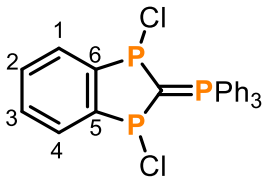
1. Experimental Section

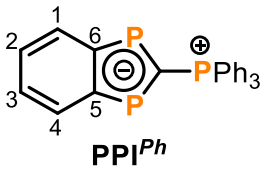
General Methods. All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques unless stated otherwise. Solvents were either obtained from an MBraun Solvent Purification System, or dried and stored according to common procedures.[1] Magnesium was activated by heating under vacuum followed by vigorous stirring for 3d under an argon atmosphere. Potassium graphite[2] and $Ph_3P{=}(C(TMS)_2)$[3] were synthesised according to a literature procedure. All other starting materials are commercially available and were used as obtained. NMR spectra were recorded with Bruker spectrometers at room temperature unless stated otherwise. No unexpected or unusually high safety hazards were encountered.

Synthetic procedures



$PPICl_2$

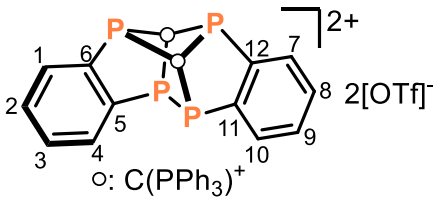
$C_6H_4(PCl_2)_2$ (2.16 g, 7.72 mmol, 1.00 eq.) was added to a solution of $Ph_3P{=}(C(TMS)_2)$ (3.25 g, 7.72 mmol, 1.00 eq.) in 1,2-difluorobenzene (DFB, 25 mL) and the mixture was stirred at room temperature for 20 h. Afterwards, the mixture was filtered to afford **$PPICl_2$** as a yellow solid (3.20 g, 86% yield). The crude product was used without further purification. **^{1}H NMR** (THF-d_8, 400.1 MHz): δ = 7.42 (ddt, $^3J_{HH}$ = 6.0 Hz, $^4J_{PP}$ = 3.2 Hz, $^5J_{PP}$ = 1.6 Hz, 2H, 2,3), 7.51 – 7.62 (m, 6H, *meta*-CH), 7.65-7.73 (m, 3H, *para*-CH), 7.74-7.87 (m, 8H, 1,4, *ortho*-CH) ppm. **^{31}P{^{1}H} NMR** (THF-d_8, 162.0 MHz): δ = 27.26 (t, $^2J_{PP}$ = 120.2 Hz, PR_3), 133.34 (d, $^2J_{PP}$ = 120.9 Hz, $C_3P_2Cl_2$) ppm.



PPI^{Ph}

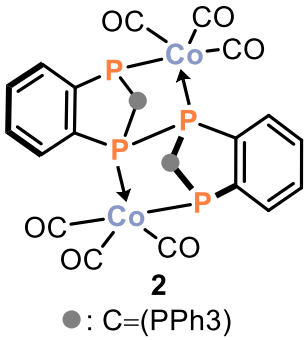
Magnesium (169 mg, 6.95 mmol, 1.10 eq.) was added to a solution of **$PPICl_2$** (3.20 g, 6.62 mmol, 1.00 eq.) in THF (25 mL). After 1 h of stirring, the mixture turned dark orange. After stirring for 20 h, volatiles were removed in vacuo and the residue was extracted with dichloromethane (DCM, 20 mL) and filtered through celite. Volatiles were again removed, and **PPI^{Ph} (2)** was obtained as a yellow solid (2.61 g, 96% yield). Crystals suitable for X-Ray diffracton measurements were obtained by layering a saturated THF solution with hexane (1:1 v/v) and storing for 2 d at -30 °C. **^{1}H NMR** (THF-d_8, 400.1 MHz): δ = 6.96 (ddt, $^3J_{HH}$ = 6.44 Hz, $^4J_{HH}$ = 3.3, $^5J_{HH}$ = 1.7 Hz, 2H, 2,3), 7.49 – 7.59 (m, 6H, *meta*-CH), 7.63 – 7.73 (m, 3H, *para*-CH), 7.77 – 7.87

(m, 6H, *ortho* -CH), 8.28 (dtd, $^{3}J_{HH}$ = 6.1 Hz, $^{4}J_{HH}$ = 3.0, $^{5}J_{HH}$ = 1.7 Hz, 2H, 1,4) ppm. **^{13}C{^{1}H} NMR** (THF-d_8, 100.6 MHz): δ = 119.51 (pt, $^{3}J_{CP}$ = 7.0 Hz, 2, 3), 126.15 (dt, $^{1}J_{CP}$ = 89.4 Hz, *ipso*-CP in PPh_3), 128.76 (d, $^{2}J_{CP}$ = 12.2 Hz, *meta*-C), 128.89-129.62 (m, 1, 4), 133.05 (d, $^{4}J_{CP}$ = 2.8 Hz, *para*-C), 134.23 (dt, $^{2}J_{CP}$ = 9.9 Hz, $^{4}J_{CP}$ = 2.8 Hz, *ortho*-C), 136.50 (q, $^{1}J_{CP}$ = 71 Hz, CP_3), 164.57 – 165.92 (m, 5, 6), ppm. **^{31}P{^{1}H} NMR** (THF-d_8, 162.0 MHz): δ = 25.77(t, $^{2}J_{PP}$ = 87.6 Hz, PR_3), 214.25 (d, $^{2}J_{PP}$ = 87.6 Hz, C_3P_2) ppm. **LIDFI-MS:** $[C_{25}H_{19}P_3]^+$ ([M]$^+$), m/z, calculated: 412.06996, found: 412.06784.



[1](OTf)$_2$

A mixture of **PPI^{Ph}** (800 mg, 1.94 mmol, 1.00 eq) and ferrocenium triflate (650 mg, 1.94 mmol, 1.00 eq.) was dissolved in DME and stirred at room temperature for 20 h. Afterwards, the mixture was filtered and the residue was washed with DME (3 x 5 mL) to obtain **[1](OTf)$_2$** as a white solid (640 mg, 59% yield). Using ferrocenium tetrafluoroborate as the oxidising agent, a significantly higher yield is obtained due to the lower solubility of the product in dme. Crystals of sufficient quality for single-crystal X-Ray diffraction measurements were obtained when a sample of [1](BF4)$_2$ was dissolved in DCM and layered with hexane. **$C_{52}H_{38}F_6O_6P_6S_2$·DME**, calculated (%): C 55.45, H 3.99; found (%): C 55.06, H 3.79. **^{1}H NMR** (CD_2Cl_2, 400.1 MHz): δ = 7.12 (p, 2H, 2, 3), 7.36 – 7.51 (m, 14 H, 8, 9, *meta*-CH), 7.53-7.62 (m, 14H, 7, 10, *ortho*-CH), 7.66 – 7.71 (m, 2H, 1, 4), 7.86 (t, $^{3}J_{HH}$ = 6.7 Hz, 6H, *para*-CH) ppm. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 100.6 MHz): δ = 51.36-53.31 (m, C_2P_2), 117.52 (d, $^{1}J_{CP}$ = 88.1 Hz, *ipso*-CP in PPh_3), 121.34 (q, $^{1}J_{CF}$ = 321.2 Hz, CF_3), 130.82 (p, 8, 9, *meta*-C, PPh_3), 131.57 (t, $^{3}J_{CP}$ = 18.7 Hz, 2, 3), 133.74 (t, $^{3}J_{CP}$ = 18.7 Hz, 1, 4), 134.36 (bs, 7, 10, *ortho*-C, PPh_3), 136.66 (s, *para*-C, PPh_3), 141.63 (pt, $^{1}J_{CP}$ = 10.5 Hz, 5, 6), 150.85 (t, $^{1}J_{CP}$ = 11.0 Hz, 11, 12) ppm. **^{31}P{^{1}H} NMR** (CD_2Cl_2, 162.0 MHz): δ = 26.9 (tdd, $^{2}J_{PP}$ = 29.2, 37.7 Hz, $^{3}J_{PP}$ = 20.3 Hz, PPh_3), 29.6 (dd, $^{2}J_{PP}$ = 29.2, $^{3}J_{PP}$ = 20.3 Hz, P_2), 45.7 (t, $^{2}J_{PP}$ = 37.8 Hz, C_2P_2), ppm.



A mixture of **PPI**^{Ph} (52 mg, 0.126 mmol, 2.00 eq.) and dicobalt octacarbonyl (21 mg, 0.063 mmol, 1.00 eq.) was suspended in acetonitrile and stirred at room temperature for 36 h. Afterwards, the mixture was filtered, and the residue was washed with acetonitrile until the filtrate was colorless (3 x 3 mL). After drying in vacuo, **2** was obtained as a yellow powder (56 mg, 77% yield). Crystals of sufficient quality for single-crystal X-Ray diffraction measurements were obtained by reacting [**1**](OTf)$_2$ with an excess of dicobalt octacarbonyl in acetonitrile upon warming to 50°C in an NMR tube. For the solid-state NMR spectroscopic measurements, different MAS frequencies were used: 13 kHz to obtain a good separation between spinning side bands and main resonances and 8 kHz to obtain a spectrum suitable for fitting with the program dmfit (see the section 3).[4] **$C_{56}Co_2H_{38}O_6P_6$**, calculated (%): C 60.56, H 3.45; found (%): C 59.90, H 3.67. **MAS ^{31}P SS NMR** (13 kHz, 121.5 MHz): δ = 15.5 (s, PPh_3), 92.7 (bs, P1), 181.5 (m, $^1J_{CoP}$ = 535 Hz, P2), ppm. **IR**: 3052 (w), 2017 (s), 1973 (s), 1939 (vs), 1588 (w), 1571 (w), 1483 (w), 1434 (m), 1310 (w), 1242 (w), 1185 (w), 1155(w), 1102 (vs), 1070 (s), 1025(w), 999(w), 939 (w), 926 (w), 838 (s), 740(s), 713(m), 690(s), 575(w), 556(s), 515(vs), 478 (s), 449(s), 436(s), 407(s).

2. X-Ray measurements & crystal structure data

The single-crystal X-ray diffraction data were recorded on Stoe StadiVari diffractometer using Mo-K_α (0.71073 Å) radiation. Semiempirical multi-scan absorption corrections were applied to the data. The structures were solved with SHELXS[5] and least-square refinements on F^2 were carried out with SHELXL.[5] The hydrogen atoms were located in idealised positions and refined isotropically with a riding model. Deposition Numbers 2389674 (**PPI**^{Ph}), 2389675 ([**1**](BF$_4$)$_2$) and 2389673 (**2**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe. Powder X-ray diffraction was used as a bulk analysis of **2**. Here, a STADI P (*Stoe & Cie GmbH*, Cu-$K_{\alpha1}$ = 1.54056 Å) with Ge monochromator, two goniometers and two L-PSD detectors (*Stoe* Mythen 1K) is used. The measurement was performed under the Debye-Sherrer geometry in short 18min measurements (2Θ = 5° - 90°) using a sample in a 0.3 mm sealed capillary prepared under argon atmosphere. The measured powder diffractogram matches the one calculated from the single-crystal structure (see Figure

S1). However, the broad baseline indicates the presence of amorphous components, hence **2** was further analysed by MAS ^{31}P SS NMR spectroscopy (see section 3, Figure S10 and S11).

Crystal data and structure refinement for **PPI^{Ph}**.

Empirical formula	$C_{25}H_{19}P_3$	
Formula weight	412.31	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.009(2) Å	α= 75.18(3)°.
	b = 10.093(2) Å	β= 67.70(3)°.
	c = 12.978(3) Å	γ = 81.28(3)°.
Volume	1170.6(5) Å^3	
Z	2	
Density (calculated)	1.170 Mg/m^3	
Absorption coefficient	0.261 mm^{-1}	
F(000)	428	
Crystal size	0.4 x 0.3 x 0.2 mm^3	
Theta range for data collection	2.412 to 25.350°.	
Index ranges	-12<=h<=11, -12<=k<=12, -15<=l<=15	
Reflections collected	13794	
Independent reflections	4269 [R(int) = 0.0156]	
Completeness to theta = 25.350°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.4678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4269 / 0 / 253	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0293, wR2 = 0.0763	
R indices (all data)	R1 = 0.0353, wR2 = 0.0788	
Largest diff. peak and hole	0.275 and -0.280 e.Å^{-3}	

Crystal data and structure refinement for [**1**]$(BF_4)_2$.

Empirical formula	$C_{52}H_{42}B_2C_{14}Cl_4F_8P_6$	
Formula weight	1168.09	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.612(3) Å	α = 98.95(3)°.
	b = 13.639(3) Å	β = 94.55(3)°.
	c = 15.969(3) Å	γ = 105.38(3)°.
Volume	2799.9(11) $Å^3$	
Z	2	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.444 mm^{-1}	
F(000)	1188	
Crystal size	0.3 x 0.3 x 0.2 mm^3	
Theta range for data collection	2.222 to 25.348°.	
Index ranges	-16<=h<=16, -16<=k<=16, -19<=l<=19	
Reflections collected	34306	
Independent reflections	10258 [R(int) = 0.0298]	
Completeness to theta = 25.348°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6452	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10258 / 0 / 654	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1011	
R indices (all data)	R1 = 0.0806, wR2 = 0.1122	
Largest diff. peak and hole	0.962 and -0.678 $e.Å^{-3}$	

Crystal data and structure refinement for **2**.

Empirical formula	$C_{56}H_{38}Co_2O_6P_6$	
Formula weight	1110.54	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.880(2) Å	α = 102.29(3)°.
	b = 11.111(2) Å	β = 101.18(3)°.
	c = 11.830(2) Å	γ = 108.62(3)°.
Volume	1270.1(5) $Å^3$	
Z	1	
Density (calculated)	1.452 Mg/m^3	
Absorption coefficient	0.893 mm^{-1}	
F(000)	566	
Crystal size	0.3 x 0.15 x 0.05 mm^3	
Theta range for data collection	2.340 to 25.028°.	
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14	
Reflections collected	11390	
Independent reflections	4602 [R(int) = 0.0375]	
Completeness to theta = 25.028°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5371	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4602 / 0 / 316	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1171	
R indices (all data)	R1 = 0.0897, wR2 = 0.1311	
Largest diff. peak and hole	0.725 and -0.319 $e.Å^{-3}$	

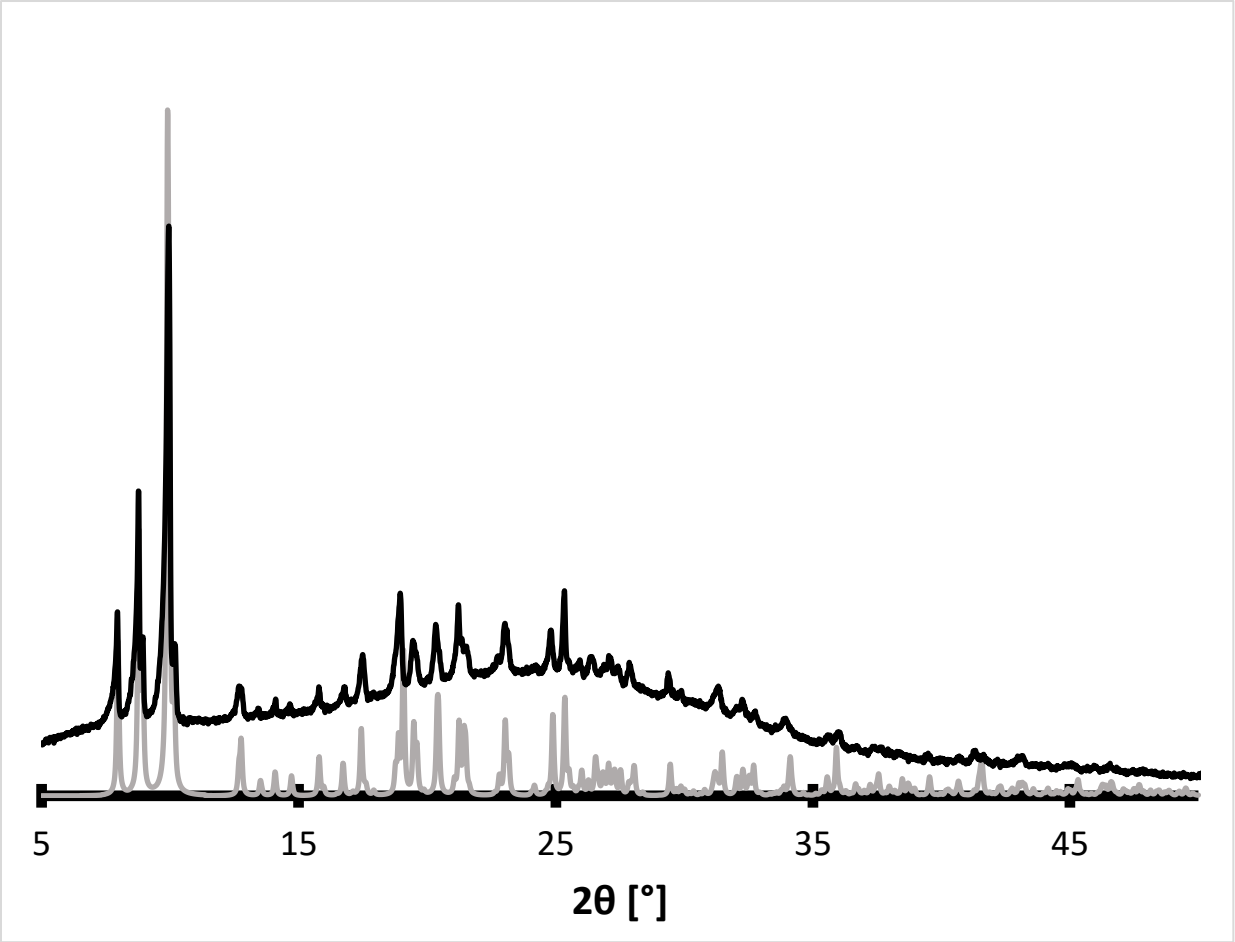


Figure S 1: Powder diffractogram of **2** (black: experimental spectrum, grey: spectrum predicted from the single-crystal structure).

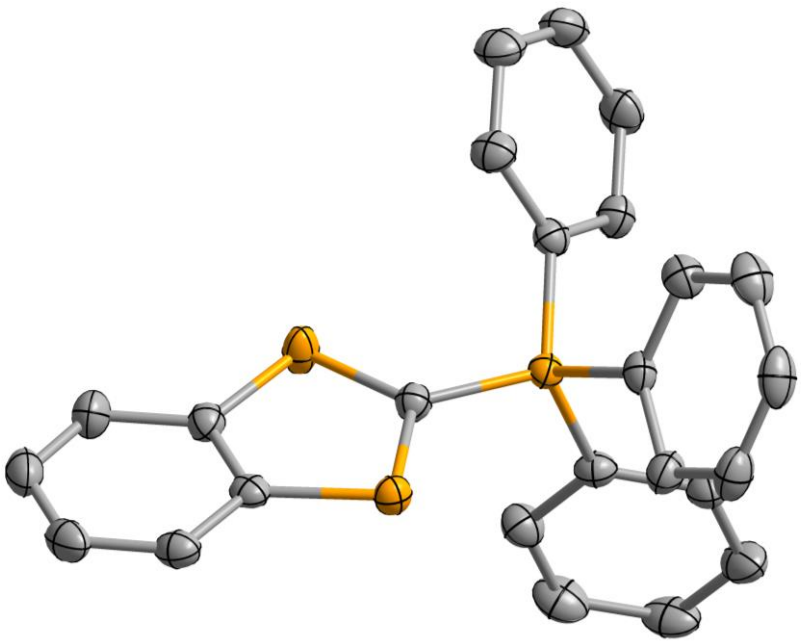


Figure S 2: Solid-state structure of **PPI^{Ph}**. Hydrogen atoms have been omitted for clarity.

3. NMR and IR spectra

$PPICl_2$

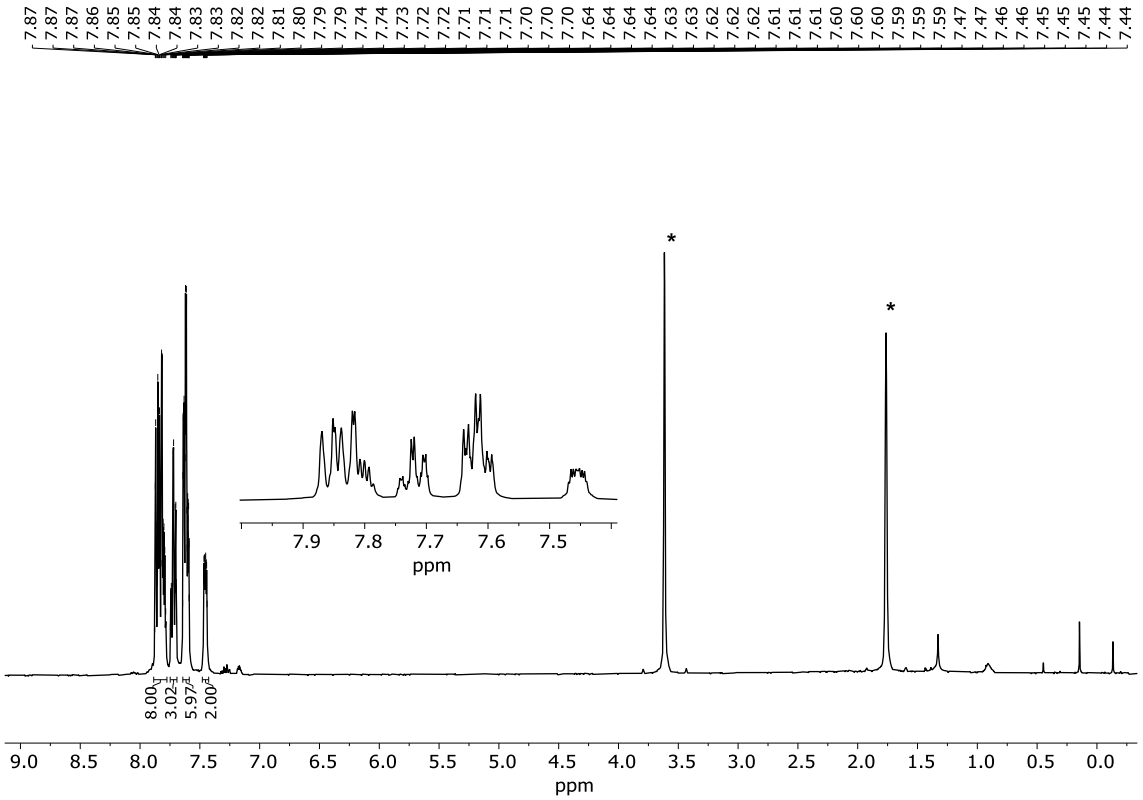


Figure S 3: ^{1}H NMR spectrum of **$PPICl_2$** in THF-d_8 (marked with a star *).

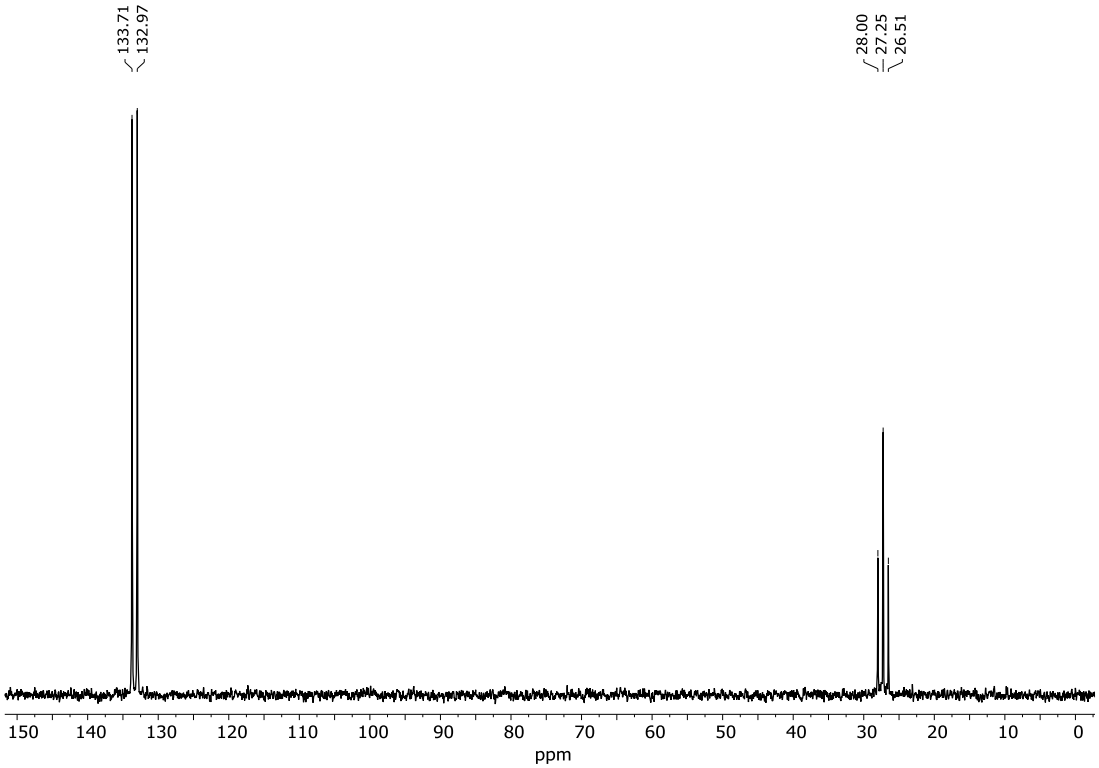


Figure S 4: $^{31}P\{^{1}H\}$ NMR spectrum of **$PPICl_2$** in THF-d_8.

PPI^{Ph}

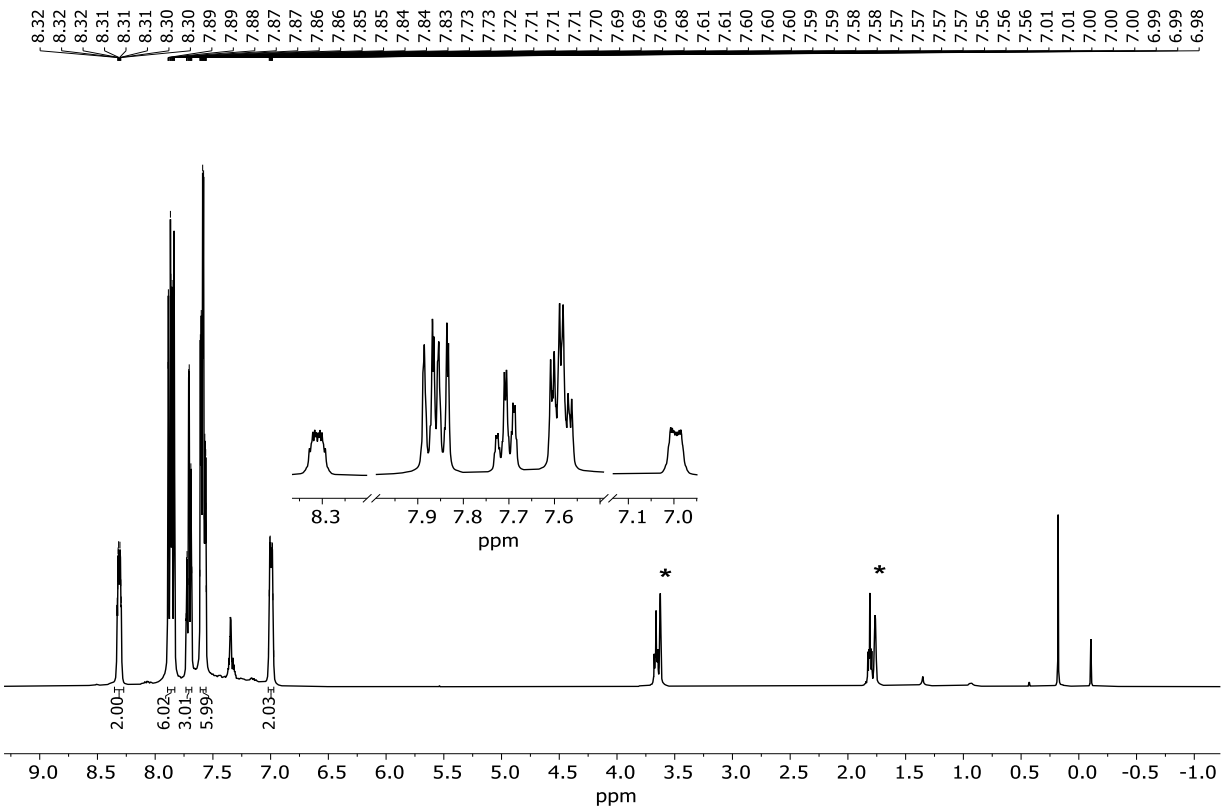


Figure S 5: ^{1}H NMR spectrum of **PPI^{Ph}** in THF-d_8 (marked with a star *).

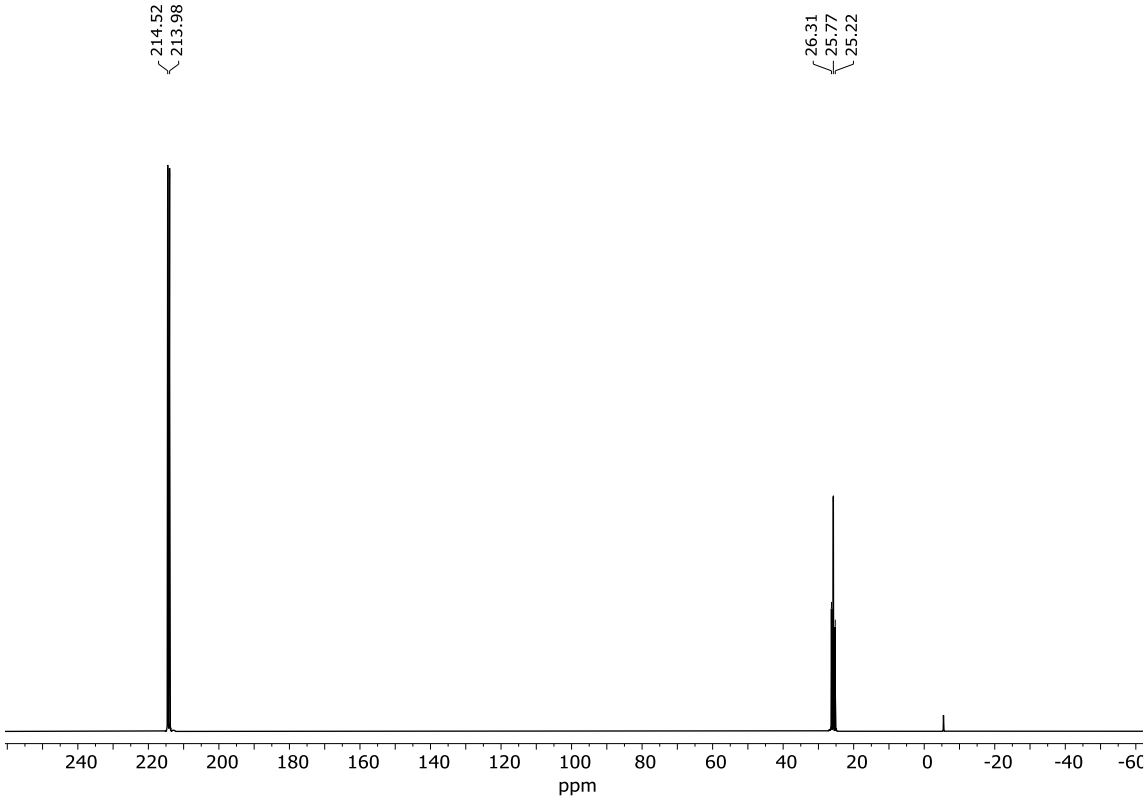


Figure S 6: ^{31}P{^{1}H} NMR spectrum of **PPI^{Ph}** in THF-d_8.

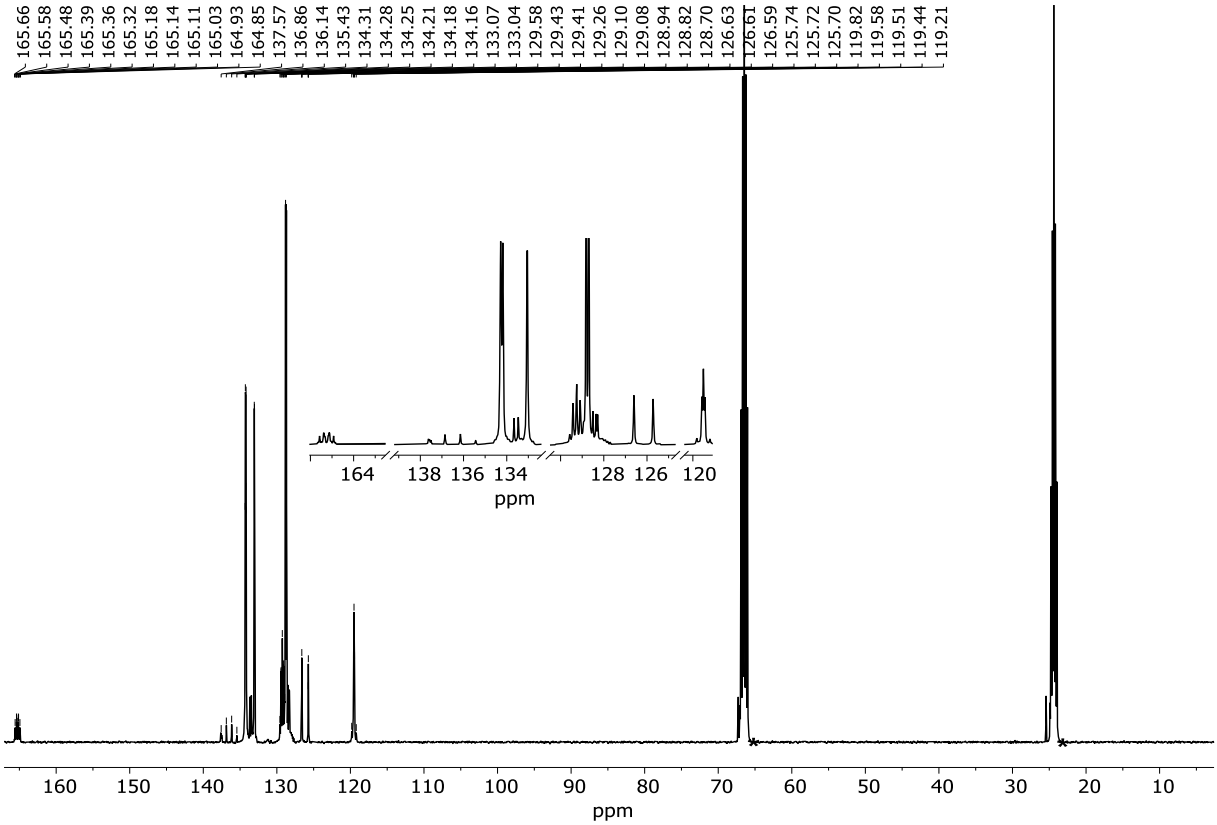


Figure S 7: $^{13}C\{^{1}H\}$ NMR spectrum of **PPI^{Ph}** in THF-d_8 (marked with a star *).

[1]OTf$_2$

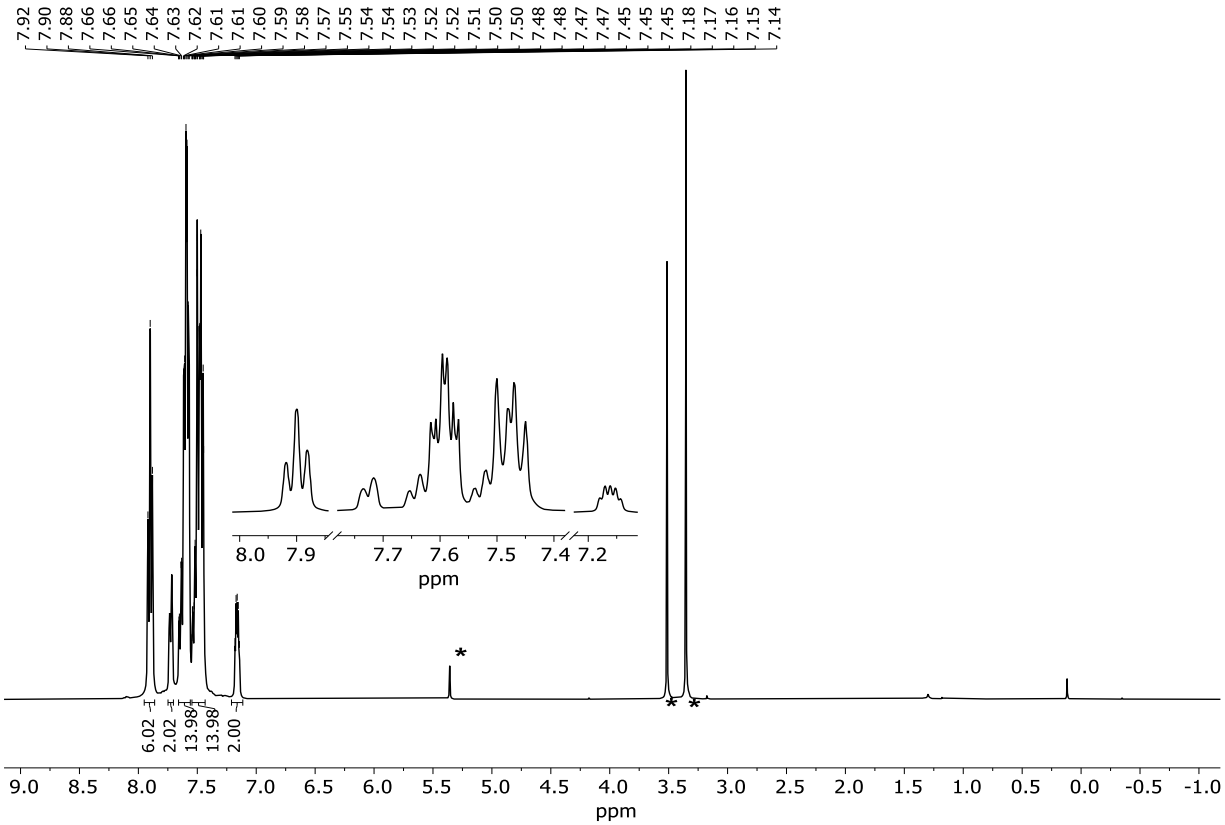


Figure S 8: ^{1}H NMR spectrum of **[1]OTf$_2$** in CD_2Cl_2 (CD_2Cl_2 and DME marked with a star *).

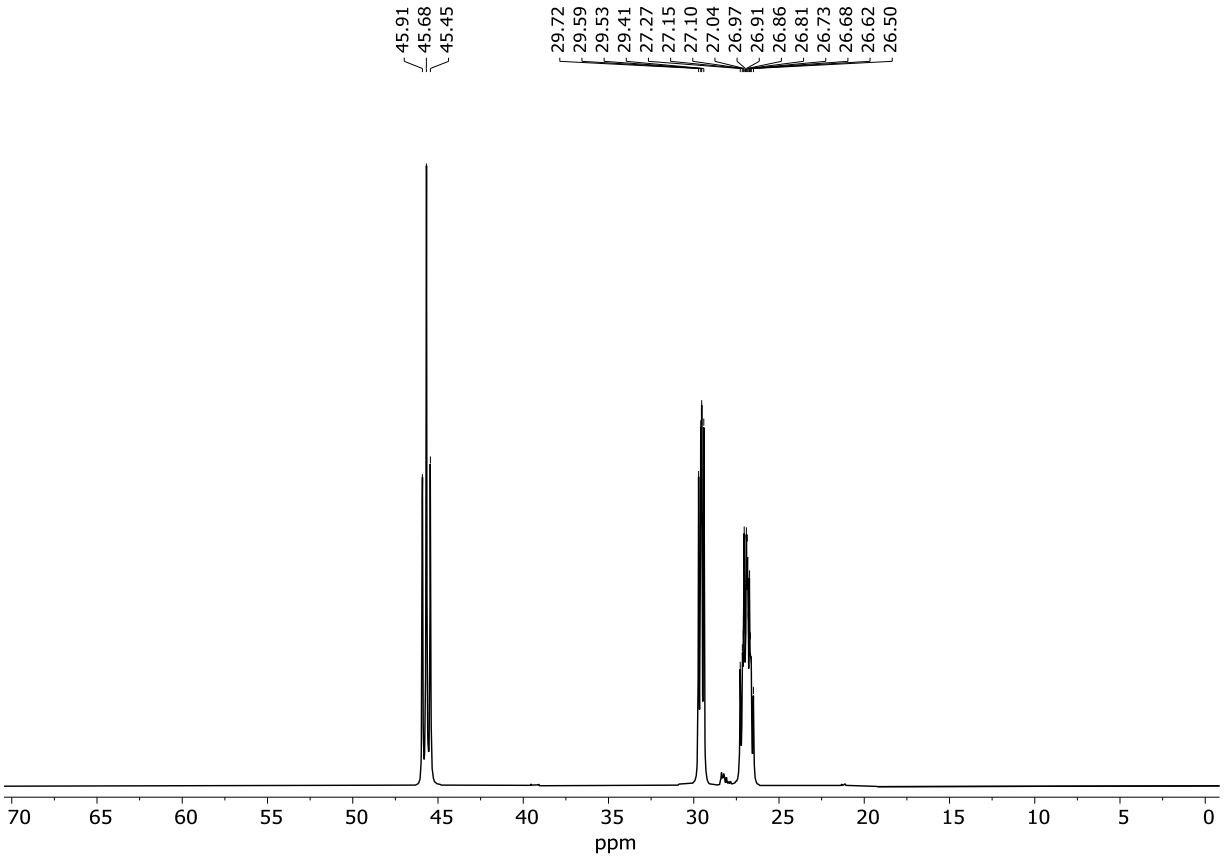


Figure S 9: $^{31}P\{^{1}H\}$ NMR spectrum of **[1]OTf$_2$** in CD_2Cl_2.

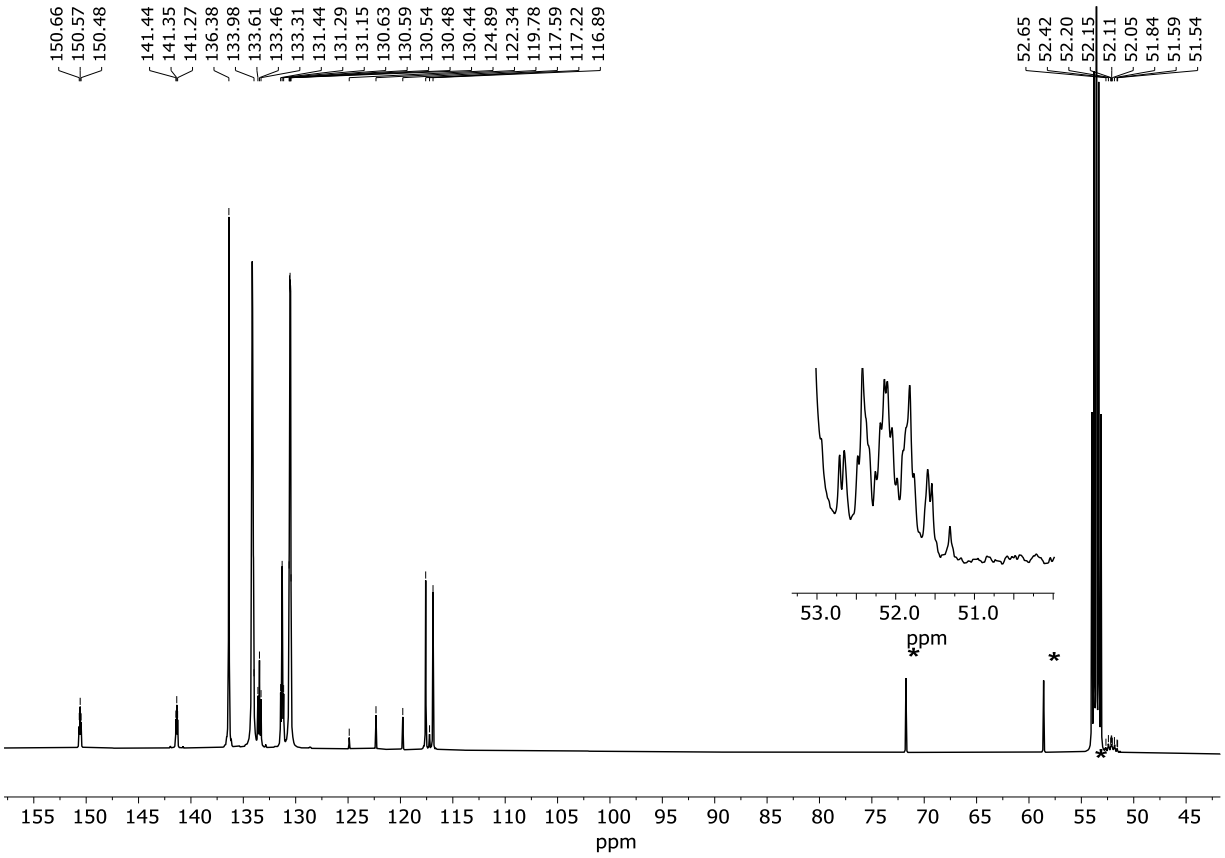


Figure S 10: $^{13}C\{^{1}H\}$ NMR spectrum of **[1]OTf$_2$** in CD_2Cl_2 (CD_2Cl_2 and DME marked with a star *).

2

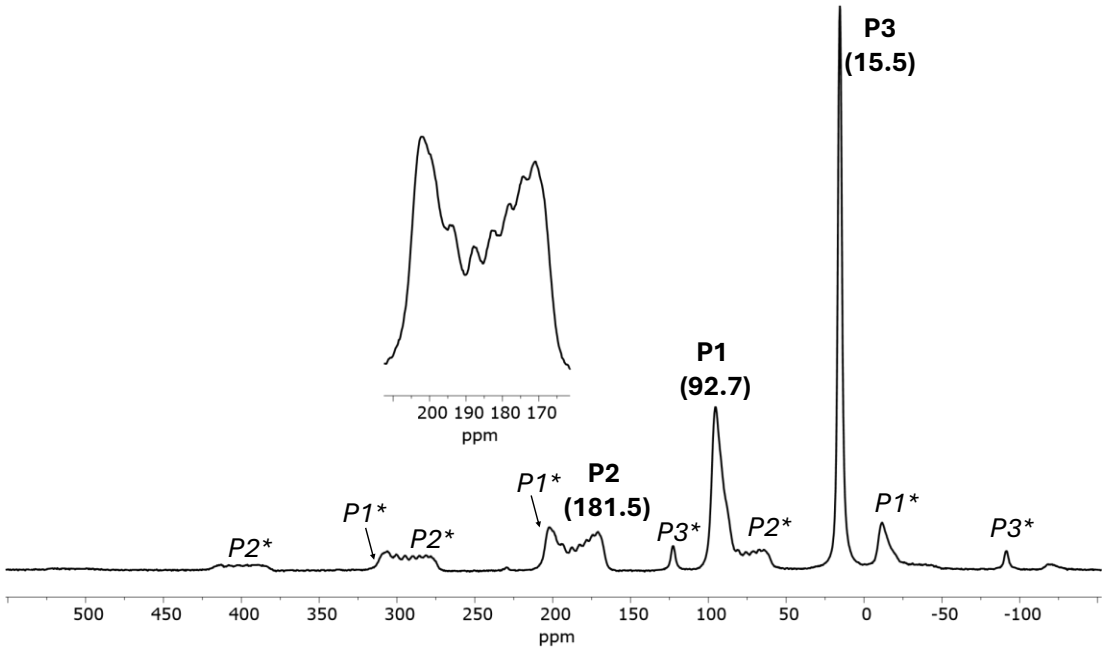


Figure S 11: MAS ^{31}P SS NMR spectrum of **2**. Spinning side bands are marked with a star (*).

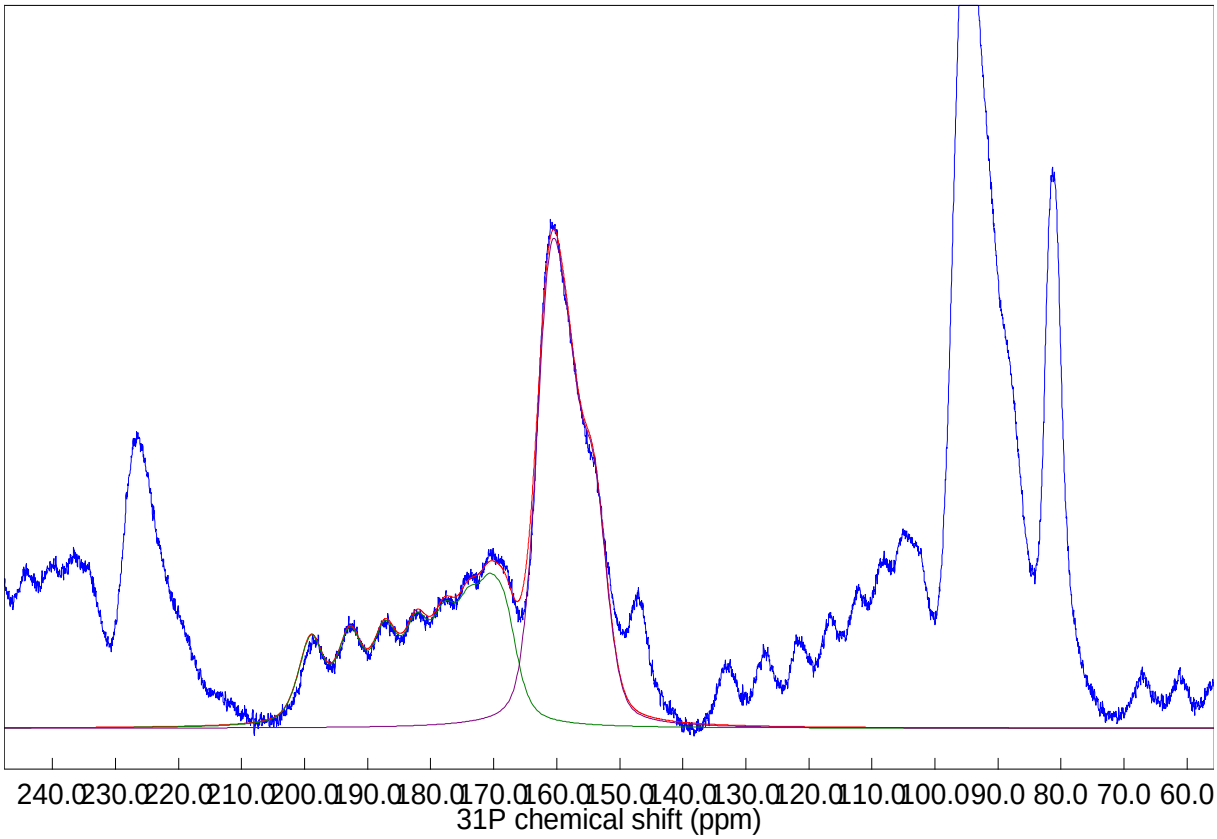


Figure S 12: Plot of the fitted resonance of P2 and a spinning side band of P1 generated by dmfit. Fit values: δ_1 = 181.5 ppm, J = 535 Hz, D_{quad} = -250 Hz; δ_2 = 158.6 ppm, J = 1 Hz, D_{quad} = 550 Hz.

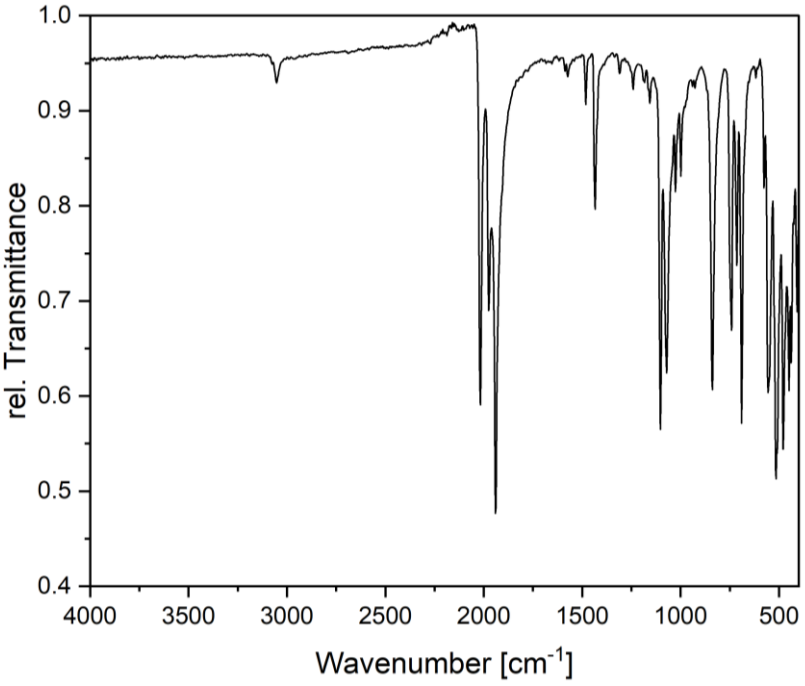


Figure S 13: ATR-IR spectrum of **2**.

4. Computational Details

4.1. Methods

All calculations were carried out with the ORCA 4.2 program package.[6,7] Unless stated otherwise, all calculations were carried out on isolated molecules (in the gas phase). Density fitting techniques, also called resolution-of-identity approximation (RI)[8], were used for GGA calculations and the RIJCOSX[9] approximation was used for hybrid-GGA DFT calculations. Atom-pairwise dispersion corrections[10,11] were used for all DFT calculations (BP86: D3BJ, M06: D3(0)). Pictures were rendered with the software ChimeraX. All geometries, thermal and entropic corrections were obtained at the BP86-D3BJ/def2-SVP level of theory. The spin-densities of [**PPI**^{Ph}]$^{\cdot+}$ and [**PPI**^{Ph}]$^{\cdot-}$ were calculated using M06/def2-TZVP.[12,13] NMR spectroscopic parameters of **2** were calculated using TPSS/def2-TZVP[14] (CP(PPP)[15] at Co) and localised orbitals of **2** were calculated using the same method but with the def2-TZVP basis set for all atoms.

4.2. NMR spectroscopic parameters of 2

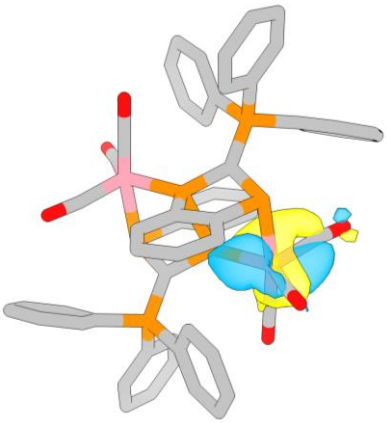
Table S1 shows the calculated NMR spectroscopic parameters of complex **2**. While the shifts of P1 and P3 are predicted with high accuracy, the calculated shift of P2 is less accurate. Still, the qualitative agreement, also with respect to the predicted J_{CoP} coupling constant allows for an assignment of the experimental spectrum.

Table S 1: Calculated NMR spectroscopic parameters of **2**.

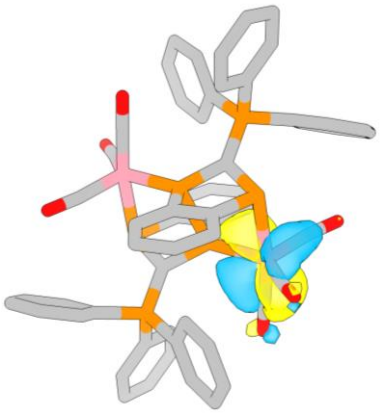
^{31}P nucleus (numbering according to Figure 3 in the main text).	Calculated absolute isotropic shielding constant [ppm]	Referenced calculated shift [ppm]	Experimental shift [ppm]
P1	209	100	92.7
P2	62 (J_{CoP} = 383 Hz)	249	181.5
P3	295	16	15.5

4.3 Electronic structure of 2

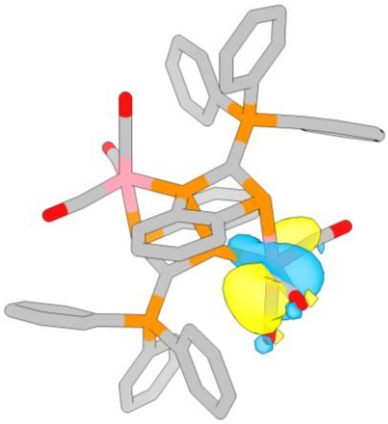
The intrinsic bond orbitals describing the electronic structure of one of the cobalt atoms are shown in Figure S 12. Here, orbitals 119, 120, 140 and 147 correspond to occupied 3d orbitals on Co. Orbital 118 is a dative bond between P2' and Co, being mostly located at P (76%). In contrast, orbital 187 corresponds to a very covalent bond between P and Co, with almost equal contributions of both centres. To gain a deeper insight into the nature of this covalent bond, CASSCF calculations were performed. Here, the two covalent Co–P bonding and respective antibonding orbitals obtained at the def2-SVP level were used as a starting point for the calculations, resulting in an active space of 4 electrons in 4 orbitals. When localised orbitals were used as the active space orbitals, orbitals displayed in Figure SX were obtained. These correspond to p-type orbitals on P and d-type orbitals on Co. From their occupation, the bond polarity can be deduced. Since the p-type orbitals display a higher occupation than the d-type orbitals (1.27 vs. 0.73) the Co–P bonds are polarised toward the **PPI** ligand making it a reduced ligand.



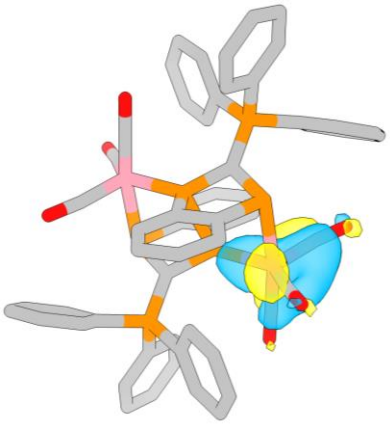
119 (85% Co)



120 (85% Co)



140 (78% Co)



147 (80% Co)

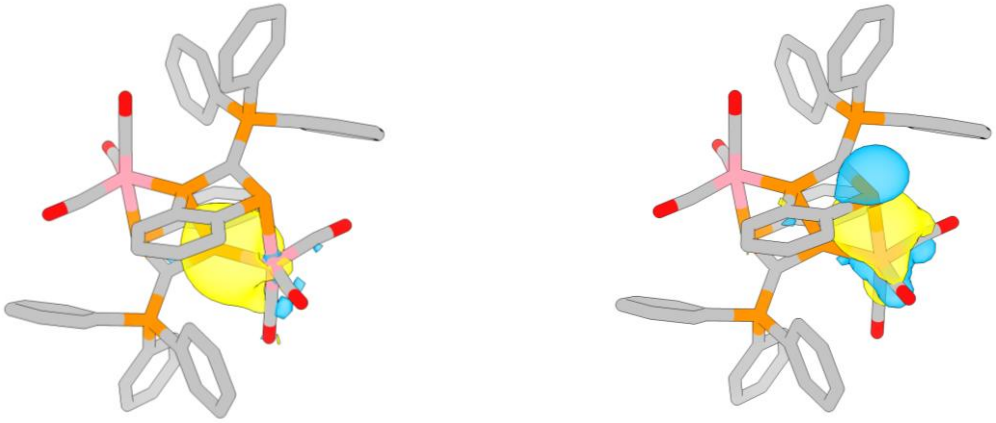
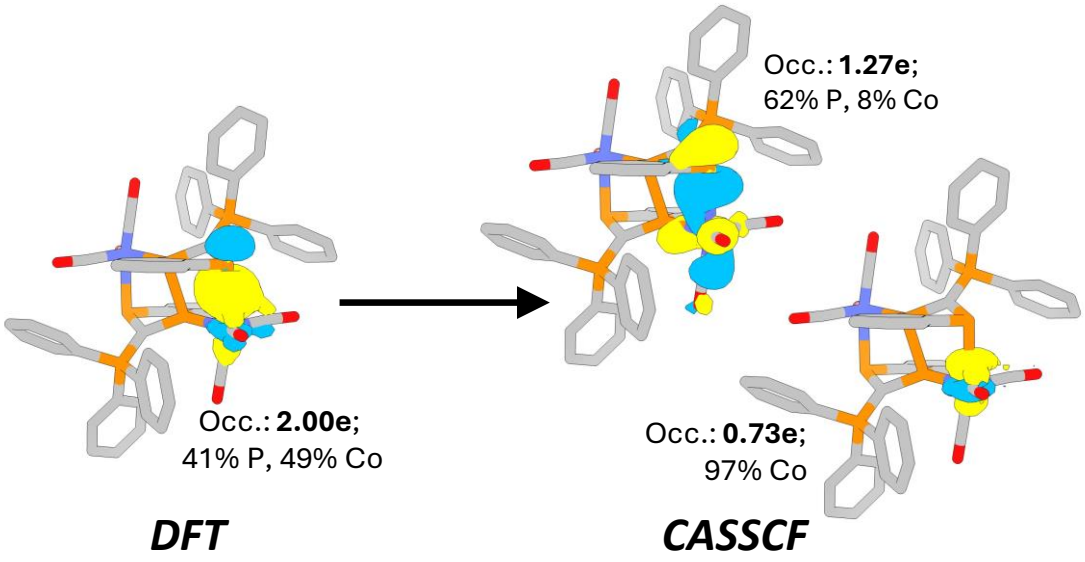


Figure S 14: Occupied intrinsic bond orbitals for one of the cobalt atoms in 2.



5. Cartesian coordinates of optimised structures

[PPI^{Ph}]$^{\cdot+}$

C	-2.23740985033153	-0.50200157645673	-1.85717089694209
C	-0.94933657866244	-0.19037616161177	-1.38041310527782
C	-2.64078850266423	-1.84159989609043	-1.99771888359433
C	-1.76266700950963	-2.89034597619820	-1.66347591989597

C	-0.46749832518705	-2.59481461038999	-1.18627700836918
C	-0.05561840700308	-1.22922759427099	-1.04340187948500
H	-0.64302947191417	0.86199716452575	-1.27332447804940
H	-3.64949500942853	-2.07415733309811	-2.36998068931751
H	-2.93144433827104	0.30999241564863	-2.12006370045539
H	-2.08808671064648	-3.93644640561822	-1.77544102572393
P	1.61401863024676	-0.94402638852364	-0.41944430242922
P	0.73753143256683	-3.85301005442202	-0.71914468280844
C	1.97400020725984	-2.66458443767323	-0.27474393120777
P	3.57568545033910	-3.22534533111043	0.28949395880383
C	4.41658149943227	-1.89261760854804	1.18246363999888
C	4.93763481084136	-0.80689199021497	0.44119540611379
C	5.54247665964344	0.26103403529048	1.11753999418500
C	5.63308344553178	0.24637336742368	2.52091893874774
C	4.51085197882299	-1.91258423808667	2.58899306571291
C	5.12241362957718	-0.83820746182958	3.25348234021890
H	5.20361565955195	-0.85213847780075	4.35034218109466
H	6.11225263195666	1.08556797312342	3.04693701113365
H	4.11796886409279	-2.76557608314640	3.16146687321071
H	5.94962579037583	1.10777989245020	0.54556283166915
H	4.88085432172855	-0.80169551829428	-0.65795400449011
C	4.63340651555662	-3.71114966812779	-1.09930603980761
C	4.06727800171670	-4.13698814425862	-2.31798871170187
C	4.90566181461523	-4.57092789858090	-3.35555853991901
C	6.29981498412283	-4.58035710311745	-3.17838231315032
C	6.86309029630501	-4.15382346488554	-1.96272424405720
C	6.03527385057261	-3.71611951568634	-0.91877882191533
H	6.47657436825859	-3.37292799014411	0.02922297198822
H	4.46679687293499	-4.89897934463132	-4.30928772941440
H	2.97568866221050	-4.12393791120384	-2.45849870563677
H	7.95479554183209	-4.15697460450247	-1.82759730768655

H	6.95383631834965	-4.91789254086475	-3.99623583480488
C	3.32975529234556	-4.64773393663318	1.38354474926242
C	2.29387015472044	-4.59742488709951	2.34473028761426
C	2.11613690238632	-5.67476271897135	3.22373098944457
C	2.95978065837211	-6.79708848877780	3.14247903727417
C	3.98451572782690	-6.84600150155364	2.18253159748346
C	4.17633658660945	-5.77193668484736	1.29971022548076
H	4.63713601766825	-7.72881650609889	2.11480983438584
H	4.97185985600528	-5.81417740967254	0.54135656322338
H	2.81276765552190	-7.64313630586955	3.83030510317264
H	1.31140892488958	-5.64084558513940	3.97292500296445
H	1.62801418882982	-3.72285549441104	2.40030015295677

[PPI^{Ph}]$^{\cdot-}$

C	-2.41962530567551	-0.55740382312095	-1.52875221708735
C	-1.18897061205266	-0.28466105553331	-0.93464477385722
C	-2.69760377814146	-1.85870957697731	-2.03263127984751
C	-1.74050185723367	-2.86728084158797	-1.93516890591312
C	-0.47294662318495	-2.61879427374670	-1.33404988615660
C	-0.18883949200337	-1.29382992666769	-0.82085159475498
H	-0.97677296102728	0.72610691665288	-0.54580125171388
H	-3.67362026221533	-2.06797773995373	-2.50089396740558
H	-3.18119197133350	0.23574474883110	-1.60983202069419
H	-1.95994209077629	-3.87498040039621	-2.32778629505130
P	1.41287434694062	-1.03115079686540	-0.06769518781614
P	0.81101614617017	-3.85275944510691	-1.14992876584654
C	1.92941987852513	-2.69917506907175	-0.39034898804799
P	3.50506904643323	-3.25069326151683	0.19911818732132
C	4.32263742441380	-1.86389857931626	1.07014850170134
C	5.04450229854752	-0.90911973585065	0.30512361324726
C	5.78260403250498	0.09168379645661	0.95241238951778
C	5.82463998955611	0.15481259203237	2.35692606837620

C	4.38943831127371	-1.81537376145821	2.48110473812880
C	5.12178160306809	-0.80739810047469	3.11961768070311
H	5.14567095149165	-0.76464348846549	4.22023744521709
H	6.40943849189884	0.94119148360180	2.85957247731876
H	3.85987306224964	-2.57864923940756	3.07173267151549
H	6.33206068529617	0.83485124382906	0.35187259733116
H	5.00646183302439	-0.95528591700807	-0.79376272761368
C	4.60974967004141	-3.76876778245899	-1.11817432286918
C	4.15551421641887	-3.99136881712907	-2.44356199267644
C	5.05194586585108	-4.37884579338468	-3.44176265925667
C	6.43254186143352	-4.54671673353159	-3.14853616553886
C	6.89354992616138	-4.29315234137252	-1.84456770807225
C	6.00867526140253	-3.88945915024406	-0.83422325105254
H	6.38951571327565	-3.64439739016559	0.16865472140409
H	4.67870349732869	-4.55801818755889	-4.46257389423030
H	3.08247359639299	-3.86787078907472	-2.66480820268450
H	7.96683613823844	-4.39293062257856	-1.61207219946730
H	7.13606935495324	-4.85531876098012	-3.93745130292695
C	3.33759504452916	-4.59368521757122	1.39034198219130
C	2.17583918795288	-4.60371256705455	2.22184530276409
C	1.98540879801232	-5.63941694338588	3.14533936117575
C	2.91955663324277	-6.68671938568614	3.26140812886392
C	4.05886011964245	-6.69246472549467	2.41540601653472
C	4.26525560705731	-5.66451392910810	1.49317780093525
H	4.78949965175720	-7.51483859969038	2.48030433326048
H	5.14353341192966	-5.68723563368071	0.83035321913534
H	2.76181365358432	-7.49786734224221	3.98899398758861
H	1.08523750486332	-5.63299290146704	3.78160713516484
H	1.43137213818027	-3.80007213501802	2.11571120118443

$[1]^{2+}$

P	-0.23751661313083	2.31405542517771	6.23484769071186
C	-1.67688375417940	3.55469173890236	-0.32172234438406
H	-2.02442199474710	4.25651054741188	0.45163123554620
P	0.89663709456166	3.88192855091616	0.74142381594099
C	0.13360467152170	3.82945417734652	2.39387904539674
P	-1.05810159502562	5.32250814266082	2.66118880662864
P	-1.85931204704628	4.38657698262691	4.58005394918458
C	0.19312934575620	6.34505951088830	3.54658000706403
P	-0.56679352274466	2.13429882856232	2.99514742395549
C	-0.30978028218909	3.20300527471732	-0.42121882338755
P	1.26547507344821	3.83683868649447	3.93241012607769
C	0.74405502005895	3.45755092029433	7.23492720814498
C	-2.37951060822944	2.27940631567714	2.83410517121752
C	1.22300318485686	5.63812514157484	4.21907684039714
C	-1.88425081114564	2.06966394727738	6.93155568197128
C	1.27607242234170	5.62423821315718	0.44314317762296
C	-2.24318317969768	2.63431971248631	8.17368523465256
H	-1.51355030287933	3.21766301013773	8.75380908525704
C	0.63499193734936	7.81057462092160	-0.39619733053951
H	-0.03143730932877	8.44078728659736	-1.00317713875977
C	0.28542696643089	4.78502854265771	7.41224505899223
H	-0.67270592417605	5.11175214377862	6.97910586188451
C	0.40954275745881	6.42628812991363	-0.32778130991712
H	-0.43040291783601	5.97366971077294	-0.87515869032538
C	4.63795839344971	2.61032343661158	-0.30464164082056
H	5.45423267330737	2.96734401796738	-0.94968863161073
C	-4.39124595441831	3.40944321260759	3.63923191547453
H	-4.87855079526942	4.16895303341085	4.26907632849927
C	-2.99400689804171	3.27059092800501	3.64222335782388
C	2.53981863912284	1.68566037306590	1.33702291204584
H	1.71624282062945	1.30946563571788	1.96233999370290

C	2.57877388767852	7.58077343617605	1.06143380824233
H	3.42499388631007	8.03235316087692	1.59909686065784
C	2.42508021078439	2.92127913615546	0.66020245376158
C	0.10281153160876	-0.38506733851872	6.80847879271035
H	-0.78901227499389	-0.27972708433814	7.44333330391899
C	4.75908529783261	1.38862487204111	0.37886748513181
H	5.67461596393143	0.78829061844786	0.26970892803769
C	0.59462226757693	0.71804397135740	6.07553891288260
C	-3.15646069062254	1.42859178343325	2.02769956899983
H	-2.67806202756045	0.65447786933509	1.40874249056905
C	1.71259626132970	8.38534157051320	0.29839363551774
H	1.88596253674505	9.47015020430074	0.23754196779856
C	2.19886413656555	6.32579601029794	4.96070608901577
H	2.99974045465832	5.77450887344471	5.47649234597273
C	2.36445458497607	6.19949113512997	1.14032819787406
H	3.03933957906281	5.57200721869961	1.74149276919868
C	1.12100544360116	8.43168534944156	4.36220841304808
H	1.09194621940213	9.53051458618055	4.41280324017592
C	2.39463223393420	-0.65718301071767	5.19202358508186
H	3.29592055903628	-0.76370106451489	4.57028829333402
C	-2.81411633936580	1.29849587264594	6.19407449732183
H	-2.53116700637307	0.84086115482123	5.23450680559954
C	0.14062043338155	7.74573476745495	3.61970144291324
H	-0.64866082632772	8.30339577924434	3.09382897007145
C	-2.59835901272744	2.99964540527009	-1.22026678960167
H	-3.66097795201816	3.27282862384003	-1.14397483308417
C	3.71028178781275	0.92804931844274	1.19474796665683
H	3.80027745913040	-0.03537617800434	1.71803098055078
C	2.13983410701476	7.72936084654310	5.03026004947311
H	2.90094683743805	8.28049727731189	5.60238169420157
C	3.47298422663594	3.38084144701600	-0.17011367049229

H	3.38104586838004	4.33511153771366	-0.70948937278871
C	-2.16644523321009	2.10159005052315	-2.21230975596441
H	-2.89389044747601	1.67093999342057	-2.91657527685770
C	-3.54346233859049	2.44151972060510	8.66589711258487
H	-3.82877610129650	2.87871898013614	9.63396498252527
C	-4.47357258894435	1.68936056146345	7.92866029204696
H	-5.49095561047924	1.54151437755155	8.32065642776070
C	0.12594305411600	2.30012938252186	-1.41701255423995
H	1.18744021430573	2.02159133035535	-1.49044614736449
C	1.97744419430026	3.04461293560486	7.78369658762939
H	2.32746723429795	2.01050860202018	7.65017063792614
C	-5.16586200328058	2.55840866603207	2.82745023478125
H	-6.26171803584634	2.65855616192763	2.82845713578888
C	-4.55523784527092	1.57764539544766	2.02552863076116
H	-5.17409414279683	0.91532613249530	1.40212745646987
C	-4.10798705702419	1.11511519777193	6.69711872766724
H	-4.83409678602156	0.51800875587801	6.12645087626902
C	1.90190263982806	-1.75912780224759	5.91445789169984
H	2.41477280780490	-2.73049210409564	5.85157843178916
C	1.74813492630057	0.58363212979072	5.26705063812456
H	2.14558069946435	1.44439463126481	4.70776448309135
C	0.76044987771008	-1.62174759650620	6.72160524282475
H	0.37823157466527	-2.48151442527845	7.29123164871253
C	2.29719943107348	5.28312289604306	8.68749435724188
H	2.90450264537097	5.99718661618876	9.26376109105543
C	-0.80801003431118	1.75336378794623	-2.30944087483778
H	-0.47107272496100	1.05053458178767	-3.08555020820148
C	1.06660791356113	5.69090289257577	8.14148793315217
H	0.71169143704295	6.72210555555145	8.28329389694317
C	2.75152770521784	3.96532189324348	8.50752720816558
H	3.71081354129385	3.64667147938703	8.94129423018169

C	-0.40622508189088	3.13453587221428	4.61489576107335

2

Co	3.51110507004929	5.30921104984493	3.53223406664628
P	2.07154850112486	4.01939961787527	4.60186589941785
P	0.93405462674602	1.66203817971105	2.81019118531098
P	-0.02710875618920	2.24622626379221	5.62835707592086
O	5.92721310408839	4.83038785062462	1.95370867715632
O	1.53434647249841	5.41088005363866	1.37780448173847
C	-0.65355322693133	1.95396412616740	1.94279758405560
O	3.59225947057592	8.13390506652326	4.32096138843307
C	0.94228219055920	-0.12715265946891	3.18841543346252
C	2.24851017194169	2.01726206577745	1.60961897863798
C	0.74356356056927	4.92289090937661	5.49867643297991
C	-1.31811979653910	3.16951208372874	2.19142978891854
H	-0.88836371363552	3.87380679600620	2.92108704310793
C	-1.18717723291135	1.02346177512943	1.02754056138729
H	-0.66700668425498	0.07073862669612	0.84322261924589
C	0.68941717839018	6.30231866500303	5.74923226189782
H	1.47863886148678	6.96424430200044	5.36786622816586
C	-0.24754333102349	4.04784616298506	6.01760996763161
C	1.94053839305138	2.32677013872564	0.26953116123110
H	0.89301143364970	2.40444205939347	-0.05351358779187
C	3.59291010822835	1.95768687503969	2.03291234640966
H	3.83130898371717	1.75812274029114	3.08481089043513
C	1.07575808412735	2.59309054673813	4.23692705167692
C	2.32591941675959	5.37138706249479	2.23212018895366
C	-1.31031526490118	4.58204746927869	6.77135986685310
H	-2.08463813150946	3.91538888734077	7.18066799587855
C	4.95539088742552	4.94813127993819	2.58874243847276
C	-0.22144005240729	-0.70427084456997	3.74257383923025

H	-1.13492373975079	-0.10178351604084	3.85530922754002
C	2.11602702411904	-0.89617009419663	3.05691206762916
H	3.02384179317777	-0.45152047318648	2.62490075669784
C	-2.51554657420289	3.45732980309961	1.51863158032580
H	-3.03622120546995	4.40732652091333	1.71214254104951
C	2.97812307688441	2.55673398488537	-0.64636254463426
H	2.73605556080641	2.81524520930727	-1.68818025101558
C	4.31735435842065	2.45823836872386	-0.23403799586568
H	5.13007255571980	2.63475821766416	-0.95481348117725
C	4.62191384947741	2.15335915556763	1.10199982206806
H	5.66573136859883	2.09822542821442	1.43864680892764
C	-2.38717939109723	1.31536287591768	0.36121772648233
H	-2.81056323447459	0.58919135719539	-0.34946093017164
C	-0.20372079188774	-2.04186714925159	4.16249386571660
H	-1.10838428628606	-2.48510471807241	4.60479368811507
C	3.52583299365957	6.99414957562186	4.08540609053628
C	-1.38020673672671	5.96874433385084	6.99568744352184
H	-2.22427426376928	6.38580457157407	7.56701843182948
C	-0.38435897735771	6.82672133378473	6.49191275606317
H	-0.44416099982920	7.91046534987007	6.67431695945043
C	-3.04973899515077	2.53181220513644	0.60589573107785
H	-3.99259844094109	2.75652064282730	0.08394163448538
C	0.96666519020433	-2.80707372692850	4.03322071680029
H	0.97932620951708	-3.85391105333981	4.37219760529525
C	2.12314540242884	-2.23397915547580	3.47933212783304
H	3.04126657637451	-2.83186895379004	3.37513218638843
P	2.96818976834946	3.07700622666670	6.48397667977823
P	4.10437632298351	5.43535909833748	8.27524659843852
P	5.06665539011277	4.85050361836546	5.45762396429099
C	5.69168192095134	5.14439177827255	9.14352940144193
C	4.09565409454096	7.22436570692935	7.89617159338188

C	2.78944046784527	5.08025493051560	9.47533337128653
C	4.29645950820166	2.17371972448776	5.58737678088361
C	6.35692824577554	3.92908879264285	8.89551233905742
H	5.92788907280623	3.22443791106913	8.16577664642904
C	6.22440435185860	6.07533053656047	10.05886621228323
H	5.70369595174709	7.02784702173384	10.24272268584363
C	4.35098304935098	0.79426912453135	5.33702446381437
H	3.56182683810043	0.13221835369821	5.71830390323306
C	5.28754189615413	3.04890087665490	5.06861913470592
C	3.09688638847800	4.77132525215050	10.81567625769951
H	4.14429196195045	4.69402804838687	11.13920877799276
C	1.44521740555584	5.13941960594671	9.05141452073678
H	1.20724947070300	5.33862212498953	7.99934351439054
C	3.96362328722162	4.50356074687751	6.84891228313293
C	6.35065480620991	2.51482473207647	4.31526117373934
H	7.12496337658795	3.18159377932612	3.90610757136497
C	5.25934123604362	7.80164061615587	7.34209974503599
H	6.17308396194663	7.19943422992265	7.22997283564506
C	2.92154999956571	7.99297860862269	8.02682274636711
H	2.01374088674355	7.54817608165625	8.45869797218064
C	7.55414110692668	3.64196597361198	9.56898625243747
H	8.07535234917798	2.69216782618859	9.37594626275285
C	2.05894884360237	4.54144869186321	11.73119066879130
H	2.30060712488024	4.28337249081595	12.77321114742728
C	0.71988138199645	4.63947114946178	11.31821814587572
H	-0.09313080796403	4.46302262173433	12.03867982757899
C	0.41584621435057	4.94382179971866	9.98193605365278
H	-0.62785680963646	4.99860205645951	9.64488105400756
C	7.42420261324965	5.78412654499813	10.72586387991533
H	7.84688565336955	6.51064710126934	11.43660300303210
C	5.24125610263104	9.13901577486373	6.92149430727670

H	6.14590133773138	9.58237748248619	6.47928115990718
C	6.42090659510166	1.12811413646692	4.09113472525080
H	7.26523846122180	0.71114920018096	3.52012467438622
C	5.42509104212351	0.26999508512857	4.59473123035874
H	5.48518336185269	-0.81376444991498	4.41251402563323
C	8.08744681440473	4.56793033434571	10.48178984767872
H	9.03014532556037	4.34376964213979	11.00426966735777
C	4.07052902069351	9.90383627340212	7.04997322105668
H	4.05757901471037	10.95049396714484	6.71045312422385
C	2.91406804133364	9.33057220563121	7.60372723585166
H	1.99567938784347	9.92816449303204	7.70727146507989
Co	1.52866498184254	1.78698772752251	7.55342246950279
O	-0.88730972392427	2.26547939954226	9.13225215690604
O	3.50561682438276	1.68486183093513	9.70766042877966
O	1.44730488956545	-1.03750915752665	6.76401944134485
C	2.71396906387194	1.72452250702881	8.85342235943710
C	0.08446798807901	2.14788600789023	8.49712214973166
C	1.51382449410629	0.10218151304828	6.99986341117792

CO

C	0.000000	0.000000	-0.004434
O	0.000000	0.000000	-1.146506

3

Co	1.832296	5.674021	2.545020
P	1.026106	4.496205	4.092593
P	0.847620	1.758263	2.803396
P	-0.062873	2.161021	5.727890
O	1.301103	4.708130	-0.178580
O	1.068026	8.483021	2.976005
C	-0.398629	2.016486	1.504225

O	4.761182	5.729218	2.663755
C	0.716301	0.005137	3.274156
C	2.499488	2.033485	2.102159
C	0.508860	4.877941	5.763989
C	-1.148516	3.207201	1.464666
H	-0.992037	3.979406	2.232526
C	-0.582066	1.021596	0.518862
H	-0.011235	0.081414	0.567133
C	0.590714	6.167141	6.339617
H	0.983279	7.003630	5.740381
C	-0.002663	3.775721	6.527342
C	2.721075	2.011468	0.712927
H	1.881250	1.875957	0.017456
C	3.568319	2.257137	2.997003
H	3.376310	2.300780	4.079594
C	0.601680	2.779288	4.212170
C	1.360006	7.363353	2.827259
C	-0.421243	4.003104	7.864254
H	-0.814449	3.165631	8.462908
C	1.494112	5.062981	0.919059
C	-0.555268	-0.508013	3.611981
H	-1.445909	0.134701	3.545855
C	1.858329	-0.815248	3.348319
H	2.844959	-0.410572	3.078039
C	-2.070723	3.407614	0.426886
H	-2.649905	4.342090	0.390384
C	4.015597	2.232798	0.218901
H	4.185911	2.248046	-0.867778
C	5.080673	2.459015	1.104874
H	6.090566	2.650073	0.712034
C	4.858091	2.464348	2.493158

H	5.688395	2.663775	3.185859
C	-1.505668	1.232703	-0.514919
H	-1.650388	0.459980	-1.284904
C	-0.675211	-1.840179	4.030796
H	-1.664419	-2.240167	4.299169
C	3.596282	5.717447	2.602203
C	-0.336521	5.283051	8.418210
H	-0.664991	5.452331	9.455266
C	0.168324	6.365689	7.656882
H	0.228767	7.368841	8.105868
C	-2.247236	2.426357	-0.562043
H	-2.970170	2.590188	-1.375609
C	0.464350	-2.660242	4.108218
H	0.365925	-3.706211	4.436290
C	1.727022	-2.149514	3.765094
H	2.617934	-2.792826	3.820983

4

Co	2.186187	5.856633	2.692192
P	1.990423	3.905252	4.603755
P	0.874852	1.680578	2.850389
P	-0.900726	2.951550	5.025682
O	1.596928	5.182417	-0.105259
O	-0.618194	6.027531	3.587286
C	-0.314851	1.948933	1.497843
O	2.786308	8.728342	2.947684
C	0.725794	-0.073003	3.343047
C	2.539663	1.854798	2.143669
C	1.058101	4.677027	5.947864
C	-0.901057	3.222518	1.358447
H	-0.703037	4.000006	2.107243

C	-0.583909	0.930828	0.559538
H	-0.138283	-0.067858	0.681229
C	1.586131	5.698123	6.770663
H	2.610371	6.063840	6.595515
C	-0.283660	4.214990	6.150681
C	2.724469	2.302688	0.822884
H	1.856484	2.539906	0.192841
C	3.653227	1.559324	2.961894
H	3.503939	1.208926	3.993831
C	0.645210	2.816156	4.161911
C	0.514579	5.919127	3.335919
C	-1.058153	4.785884	7.194134
H	-2.089947	4.437313	7.360586
C	1.835061	5.421137	1.010572
C	-0.160433	-0.450082	4.372316
H	-0.727160	0.322436	4.918593
C	1.475192	-1.055071	2.658646
H	2.183248	-0.759577	1.869639
C	-1.745941	3.479675	0.268205
H	-2.199782	4.475636	0.158751
C	4.025848	2.466950	0.322749
H	4.169292	2.834740	-0.703916
C	5.133651	2.177242	1.134137
H	6.152531	2.317409	0.743086
C	4.947095	1.720304	2.450714
H	5.816089	1.503916	3.089220
C	-1.431412	1.197177	-0.525652
H	-1.646130	0.404790	-1.258489
C	-0.300043	-1.805209	4.706799
H	-0.989056	-2.096097	5.514005
C	2.557320	7.592856	2.858876

C	-0.518414	5.789594	8.001092
H	-1.127384	6.231073	8.805095
C	0.803480	6.250227	7.788830
H	1.215219	7.047356	8.426492
C	-2.008125	2.471581	-0.673654
H	-2.671587	2.676650	-1.527620
C	0.439016	-2.784772	4.021122
H	0.327654	-3.846495	4.289111
C	1.327407	-2.408513	2.999672
H	1.915240	-3.171993	2.467939
C	3.869166	5.245034	2.887176
O	4.982427	4.915040	2.943474

[$Co_2(CO)_8$]

Co	1.781540	1.390492	5.374674
O	2.388044	4.186391	6.141717
O	0.686151	-1.180197	4.433846
O	-0.728129	1.317920	6.946502
C	1.046182	-0.067183	4.306850
C	2.144239	3.101455	5.828416
C	0.244273	1.347817	6.323323
C	2.953256	0.384724	6.290669
O	3.688035	-0.226349	6.940169
Co	1.195406	1.306941	2.939326
C	2.903223	1.665547	3.810290
O	4.015644	1.928709	3.531479
C	1.850130	0.243077	1.650529
C	-0.602744	1.215894	2.778189
C	1.282339	2.986798	2.276205
O	2.220505	-0.407559	0.770364
O	-1.748386	1.145683	2.647460

O 1.340323 4.050518 1.829572

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