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Supporting Information

Di-*tert*-butyldiphosphatetrahedrane as a Source of 1,2-Diphosphacyclobutadiene Ligands

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Supporting Information

The Supporting Information contains:

1 Additional Experiments

Reaction of [K(thf)$_{0.2}$][Co(η^4-cod)$_2$] with 1:

To a cold (−80 °C) solution of [K(thf)$_{0.2}$][Co(η^4-cod)$_2$] (50.0 mg, 0.15 mmol) was added (*t*BuCP)$_2$ (0.84 mL, 0.4 M in toluene, 0.33 mmol, 2.2 eq.). The solution was stirred overnight while allowing it to warm to ambient temperature and then analysed by ^{31}P{^{1}H} NMR spectroscopy (Figure S16). Subsequently, the solvent was removed and the brown residue was dried *in vacuo*. The residue was washed with *n*-hexane (5 mL) and extracted with 1,4-dioxane (ca. 0.5 mL). Slow diffusion of *n*-hexane into this 1,4-dioxane solution afforded yellow crystals of both **3** and **3′**.

General procedure for reactions of [K(dioxane)][(^{Dipp}BIAN)Co(1,2-*t*Bu$_2$C$_2$P$_2$)] (4) and [K(thf)$_3$][(^{Dipp}BIAN)Co(1,3-*t*Bu$_2$C$_2$P$_2$)] (5) with electrophiles:

To a cold (−80 °C) solution of [K(1,4-dioxane)][(^{Dipp}BIAN)Co(1,2-*t*Bu$_2$C$_2$P$_2$)] (**4**) or [K(thf)$_3$][(^{Dipp}BIAN)Co(1,3-*t*Bu$_2$C$_2$P$_2$)] (**5**) (ca. 0.03 mmol, 1.0 eq.) in THF (1 mL) was added reagent (see Table S1, 1.05 eq.). Subsequently, the reaction was stirred overnight while allowing it to warm to room temperature. The solution was transferred to an NMR tube and analysed by ^{31}P{^{1}H} NMR spectroscopy.

^{31}P{^{1}H} NMR spectra for the reactions are given in **Figure S18** and **Figure S19**.

Table S1. Reagents and stock solutions used for reactivity studies of **4** and **5**.

Reagent	Stock solution
HCl	0.4 M in 1,4-dioxane
MeI	0.1 M in toluene
Me_3SiCl	0.5 M in toluene
Ph_2PCl	0.08 M in toluene
Cy_2PCl	0.11 M in toluene

2 NMR Spectra

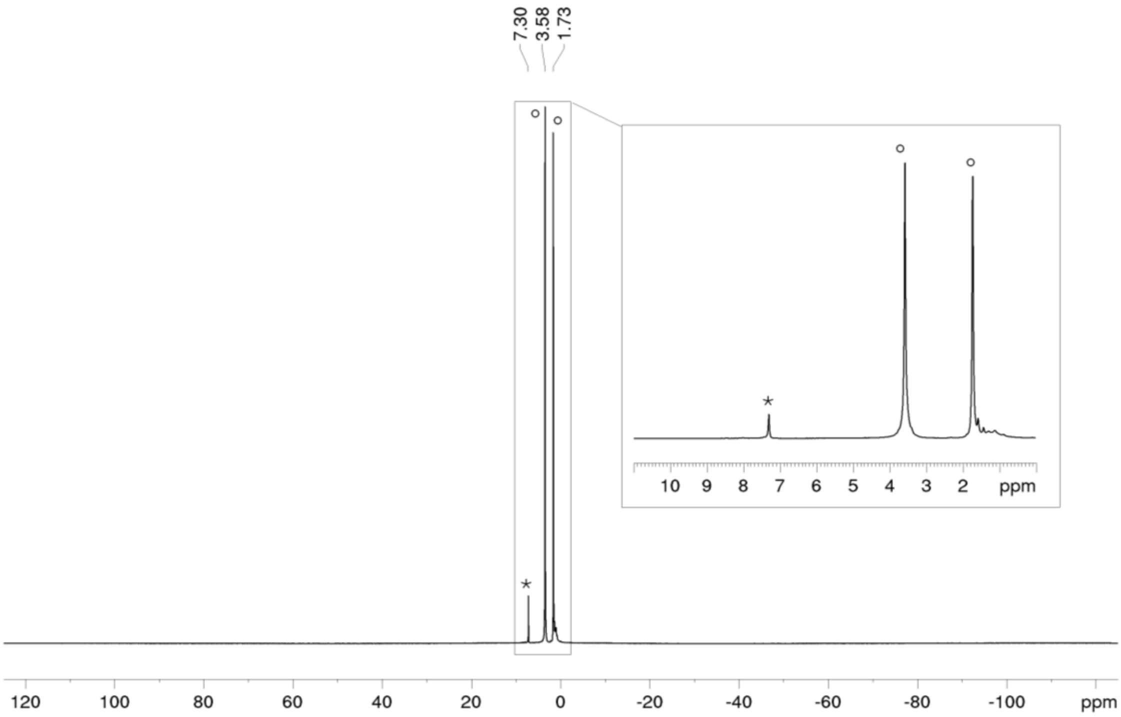


Figure S1. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **2** *residual C_6H_6, °THF-d_8.

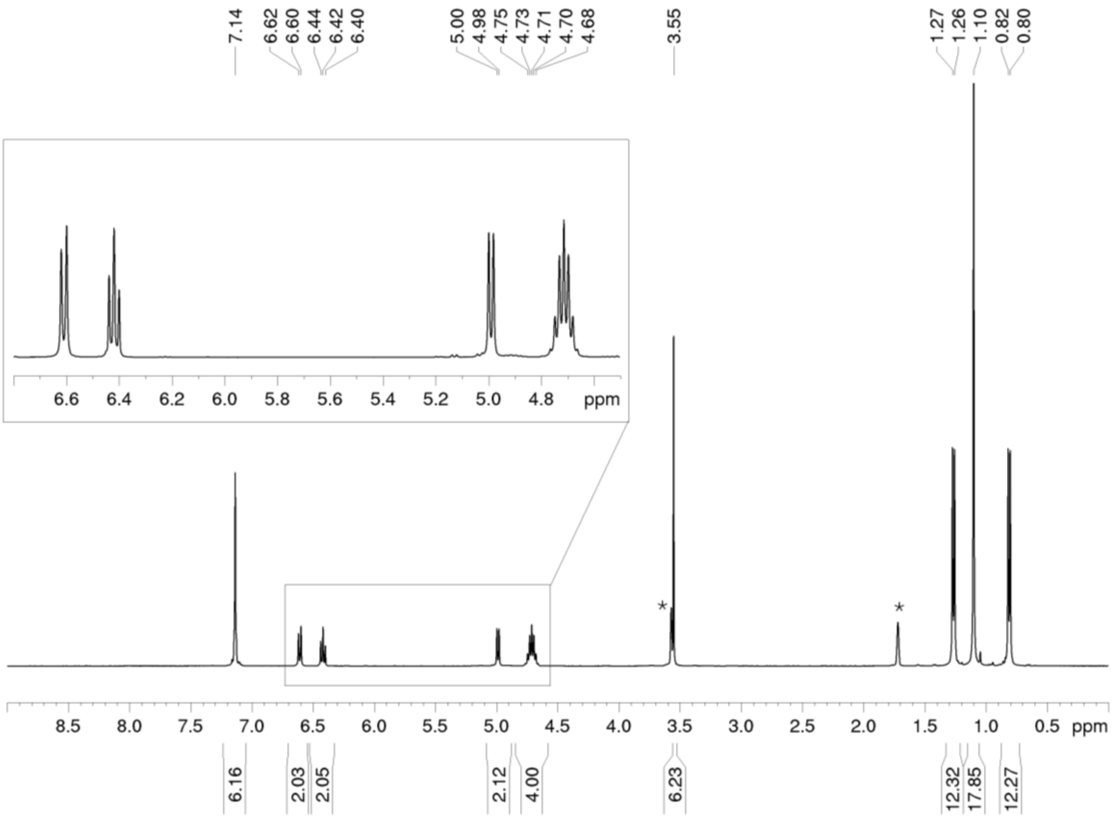


Figure S2. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **4** *THF-d_8.

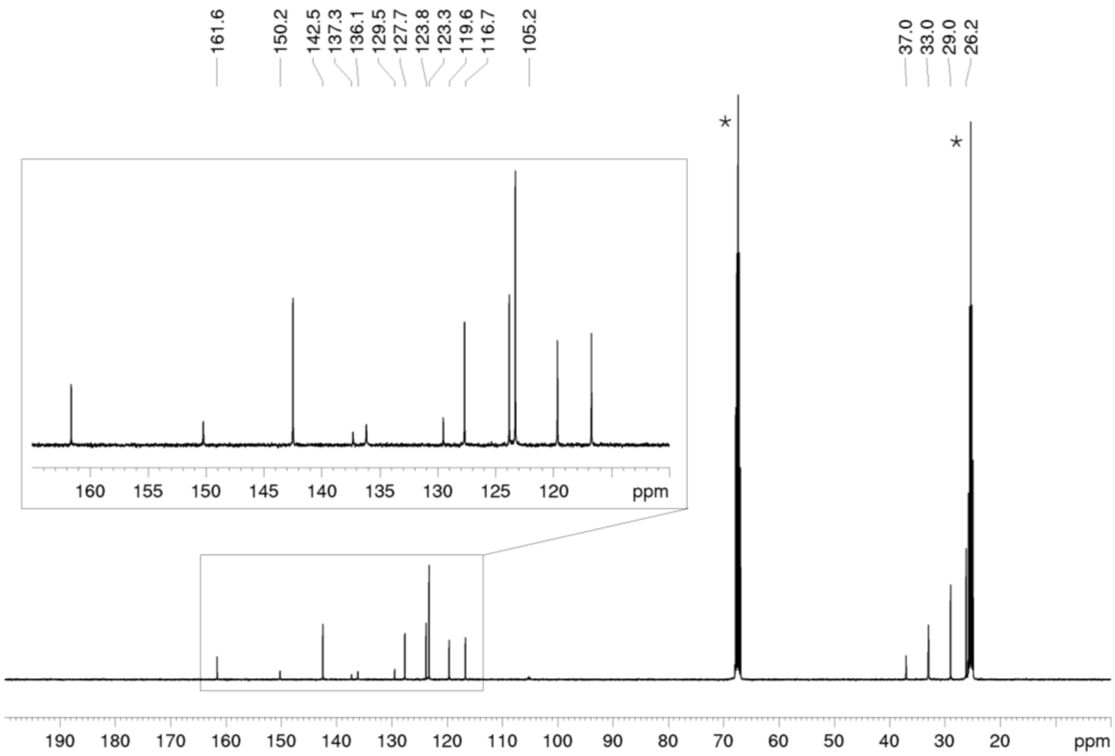


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, THF-d_8) of **4**; *THF-d_8.

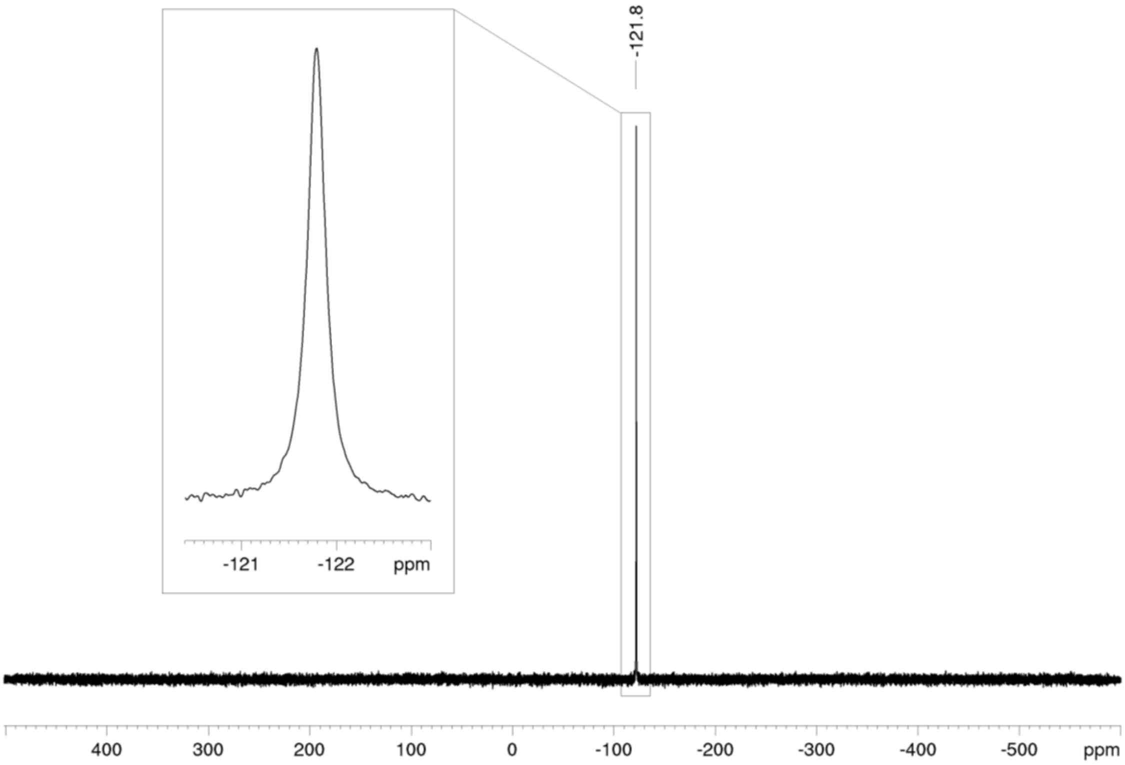


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **4**.

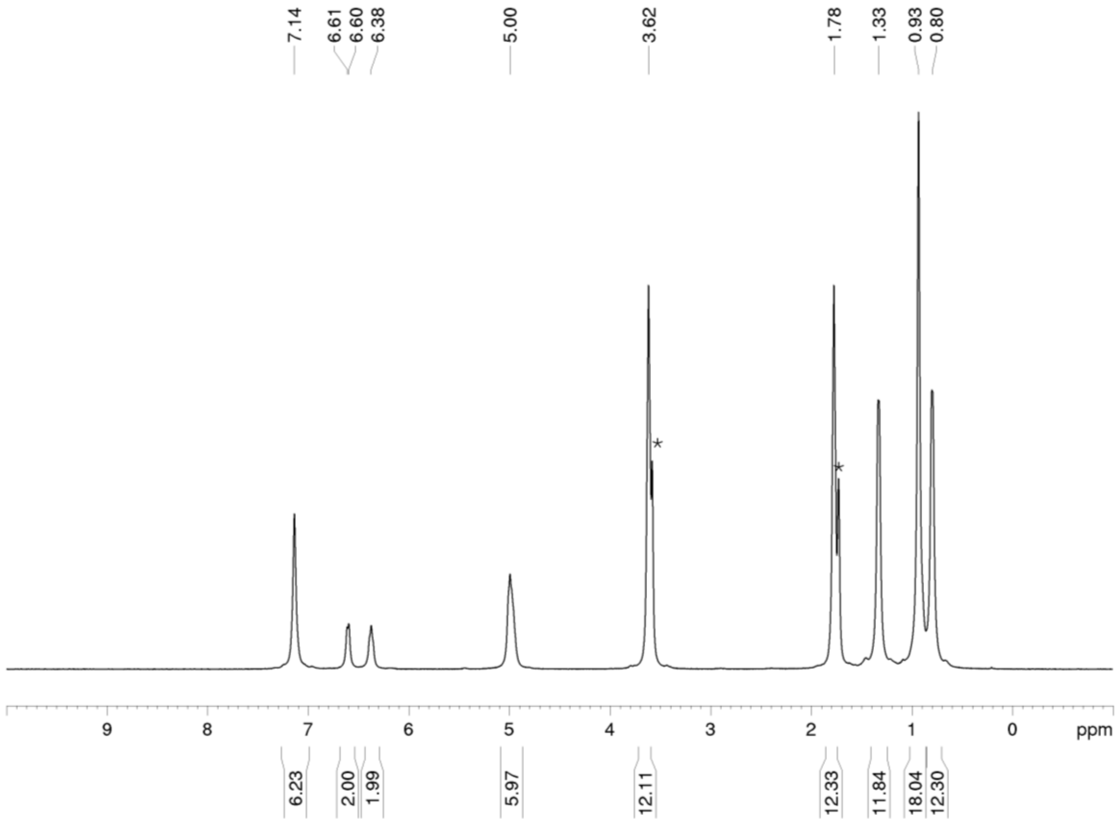


Figure S5. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **5** *THF-d_8.

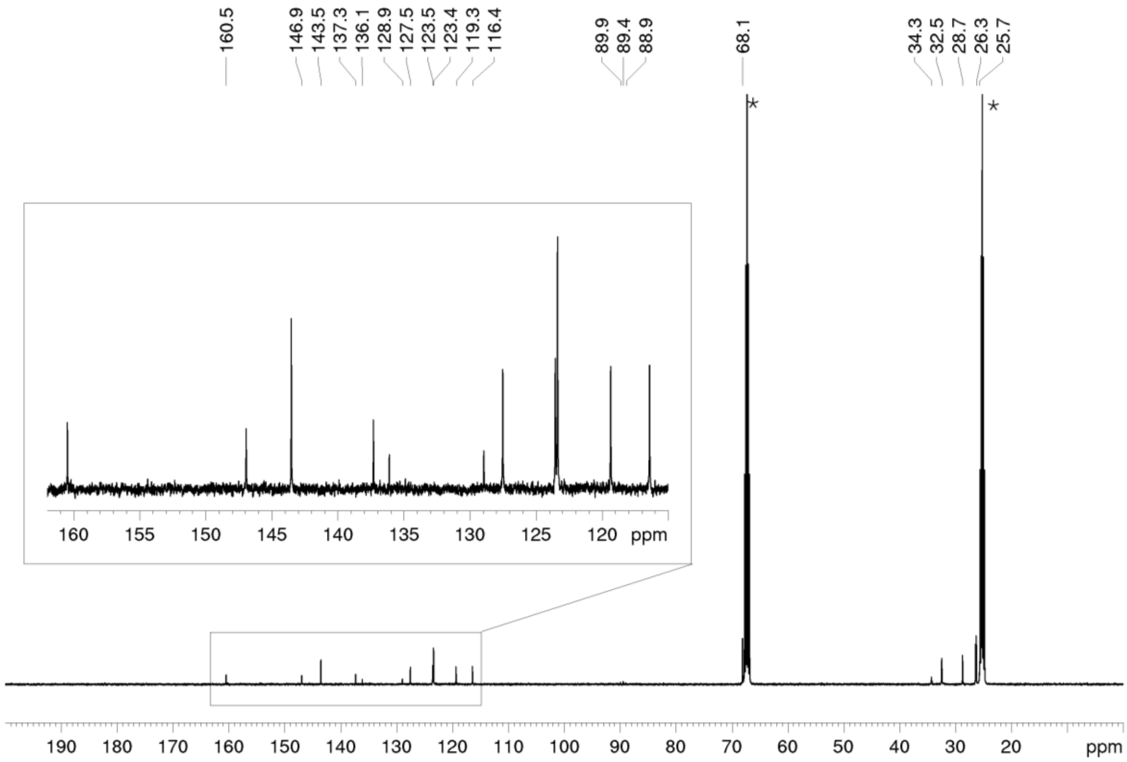


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, THF-d_8) of **5**; *THF-d_8.

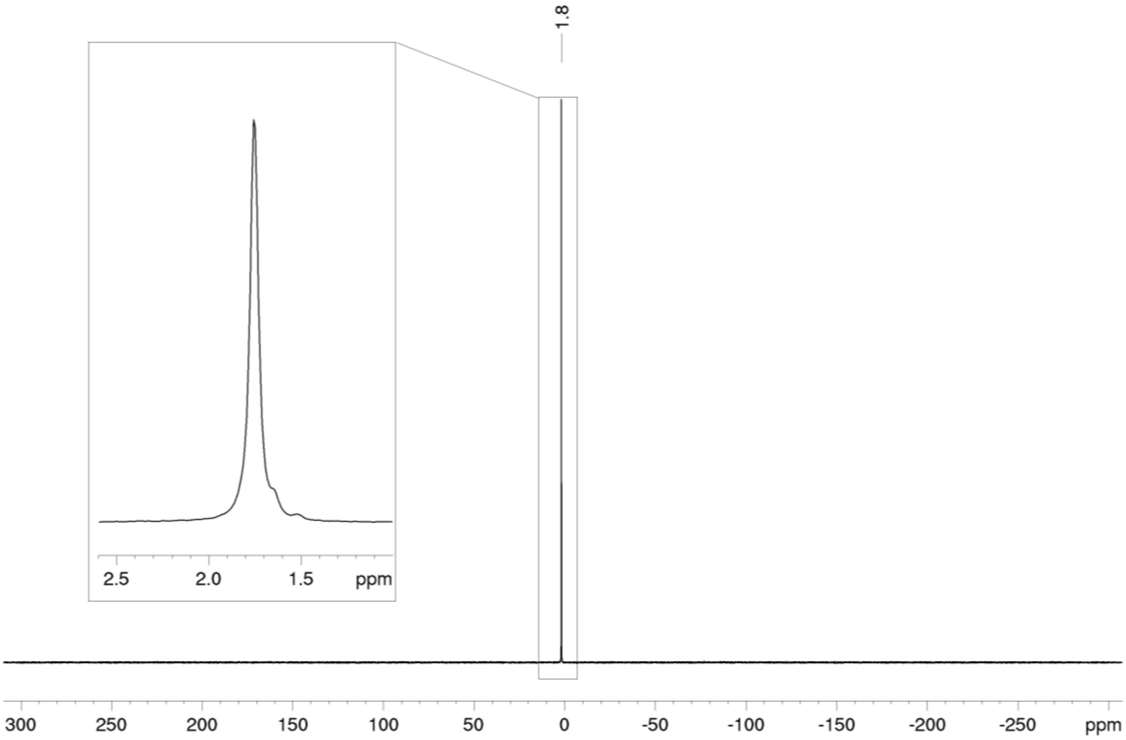


Figure S7. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **5**.

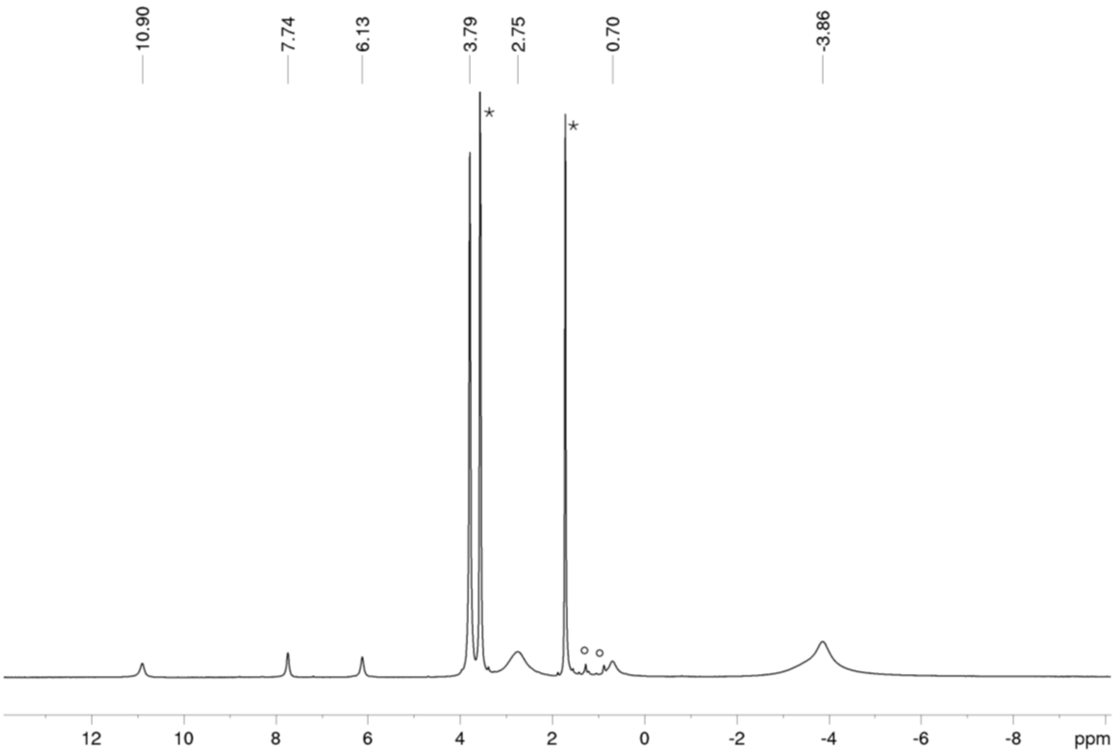


Figure S8. ^1H NMR spectrum (400 MHz, 300 K, THF-d_8) of **6** *THF-d_8, °*n*-hexane.

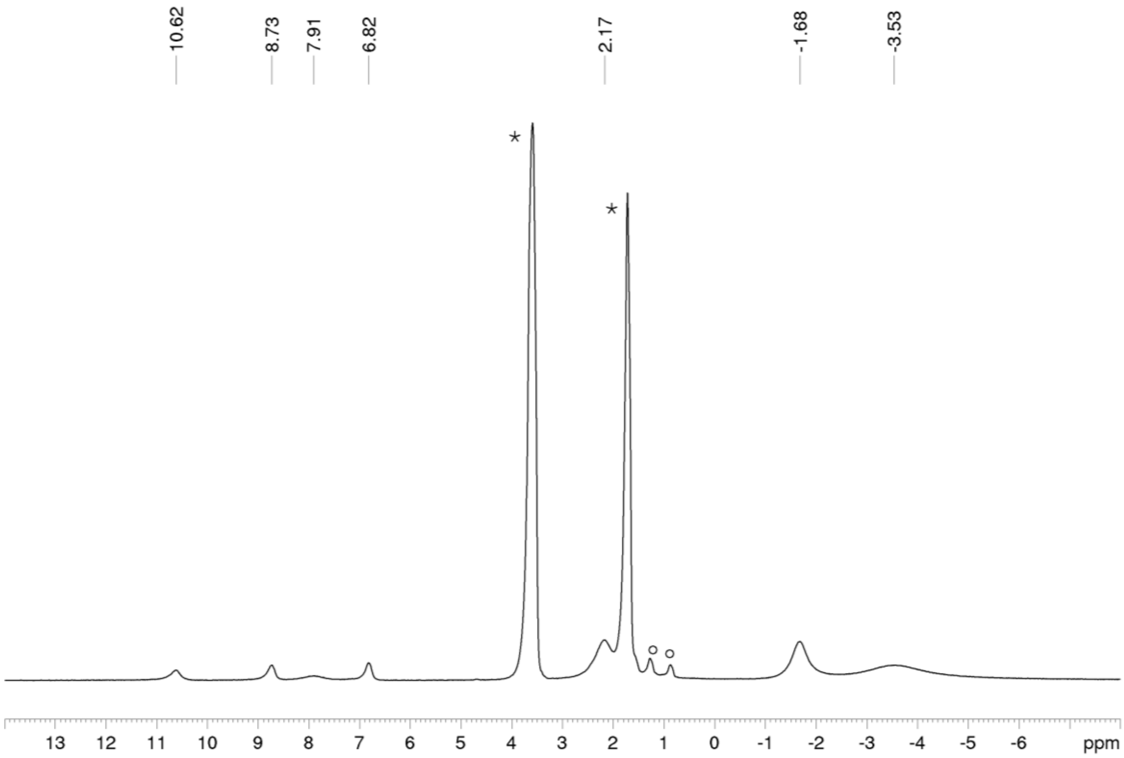


Figure S9. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **7** *THF-d_8, °*n*-hexane.

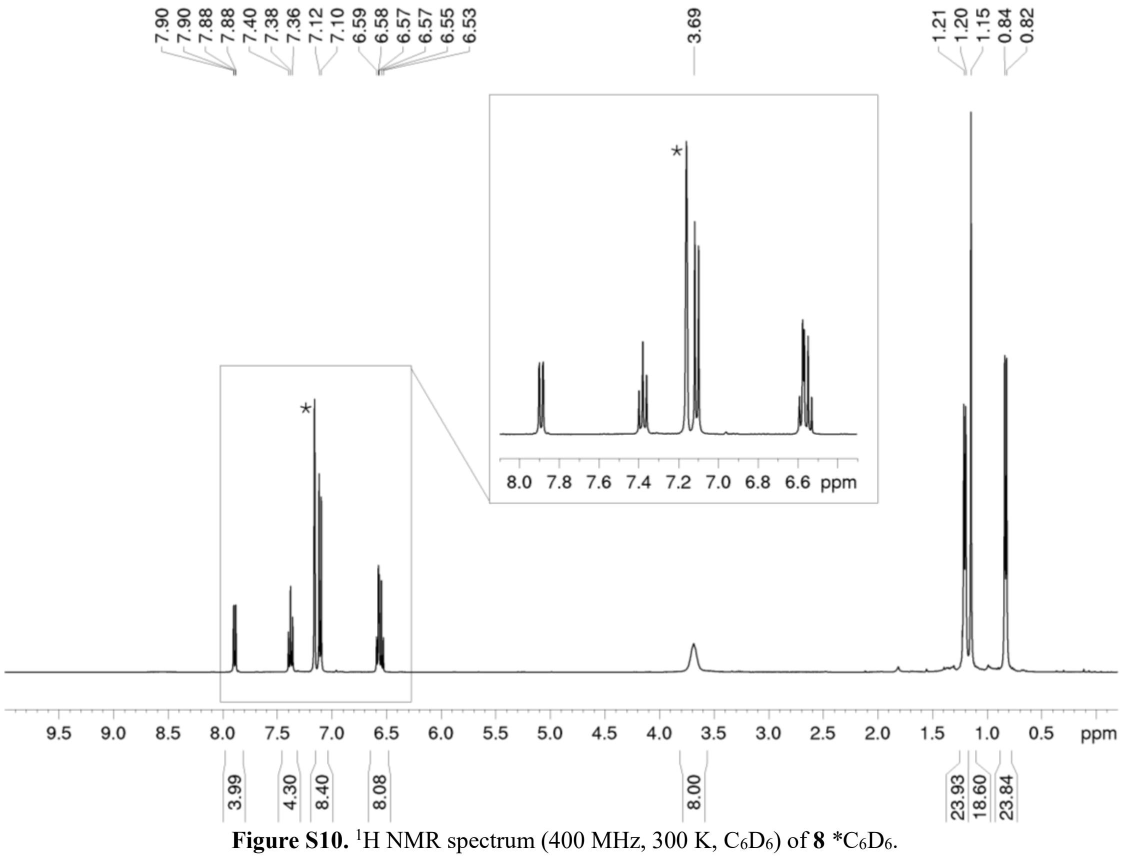


Figure S10. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **8** *C_6D_6.

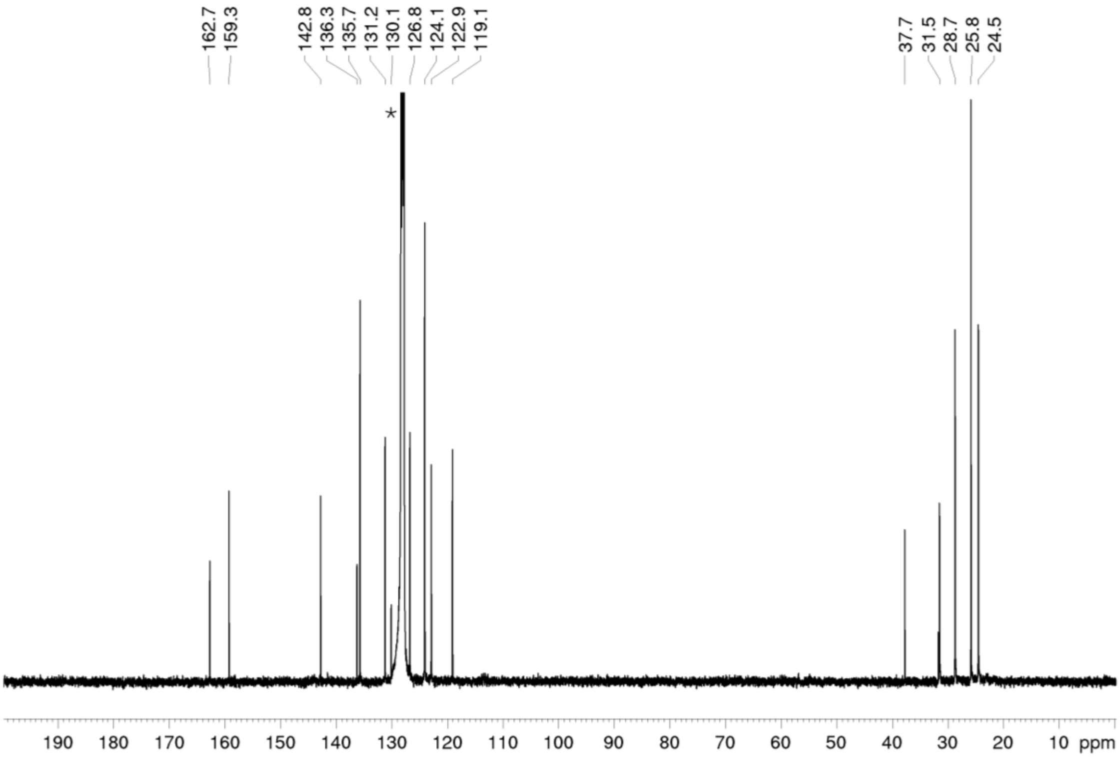


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **8**; *C_6D_6.

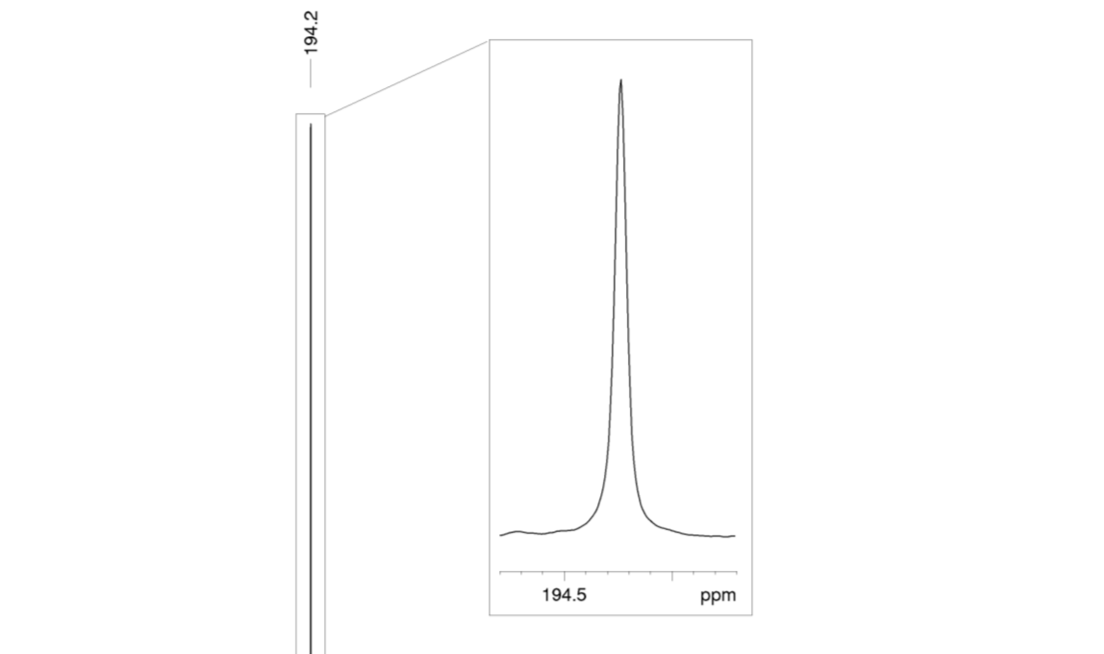


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **8**.

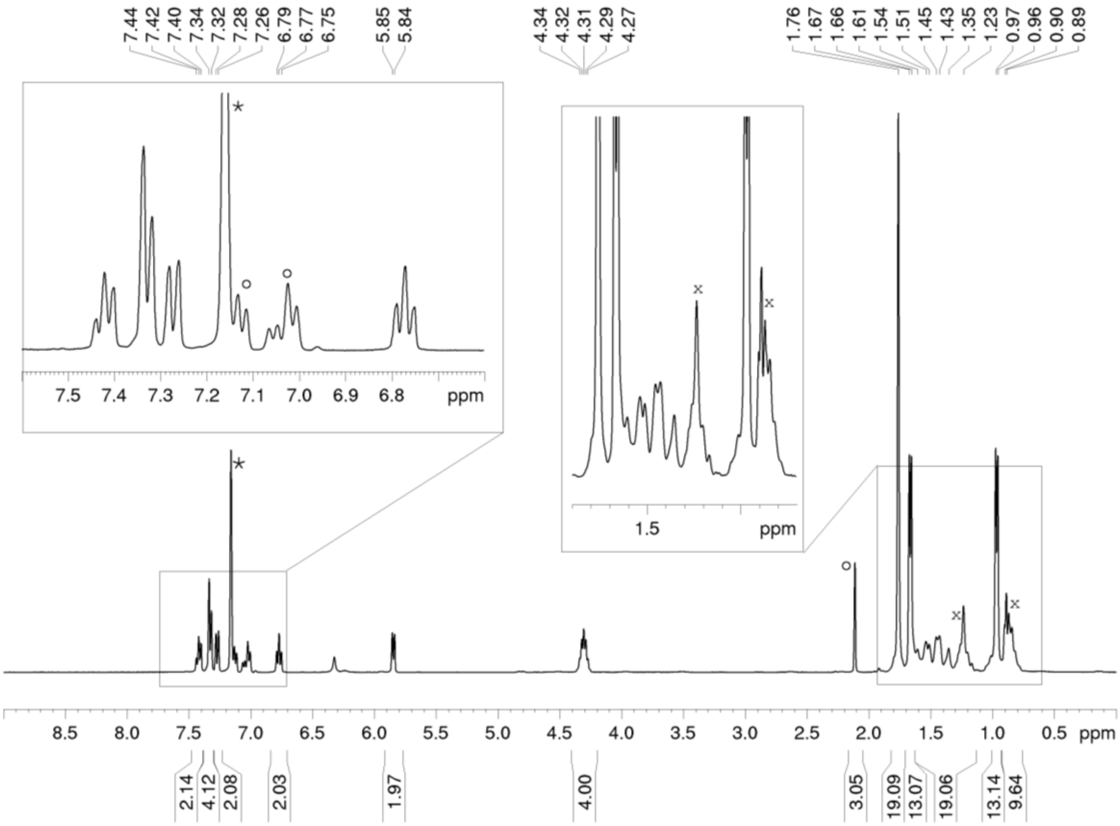


Figure S13. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **9** *C_6D_6, °residual toluene, ^{x}residual *n*-hexane.

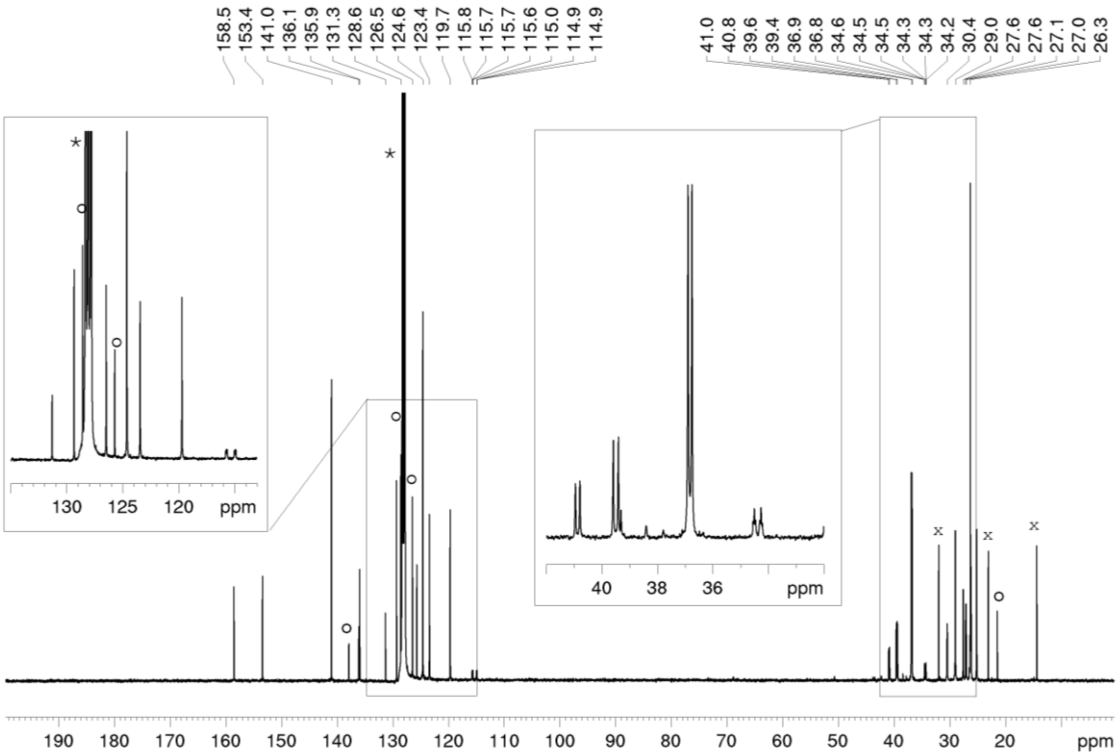


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **9**; *C_6D_6,°residual toluene, ^{x}residual *n*-hexane.

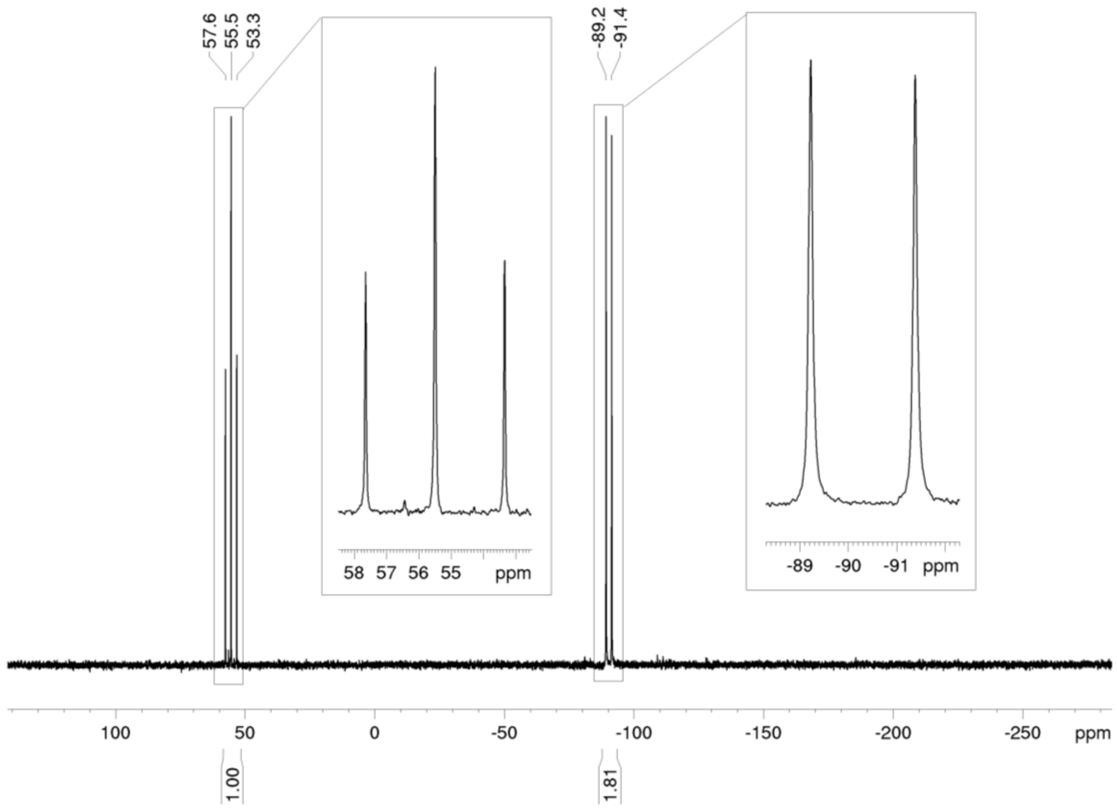


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **9**.

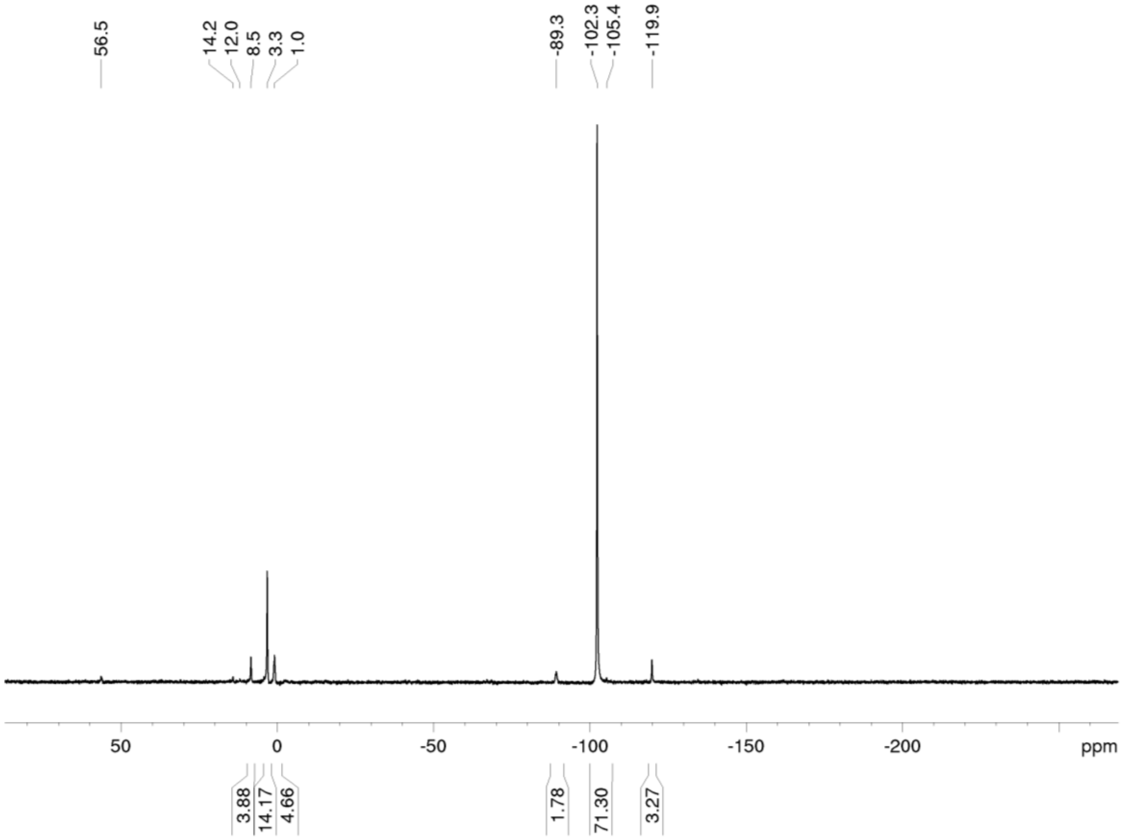


Figure S16. $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, 300 K, C_6D_6) of the reaction of $[K(thf)_{0.2}][Co(\eta^4\text{-cod})_2]$ with **1**.

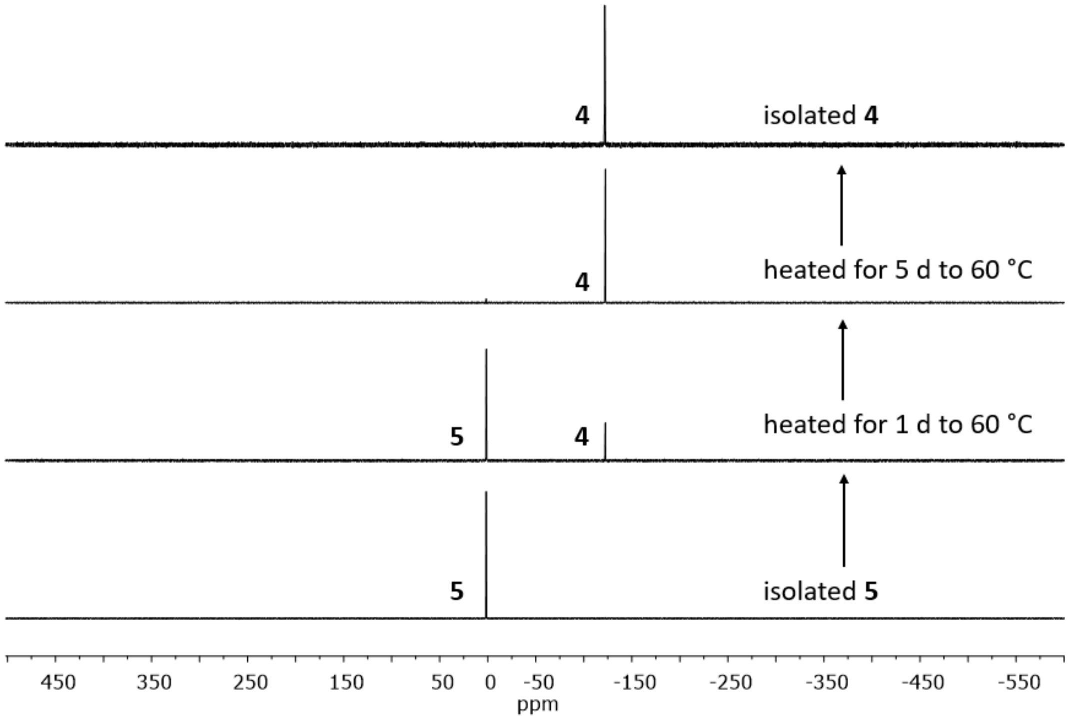


Figure S17. $^{31}P\{^1H\}$ NMR spectra (162 MHz, 300 K, C_6D_6) of the conversion of **5** into **4** upon heating.

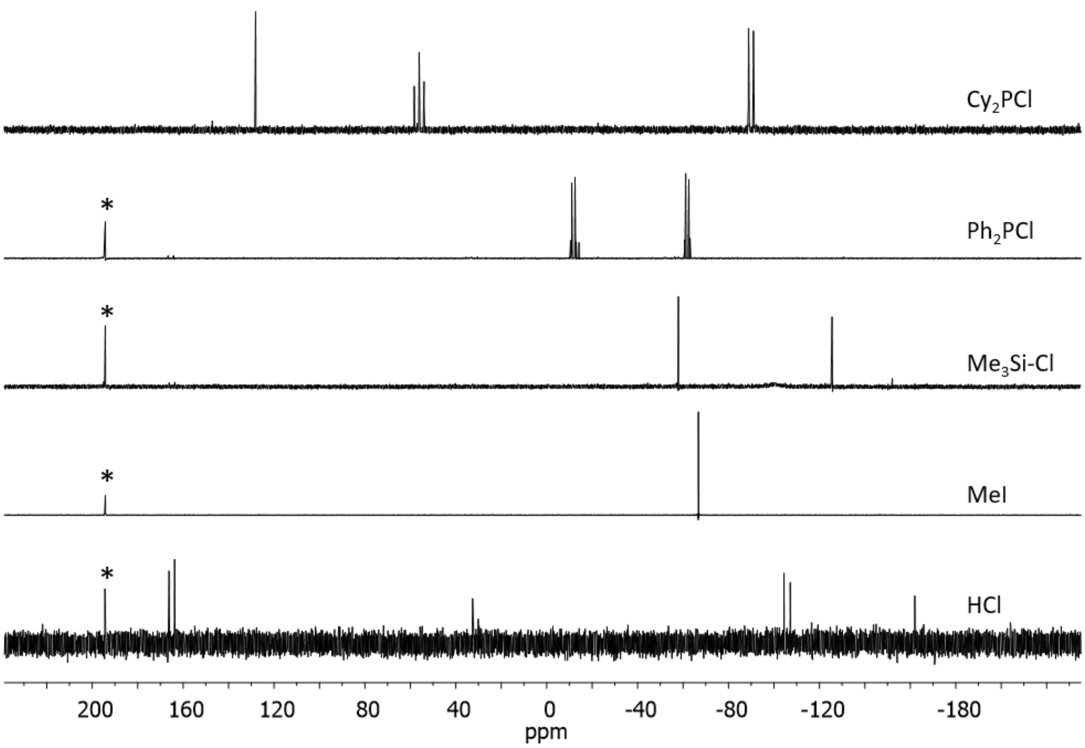


Figure S18. $^{31}P\{^1H\}$ NMR spectra (162 MHz, 300 K, C_6D_6) of reactions of **4** with different electrophiles; ***8**.

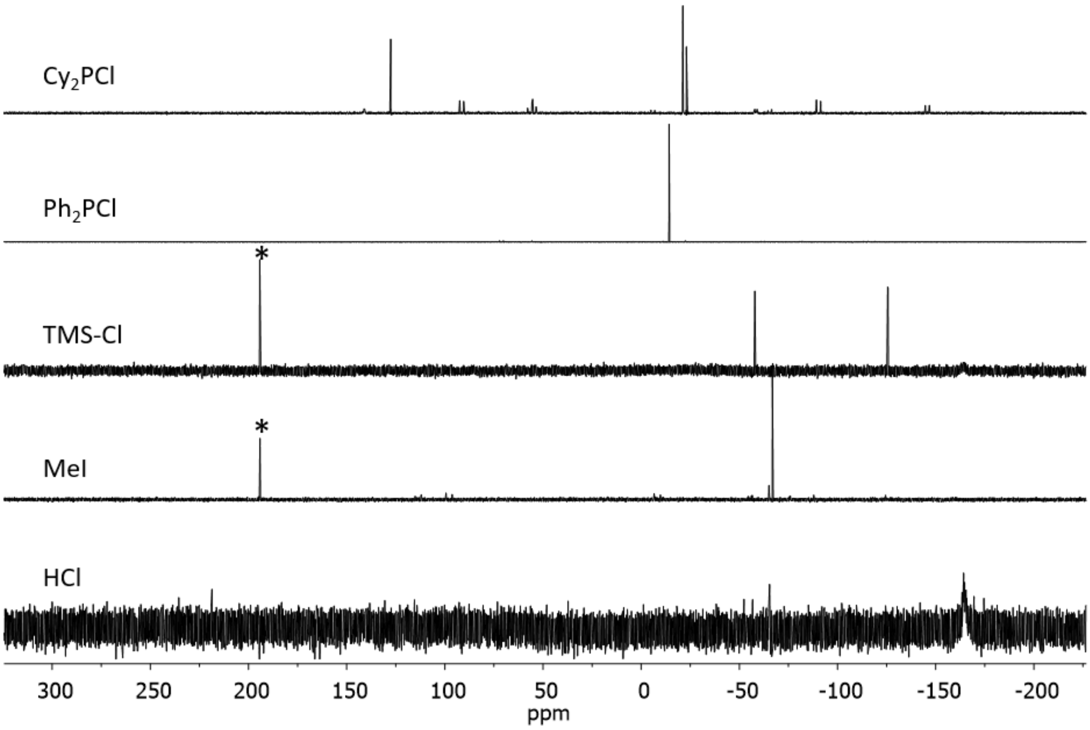


Figure S19. $^{31}P\{^1H\}$ NMR spectra (162 MHz, 300 K, C_6D_6) of reactions of **5** with different electrophiles; ***8**.

3 UV/Vis Spectra

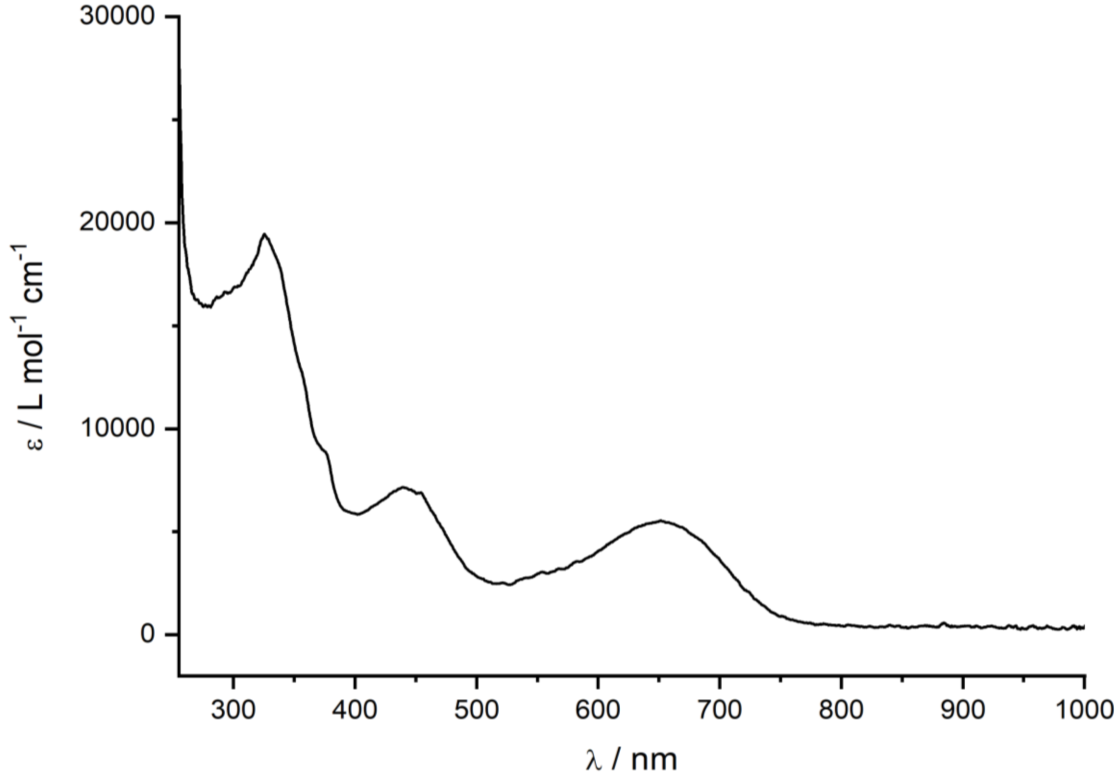


Figure S20. UV/Vis spectrum of **2** recorded in THF.

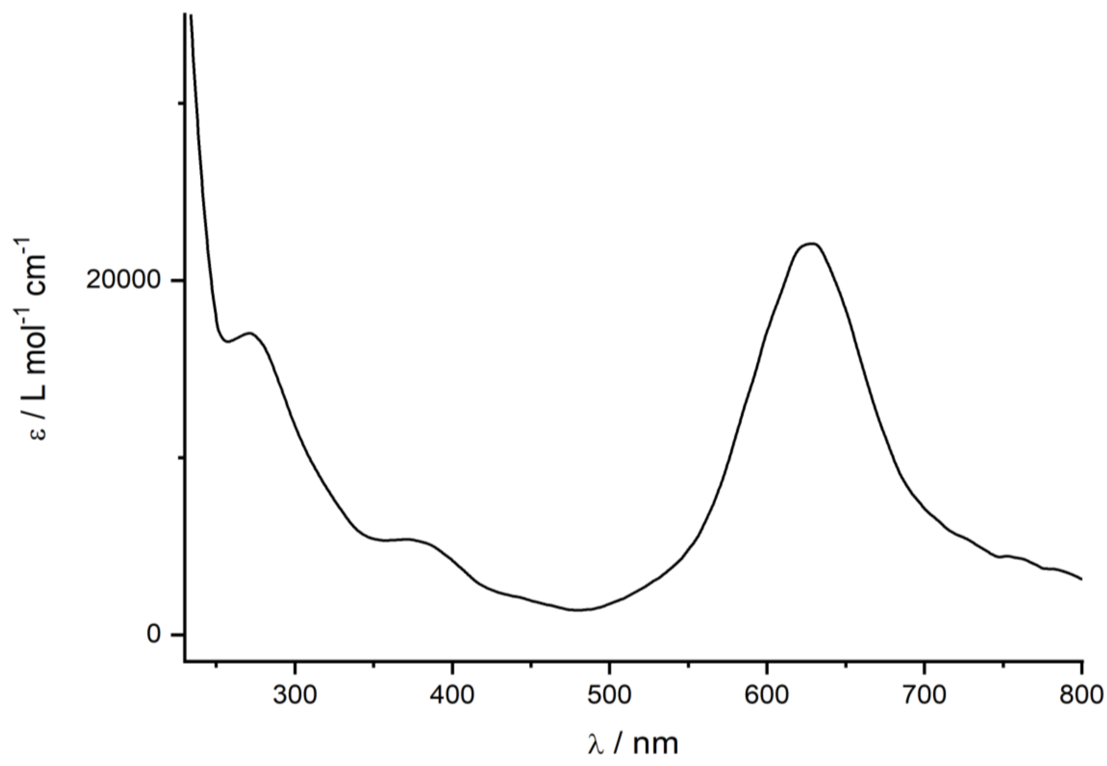


Figure S21. UV/Vis spectrum of **4** recorded in THF.

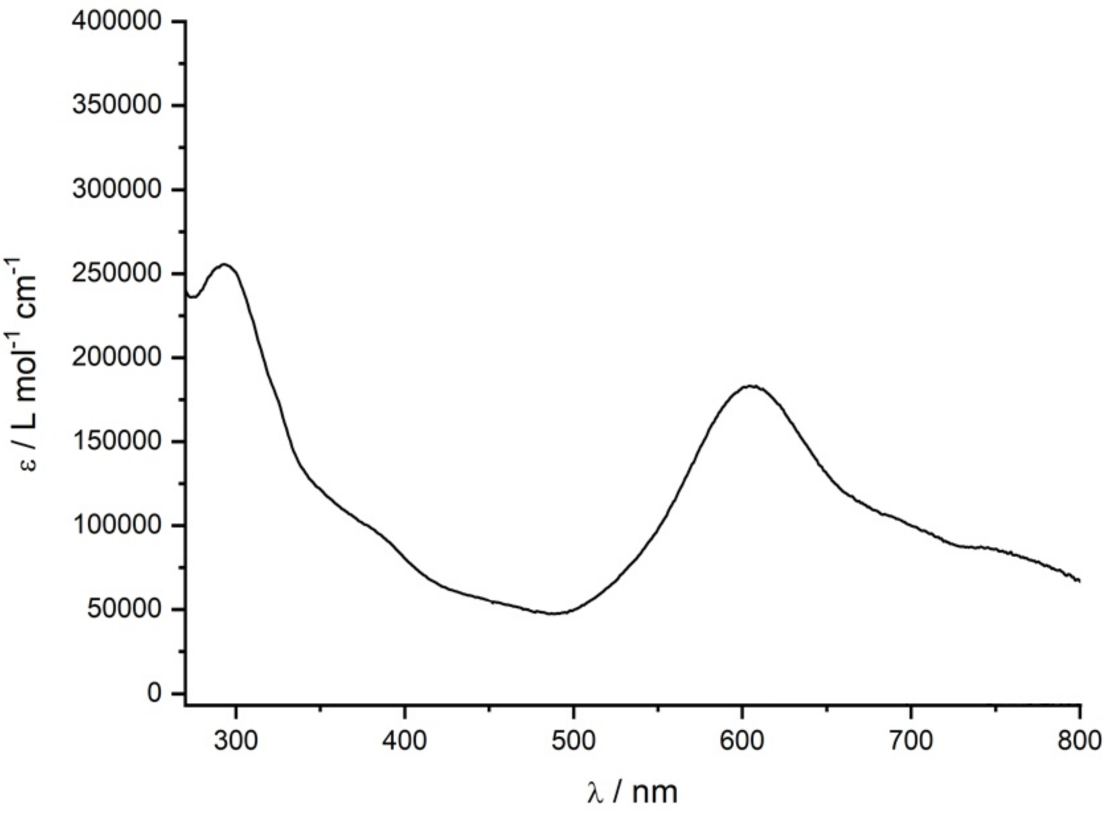


Figure S22. UV/Vis spectrum of **5** recorded in THF.

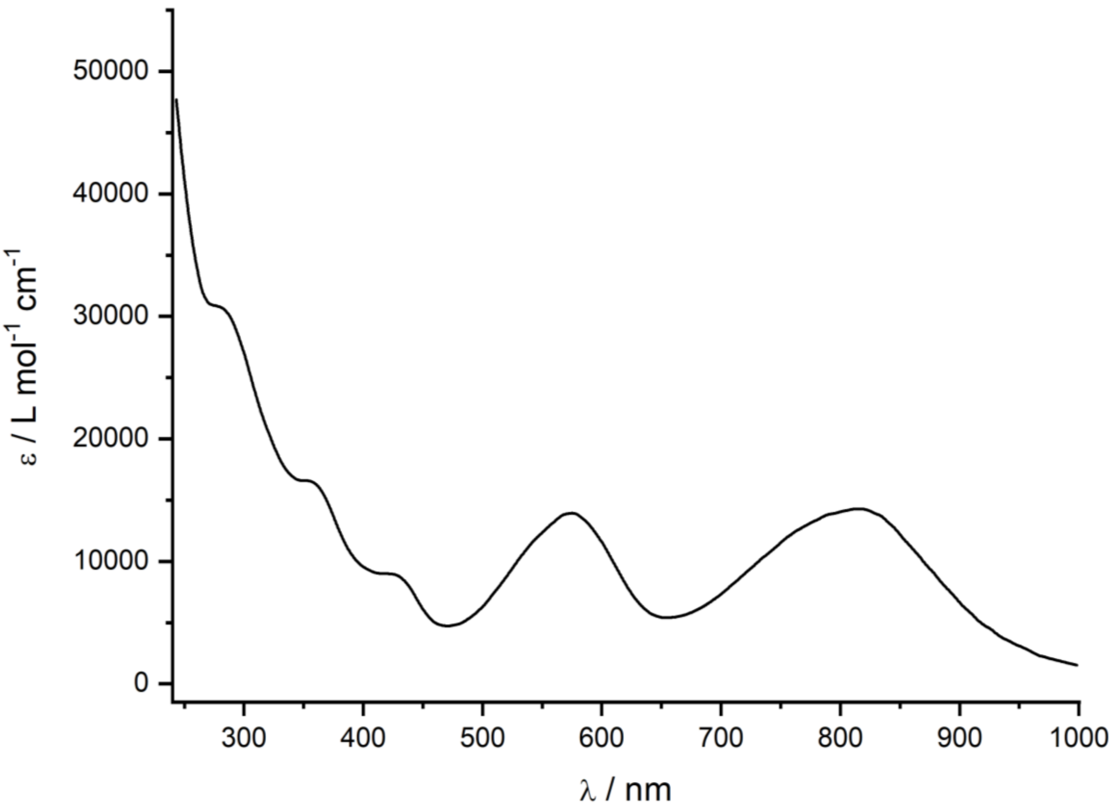


Figure S23. UV/Vis spectrum of **6** recorded in THF.

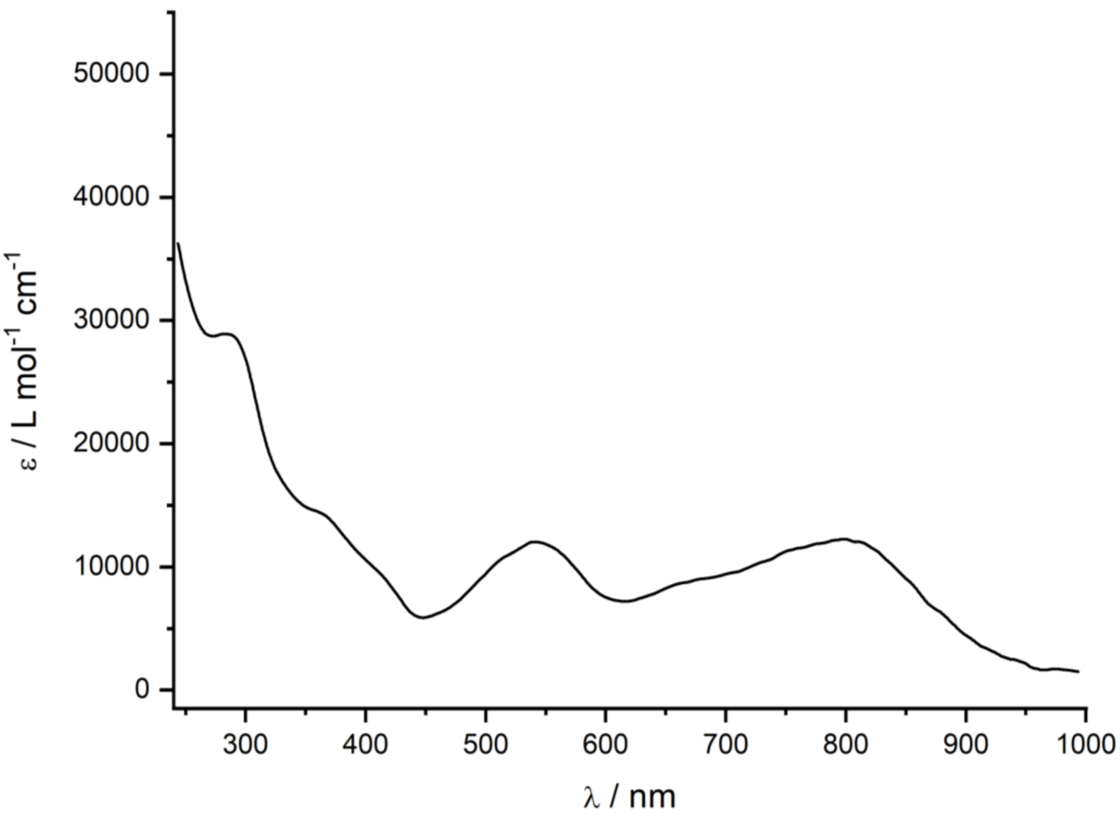


Figure S24. UV/Vis spectrum of **7** recorded in THF.

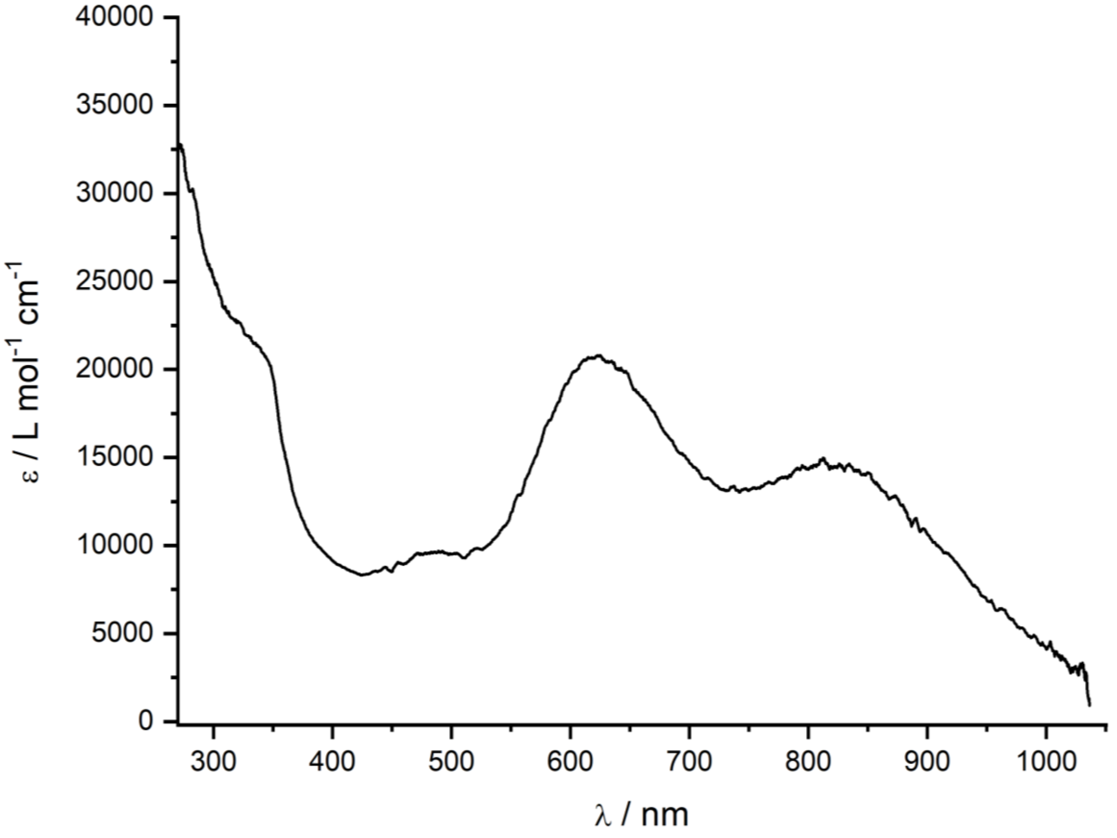


Figure S25. UV/Vis spectrum of **8** recorded in THF.

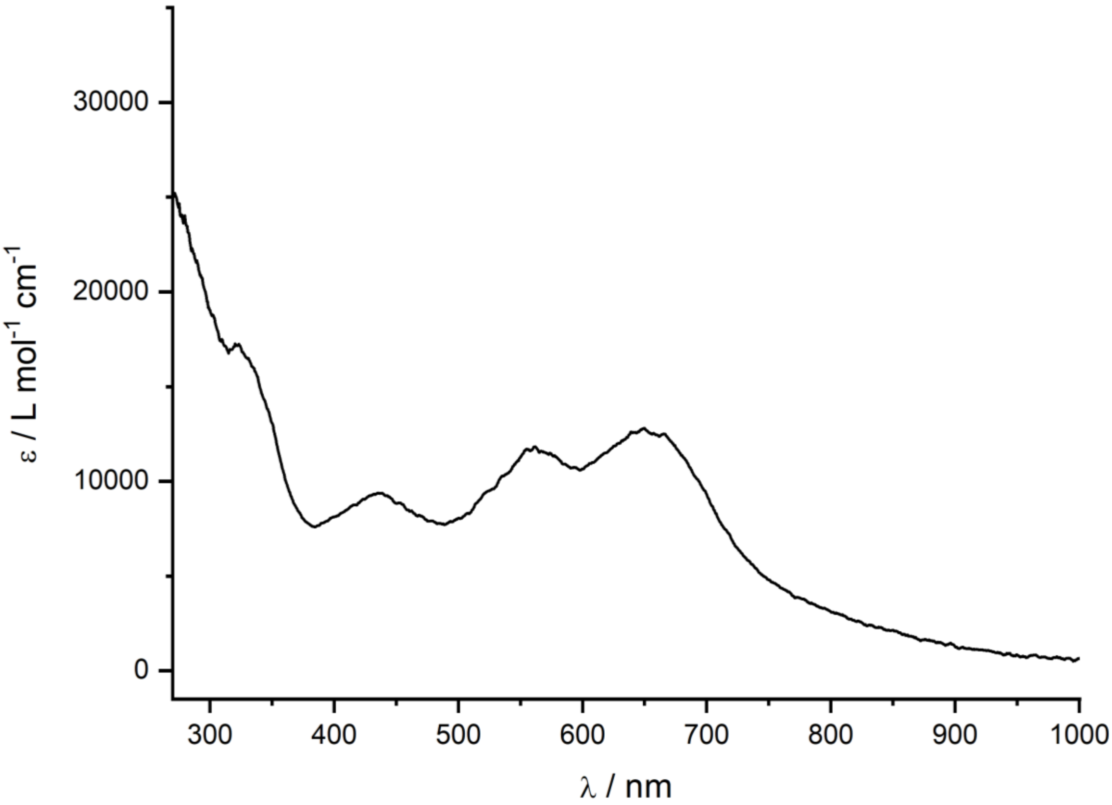


Figure S26. UV/Vis spectrum of **9** recorded in THF.

4 Zero-field ^{57}Fe-Mössbauer Spectra

Zero-field ^{57}Fe-Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) at a temperature of 77 K in constant acceleration mode. ^{57}Co/Rh was used as γ-radiation source. WinNormos for Igor Pro software was used for the quantitative evaluation of the spectral parameters (least squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.21 mm·s^{-1} (full width at half maximum, FWHM). The temperature of the sample was controlled by a MBBC-HE0106 MÖSSBAUER He/N_2 cryostat within an accuracy of +/– 0.3 K. Least-square fitting of the Lorentzian signals was carried out with the “Mfit” software, developed by Dr. Eckhard Bill (MPI CEC, Mülheim/Ruhr). The isomer shifts were reported relative to a α-iron reference at 300 K.[1]

5 EPR Spectroscopy

X-band EPR spectra were acquired on a Bruker EMX X-band spectrometer, equipped with an ER 4112HV-CF100 cryostat, and further analyzed and simulated using EasySpin,[2] via the cwEPR 3.2 GUI.[3]

6 Magnetic Measurements

Magnetism data of multiple microcrystalline and powdered samples (15–30 mg) were collected on a Quantum Design MPMS-3 SQUID magnetometer. All samples were loaded within polycarbonate gel capsules, if not stated otherwise. Additional measurements for compound **2** were performed on a sample (24.0 mg) contained within a flame-sealed NMR tube and fixated in a plastic straw. DC susceptibility was recorded in the temperature range of 2–300 K with an applied DC field of 1 T, if not stated otherwise, or by means of field-dependent measurements in the temperature range of 2–150 K under DC magnetic fields of 0.1, 1.0, 3.0, and 5.0 T, respectively. Values of the magnetic susceptibility were corrected for core diamagnetism of the sample using tabulated Pascal's constants.[4]

Several independent samples of the iron complexes **2**, **6** and **7** were studied. Unfortunately, the obtained data showed a strong temperature and field-dependence of μ_{eff}, which could not be explained (see Figure S27- Figure S30 for complex **2**). It is speculated that the samples contain minor impurities of Fe nanoparticles. The samples used for SQUID measurements were recrystallised twice. Furthermore, the crystalline compounds were dissolved in the appropriate solvent, filtered to remove undissolved material/impurities, and the thoroughly dried residue was measured again. This was made to avoid crystallinity effects, which might give rise to phenomena similar to the observed ones at weaker magnetic fields.

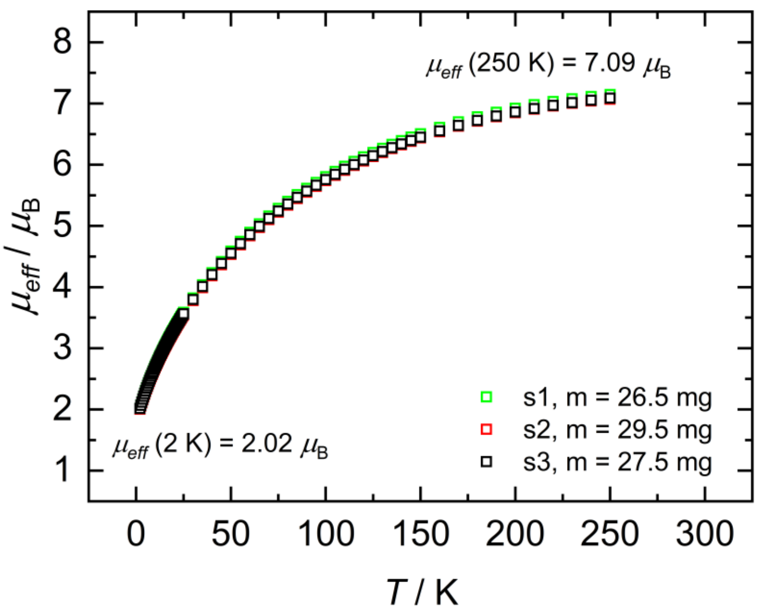


Figure S27. SQUID DC Field measurements at 1 T, 2-250 K, for compound **2**, samples 1, 2 and 3 (squares).

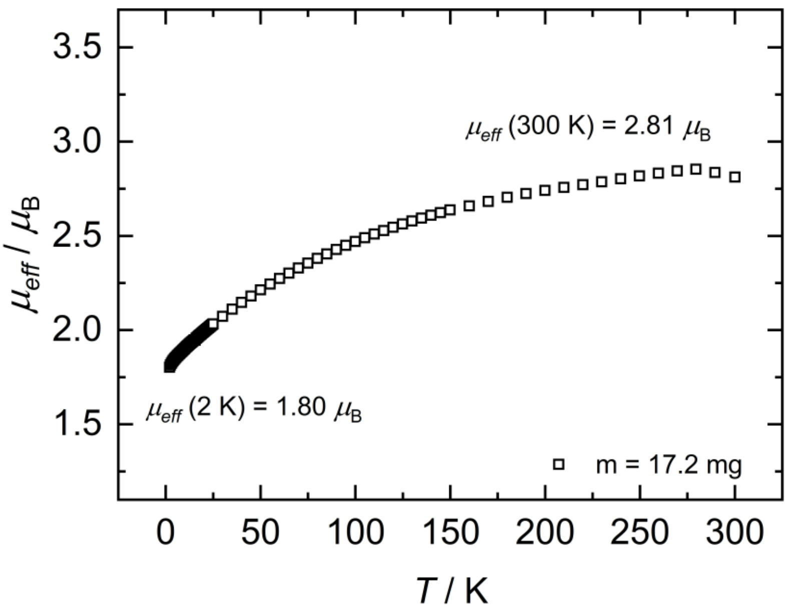


Figure S28. SQUID DC Field measurement at 1 T, 2-300 K, for compound **2**, sample 4 (black squares).

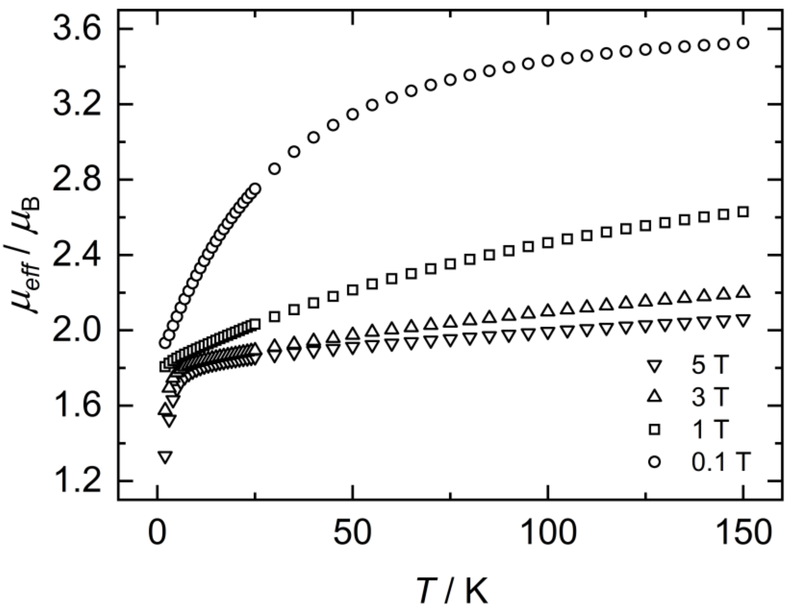


Figure S29. SQUID DC Field VTVF measurement for compound **2**, sample 4, measured at H = 5 T, 3 T, 1, 0.1 T (m = 17.2 mg, T = 2–150 K).

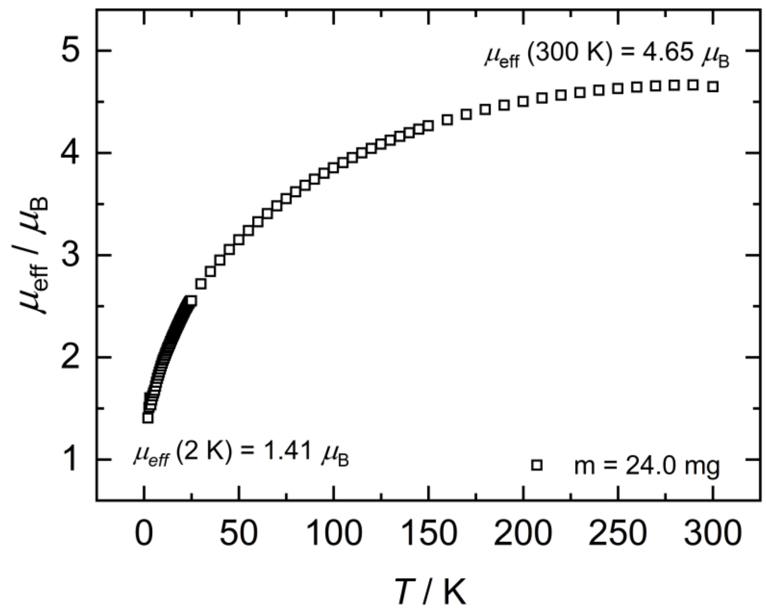


Figure S30. SQUID DC Field measurement at 1 T, 2-300 K, for compound **2** (black squares), sample 5 (in flame sealed NMR tube).

7 Single Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku Oxford Diffraction SuperNova Atlas, GV1000 Titan[S2] or Xcalibur Gemini Ultra (AtlasS2) diffractometers. Cu-K_{α} radiation (λ = 1.54184 Å) was used except for compound **7** (Cu-K_{β}; λ = 1.387 Å) Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[5] or analytical ones[6] were applied to the data. The structures were solved with SHELXT[7] solution program using dual methods and by using Olex2 as the graphical interface.[8] The models were refined with ShelXL[9] using full matrix least squares minimisation on F^2.[10] The hydrogen atoms were located in idealised positions and refined isotropically with a riding model.

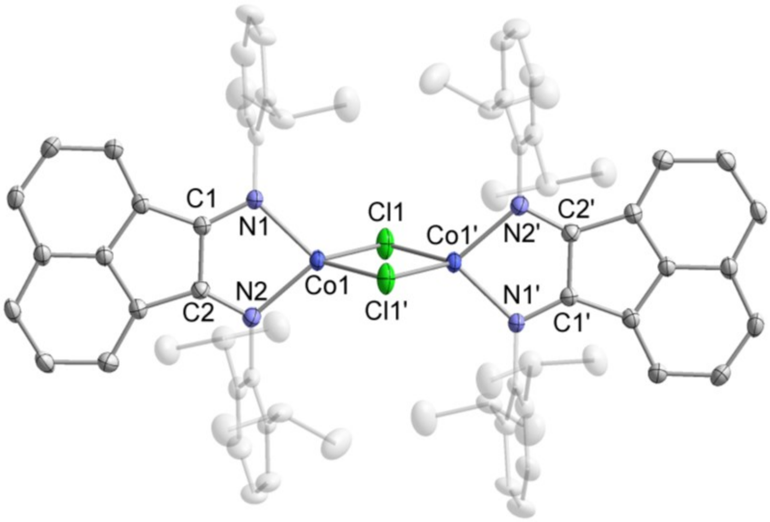


Figure S31. Molecular structure of [(^{Dipp}BIAN)CoCl]$_2$ in the solid state. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]:Co1−Cl1 2.3000(5), Co1−Cl1′ 2.2786(5), Co1−N1 1.9606(15), Co1−N2 1.9652(17), N1−C1 1.320(2), N2−C2 1.327(3), C1−C2 1.441(2), Cl1−Co1−Cl1′ 96.169(19), N1−Co1−Cl1 126.11(5), N1−Co1−Cl1′ 112.69(5), N1−Co1−N2 85.06(7), N2−Co1−Cl1 120.69(5), N2−Co1−Cl1′ 118.54(5).

The following section provides figures of the molecular structures of metalate salts with additional potassium counterions (+ sequestering agents and solvate molecules) which were not given in section 8.2 itself.

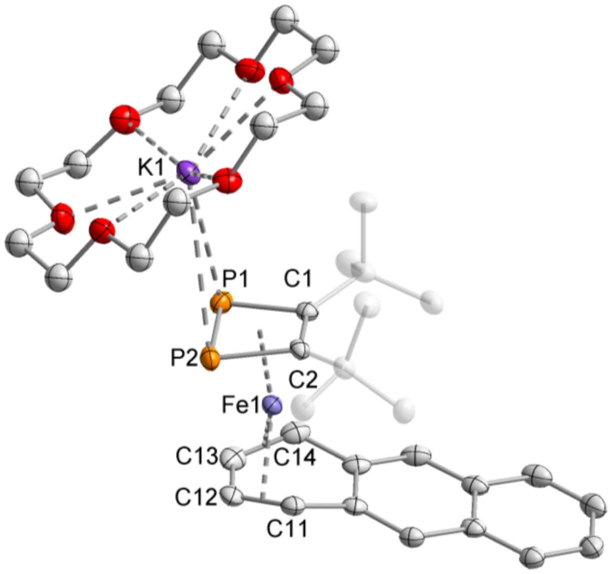


Figure S32. Molecular structure of **2** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1−P2 2.1738(6), P1−C1 1.8328(15), P2−C2 1.8274(14), C1−C2 1.440(2), Fe−(C2P2centroid) 1.783(2), C11−C12 1.428(2), C12−C13 1.403(2), C13−C14 1.432(2), P1−K1 3.4460(5), P2−K1 3.7961(5) C1−P1−P2 78.03(5), C2−P2−P1 78.85(5), C2−C1−P1 101.97(10), C1−C2−P2 101.14(10).

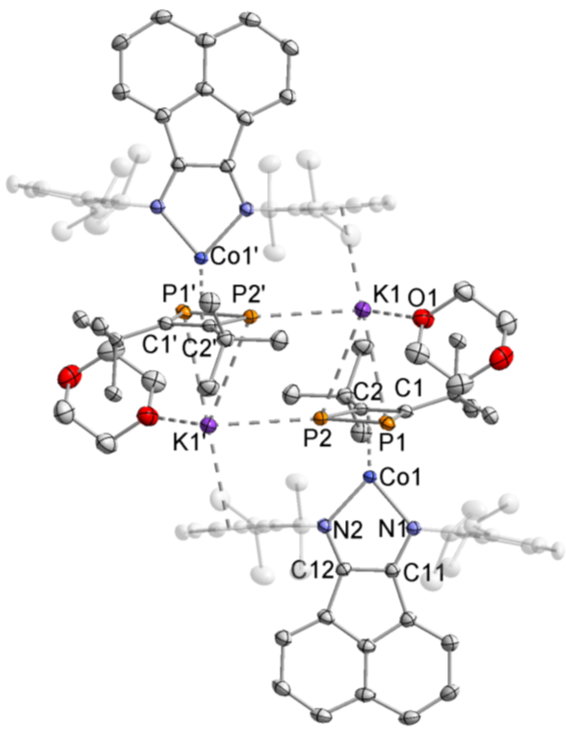


Figure S33. Molecular structure of **4** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent of crystallisation are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1−P2 2.1765(8), P1−C1 1.838(2), P2−C2 1.815(2), C1−C2 1.441(3), N1−C11 1.353(3), N2−C12 1.347(3), C12−C11 1.403(3), Co1−N1 1.9382(18), Co1−N2 1.9074(18), Co−($C_2P_2^{centroid}$) 1.775(2), K1−P1 3.3087(7), K1−P2 3.4513(7), K1−P2′ 3.2213(8), K1−O1 2.7208(19), K1−($Dipp^{centroid}$) 3.002(1), C2−C1−P1 102.62(16), C1−C2−P2 100.60(16), C1−P1−P2 77.11(7), C2−P2−P1 79.66(8).

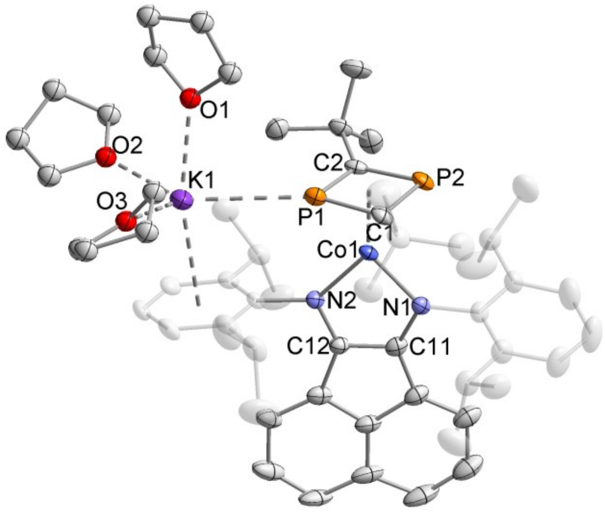


Figure S34. Molecular structure of **5**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent of crystallisation are omitted for clarity. Only one of two crystallographically independent molecules is shown. Selected bond lengths [Å] and angles [°]: P1−C1 1.802(4), P1−C2 1.787(5), P2−C1 1.787(4), P2−C2 1.802(4), N1−C11 1.358(6), N2−C12 1.352(5), C12−C11 1.397(6), Co1−N1 1.929(3), Co1−N2 1.909(4), Co−($C_2P_2^{centroid}$) 1.780(2), K1−P1 3.3944(15), K1−O1 2.733(4), K1−O2 2.662(4), K1−O3 2.805(15), K−($Dipp^{centroid}$) 2.957(1), P2−C1−P1 98.4(2), P1−C2−P2 98.4(2), C2−P1−C1 81.45(19), C1−P2−C2 81.4(2).

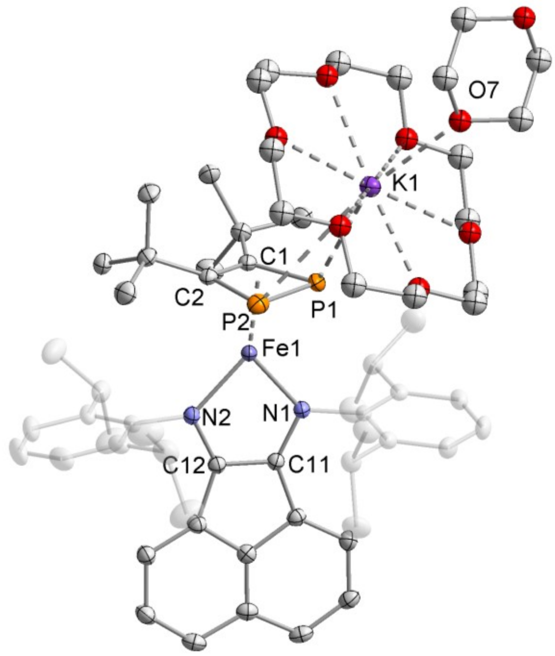


Figure S35. Molecular structure of **6** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent of crystallisation are omitted for clarity. Only one of two crystallographically independent molecules is shown. Selected bond lengths [Å] and angles [°]: P1−P2 2.173(5), P1−C1 1.819(9), P2−C2 1.776(10), C1−C2 1.434(13), N1−C11 1.369(9), N2−C12 1.350(9), C12−C11 1.413(10), Fe1−N1 1.959(6), Fe1−N2 1.958(7), Fe−($C_2P_2^{centroid}$) 1.823(3), K1−P1 3.3389(4), K1−P2 3.7883(4), K1−O7 2.7559(12), C2−C1−P1 100.8(7), C1−C2−P2 103.0(7), C1−P1−P2 77.7(3), C2−P2−P1 78.5(3).

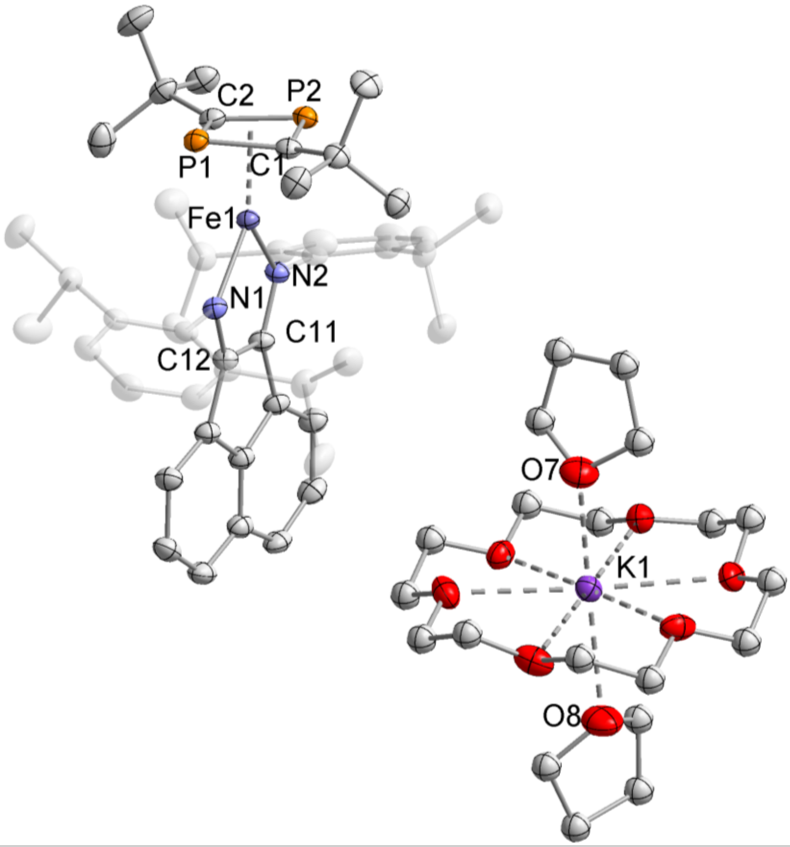


Figure S36. Molecular structure of **7** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent of crystallisation are omitted for clarity. Selected bond lengths [Å] and angles [°] P1−C1 1.799(2), P1−C2 1.795(2), P2−C1 1.790(2), P2−C2 1.791(2), N1−C11 1.367(3), N2−C12 1.366(2), C12−C11 1.385(3), Fe1−N1 1.9421(16), Fe1−N2 1.9331(17), Fe−($C_2P_2^{centroid}$) 1.803(3), K1−O7 2.7454(16), K1−O8 2.7333(17), P2−C1−P1 98.94(10), P2−C2−P1 99.01(10), C2−P1−C1 80.54(9), C1−P2−C2 80.89(10).

Table S2. Crystallographic data and structure refinement for compounds **2-9** and [(^{Dipp}BIAN)CoCl]$_2$

Compound	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**[(^{Dipp}BIAN)CoCl]$_2$**
CCDC	2101038	2101036	2101043	2101039	2101037	2101042	2101040	2101041	2101044
Empirical formula	$C_{42}H_{58}FeKO_6P_2$	$C_{36}H_{68}CoKO_8P_4$	$C_{50}H_{66}CoKN_2O_2P_2$	$C_{60}H_{86.39}CoKN_2O_{3.5}P_2$	$C_{62}H_{90}FeKN_2O_8P_2$	$C_{70}H_{105.8}FeKN_2O_{9.2}P_2$	$C_{106}Co_2H_{154}N_4P_2$	$C_{61}H_{87}CoN_2P_3$	$C_{72}H_{80}Cl_2Co_2N_4$
Formula weight	815.77	850.81	887.01	1051.64	1148.24	1276.45	1664.12	1000.16	1190.16
Temperature/K	123.0(1)	123.0(1)	123.0(1)	122.9(6)	123.0(1)	123.0(1)	123.01(10)	123.0(1)	123.0(1)
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	Pn	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	11.5384(4)	10.3092(4)	17.0200(3)	15.45098(15)	20.6034(2)	13.0809(4)	19.7108(3)	13.0484(2)	16.1977(2)
b/Å	13.2644(4)	10.6450(6)	12.9087(3)	21.02068(18)	14.1129(2)	14.4445(5)	22.8080(3)	12.0775(2)	12.1792(2)
c/Å	14.6464(5)	11.4046(5)	21.7442(4)	18.21942(14)	22.1268(2)	19.5071(9)	17.6768(3)	35.3534(5)	16.2781(2)
α/°	70.660(3)	73.824(4)	90	90	90	84.648(3)	90	90	90
β/°	83.052(3)	63.657(4)	95.861(2)	102.4732(9)	100.215(1)	73.288(4)	95.0430(10)	97.1380(10)	94.0090(10)
γ/°	85.943(3)	86.201(4)	90	90	90	85.656(3)	90	90	90
Volume/Å^3	2098.48(13)	1074.79(10)	4752.36(16)	5777.82(9)	6331.91(12)	3510.1(2)	7916.1(2)	5528.23(15)	3203.41(8)
Z	2	1	4	4	4	2	4	4	2
ρ_{calc}g/cm^3	1.291	1.314	1.240	1.209	1.205	1.208	1.396	1.202	1.234
μ/mm^{-1}	4.841	5.772	4.550	3.837	3.384	2.331	4.087	3.540	5.151
F(000)	866.0	454.0	1888.0	2257.0	2460.0	1374.0	3608.0	2156.0	1256.0
Crystal size/mm^3	0.468 × 0.152 × 0.122	0.208 × 0.123 × 0.024	0.388 × 0.214 × 0.077	0.2552 × 0.1527 × 0.0443	0.514 × 0.284 × 0.227	0.412 × 0.255 × 0.125	0.574 × 0.31 × 0.195	0.645 × 0.588 × 0.278	0.808 × 0.339 × 0.252
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKβ (λ = 1.39222)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.066 to 143.938	8.668 to 147.664	6.95 to 147.086	7.212 to 133.528	7.632 to 145.78	5.556 to 120.254	8.03 to 145.366	6.978 to 145.73	7.444 to 143.542
Index ranges	-12 ≤ h ≤ 14, -16 ≤ k ≤ 16, -10 ≤ l ≤ 17	-12 ≤ h ≤ 10, -13 ≤ k ≤ 13, -12 ≤ l ≤ 14	-18 ≤ h ≤ 20, -15 ≤ k ≤ 16, -24 ≤ l ≤ 26	-18 ≤ h ≤ 18, -24 ≤ k ≤ 25, -18 ≤ l ≤ 21	-25 ≤ h ≤ 25, -16 ≤ k ≤ 17, -26 ≤ l ≤ 27	-13 ≤ h ≤ 16, -17 ≤ k ≤ 11, -23 ≤ l ≤ 24	-21 ≤ h ≤ 24, -22 ≤ k ≤ 27, -21 ≤ l ≤ 19	-16 ≤ h ≤ 16, -14 ≤ k ≤ 9, -43 ≤ l ≤ 41	-16 ≤ h ≤ 19, -10 ≤ k ≤ 14, -19 ≤ l ≤ 20
Reflections collected	14008	7017	18700	70293	26851	23140	14820	21796	14413
Independent reflections	7918 [R_{int} = 0.0237, R_{sigma} = 0.0343]	4178 [R_{int} = 0.0287, R_{sigma} = 0.0396]	9221 [R_{int} = 0.0330, R_{sigma} = 0.0439]	17913 [R_{int} = 0.0384, R_{sigma} = 0.0348]	12301 [R_{int} = 0.0168, R_{sigma} = 0.0202]	13609 [R_{int} = 0.0200, R_{sigma} = 0.0318]	7570 [R_{int} = 0.0210, R_{sigma} = 0.0287]	10682 [R_{int} = 0.0237, R_{sigma} = 0.0293]	6116 [R_{int} = 0.0396, R_{sigma} = 0.0389]
Data/restraints/para-meters	7918/132/521	4178/0/235	9221/0/537	17913/525/1475	12301/0/699	13609/115/846	7570/0/417	10682/0/619	6116/0/369
Goodness-of-fit on F^2	1.037	1.034	1.018	1.023	1.026	1.031	1.063	1.028	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0733	R_1 = 0.0325, wR_2 = 0.0792	R_1 = 0.0420, wR_2 = 0.0979	R_1 = 0.0352, wR_2 = 0.0838	R_1 = 0.0287, wR_2 = 0.0726	R_1 = 0.0391, wR_2 = 0.1011	R_1 = 0.0383, wR_2 = 0.1022	R_1 = 0.0401, wR_2 = 0.1015	R_1 = 0.0483, wR_2 = 0.1283
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0747	R_1 = 0.0357, wR_2 = 0.0822	R_1 = 0.0515, wR_2 = 0.1032	R_1 = 0.0412, wR_2 = 0.0870	R_1 = 0.0307, wR_2 = 0.0740	R_1 = 0.0442, wR_2 = 0.1056	R_1 = 0.0405, wR_2 = 0.1040	R_1 = 0.0433, wR_2 = 0.1040	R_1 = 0.0501, wR_2 = 0.1307
Largest diff. peak/hole / e Å^{-3}	0.38/-0.21	0.30/-0.30	0.44/-0.47	0.41/-0.26	0.29/-0.24	0.61/-0.69	0.32/-0.36	0.56/-0.40	0.60/-0.49
Flack parameter	/		/	-0.0321(13)	/	/		/	/

8 Quantum Chemical Calculations

General Methods

All calculations were performed with the ORCA program package.[11] All geometry optimisations were performed at the BP86-D3BJ/def2-TZVP level of theory in the gas phase.[12–14,15] Density fitting techniques, also called resolution-of-identity approximation (RI)[16] were used for GGA calculations, whereas the RIJCOSX[17] approximation was used for hybrid-DFT and CASSCF calculations

Calculations were performed on the anions only (cations were omitted). In addition, the aryl substituents at the 2,6-di-*iso*-propylphenyl (Dipp) moieties were truncated to 2,6-dimethylphenyl rings (Dmp). Single point calculations on the energies of $[(^{Dmp}BIAN)Co(1,2\text{-}t Bu_2C_2P_2)]^-$ and $[(^{Dmp}BIAN)Co(1,3\text{-}t Bu_2C_2P_2)]^-$ have been carried out at the RI-PWPB95/def2-TZVP level of theory. The differences in energies for $[(^{Dmp}BIAN)Co(1,2\text{-}t Bu_2C_2P_2)]^-$ and $[(^{Dmp}BIAN)Co(1,3\text{-}t Bu_2C_2P_2)]^-$ are smaller than 1 kcal·mol^{-1}.

Frequency analysis of **3**, **3′** and the mixed isomer $[Co(1,2\text{-}t Bu_2C_2P_2)(1,3\text{-}t Bu_2C_2P_2)]^-$ were performed on the BP86-D3BJ/def2-TZVP level of theory.[12–14] The minimum structures and corresponding energies are depicted in Figure S37.

EPR parameters were calculated at the CASSCF-NEVPT2/DKH-def2-TZVP level of theory (state-averaged over 15 states). For the iron complexes **6** and **7** an active space of nine electrons in nine orbitals were chosen. Here, the initial guess orbitals consisted of the five 3d-orbitals of Fe, two ligand orbitals and two orbitals of the 4d-shell of Fe (so called double-shell). The resulting orbitals are shown in Figure S38 and Figure S39. For **2**, the guess orbitals consisted of the five 3d orbitals on Fe, two ligand orbitals and three orbitals of the 4d-shell of Fe. The resulting orbitals are shown in Figure S40. For all complexes, the experimental g-tensors are well reproduced when 14 excited states were included in the spin-orbit coupling procedure. An example input file is given below:

```
! RIJCOSX DKH DKH-def2-TZVPP def2/JK Grid5 NoFinalGrid Gridx5
! MOREAD
%moinp "1.gbw"
%casscf
trafostep rimo
nel     9
norb    10
mult    2
nroots 15
nevpt2 true
nevpt
D4Tpre 1e-14
D3Tpre 1e-14
```

```
end
rel
dosoc true
gtensor true
end
end
```

For the calculation of Mössbauer parameters, the ground-states of the three iron complexes were calculated using the TZVP basis on C, H, N and P and the CP(PPP)[18] basis on Fe. The active spaces were constructed in the same manner as described above. An example input file is given below:

```
! RIJCOSX TZVP def2/JK Grid5 NoFinalGrid Gridx5
! MOREAD
%moinp "1.gbw"
%basis newgto Fe "CP(PPP)" end
end
%method
SpecialGridAtoms 26
SpecialGridIntAcc 7
end
%output
Print[ P_Basis ] 2
Print[ P_MOs ] 1
end
%casscf
trafostep rimo
nel     9
norb    10
mult    2
nroots 1
end
```

The active space of the cobalt complexes consists of ten electrons in ten orbitals (using TZVP on C, H, N and P and CP(PPP) on Co). The initial guess orbitals consisted of the five 3d orbitals on Co, two ligand orbitals and three orbitals of the 4d-shell of Co. The resulting orbitals are shown in Figure S41 and Figure S42.

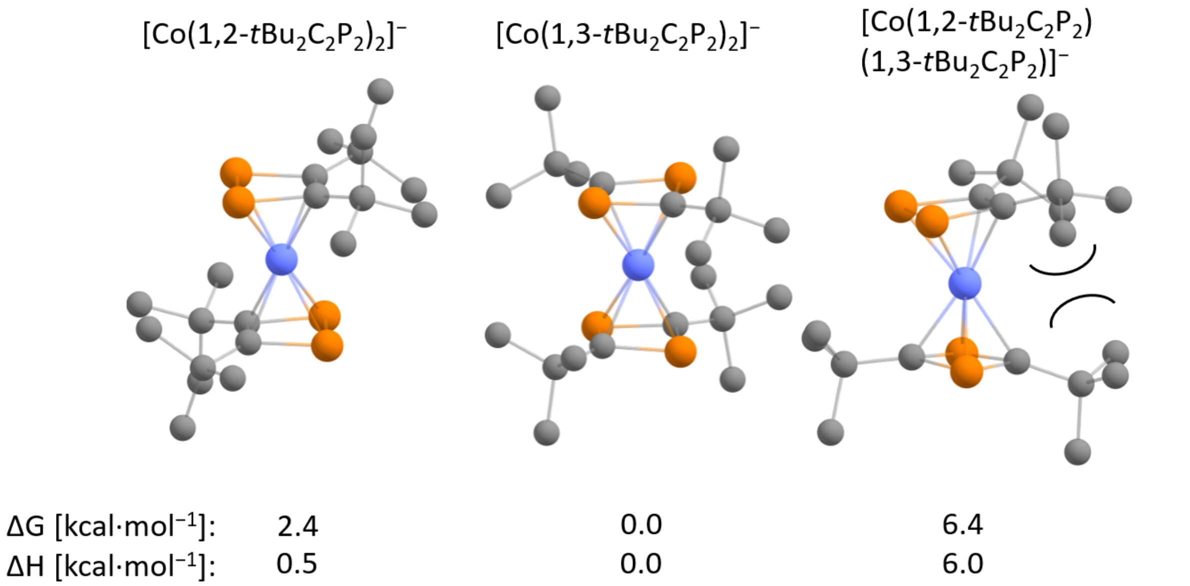


Figure S37. Optimised geometries, enthalpies and Gibb's energies for $[Co(1,2\text{-}t\mathrm{Bu}_2C_2P_2)_2]^-$, $[Co(1,3\text{-}t\mathrm{Bu}_2C_2P_2)_2]^-$ and the mixed isomer $[Co(1,2\text{-}t\mathrm{Bu}_2C_2P_2)(1,3\text{-}t\mathrm{Bu}_2C_2P_2)]^-$ calculated at the BP86-D3BJ/def2-TZVP level of theory.

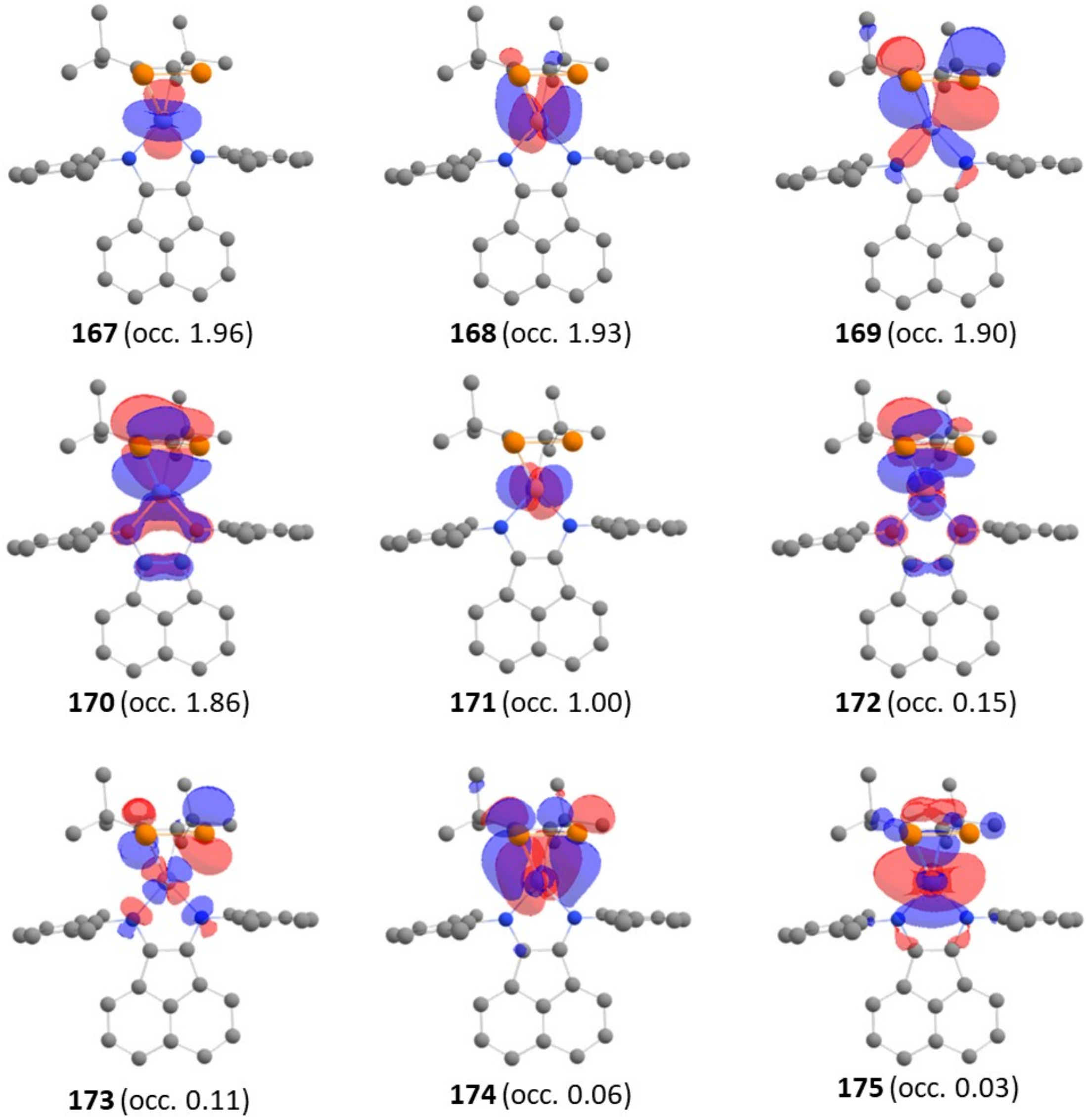


Figure S38. Natural orbitals of the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Fe] on $[(^{Dmp}BIAN)Fe(1,2\text{-}t\mathrm{Bu}_2C_2P_2)]^{-}$. The occupancy of each orbital is given in parentheses. Surface isovalue = 0.03.

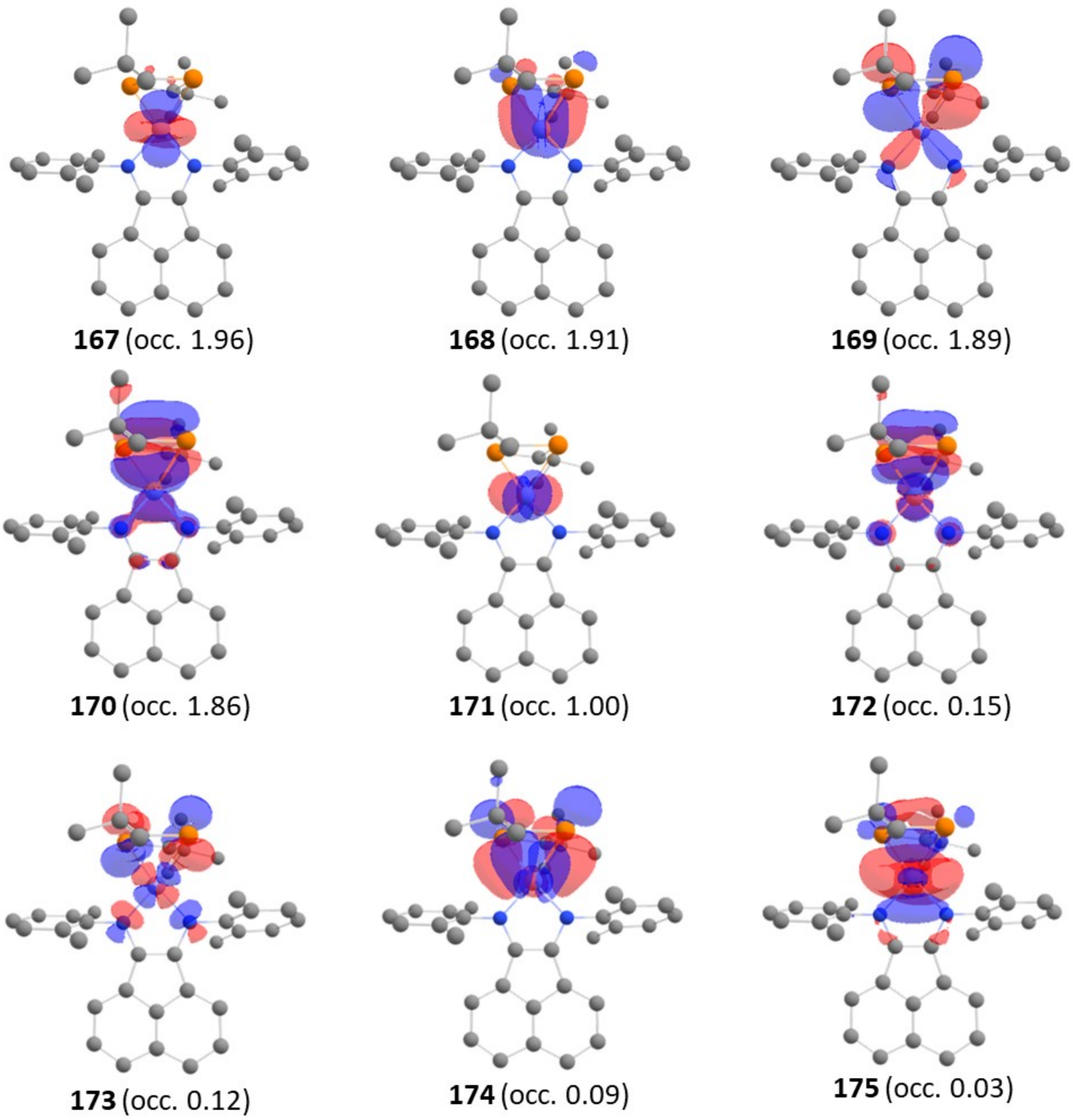


Figure S39. Natural orbitals of the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Fe] on [(^{Dmp}BIAN)Fe(1,3-*t*$Bu_2C_2P_2$)]$^-$. The occupancy of each orbital is given in parentheses. Surface isovalue = 0.03.

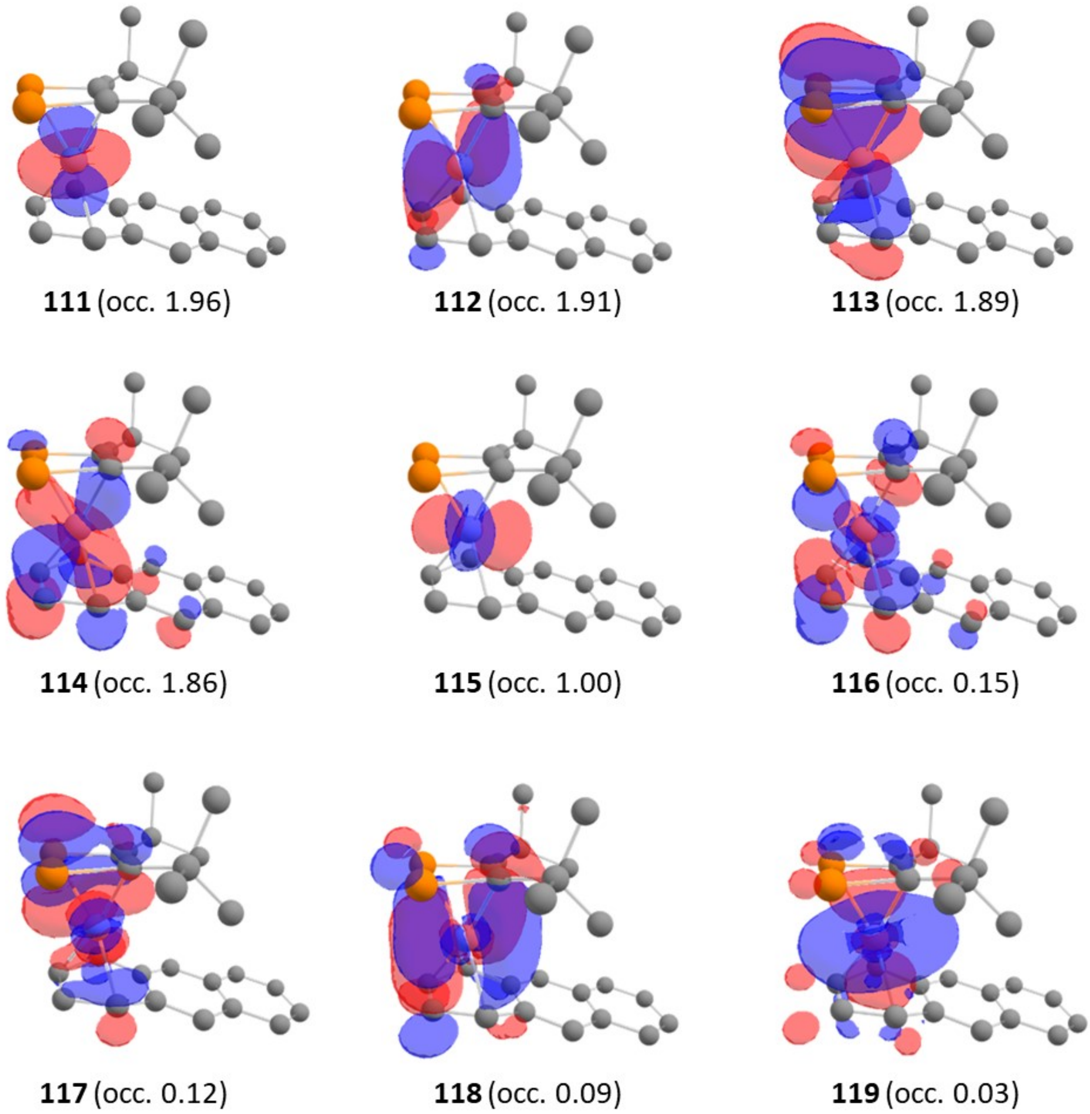
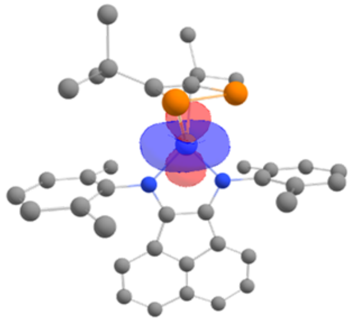
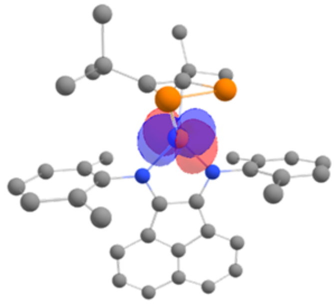
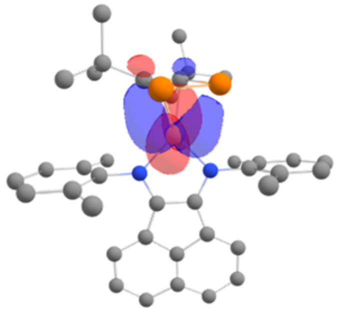
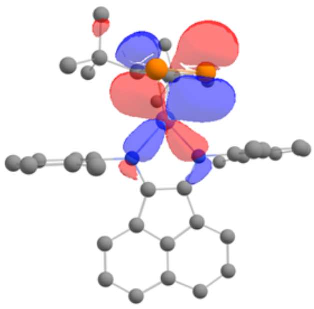


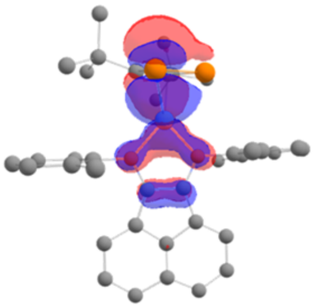
Figure S40. Natural orbitals of the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Fe] on $[Fe(1,2\text{-}t Bu_2C_2P_2)(anthracene)]^{-}$. The occupancy of each orbital is given in parentheses. Surface isovalue = 0.03.

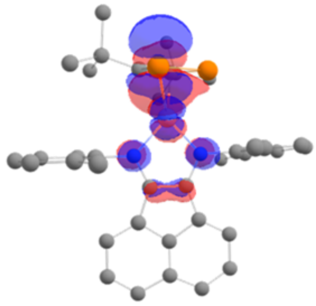

167 (occ. 1.97)

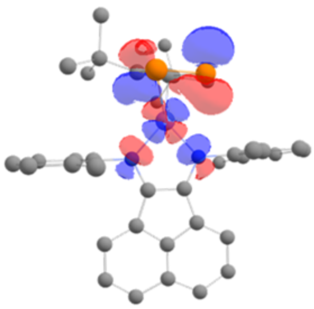

168 (occ. 1.96)

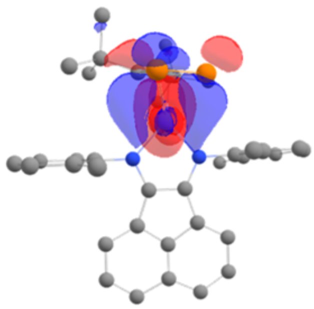

169 (occ. 1.94)

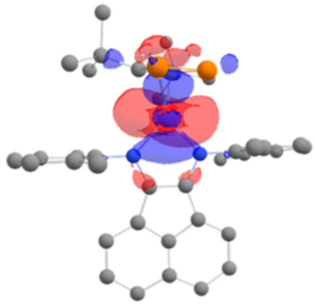

170 (occ. 1.91)


171 (occ. 1.89)


172 (occ. 0.12)


173 (occ. 0.10)


174 (occ. 0.05)


175 (occ. 0.03)

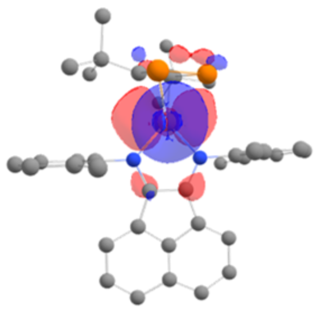

176 (occ. 0.02)

Figure S41. Natural orbitals of the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Co] on [(^{Dmp}BIAN)Co(1,2-tBu$_2$C$_2$P$_2$)]$^{-}$. The occupancy of each orbital is given in parentheses.
Surface isovalue = 0.03.

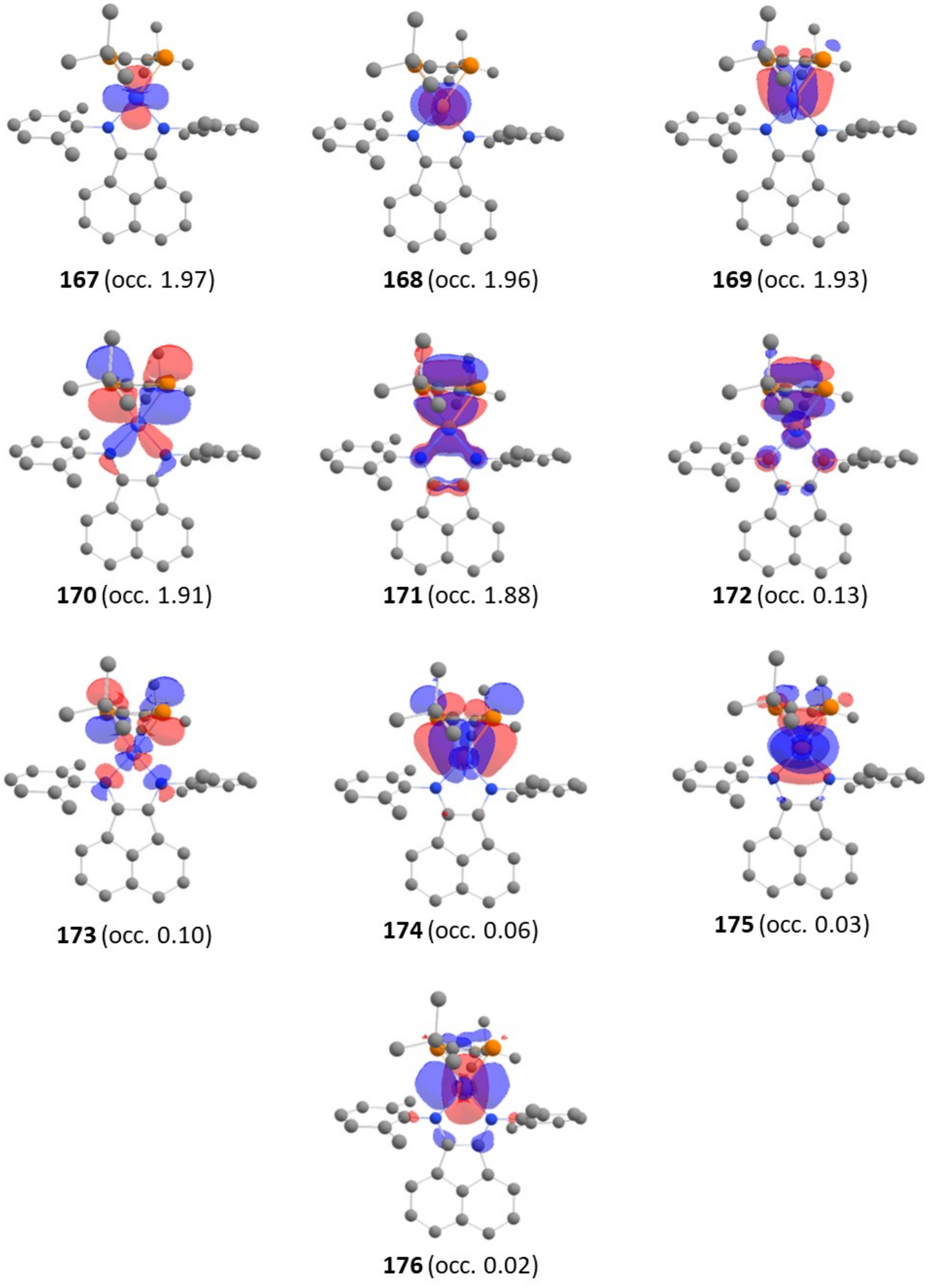


Figure S42. Natural orbitals of the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Co] on [(^{Dmp}BIAN)Co(1,3-*t*$Bu_2C_2P_2$)]$^-$. The occupancy of each orbital is given in parentheses. Surface isovalue = 0.03.

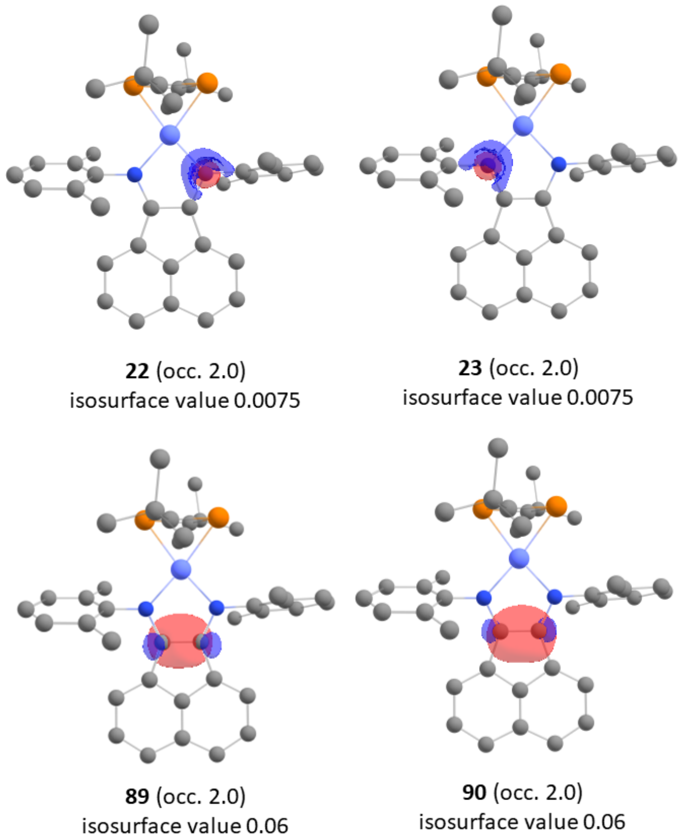


Figure S43. Selected localised molecular orbitals below the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Co] on [(^{Dmp}BIAN)Co(1,3-*t*$Bu_2C_2P_2$)]$^-$. The occupancy of each orbital is given in parentheses (2.0). These orbitals represent the lone pairs on the N atoms as well as the connecting C=C double bond of the ^{Dmp}BIAN ligand.

Cartesian Coordinates for Optimised Structures

[(^{Dmp}BIAN)Co(1,2-*t*$Bu_2C_2P_2$)]$^-$:

Co	6.90410033514340	6.15330831951012	11.35984907085909
P	6.85052854423478	5.02699910811742	9.37339781624692
P	8.72160413127847	5.04152986710298	10.52207610126049
N	7.11729654968343	6.87669170275783	13.11422124236625
N	5.19967926345825	5.61041152469170	11.99296201596355
C	6.03546147308029	6.65470670107382	13.90116183541723
C	5.69307966541484	6.90911031101124	15.29818310409287
C	5.57983610799920	7.54458678549787	17.63204603906584
H	6.05786196493332	8.02430118106321	18.48945396099681
C	4.31854638067479	6.98954199565647	17.79012281460207
H	3.81425846066238	7.03153339184449	18.75825425010385
C	6.28960865519491	7.51529229353724	16.39817786365691
H	7.28376620440376	7.95843239880452	16.33379840849716
C	2.67065578533189	5.11334892988506	14.29375310727060
H	2.25791345004648	4.62516116028709	13.41031342867678
C	3.91518567994650	5.73349710631086	14.26279184468772
C	4.38828588288716	6.33809843281035	15.47657067287007
C	8.21960644408367	7.49306845893977	13.75466467072679
C	4.97299090749219	5.95858349281301	13.28370087976165
C	3.67883331108848	6.35111311807890	16.68141699693368
C	2.39829836889404	5.71325474735205	16.67445420838340
H	1.79616825870646	5.69157879720472	17.58557771198745

C	9.09564792592480	5.19232500251529	14.31238375742943
C	4.30532646293926	3.47540782467546	11.20327526030827
C	4.17698172760161	4.87563705537802	11.33783436644646
C	1.93227075706501	5.11907696991361	15.51087216970452
H	0.95490959864066	4.63067096039952	15.52174192294777
C	2.03430578203762	4.79826256455945	10.21474043883759
H	1.14739759963273	5.31579447037871	9.84027561783998
C	8.27353041601097	8.89923753300532	13.84539499762759
C	2.16791579952016	3.42172605433411	10.03848958265284
H	1.39309337830857	2.85633352845760	9.51715014262881
C	3.02033513688691	5.54113987786466	10.87778702577472
C	9.66014090580130	7.79137095772047	10.19244122413044
C	9.21096464187680	6.68798981007203	14.35755730672035
C	3.29398803402248	2.76879263918342	10.54539148809664
H	3.39444045412690	1.68631426728574	10.43411180832682
C	8.47933064854831	6.81737504059852	10.16027518543820
C	10.28600032672213	7.31794331483808	14.99546814005030
H	11.06135067048445	6.70091907219318	15.45579836343070
C	2.82701793092870	7.00925860998901	11.14064965128964
C	7.12966003520770	9.72612461664466	13.32810094009418
C	5.49670100230115	2.76819165164850	11.78287449028547
C	5.95521800230328	9.00817376781846	9.68782482435734
H	5.28841733332040	9.71434261246803	9.16601746843397
H	6.81839145841181	9.56633931962791	10.06226359079489
H	5.42529420763196	8.59805688805060	10.55759077839453
C	6.36836258100917	7.86437228828989	8.74461207509880
C	5.07914881460985	7.19232821488153	8.23378432482787
H	4.54703720013848	6.68144321987435	9.04667872605347
H	5.30195775318358	6.44168686874887	7.46182908832248
H	4.40710303598199	7.94856218104746	7.79897882431884
C	7.21784624922063	6.80536177584284	9.45106124075678
C	9.37364629082458	9.49211597181150	14.47719056792766
H	9.42842947029165	10.58212122843928	14.53302725649262
C	7.10774131808402	8.43428052680847	7.51674631420465
H	6.43497097332104	9.08566801919175	6.93504689231894
H	7.44640106375585	7.61774123117723	6.86185720614343
H	7.98497003742150	9.02851942072771	7.80234930929246
C	9.30732779208324	9.27436110847634	10.38095449707712
H	8.74432021292652	9.67872012154368	9.53141887975804
H	10.23415327145906	9.86315231296276	10.47261360725231
H	8.72414096867807	9.42506646407745	11.29597447778957
C	10.38084419573862	8.71023300182208	15.04422569290436
H	11.23430481817923	9.18491494977524	15.53199896825722
C	10.40032613076916	7.61748004964382	8.84313333852055
H	10.74547475875469	6.57892730675396	8.73638028986237
H	11.27661968938951	8.28558229853713	8.79901678549293
H	9.74599719533527	7.84351304454778	7.99162800497466
C	10.64572250593740	7.40656208143785	11.30858740914122
H	10.24208297316871	7.63887905978487	12.29816474707218
H	11.58654846632526	7.96508519398348	11.18250069499626
H	10.87990220207467	6.33168561012090	11.27641047274199
H	9.05319002450067	4.83761543703108	13.26986034439762
H	8.16228629089701	4.85660311881229	14.78915363554364
H	9.94487316172646	4.71964135839062	14.82446169971786
H	2.10924263757336	7.44490648627380	10.43186712405042
H	3.77753305044713	7.55152978123594	11.06788254188388

H	2.44713840613536	7.17550478256274	12.16171242771999
H	6.74937196410896	9.32292709095073	12.38085901264360
H	7.42797085034573	10.77431509577731	13.18794286342728
H	6.28668901477806	9.69947408977570	14.03767323423495
H	5.39758194352531	1.67989055282199	11.66953417236452
H	5.61560962368729	3.00764505297470	12.84985668989972
H	6.42507700271857	3.09864936911372	11.29333797604913

[(^{Dmp}BIAN)Co(1,3-*t*Bu$_2$C$_2$P$_2$)]$^-$:

Co	6.26070922590476	11.32572283032820	5.27742212988500
P	4.15004124365782	11.88083782934124	4.67375583633794
P	4.95161832354998	10.69317144382055	7.01216813378952
N	7.19410913413078	11.43645665370285	3.61996476909215
N	8.00182066578069	11.28072041184108	6.04948723416630
C	8.40997627371591	11.32386518502813	7.40521951536092
C	6.71297040212706	11.38648782118310	2.28879735323745
C	9.70278957711900	11.49879973191258	2.89396066833462
C	12.17238199668425	11.43823782793786	3.31843095343529
C	4.49847392936869	10.23602958719674	5.32674019418981
C	8.37029160870586	10.15690533777094	8.19960540652490
C	6.15915994591103	12.53765119328885	1.68694936446094
C	8.54386694592435	11.43037727798221	3.78109628375868
C	10.84605141819635	11.41796658205538	3.75816537219258
C	10.44818416306416	11.31294695790180	5.13347177956961
C	5.68841207113831	12.44929188316975	0.37137952031082
H	5.26066174112437	13.34036797563761	-0.09497411088058
C	11.45260664868216	11.21088546978924	6.08855981097496
H	11.21978217348819	11.12555948844768	7.15047716164138
C	9.93451488728607	11.61945219153466	1.52904259376566
H	9.11116187678216	11.68817668611841	0.81731698031860
C	6.84266038528203	10.18423894907579	1.55356241483093
C	8.98749480674103	11.34131907711872	5.11507790451288
C	7.93047240051437	8.84757732748992	7.61213272871789
C	8.90910290848689	12.53673390698074	7.93682850908277
C	4.14236893721438	8.88111715874395	4.76778857045525
C	4.77297753515159	12.34153134608666	6.30246922838082
C	13.18083017530498	11.33613796024787	4.32841592698277
H	14.23621130357948	11.34654281012139	4.04682279651896
C	6.35537848945507	10.13662488500324	0.24227295156273
H	6.43693023002657	9.20117404111779	-0.31690503884364
C	12.37464146513130	11.55813021179551	1.90693953151579
H	13.38900026753220	11.57863926860433	1.50211623078903
C	11.27969106832394	11.64729258492849	1.06102405929190
H	11.44841344321545	11.74028422063766	-0.01446388679544
C	6.10560212358216	13.83881669095645	2.43344308641720
C	9.30022935913000	12.57704870641757	9.28021118318387
H	9.66550352056267	13.51987621099466	9.69498203428875
C	5.77271869409800	11.25743814274555	-0.34972880446930
H	5.39584642027239	11.20589657025590	-1.37302508000354
C	2.77461134732039	8.46595642985899	5.35599596034576
H	2.82898346843725	8.40381238019685	6.45264821909972
H	2.45925253549329	7.48502626602982	4.96245002486285
H	2.00707690323936	9.20971768935697	5.09610956414294
C	8.77609227238991	10.23853941585278	9.53706637348503
H	8.74620419094751	9.33523805488181	10.15155266469840

C	4.77043314323634	13.69008760921619	6.97809272038279
C	9.03972256145406	13.75621073535978	7.06610911124945
C	5.19647011067122	7.83949577125819	5.17753635540594
H	6.19291109811242	8.14243415529574	4.83106676664316
H	4.95608586783250	6.84905074497259	4.75862583046194
H	5.24117961715978	7.74497778671151	6.27285667971607
C	12.81108141827137	11.22397145439638	5.65999242845187
H	13.59129843641451	11.14481476990055	6.42076439631871
C	7.51242295239111	8.98407186816339	2.16489803492622
C	5.59013837039656	13.63956006219034	8.27562434359800
H	5.16571282505645	12.90160808809139	8.97300205872536
H	5.59388332992412	14.62181134566617	8.77460817361273
H	6.62665931183725	13.34422287619785	8.08084921556305
C	4.02002519827140	8.94866705104892	3.23838630319529
H	3.23084951277362	9.65751429588513	2.94526925844012
H	3.76649711149304	7.96053952734941	2.82253992460327
H	4.95210088945249	9.29223068877473	2.77728024530570
C	3.30814304132676	14.04802581535552	7.32782144000039
H	2.69505923687511	14.09914003982877	6.41624739575107
H	3.25534253271155	15.02146971000822	7.84360704314154
H	2.87475340971093	13.28017398182852	7.98536857096486
C	9.22918945826373	11.43955257703991	10.08459443572310
H	9.53670259988344	11.48565940628420	11.13108482427860
C	5.33206233462841	14.76246311375892	6.03029055696141
H	6.35215033356020	14.50356331614193	5.71874759078093
H	5.34501008684248	15.75139599493458	6.51624610878880
H	4.71679834323045	14.83616047336357	5.12091783126813
H	8.31110369877002	8.72369030052822	6.58972138231443
H	6.83246017984148	8.81204735486507	7.54211668632731
H	8.27202680486504	8.00711778030914	8.23289988805403
H	5.98586214347861	14.68246784335297	1.73893720727513
H	7.01181640962606	13.98763990946257	3.03502865144446
H	5.26008170636710	13.83989925440149	3.13862330615467
H	8.22962986579658	13.79545981482346	6.32612467849636
H	9.98364431253846	13.73313195347533	6.49877089464700
H	9.02370676670528	14.67351008650868	7.67094398892545
H	7.16317353701814	8.05600273000463	1.69135389593471
H	7.31591994931777	8.93715130745064	3.24405506371785
H	8.60599299011997	9.04202773430712	2.04538260892928

[(^{Dmp}BIAN)Fe(1,3-*t*Bu$_2$C$_2$P$_2$)]$^{-}$:

Fe	6.24556596645472	11.32929160284019	5.28185116683388
P	4.09761759421678	11.89817126437982	4.69559311838341
P	4.90049629740832	10.67921605894511	7.02760697663079
N	7.19565114125721	11.42298583672634	3.60543826045029
N	8.01124235125749	11.29645121302279	6.05832826275177
C	8.42894374155150	11.34259768713790	7.41093908539656
C	6.72677640650530	11.36559949523953	2.26999499172361
C	9.70901742228471	11.50685549449432	2.89202144757708
C	12.17792488212975	11.43976192623314	3.31210420959331
C	4.46842164440188	10.24658975754285	5.32526778464737
C	8.38408912207884	10.18021713883584	8.21208424460460
C	6.16985417898182	12.51074095312424	1.65871889723631
C	8.54943921285927	11.43038676783484	3.78061116747738
C	10.85352499075242	11.41953311977669	3.75257857081753

C	10.45454851560004	11.30834995990963	5.12636665006077
C	5.70672185482344	12.41357571965859	0.34117017670838
H	5.27508724504410	13.29951876497470	-0.13138808521137
C	11.45849296405191	11.20053458451407	6.07985156458191
H	11.22637987385832	11.11055663384509	7.14157681626179
C	9.93806338164895	11.63336627870689	1.52825060939022
H	9.11382835428210	11.70732072644562	0.81809770837577
C	6.86688689019575	10.16088555208873	1.54095158771478
C	8.99250212834393	11.34639945767869	5.11017145994339
C	7.93641930153422	8.87026837935619	7.63130106217014
C	8.93513166222887	12.55553377245447	7.93628462073608
C	4.10831784754053	8.89704932383821	4.75104472957316
C	4.74897907423150	12.33539127546023	6.32518949105606
C	13.18791282906480	11.32982849341405	4.32071854049299
H	14.24303739078913	11.33707177590740	4.03813377109643
C	6.38919136903038	10.10451155730909	0.22638298850088
H	6.48016059374794	9.16719223639531	-0.32830203398458
C	12.37906963887025	11.56727071535603	1.90058072110183
H	13.39307381894990	11.59114865476036	1.49498107062947
C	11.28371490608600	11.66219752174879	1.05722257044387
H	11.45009172688724	11.76142720167598	-0.01800096565004
C	6.10775442981389	13.81419115244378	2.40048479011386
C	9.33040805957833	12.60038633642241	9.27807971475229
H	9.70227005940249	13.54328887766435	9.68700417823503
C	5.80363611191885	11.21907721457693	-0.37444923769906
H	5.43257778891646	11.16040946047251	-1.39950179918278
C	2.73254855814399	8.48154749133635	5.31913109207684
H	2.77382713061813	8.41050123210725	6.41587335567937
H	2.41809625500908	7.50501901121867	4.91401938913698
H	1.97104687282251	9.23045166273813	5.05672486620329
C	8.79215988692082	10.26658510390205	9.54874448820842
H	8.75733537542857	9.36706261830467	10.16860132963427
C	4.75314025411568	13.67758062413302	7.01732646118588
C	9.06329600141103	13.77103831404556	7.05973744135095
C	5.15383535073911	7.84782483795217	5.16406934222381
H	6.15318677226066	8.14043189905169	4.81573676355492
H	4.90607297870821	6.85866252374527	4.74630436010712
H	5.19771419218002	7.75443382239862	6.25964659857152
C	12.81840459802740	11.21230080878398	5.65099110461329
H	13.59798844810182	11.12671973906139	6.41165263287546
C	7.53659773519968	8.96679333167522	2.16385319779246
C	5.58813547812664	13.61156787788666	8.30443235197568
H	5.17517775218940	12.86132536775004	8.99566832632849
H	5.59311251578442	14.58608552158728	8.81826678477905
H	6.62378695100841	13.32389118519102	8.09360835776894
C	4.00647310710742	8.97858491726728	3.22080692249488
H	3.23011085978754	9.69959314048442	2.92321780329299
H	3.74624558922647	7.99724297401715	2.79307215980824
H	4.94913750653484	9.31404241317282	2.77537664871111
C	3.29608711551360	14.03563312923269	7.38722300556243
H	2.67252737475615	14.09729835682511	6.48337788645793
H	3.25072424501385	15.00373490743920	7.91379259089185
H	2.86855017564099	13.26153982539598	8.04115199768633
C	9.25459341503735	11.46743503943770	10.08881279214908
H	9.56366343231172	11.51726584418401	11.13467525267805
C	5.30761174791537	14.75903042489849	6.07524102876976

H	6.33375134993314	14.51455260631928	5.76996550932795
H	5.30769616957735	15.74644147805333	6.56447252473309
H	4.69660688320881	14.82917243754355	5.16254544936491
H	8.34696269971417	8.72199913700051	6.62333601204151
H	6.84033003607792	8.85584987658449	7.52738685428083
H	8.24211302356423	8.03306746586583	8.27457556969878
H	5.88080579885077	14.64331310984981	1.71569787614014
H	7.05446405524736	14.02160400418841	2.91824268865599
H	5.32957280719415	13.77108563722090	3.17791377992951
H	8.23980719778001	13.81736936636713	6.33461292589188
H	9.99536915969733	13.73614575413703	6.47379992456961
H	9.06828846728205	14.69009692643507	7.66187391395561
H	7.20703244106628	8.03622667803505	1.68127842578633
H	7.31734854166093	8.91454930035522	3.23859294477791
H	8.63182092492524	9.03579233360872	2.06843838394143

[(^{Dmp}BIAN)Fe(1,2-*t*Bu$_2$C$_2$P$_2$)]$^-$:

Fe	6.95933952896180	6.12005865212629	11.38242106026567
P	6.97214841134604	4.96648613498811	9.36619641316097
P	8.83919599227014	5.07967634310467	10.53044211100740
N	7.16166486276801	6.79716828463087	13.17457611913803
N	5.19452082762216	5.63510767625741	11.98584855147564
C	6.03627593103217	6.63360372832158	13.92578107932763
C	5.66536142327007	6.91296268529047	15.31311182220455
C	5.51856582195918	7.55760554330462	17.64394131056465
H	5.99280313861942	8.02507743176316	18.51007342443224
C	4.23712336865899	7.04647416159285	17.77397276394843
H	3.71056301705265	7.11050501509820	18.72889372025779
C	6.25560558242183	7.49935571401458	16.42508027744439
H	7.26525010548129	7.90913634827053	16.38287884616559
C	2.62086315714437	5.20286744298693	14.24781857190061
H	2.21700519224207	4.71645507544459	13.35928569748799
C	3.88031095351229	5.78911006550822	14.24244394197955
C	4.33931086201521	6.38640500833943	15.46432050125815
C	8.26148518977445	7.41166541066242	13.81874968089696
C	4.96909648766364	5.98016254279599	13.28547148137423
C	3.60440520345126	6.42457766360337	16.65097499846557
C	2.30618348378729	5.82280964870985	16.61797377813978
H	1.68394447656267	5.82045701404169	17.51574297619942
C	9.25248338193897	5.11799833151745	14.27728581938408
C	4.29513863148711	3.50077421051104	11.19891737617360
C	4.17029579047025	4.90258155115756	11.32958214928092
C	1.85201682083112	5.23583316744472	15.44769212103935
H	0.86259192486109	4.77260209473963	15.43706667677175
C	2.03083871694465	4.82218096102531	10.19570130419419
H	1.14576685474955	5.33963980357510	9.81671350719236
C	8.29251172356508	8.82050632806498	13.93669847361471
C	2.16383605553988	3.44545866929213	10.02267909892350
H	1.39136633643952	2.87952481911517	9.49840114775085
C	3.01509821105510	5.56583094411613	10.86077826580859
C	9.65467747551857	7.86342952314550	10.18973200250734
C	9.29624209198223	6.61972377156898	14.36068718980522
C	3.28701004716759	2.79342766244038	10.53641824625682
H	3.38681021279844	1.71054812676783	10.42868568276222
C	8.51200635515251	6.84260019773478	10.16724794829527

C	10.37843755927535	7.26224375820934	14.97705244405615
H	11.18581144551830	6.65395921230832	15.39265224563027
C	2.81444704832003	7.03372225772881	11.11944409090006
C	7.13433525437166	9.64066425568708	13.44063898517612
C	5.47648941809030	2.78827650716197	11.79253378756301
C	5.92083077954573	8.92631633335064	9.67063879375951
H	5.22019579410920	9.59888062489288	9.14876423384628
H	6.76504381546997	9.52421042479906	10.02617403766483
H	5.41641179014252	8.50996759457774	10.55255572490402
C	6.36539992651192	7.78521404870296	8.73720993466081
C	5.09655991286044	7.06688790264958	8.24111424874668
H	4.57490282841821	6.56368986150383	9.06530773512292
H	5.34165152578288	6.30285855302875	7.48914988122877
H	4.40601185809855	7.79316912301511	7.78445301280226
C	7.25379742998338	6.76174664639580	9.45133761751222
C	9.39743191833264	9.42385525944716	14.54604506139592
H	9.43365312632968	10.51370765893260	14.61811538894572
C	7.08155247131255	8.36649553062168	7.50146027988308
H	6.39009278067254	8.99935603728650	6.92112006204877
H	7.43583402599178	7.55475844445971	6.84896867818400
H	7.94632861545995	8.98216159657574	7.77959374728294
C	9.24177890760063	9.33212206207921	10.36943118876332
H	8.67546368966684	9.71339490414007	9.51104498823605
H	10.14397366662706	9.95670322275463	10.47095665686771
H	8.64071812365814	9.46292457469241	11.27675950646105
C	10.44116444167564	8.65269294478662	15.06254222943712
H	11.29929100965682	9.13587446608958	15.53352311418075
C	10.40927601063921	7.71376477068382	8.84576969884152
H	10.80574648966611	6.69259303048510	8.75116692205435
H	11.25141383905756	8.42433178875541	8.79721036126768
H	9.74838730023857	7.89731855956736	7.98919683898990
C	10.64940075859293	7.52796007205560	11.31403214463431
H	10.22579713575366	7.73898672037568	12.30012343616788
H	11.56231024707199	8.13261610106071	11.19599312922729
H	10.93710719428469	6.46610009815787	11.28325769957640
H	8.26196672707425	4.76717995736582	13.96989273665821
H	9.51423694273974	4.66918267672395	15.24753096504622
H	9.96694623635642	4.74856924966059	13.52516196397598
H	2.12615223592508	7.47308900463545	10.38419308864734
H	3.76681916973853	7.57488876154881	11.08553277963112
H	2.39371858253851	7.19748895009172	12.12481967830459
H	6.75976553912832	9.25222176218941	12.48394236618136
H	7.41971207440929	10.69486443072638	13.32015417830058
H	6.29021099338836	9.59082684980550	14.14715225582453
H	5.37611911263758	1.70071916590530	11.67323460084858
H	5.58062491477752	3.02169361043654	12.86256795414981
H	6.41110568438037	3.11738288081863	11.31376338955604

A. **[Fe(1,2-*t*Bu$_2$C$_2$P$_2$)(anthracene)]$^-$:**

Fe	5.42992338896547	10.21329259797338	4.09655246495137
P	3.27081912469223	9.37074297810374	3.88260991763509
P	4.71462146743912	8.23481996598950	5.06855804286578
C	8.75893610634255	12.32604842142458	1.50258150806364
C	5.54014543097296	8.28562032369459	3.43340444799700
C	9.06964322496417	11.04561880204657	3.58394123244978
H	9.70313536155170	10.42758732850495	4.22608779934441

C	5.51726888730192	12.24124760088973	3.50485015137721
H	4.83834281913736	12.73893131970857	2.80900995158177
C	7.76284188319901	11.31980536132664	3.97969350717611
C	6.91353552165672	12.12086978550977	3.11512082974346
C	7.43747581846268	12.62337250404024	1.92973466437242
H	6.80018913780467	13.22655790272626	1.27723649256286
C	9.59482022297998	11.50956036933791	2.34927373978894
C	4.40291201004026	9.31757749313681	1.14872477852717
C	5.10837478779764	12.07905321555021	4.86529298930349
H	4.12986165877882	12.42255482522647	5.20013906772663
C	9.28714766728218	12.78974406262612	0.27296216281347
H	8.64774540556294	13.40249223160152	-0.36791670310972
C	4.58430704658751	9.04199446632838	2.64768049829269
C	5.52454154543554	10.16934050410594	0.53152610606912
H	5.48052396793526	11.18996467553065	0.92677158871565
H	5.40890397159222	10.21756811426729	-0.56451556056025
H	6.52421798009941	9.78845990622380	0.75286573696628
C	6.75573639660870	7.41167888354831	3.12029991955503
C	5.94549887691943	11.32385256020950	5.72100536783477
H	5.63195637664804	11.07316350822020	6.73405338263058
C	7.14074777466973	10.76332556169740	5.16537276875521
H	7.73677957305419	10.09367492316436	5.78735458170814
C	6.25257530836751	5.98863561159257	2.78726256281905
H	5.68268177761453	5.58239048518786	3.63566589593460
H	7.10001032707451	5.31506929171676	2.57660365926648
H	5.59001736627465	5.99531643470544	1.91177323787653
C	3.09278598345542	10.10281632821169	0.94591418359401
H	2.21751841709211	9.51387435698520	1.25558950100181
H	2.97693409969083	10.37342457719761	-0.11577399377262
H	3.10304656562731	11.02860263391476	1.53978884166466
C	10.90743569794161	11.20414263362206	1.91142534432964
H	11.53538813684963	10.57872868797772	2.55130047953862
C	10.58101402466190	12.47861746671254	-0.12415713861945
H	10.96461791871884	12.84840400560212	-1.07716195927714
C	7.64101211700184	7.92550247155637	1.97441596959691
H	7.13341859676342	7.87737942579475	1.00368754961084
H	8.54847049922447	7.30418772764594	1.90020859126669
H	7.95809965098120	8.96119370595715	2.15778009867135
C	11.39723761242334	11.67881428833602	0.70200196973623
H	12.41299760075058	11.42971084918711	0.38825973579620
C	4.26913669751848	7.98153376151916	0.39041201193845
H	5.21451453211875	7.42411386822805	0.38498894602883
H	3.97830228677105	8.16090458166007	-0.65796545687338
H	3.50305724548729	7.34782270355695	0.86128464914671
C	7.64693319508260	7.31854023495724	4.37305686827100
H	8.11873189224048	8.28648839904366	4.58065687025429
H	8.43786473039856	6.56739538319608	4.21866949613474
H	7.06074428538640	7.02756989322120	5.25794065092669

$[Co(1,2\text{-}t\mathrm{Bu}_2C_2P_2)_2]^-$:

P	6.64938391058229	7.55525715681854	8.00177373498066
P	4.49445918522593	7.91779672906008	7.73986252497686
C	6.49510260587596	9.30413377752347	8.52056972282425
C	5.07642909999820	9.53631892693298	8.34011995774395
C	4.51947211114347	11.90099945722442	9.23398232335246

H	4.63464686108104	11.51740937753246	10.25727074739976
H	3.71277542217134	12.65220509769370	9.23269695057302
H	5.44320091168956	12.41204660368133	8.93420166662225
C	4.16060121524240	10.75917427860493	8.27492444761793
C	4.18994544820989	11.28673079470589	6.82121149155081
H	5.20615102363349	11.58125951611109	6.52542652990906
H	3.52870246902273	12.16274572359091	6.71344811486487
H	3.85191006159741	10.50263275100064	6.12830451932694
C	7.71631259251636	10.20396288945178	8.75142928881772
C	2.71647301594247	10.33081742711116	8.59684075049428
H	2.40814037512657	9.47668821407003	7.97425990861737
H	2.02402793182692	11.16621386031512	8.40339655343891
H	2.63662444198264	10.03292441781177	9.65121836948773
C	8.96633315851741	9.31300661708705	8.88423560451054
H	8.86199415728061	8.64239675437981	9.74848500012303
H	9.85888589209567	9.94057549159707	9.03596591613360
H	9.12120212169748	8.69710437839624	7.98642488591223
C	7.68038197010441	11.07783947214667	10.01826890510897
H	6.82365882887970	11.75442329164771	10.04789514977531
H	8.59768140163681	11.68920763658929	10.06664788407832
H	7.63524571933187	10.43767999534191	10.90937339436188
C	7.89245295365262	11.10324861744877	7.50892953942038
H	7.89993818663448	10.49487070131208	6.59233314853057
H	8.84030782859175	11.66352041059897	7.56706379499048
H	7.07353860106217	11.83107613323309	7.42763967246027
Co	5.41335595384599	8.15892285419413	9.81538667086170
P	4.17730265537511	8.76256466205733	11.62899081900202
P	6.33222662184621	8.40005835068470	11.89091738400542
C	4.33160823843264	7.01369336811577	11.11018700334786
C	5.75029193821326	6.78152599577879	11.29065549920037
C	6.30755145858268	4.41686284206775	10.39680166953154
H	6.19240658766219	4.80044875584104	9.37350876073599
H	7.11434906275918	3.66576567801498	10.39814352068256
H	5.38387081665006	3.90568877880106	10.69650486943530
C	6.66619589849060	5.55872117400287	11.35590026935190
C	6.63677734486310	5.03114809861139	12.80960562273374
H	5.62057277804889	4.73652948209645	13.10530390460146
H	7.29808769694851	4.15518962916903	12.91741486372818
H	6.97468799751399	5.81526862835548	13.50254785312610
C	3.11036345745693	6.11390930269720	10.87931217890680
C	8.11031367509772	5.98721070732250	11.03412520345048
H	8.41850765922480	6.84136543301499	11.65673971131119
H	8.80281786139917	5.15187738886849	11.22763203226719
H	8.19023579207773	6.28511557421947	9.97975664788824
C	1.86038728119064	7.00494641105136	10.74665318325479
H	1.96471177361531	7.67561831459174	9.88244993606924
H	0.96778932665142	6.37744025516681	10.59493017192588
H	1.70561222887339	7.62078704307267	11.64452246983146
C	3.14613807066714	5.24014890955145	9.61238768454899
H	4.00277864956505	4.56347451082967	9.58265099730100
H	2.22876845685474	4.62888743520280	9.56399869155777
H	3.19129789739262	5.88038763028657	8.72134062109439
C	2.93423305905211	5.21453984569190	12.12175508297020
H	2.92682381738597	5.82285071945895	13.03839639001513
H	1.98634546420044	4.65432342120910	12.06362338224147
H	3.75311097770871	4.48666230095461	12.20295640701719

[Co(1,3-*t*Bu$_2$C$_2$P$_2$)$_2$]$^-$:

Co	4.77915327914802	5.96659674678014	6.20688184845955
P	6.61071027853583	5.12606097718256	7.22523026189821
P	4.34180269677009	3.76340978665667	6.45123519877359
P	3.52266194963722	7.74424807387785	6.80558102541787
P	4.65238307755447	7.23628133839241	4.34302735393108
C	4.95626774347235	4.73849117856493	7.84570280871896
C	5.92090665425435	4.31563124972012	5.76261328825507
C	5.08982631998917	7.97930437933080	5.93311973530431
C	3.16033925494209	6.83606022882922	5.28408803325726
C	4.40712632526285	4.85589769469377	9.24688794626532
C	4.86141619162523	3.60512196954168	10.03422024858716
H	4.48532477833418	2.69211042108751	9.54990863042658
H	4.48708652404900	3.63400637151311	11.07113704035608
H	5.95945398810515	3.54701117858377	10.05822895817323
C	4.95259760200757	6.11334318383000	9.94140040134323
H	6.05330097484440	6.11873621451569	9.93181870460180
H	4.61782304664716	6.15559394240598	10.99065265633964
H	4.60118908739832	7.01259813903854	9.41855463637295
C	2.87147299308306	4.90800851432951	9.22855074564522
H	2.53427980632277	5.82455015041354	8.72683994134914
H	2.46823277176504	4.89148185797072	10.25425705585169
H	2.45758643958417	4.04649214834811	8.68272755462687
C	6.60918046897777	3.88729717139428	4.48931720222079
C	7.33113960799416	2.55023790090350	4.77447463930693
H	8.06618061290823	2.67878985365208	5.58237719726348
H	7.85538283891393	2.18528480179243	3.87552971903304
H	6.60743035974953	1.78633633959965	5.09423807755114
C	7.64468571878370	4.93371680190296	4.04883024020361
H	7.13955531011073	5.87192719000585	3.78416850473572
H	8.21436655243888	4.57577767712225	3.17570317374844
H	8.35762350251913	5.14514956623090	4.86039064489023
C	5.58605043658680	3.67705484677485	3.36223019396852
H	4.81044223924124	2.95780927241032	3.66704677131487
H	6.07866454107417	3.28814988451818	2.45623742911043
H	5.09398291552751	4.62846698240850	3.12063860439856
C	6.25637972978233	8.87001960400489	6.28581542200284
C	6.50899444374711	8.86287598742107	7.80157640775408
H	5.59314389496568	9.12869460380764	8.35139406001029
H	7.29395093360803	9.58873508731667	8.06957256822736
H	6.82319318825104	7.86143666507462	8.12401396035566
C	7.52887615856476	8.41628617642127	5.55392913337091
H	7.81876686873882	7.41296153694629	5.89278001335167
H	8.36007947942707	9.11344990918804	5.74874914079995
H	7.36187799332342	8.37674478255677	4.46661040459239
C	5.90040447035283	10.30675636492637	5.83929582506229
H	5.70784907051968	10.33346797890953	4.75680863575349
H	6.72163737437596	11.00604997459824	6.06888248299517
H	4.99111886617228	10.65143041796471	6.35303253780776
C	1.85275999530321	6.25440387894149	4.80390874416271
C	2.09556893546767	5.17900392993694	3.73330261531901
H	2.69449639743522	5.58237348584655	2.90243062404069
H	1.13993035150073	4.81437911389806	3.32250345286983
H	2.64181071635812	4.33287180336028	4.17053810363977

C	1.06646697041145	5.64145995980781	5.97338490127615
H	1.61332789585157	4.78258515999564	6.38415295205155
H	0.07073350958321	5.30634638173749	5.64010642733725
H	0.92903504672394	6.37701485090235	6.78057611477055
C	1.02590562618793	7.40586963993404	4.18736132779061
H	0.84062619118932	8.18748511169779	4.93863916115960
H	0.05539421220542	7.03876659056682	3.81392971002435
H	1.57354479179491	7.86459696991624	3.35105880177348

[Co(1,2-*t*Bu$_2$C$_2$P$_2$)(1,3-*t*Bu$_2$C$_2$P$_2$)]$^-$:

P	7.20418158499781	7.79485466349769	8.44774990855626
P	5.05488928320007	7.66107954504914	7.99442538308555
C	6.68129509846732	9.53886757383435	8.61537729760361
C	5.27257491397685	9.45560337023367	8.30532972909033
C	4.26372983816780	11.81641946801524	8.58036483728892
H	4.31265295157375	11.70554497905687	9.67030686054394
H	3.36900607416202	12.41110911522929	8.33414905060018
H	5.14120600522142	12.38843586960155	8.25309515891487
C	4.18553014788925	10.44503544227665	7.89646353429595
C	4.27895361643435	10.64964658736817	6.36602147338073
H	5.25159458884145	11.07401455993212	6.08106718034433
H	3.48584843267751	11.33116341818638	6.01482840914716
H	4.16810218123028	9.68506198367601	5.85021723539291
C	7.69707090677457	10.67548854492578	8.76951688104048
C	2.81142717516135	9.82386619193288	8.20975302193320
H	2.69481960258403	8.85902677392538	7.69388395122117
H	2.00220680272113	10.49475133353598	7.87889952944151
H	2.70671909830448	9.63128394030434	9.28393694248276
C	9.08152805285340	10.06612222476179	9.06608167194825
H	9.03850120762814	9.45017893559143	9.97618399579329
H	9.81861228806667	10.87021176223574	9.22097614946153
H	9.42763272055877	9.43060057849915	8.23831173492039
C	7.38994110528164	11.62774554877640	9.93396012925499
H	6.41941799761203	12.11894089313429	9.82649468314196
H	8.16373706954934	12.41151660718870	9.99763752762636
H	7.38237315756835	11.06041811853722	10.87292826366941
C	7.79363986418102	11.45826044917251	7.44457681166666
H	7.99621084748397	10.77145136482640	6.60931941607113
H	8.60733718625451	12.20107127684680	7.49044706588591
H	6.86047550812124	11.99300577738958	7.22309599305666
Co	5.69672699939180	8.42038418099407	10.02703995132127
P	6.59496704473718	8.39704792942191	12.09309816261063
C	5.81976732196286	6.91940352372522	11.39043598991059
C	5.75659079124251	4.78667876474564	10.05766550653011
H	6.12505207160999	5.23957872424945	9.12733937700964
H	6.03110425446006	3.71845674970949	10.06302604812025
H	4.65917720255900	4.86391668524682	10.05301887880051
C	6.34964005608019	5.50778664372072	11.27952688740929
C	5.92096719232715	4.75262258249800	12.55999269312719
H	4.82419756949841	4.72186522638064	12.63806846113489
H	6.30394538520184	3.71825809853108	12.55387957281593
H	6.30893572778226	5.26567711366666	13.45238923327834
C	7.88436872173649	5.50004742238514	11.19559015091548
H	8.32266797466788	6.00757737405836	12.06900237561862
H	8.26628914613990	4.46611962338033	11.17058571680001

H	8.21824093848613	6.02876184500308	10.29229333598866
C	4.91064102881199	9.02788411439613	11.88193237893699
P	4.10775526125241	7.50614839246665	11.32451106990744
C	4.24364641514248	10.18816207369655	12.59374882762676
C	4.03001246320984	9.75075123478088	14.06421107531365
H	3.41330316594468	8.84125254325311	14.10494177920825
H	3.52865887158419	10.54556244988692	14.64292380069710
H	4.99626581020444	9.52470970687079	14.53777122836311
C	5.11639349306834	11.45088584492622	12.59398237735008
H	6.12026885685338	11.22865036139558	12.98664551250920
H	4.66650968056359	12.23470567669299	13.22540436421371
H	5.23524126561692	11.84808496614559	11.57996243516065
C	2.86723752680400	10.50417397801979	11.98791718165785
H	2.24211390042749	9.59857590699798	11.95780276310292
H	2.96128804031358	10.88199102242848	10.96341295037234
H	2.34258051477450	11.26494234278417	12.58883008732809

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