-1.432212	-0.910859
P	1.251372	-1.666643	0.855864
C	-0.559297	-1.653338	0.860945
P	-0.864154	-1.666643	-0.923883
C	-2.059001	1.953981	-1.477218
C	2.001020	1.953981	1.938390
C	-1.506081	-1.925014	1.986356
C	1.894057	-1.420608	-2.055276
H	-2.357087	3.010050	-1.596191
H	-1.805596	1.566569	-2.474095
H	-2.939826	1.398307	-1.125875
H	2.169250	3.010050	2.211719
H	1.805598	1.398307	2.866347
H	2.939826	1.566569	1.518127
H	-1.636415	-3.010050	2.141280
H	-1.144895	-1.496047	2.931659
H	-2.499250	-1.496047	1.792270
H	2.154247	-2.447710	-2.364556
H	1.474890	-0.906489	-2.931659
H	2.829244	-0.906489	-1.792270



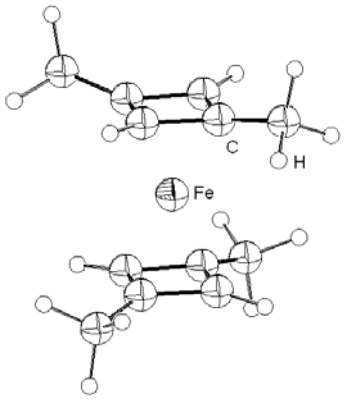
2P

$[Fe(\eta^6\text{-}P_3C_3Me_3)(\eta^2\text{-}PCMe)]^-$

S=1/2, E = -1801.407660, C_1

C	-1.428049	1.787388	-1.058577
P	-1.425355	1.693334	0.703095
C	0.268122	1.799077	1.189561
P	1.785030	2.018927	0.316631
C	1.354907	2.019194	-1.396687
P	-0.177535	2.003881	-2.277916
Fe	0.221422	0.454258	-0.510107
P	-0.125842	-1.657839	-1.277113

	C	0.826470	-1.266555	0.025691
	C	1.687541	-1.887643	1.067110
	C	2.566618	1.952765	-2.315457
	C	-2.795969	1.504335	-1.661750
	C	0.470571	1.563239	2.679691
	H	1.219853	-1.772563	2.057403
	H	1.865174	-2.962144	0.900541
	H	2.659981	-1.376926	1.127712
	H	2.336632	1.401521	-3.237451
	H	3.408737	1.443707	-1.826527
	H	2.903458	2.962145	-2.600817
	H	-2.709581	0.961826	-2.612370
	H	-3.408737	0.892583	-0.985691
	H	-3.340809	2.442008	-1.854614
	H	1.461565	1.138513	2.889766
	H	-0.283159	0.873464	3.083664
	H	0.389314	2.509607	3.237451

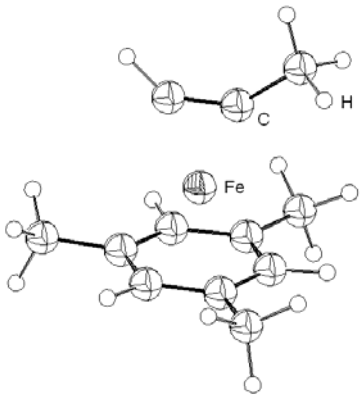


1C

$[Fe(\eta^4\text{-}C_4Me_2H_2)_2]^-$

S=1/2, E = -590.736954, D_{2d}

	C	-0.703313	1.687227	-0.749974
	C	-0.705874	1.691600	0.716466
	C	0.760537	1.687227	0.706844
	C	0.762604	1.648814	-0.759100
	Fe	0.003741	-0.028219	0.003426
	C	0.707125	-1.764884	-0.703353
	C	0.717056	-1.726645	0.762563
	C	-0.749385	-1.722446	0.760187
	C	-0.758822	-1.726645	-0.706225
	C	1.800708	1.875755	-1.802215
	C	-1.736523	1.978820	1.752090
	C	1.752918	-1.983726	1.800904
	C	-1.802139	-1.983726	-1.737075
	H	-1.471411	1.781135	-1.517105
	H	1.531358	1.781135	1.471239
	H	1.471365	-1.881099	-1.471282
	H	-1.516348	-1.794047	1.530853
	H	1.984764	2.953415	-1.987160
	H	2.762585	1.427291	-1.513436
	H	1.507301	1.427291	-2.762690
	H	-1.889189	3.066290	1.905493
	H	-2.711116	1.550203	1.476089
	H	-1.455832	1.550203	2.725343
	H	1.906431	-3.066290	1.985071
	H	2.726080	-1.563381	1.507670
	H	1.477090	-1.526989	2.762689
	H	-1.987043	-3.066290	-1.889700
	H	-2.762585	-1.526989	-1.456619
	H	-1.513594	-1.563381	-2.711637



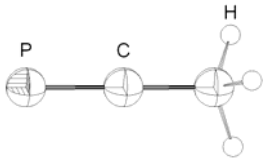
2C

$[Fe(\eta^6\text{-}C_6Me_3H_3)(\eta^2\text{-}C_2MeH)]^-$

S=1/2, E = -590.774490, C_s

	C	-1.244170	2.156458	-1.164078
	C	-1.241169	2.156920	0.264955
	C	-0.019905	2.156458	1.007018
	C	1.211416	2.185482	0.292723
	C	1.241049	2.157202	-1.134750
	C	0.004232	2.185482	-1.848081
	Fe	-0.006202	0.651326	-0.431435
	C	0.586885	-1.124723	-0.765872
	C	-0.556793	-1.145329	-0.120960
	H	-2.188890	2.069454	0.799368
	H	2.150474	2.111892	0.845583
	H	0.017095	2.111892	-2.937723
	H	1.305383	-1.848703	-1.171028
	C	-1.561563	-2.084910	0.445623
	H	-2.555157	-1.920410	-0.002910
	H	-1.299347	-3.150503	0.297761
	H	-1.691920	-1.920410	1.527943
	C	2.549752	2.114367	-1.872718

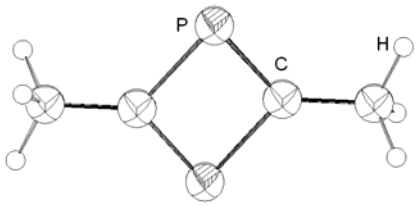
	H	2.445112	1.586378	-2.830078
	H	2.934615	3.127151	-2.089740
	H	3.314812	1.586378	-1.287764
	C	-2.540763	2.131874	-1.927357
	H	-2.927292	3.150502	-2.111875
	H	-2.417162	1.642899	-2.903212
	H	-3.314813	1.580412	-1.376991
	C	-0.037731	2.131874	2.511488
	H	-0.079861	3.150502	2.937723
	H	-0.909231	1.580412	2.889036
	H	0.861265	1.642899	2.910708

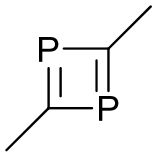


MeC≡P

S=0, E = -419.242870, C_{3v}

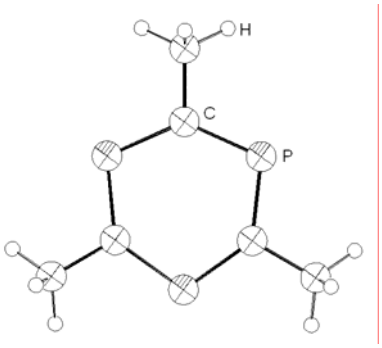
	C	0.000000	0.256617	-1.307823
	C	0.000000	0.256617	0.143360
	P	0.000000	0.256617	1.701114
	H	0.000000	-0.769852	-1.701114
	H	-0.888949	0.769852	-1.701114
	H	0.888949	0.769852	-1.701114

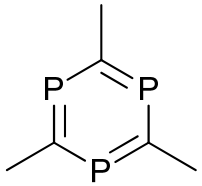




S=0, energy = -838.498583, C_{2h}

	C	-0.948512	0.000000	-0.686830
	P	-0.939977	0.000000	1.005201
	C	0.948512	0.000000	0.686830
	P	0.939977	0.000000	-1.005201
	C	-2.029485	0.000000	-1.688296
	C	2.029485	0.000000	1.688296
	H	-1.944547	0.878241	-2.349370
	H	-1.944547	-0.878241	-2.349370
	H	-3.027998	0.000000	-1.232906
	H	1.944547	0.878241	2.349370
	H	1.944547	-0.878241	2.349370
	H	3.027998	0.000000	1.232906





S=0, E = -1257.834667, C_{3v}

	C	-1.382140	-0.269470	-1.089765
	P	-1.381525	-0.269720	0.655014
	C	0.273761	-0.269470	1.206631
	P	1.783891	-0.316566	0.333968
	C	1.434260	-0.311152	-1.375412
	P	-0.077213	-0.316566	-2.247003
	C	2.663982	-0.312198	-2.262148
	C	-2.764324	-0.231863	-1.711594
	C	0.427246	-0.231863	2.714459
	H	2.473087	-0.808518	-3.221844
	H	3.514272	-0.808518	-1.777933
	H	2.974456	0.718869	-2.486027
	H	-2.784582	-0.730708	-2.688597
	H	-3.514272	-0.704499	-1.065079
	H	-3.083081	0.808518	-1.871655
	H	1.347847	-0.730708	3.042236
	H	-0.423029	-0.704499	3.221843
	H	0.478444	0.808518	3.067453

Fe^-

S=1/2, E = -124.035272, O_h

	Fe	0.000000	0.000000	0.000000

2. EPR spectroscopy and EPR parameter calculations

Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). The spectra were simulated by iteration of the anisotropic *g* values, (super)hyperfine coupling constants and line widths using the W95EPR program (available upon request from Prof. Frank Neese, University of Bonn).

The geometry of the full atom model of $[Fe(\eta^6\text{-}C_6Ph_6)(\eta^2\text{-}C_2Ph_2)]^-$ (**2**) was fully optimized as a minimum with the Turbomole program[S4a] coupled to the PQS Baker optimizers[S5] at the bp86 level[S6] using the Turbomole SV(P) basis.[S4c,f] EPR parameters[S7] (Table S1) were subsequently calculated with the ADF[S8] program system using the BP86 functional and the OPBE functional with the ZORA/TZP basis set supplied with the program (all electron, core double zeta, valence triple zeta polarized basis set on all atoms), using the coordinates from the structures optimized in Turbomole as input. Orbital and spin density plots were generated with Molden.[S9]

Table S1. Experimental and DFT calculated g-values of **2**

	g_{11}	g_{22}	g_{33}	σ [(d)]
Exp[(a)]	2.114	2.010	2.003	
DFT BP86[(b)]	2.095	1.996	1.992	110%
DFT OPBE[(c)]	2.106	1.995	1.991	122%

(a) Values obtained by least square curve fitting of the experimental spectrum
(b) ADF (BP86, TZP) using a Turbomole optimized geometry of the full atom model as input.
(c) ADF (OPBE, TZP) using a Turbomole optimized geometry of the full atom model as input.
(d) Spin density at the Fe nucleus (negative spin density at the aromatic C_6Ph_6 ligand compensates for the excess of positive spin density at Fe).

Cartesian coordinates of the DFT optimized structure of **2** (full atom model)
S = 1/2, Energy = -3420.367623 au

C	1.4426927	-0.0720557	1.2146455	C	-3.1745102	-3.9730033	2.3780098
C	-1.4448093	0.0734442	1.2180778	C	-2.2065982	-4.6438286	0.2568913
C	0.6568948	-1.2888879	1.2036902	H	-0.8198583	-3.223017	-0.6437478
C	0.7858956	1.2163306	1.2165171	H	-2.5425372	-2.040358	3.145214
C	-0.6590567	1.29025	1.2079627	H	-3.8395268	-4.1721254	3.2361765
C	-0.7880517	-1.2149366	1.2155829	H	-2.1043807	-5.3740236	-0.5641892
Fe	-0.002612	0.0022507	-0.3414217	H	-3.6304581	-5.8592042	1.3794686
C	0.6278213	0.2265357	-2.1369246	C	-2.9411635	0.151883	1.2840659
C	-0.632829	-0.222275	-2.1375558	C	-5.773262	0.2749864	1.4749503
C	-1.5909258	-2.4820618	1.2400755	C	-3.571655	0.6772821	2.4360549
C	-3.0582766	-4.9161426	1.3421517	C	-3.759062	-0.3051959	0.2284335
C	-1.484717	-3.4406755	0.2071329	C	-5.1590471	-0.246915	0.3230291
C	-2.4470969	-2.7724075	2.3271635	C	-4.9711449	0.7399985	2.5322773

	H	-2.9468502	1.0443294	3.2672246		H	-3.4961123	4.5211684	-0.7098811
	H	-3.2793223	-0.69461	-0.6828299		H	-3.229339	6.0911322	1.2400125
	H	-5.7740871	-0.6070765	-0.5192949	315	C	1.588575	2.4835207	1.2424225
280	H	-5.4384293	1.1583177	3.4407256		C	3.0548926	4.9180794	1.3479385
	H	-6.8735387	0.3251664	1.5468036		C	1.4790252	3.4452746	0.2127601
	C	1.3567176	-2.6154092	1.1997711		C	2.4477393	2.7708786	2.3279351
	C	2.7051912	-5.1173632	1.2131573		C	3.1746385	3.97171	2.3804437
	C	2.1823858	-3.0016129	0.1190453	320	C	2.2003025	4.6486965	0.2642499
285	C	1.2204599	-3.5108446	2.2857319		H	0.8118347	3.2299029	-0.6368875
	C	1.8842416	-4.7485475	2.2935131		H	2.545846	2.036331	3.1434044
	C	2.85142	-4.2359926	0.1266388		H	3.8419718	4.1685209	3.2373227
	H	2.2812469	-2.316749	-0.7385482		H	2.0953607	5.3814357	-0.5542154
	H	0.5777929	-3.2271468	3.1353037	325	H	3.6265878	5.8613784	1.3866357
290	H	1.7575969	-5.4309526	3.1516967		C	-1.6635426	-0.4802534	-3.1357746
	H	3.4890427	-4.5146562	-0.7298526		C	-3.6751292	-0.9527973	-5.1146105
	H	3.2267559	-6.0900615	1.2162287		C	-2.519684	-1.6141733	-3.0677569
	C	2.9391982	-0.150392	1.2763583		C	-1.8571269	0.4139302	-4.2289748
	C	5.7718938	-0.2736792	1.4588517	330	C	-2.8467458	0.1840233	-5.1946182
295	C	3.5730216	-0.6818812	2.4237495		C	-3.4989688	-1.8506373	-4.0451926
	C	3.7541201	0.3129247	0.2211026		H	-2.3945371	-2.3201982	-2.2313117
	C	5.1543592	0.2545462	0.3115797		H	-1.2104912	1.3039169	-4.2990605
	C	4.9727966	-0.7447286	2.5157807		H	-2.9720807	0.8997507	-6.0262815
	H	2.950681	-1.0537974	3.2545861	335	H	-4.1392312	-2.7469319	-3.9659379
300	H	3.2719851	0.7075001	-0.6866658		H	-4.4528104	-1.1342356	-5.8761349
	H	5.7668892	0.6195249	-0.5304747		C	1.6635527	0.4808274	-3.1308599
	H	5.4426763	-1.1679873	3.4206202		C	3.6889178	0.9427295	-5.0981615
	H	6.8723826	-0.3240593	1.5273823		C	1.8732827	-0.4259601	-4.210423
	C	-1.3590657	2.6166919	1.209348	340	C	2.5098274	1.6224714	-3.0709425
305	C	-2.7077052	5.1184879	1.2329822		C	3.4961218	1.8534336	-4.0426913
	C	-2.187299	3.005857	0.1316485		C	2.8698445	-0.2012424	-5.1702693
	C	-1.2202483	3.5091277	2.2974893		H	1.234125	-1.3217836	-4.2741792
	C	-1.8841111	4.7467532	2.310333		H	2.3706507	2.3394182	-2.2458838
	C	-2.8564581	4.2401441	0.144323	345	H	4.1283797	2.7558871	-3.9701028
310	H	-2.2879433	2.3234342	-0.7276988		H	3.0085437	-0.9273569	-5.9908016
	H	-0.5754527	3.2231674	3.1446869		H	4.4722525	1.1197284	-5.8549852
	H	-1.7554132	5.4268206	3.1700756					

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