Electronic Supplementary Material (ESI) for Chemical Science.

Formation of an imidazoliumyl-substituted $[(L_C)_4P_4]^{4+}$ tetracation and transition metal mediated fragmentation and insertion reaction (L_C = NHC)

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Supporting Information

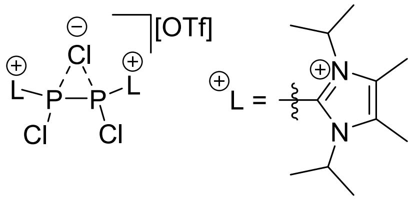
This PDF file includes:

S1. General remarks

General Considerations: All reported relevant compounds are fully characterized by multinuclear NMR spectroscopy, IR- and Raman spectroscopy, elemental analysis and X-ray crystallography. Manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified nitrogen or nitrogen or argon, respectively. Dry, oxygen-free solvents (CH_2Cl_2, CH_3CN, C_6H_5F, *o*-$C_6H_4F_2$ (distilled from CaH_2), *n*-hexane, *n*-pentane (distilled from potassium)) were employed. Deuterated benzene (C_6D_6) was purchased from Sigma-Aldrich and distilled from potassium. Anhydrous deuterated acetonitrile (CD_3CN) and dichloromethane (CD_2Cl_2) were purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored over molecular sieves (4 Å: CH_2Cl_2, CD_2Cl_2, C_6H_5F, $C_6H_4F_2$, C_6D_6, *n*-hexane; 3 Å: CH_3CN, CD_3CN)). All glassware was oven-dried at 160 °C prior to use. Compounds **4**[OTf][S1], **6**[S2] and AuCl(tht)[S3] were prepared according to procedures given by literature. Reagents $Fe_2(CO_9)$, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ were purchased from Sigma Aldrich and used as received. NMR spectra were measured on a Bruker AVANCE III HD Nanobay (^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{31}P (161.98 MHz) ^{19}F (376.50 MHz), ^{29}Si (79.94 MHz), ^{195}Pt (86.01 MHz)) 400 MHz UltraSield or on a Bruker AVANCE III HDX, 500 MHz Ascend (^1H (500.13 MHz), ^{13}C (125.75 MHz), ^{31}P (202.45 MHz) ^{19}F (470.59 MHz)). All ^{13}C NMR spectra were exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the ^{13}C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to $\delta_{TMS} = 0.00$ ppm (^1H, ^{13}C, ^{29}Si), $\delta_{CFCl3} = 0.00$ ppm (^{19}F), $\delta_{H3PO4(85\%)} = 0.00$ ppm (^{31}P) and $\delta_{K2PtCl6} = 0.00$ ppm (^{195}Pt). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. For P_7 compound **6**$^{3+}$ which gives rise to a higher order spin-system in the $^{31}P\{^1H\}$ NMR spectrum, the resolution-enhanced $^{31}P\{^1H\}$ spectrum was transferred to the software gNMR, version 5.0.[S3] The full line shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum. ^1J(PP) coupling constants were set to negative values,[S5] and all other signs of the coupling constants were obtained accordingly. The designation of the spin system was performed by convention. The furthest down field resonance is denoted by the latest letter in the alphabet, and the furthest upfield by the earliest letter. Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on a Vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS mode.

S2. Experimental details

S2.1. Reaction of 4[OTf] with Mg to 5[OTf]



Compound **4**[OTf] (160 mg, 0.37 mmol) and Mg (10 mg, 0.40 mmol) were combined together and THF (4 ml) was added. The suspension turned into a yellowish solution after 30 min reaction time at room temperature. After 12 h the yellow suspension was filtered and the filtrate was concentrated to 2 ml and stored at –35 °C. NMR spectroscopic investigation of the filtrate revealed the formation of compound **5**[OTf]. Single crystals suitable for X-ray analysis were obtained from the filtrate which was stored at –35 °C.

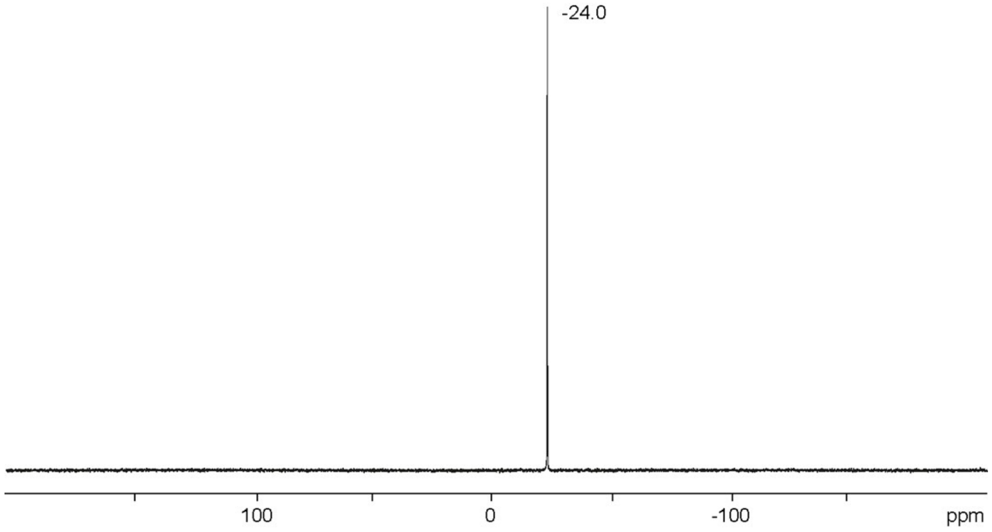


Figure S1. ^{31}P NMR spectrum of **5**[OTf] (300 K, C_6D_6 capillary).

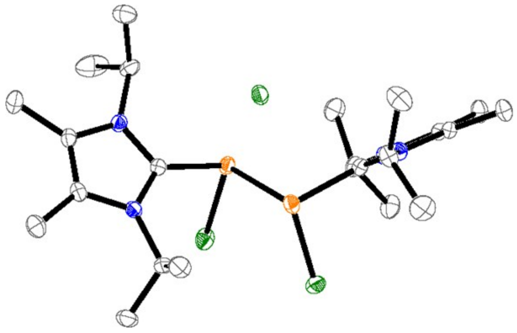
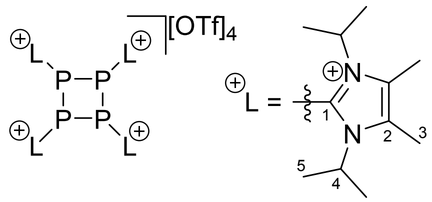


Figure S2. Molecular structure of **5**$^+$ in **5**[OTf]·CH_2Cl_2; hydrogen atoms, solvate molecule and anion are omitted for clarity and thermal ellipsoids are displayed at 50% probability.

S2.2. Preparation of $[(L_C)_4P_4][OTf]_4$ ($3[OTf]_4$)



A fluorobenzene solution (4 ml) of 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**6**) (254 mg, 1.12 mmol) was added dropwise to a solution of **4**[OTf] (484 mg, 1.12 mmol) in fluorobenzene (6 ml). During the addition the reaction solution turned into a red suspension. The red suspension was stirred for 12 h. After Filtration and washing the residue with fluorobenzene (3 x 3 ml) **3**$[OTf]_4$ was dried *in vacuo* and obtained as colorless, air and moisture sensitive solid.

Yield: 345 mg (86%); **m.p.**: 259 °C - 261 °C; **Raman** (50 mW, in cm^{-1}): ν = 2983(17), 2948(27), 1609(26), 1454(14), 1411(26), 1389(15), 1354(29), 1307(9), 1273(100), 1252(16), 12248(, 1190(6), 1151(19), 1107(5), 1091(10), 1032(19), 1012(5), 978(5), 961(5), 887(7), 796(11), 755(12), 696(7), 584(7), 574(9), 545(8), 506(26), 460(10), 447(10), 414(7), 403(8), 394(9), 360(15), 348(17), 313(11), 281(9), 212(9); **IR** (ATR, in cm^{-1}): ν = 3394(vw), 2997(vw), 2947(vw), 1732(vw), 1685(vw), 1607(w), 1545(vw), 1489(w), 1468(w), 1444(w), 1410(w), 1398(w), 1377(w), 1340(w), 1266(s), 1246(vs), 1220(s), 1145(s), 1091(w), 1027(vs), 976(w), 934(w), 904(vw), 845(vw), 795(w), 753(w), 690(w), 634(vs), 572(m), 516(s), 483(vw), 467(vw), 398(w), 372(vw); **^{1}H NMR** (CD_3CN, 300 K, in ppm): δ = 1.68 (48H, d, $^3J_{HH}$ = 6.81 Hz, 5H), 2.46 (24H, s, H3), 5.64 (8H, s(br), H4); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 10.65 (8C, s, C3), 20.81 (16C, s, C5), 55.21 (8C, s(br), C4), 120.95 (4C, q, $^1J_{CF}$ = 323 Hz, -CF_3), 133.34 (4C, s(br), C1), 134.90 (8C, s, C2); ^{19}F NMR (CD_3CN, 300 K, in ppm): δ = –79.3 (12F, s, -CF_3); **^{31}P NMR** (CD_3CN, 300 K, in ppm): δ = –55.7 (4P, s); **elemental analysis**: calculated for $C_{48}H_{80}F_{12}N_8O_{12}P_4S_4$: C: 40.0, N: 7.8, H: 5.6, S: 8.9; found: C: 39.8, N: 7.8, H: 5.4, S: 9.3.

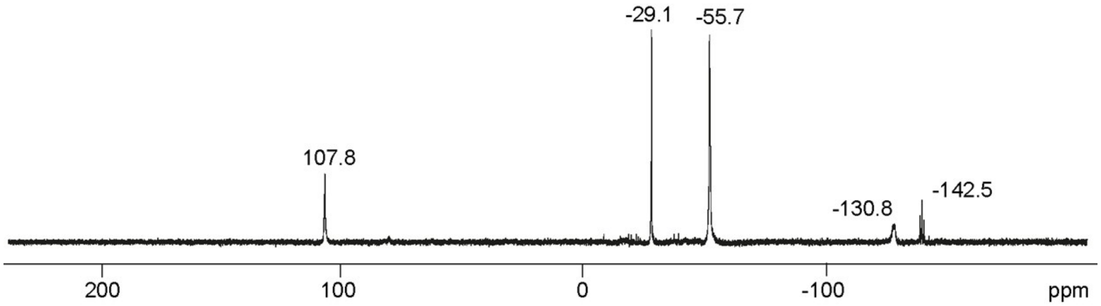


Figure S3. ^{31}P NMR spectrum of the reaction of **4**[OTf] with **6** after 3 h (240 K, THF-d$_8$). The resonances can be assigned as follows: δ(P) = 107.8 ppm to **4**$^+$; δ(P) = –29.1 ppm to intermediate **7**$^{2+}$; δ(P) = –55.7 ppm to **3**$^{4+}$; and AB$_2$ spin system δ(P$_A$) = –142.5 ppm, δ(P$_B$) = –130.8 ppm to **8**$^{3+}$.

S2.3. Reaction of 4[OTf] with 6 and one equivalent of *n*Bu$_4$N[Cl]

Compound **4**[OTf] (40 mg, 0.09 mmol), **6** (21 mg, 0.09 mmol) and *n*Bu$_4$N[Cl] (25 mg, 0.09 mmol) were combined and 1.5 ml THF was added. The vigorously stirred reaction mixture turned immediately red upon addion of the solvent and slowly into orange. After 12 h the supernatant was investigated by means of ^{31}P NMR spectroscopy which revealed three singlet resonaces at δ(P) = –124.3 ppm, δ(P) = –54.8 ppm and δ(P) = –30.3 ppm which we assign to **10**$^+$, **3**$^{4+}$ and **7**$^{2+}$, respectively. After 30 h, the ^{31}P NMR spectrum gives rise to an additional resonance at δ(P) = –21.8 ppm being assigned to chloride-bridged cation **5**$^+$. From this reaction we conclude that the addition of a chloride source quenches the reduction process by the reaction with **6** and slowly forms chloride-bridged cation **5**$^+$ by the reaction with **7**$^{2+}$. In addition, we observe a Cl$^–$ induced degradation[S6] leading to the formation of **10**$^+$.

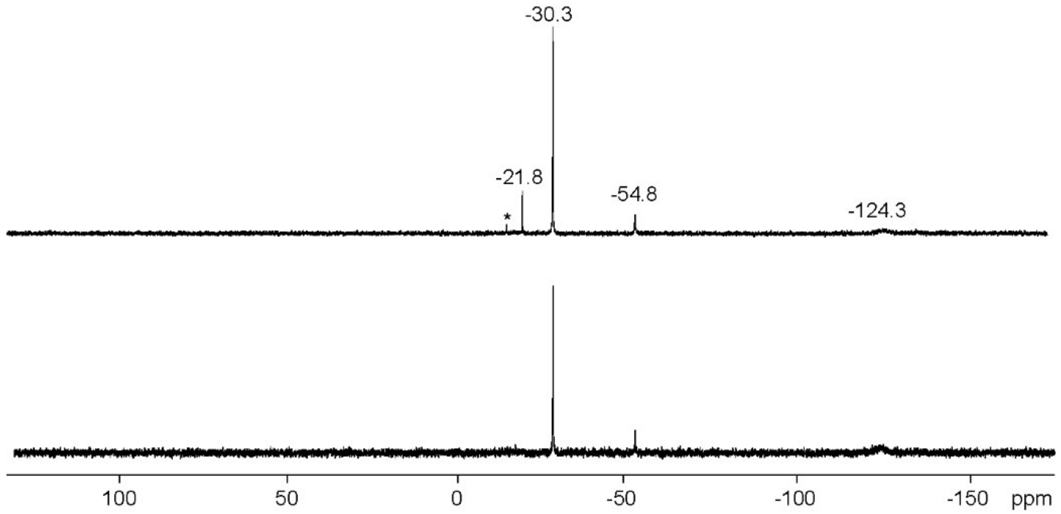
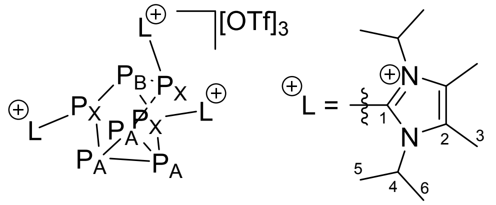


Figure S4. ^{31}P NMR spectra of the reaction of **4**[OTf] with **6** and one equivalent of *n*Bu$_4$N[Cl] after 12 h (bottom; top; 300 K, C$_6$D$_6$-capillary) and after 30 h (top; 300 K, THF-d$_8$). The resonances can be assigned as follows: δ(P) = –124.3 ppm to **10**$^+$; δ(P) = –54.8 ppm to **3**$^{4+}$; δ(P) = –30.3 ppm to **7**$^{2+}$ and δ(P) = –21.8 ppm to **5**$^+$.

S2.4. Preparation of [(L$_C$)$_3$P$_7$][OTf]$_3$ (9[OTf]$_3$)



3[OTf]$_4$ (160.0 mg, 0.11 mmol) was dissolved in CH$_3$CN (2 ml) and a yellow solution of **6** (25 mg, 0.11 mmol) in CH$_3$CN (1.5 ml) was slowly added at room temperature accompanied by a color change to red-orange. The reaction mixture was stirred for 8 h and the solvent was removed *in vacuo*. The crude material was suspended in THF (2 ml) and filtered. The precipitate was washed with THF (2 x 1 ml) and dried *in vacuo*. P$_7$ compound **9**[OTf]$_3$ was obtained as colorless, air and moisture sensitive powder.

Yield: 41 mg, (61%); **m.p.**: 249 °C – 251 °C; **Raman (**50 mW, in cm^{-1}): v = 2975(23), 2941(31), 2741(8), 1614(42), 1455(39), 1400(51), 1356(56), 1246(100), 1222(32), 1191(31), 1152(43), 1089(36), 1031(50), 980(29), 886(33), 791(39), 753(38), 677(32), 572(37), 545(37), 510(37), 456(57), 402(36), 380(6), 361(11), 346(7), 310(6), 275(17), 216(6); **IR** (ATR, in cm^{-1}): v = 2992(vw), 2942(vw), 1612(vw), 1459(vw), 3196(w), 1377(vw), 1256(vs), 1220(w), 1137(s), 1027(s), 978(vw), 903(vw), 804(vw), 790(vw), 752(w), 689(vw), 634(vs), 570(w), 515(m), 463(vw); **^{1}H NMR** (CD$_3$CN, 260 K, in ppm): δ = 1.54 (18H, d, $^3J_{HH}$ = , HX), 1.62 (18H, d, $^3J_{HH}$ = , HX), 2.44 (18H, s, HX), 4.86 (6H, s(br), HX); **^{13}C{^{1}H}** NMR (CD$_3$CN, 260 K, in ppm): δ = 10.52

(6C, s, C3), 19.96 (6C, s, C5), 20.10 (6C, s, C6), 54.60 (2C, s, C4), 55.15 (6C, s, C4), 120.93 (3C, q, $^1J_{CF}$ = 321 Hz, -CF$_3$), 133.23 (6C, s, C2), 133.30 (3C, *pseudo* d, $^1J_{CP}$ = 82 Hz, C1); **^{19}F NMR** (CD$_3$CN, 260 K, in ppm): δ = –79.1 (9F, s, -CF$_3$); **^{31}P NMR** (CD$_3$CN, 260 K, in ppm): AA´A´´BXX´X´´ spin system δ(P$_A$) = –178.5 (3P), δ(P$_B$) = –164.9 (1P), δ(P$_X$) = 13.2 (3P); **elemental analysis**: calculated for $C_{36}H_{60}F_9N_6O_9P_7S_3$: C: 35.9, N: 7.0, H: 5.0, S: 8.0; found: C: 36.2, N: 6.9, H: 4.9, S: 8.1.

Table S1: Parameter of the iteratively fitted ^{31}P NMR spectrum of the AA´A´´BXX´X´´ spin system of **9**$^{3+}$.

	iterated parameter	value
chemical shift	δ_A	-178.7 ppm
	δ_B	-165.2 ppm
	δ_X	12.9 ppm
line widths	$\nu_{1/2}$(A)	14.5 Hz
	$\nu_{1/2}$(B)	12.2 Hz
	$\nu_{1/2}$(X)	14.1 Hz
coupling constants	^1J(AX) = ^1J(A´X´) = ^1J(A´´X´´)	-406.1 Hz
	^1J(AA´) = ^1J(A´A´´) = ^1J(A´´A)	-211.1 Hz
	^1J(BX) = ^1J(B´X´) = ^1J(BX´´)	-354.6 Hz
	^2J(AB) = ^2J(A´B) = ^2J(A´´B)	31.0 Hz
	^2J(AX´) = ^2J(A´X´´) = ^2J(A´´X)	5.6 Hz
	^2J(XX´) = ^2J(X´X´´) = ^2J(X´´X)	-5.9 Hz

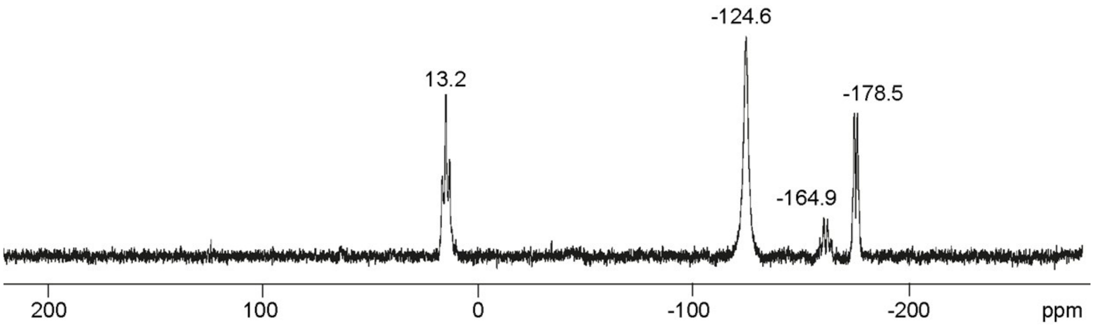
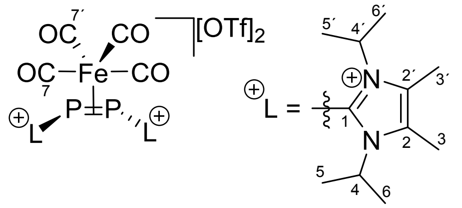


Figure S5. ^{31}P NMR spectrum of the reaction of **3**[OTf]$_4$ with **6** after 8 h (300 K, C$_6$D$_6$ capillary). The resonances can be assigned as follows: δ(P) = –124.6 ppm to **10**$^+$; and AA´A´´BXX´X´´ spin system δ(P$_A$) = δ(P$_A$) = –178.5 ppm, δ(P$_B$) = –164.9 ppm, δ(P$_X$) = 13.2 ppm to **9**$^{3+}$.

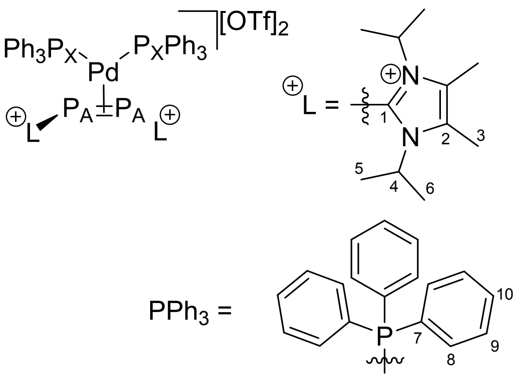
S2.5. Preparation of $[(\eta_2\text{-}L_CP{=}PL_C)Fe(CO)_4][OTf]_2$ (12$[OTf]_2$)



3$[OTf]_4$ (176.0 mg, 0.12 mmol) and $Fe_2(CO)_9$ (95.2 mg, 0.25 mmol) were combined in a sealed tube and 2 mL acetonitrile as well as 1.5 mL THF were added. The reaction mixture was stirred at ambient temperature for 12 h and turned into a yellow solution. After the addition of Et_2O (10 ml) a yellow precipitate was formed. After filtration the solid was dried *in vacuo* and **12**$[OTf]_2$ was obtained as yellow, air and moisture sensitive powder.

Yield: 208 mg, (98%); **m.p.**: 176 °C – 178 °C; **Raman (**50 mW, in cm^{-1}): ν = 2979(5), 2950(30), 2116(35), 2076(26), 2051(21), 1622(29), 1448(13), 1409(34), 1352(67), 1285(100), 1223(5), 1153(12), 1084(11), 1032(33), 884(11), 785(15), 753(11), 700(5), 609(5), 584(5), 572(6), 548(5), 512(26), 489(7), 454(9), 424(5), 410(10), 384(19), 347(10), 313(24), 292(6), 272(5), 212(5); **IR** (ATR, in cm^{-1}): ν = 2989 (vw), 2944 (w), 2115 (m), 2074 (m), 2048 (s), 1621 (w), 1449 (w), 1395 (w), 1379 (w), 1305 (vw), 1261 (vs), 1221 (m), 1142 (s), 1115 (m), 1030 (s), 976 (w), 903 (vw), 784 (vw), 752 (w), 700 (w), 636 (vs), 602 (s), 582 (s), 571 (s), 516 (m), 489 (m), 446 (w), 421 (w), 411 (w), 398 (w), 380 (w), 368 (w), 359 (w); **^{1}H NMR** (CD_2Cl_2, 260 K, in ppm): δ = 1.73 (24H, s(br), H5, H5´, H6, H6´), 2.43 (12H, s(br), H3, H3´), 5.46 (2H, s(br), H4), 5.89 (2H, s(br), H4´); **^{13}C{^{1}H}** NMR (CD_2Cl_2, 260 K, in ppm): δ = 11.08 (2C, s, C3), 11.31 (2C, s, C3´), 20.85 (2C, s, C5), 20.92 (2C, s, C5´), 21.20 (2C, s, C6), 21.55 (2C, s, C6´), 54.60 (2C, s, C4), 54.94 (2C, s, C4´), 121.06 (2C, q(br), $^1J_{CF}$ = 321 Hz, -CF_3), 131,44 (2C, s, C2), 133.15 (2C, s, C2´), 143.02 (2C, *pseudo* t, $^1J_{CP}$ = 56 Hz, C1), 200.18 (2C, *pseudo* t, $^2J_{CP}$ = 6 Hz, C7), 201.42 (2C, s, C7´); **^{19}F NMR** (CD_2Cl_2, 260 K, in ppm): δ = –78.9 (6F, s, -CF_3); **^{31}P NMR** (CD_2Cl_2, 260 K, in ppm): δ = –49.8 (2P, s); **elemental analysis**: calculated for $C_{28}H_{40}F_6FeN_4O_{10}P_2S_2$: C: 37.8, N: 6.3, H: 4.5, S: 7.2; found: C: 37.4, N: 6.4, H: 4.2, S: 6.8.

S2.6. Preparation of [(η_2-L$_C$P=PL$_C$)Pd(PPh$_3$)$_4$][OTf]$_2$ (13[OTf]$_2$)



A THF suspension (4 ml) of Pd(PPh$_3$)$_4$ (170 mg, 0.14 mmol) was added to a stirred solution of **3**[OTf]$_4$ (106 mg, 0.07 mmol) in acetonitrile (3 ml). The color of the reaction mixture turned immediately red after the addition of the metal containing suspension. Stirring overnight and removing the volatiles *in vacuo* produced an red oil. This oil was washed several times with Et$_2$O (4 x 2 ml) until the oil turned into a precipitate. The precipitate was filtered, washed with *n*-hexane (2 ml) and subsequently dried *in vacuo*. **12**[OTf]$_2$ was obtained as red, air and moisture sensitive solid.

Yield: 174 mg (93%); **m.p.**: 182 °C – 184 °C; **Raman** (50 mW, in cm^{-1}): ν = 3060(38), 2988(5), 2945(23), 1621(19), 1586(57), 1439(9), 1407(28), 1343(33), 1281(100), 1186(6), 1149(14), 1095(29), 1030(42), 1000(90), 883(5), 785(14), 752(10), 700(9), 618(9), 572(7), 552(5), 525(38), 452(5), 401(5), 347(10), 312(5), 278(5), 257(10), 176(9); **IR** (ATR, in cm^{-1}): ν = 3055(vw), 2983(vw), 1618(vw), 1479(vw), 1435(w), 1388(vw), 1375(vw), 1262(vs), 1220(w), 1140(w), 1093(vw), 1029(s), 998(vw), 901(vw), 747(m), 694(s), 635(vs), 570(w), 515(vs), 505(vw), 490(vw), 449(vw), 432(vw), 418(vw); **^{1}H NMR** (CD$_3$CN, 300 K, in ppm): δ = 1.28 (12H, d, $^3J_{HH}$ = 6.98 Hz, H5), 1.33 (12H, s, H6), 2.30 (12H, s(br), H3), 5.41 (4H, s(br), H4) 7.11-7.20 (12H, m, H8), 7.28 (12H, t(br), $^3J_{HH}$ = 7.41 Hz, H9), 7.46 (6H, t(br), $^3J_{HH}$ = 7.41 Hz, H10); **^{13}C{^{1}H}** NMR (CD$_3$CN, 300 K, in ppm): δ = 10.29 (4C, s, C3), 20.36 (4C, s, C5), 21.02 (4C, s, C6), 53.43 (4C, s(br), C4), 121.64 (2C, q, $^1J_{CF}$ = 321 Hz, -CF$_3$), 129.05 (12C, *pseudo* t, J_{CP} = 5 Hz, C9), 130.53 (4C, s(br), C2), 131.21 (6C, s, C10), 132.23 (6C, d, $^1J_{CP}$ = 42 Hz, C7), 133.63 (12C, *pseudo* t, J_{CP} = 7 Hz, C8), 143.56-145.11 (2C, m, C1); **^{19}F NMR** (CD$_3$CN, 300 K, in ppm): δ = -79.3 (6F, s, -CF$_3$); **^{31}P NMR** (CD$_3$CN, 300 K, in ppm): δ(P$_A$) = 10.2 (2P, s(br), δ(P$_X$) = 23.5 (2P, $^2J_{PP}$ = 29 Hz); **elemental analysis**: calculated for $C_{60}H_{70}F_6N_4O_6P_2S_2Pd$: C: 53.3, N: 4.2, H: 5.2, S: 4.7; found: C: 53.0, N: 4.2, H: 4.9, S: 4.4.

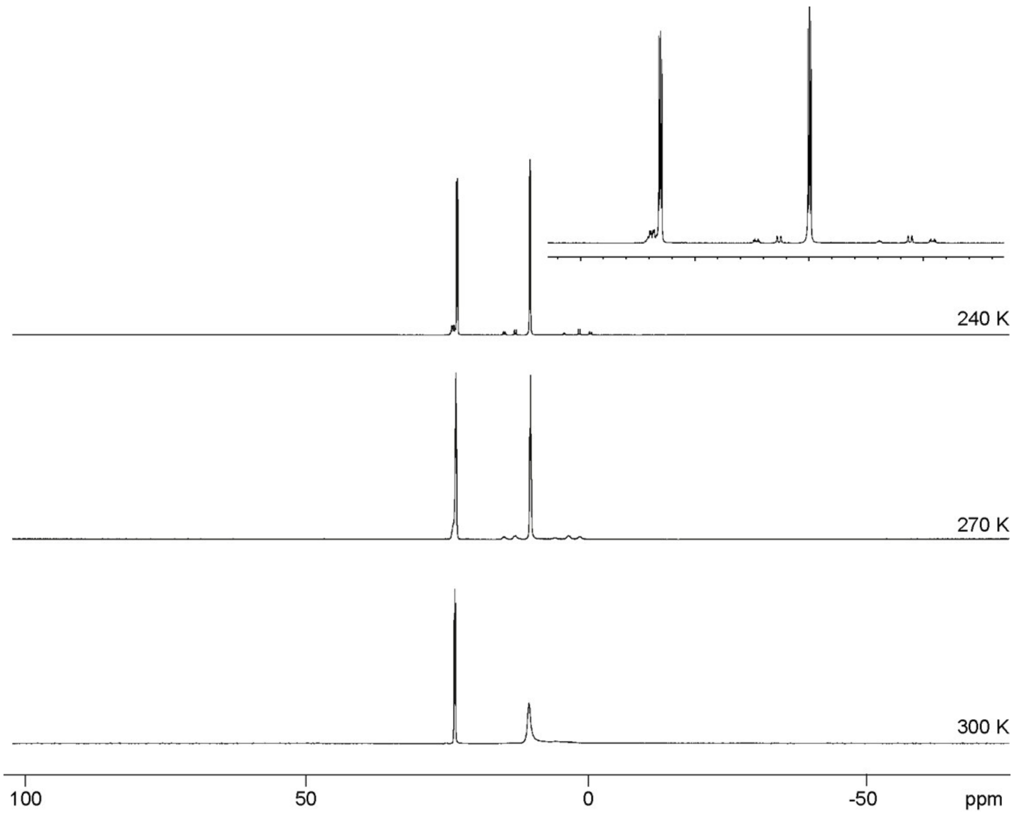
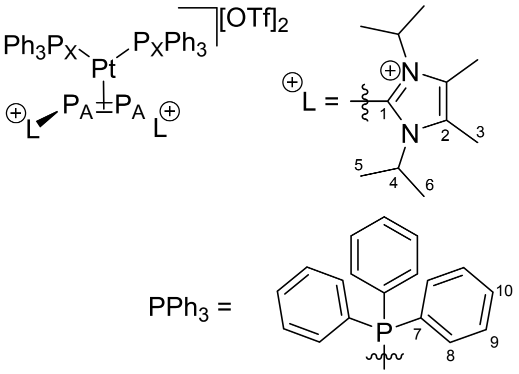


Figure S6. Variable temperature ^{31}P NMR spectra of **13**[OTf]$_2$ (CD_3CN). The extension at 240 K reveals the spin system of higher order which we attribute to a rotational isomer of **13**[OTf]$_2$.

S2.7. Preparation of $[(\eta_2\text{-}L_CP{=}PL_C)Pt(PPh_3)_4][OTf]_2$ (14[OTf]$_2$)



A THF suspension (4 ml) of $Pt(PPh_3)_4$ (155 mg, 0.124 mmol) was added to a stirred solution of **3**[OTf]$_4$ (90 mg, 0.062 mmol) in acetonitrile (3 ml). After five minutes of stirring, the color changed from yellow to orange. Stirring overnight and removing the volatiles *in vacuo* produced an orange oil. This oil was dissolved in CH_2Cl_2 (2 ml) and *n*-hexane (6 ml) was added until a precipitate was formed. The precipitate was filtered, washed with *n*-hexane (2 x 2 ml) and subsequently dried *in vacuo*. **14**[OTf]$_2$ was obtained as yellow, air and moisture sensitive solid.

Yield: 157 mg (88%); **m.p.**: 159 °C – 161 °C; **Raman** (50 mW, in cm^{-1}): ν = 3060(43), 2988(20), 2941(36), 1622(26), 1586(64), 1574(22), 1443(27), 1409(35), 1343(50), 1282(100), 1223(11), 1187(16), 1150(21), 1096(34), 1031(65), 1001(98), 883(12), 784(22), 752(17), 701(12), 688(13), 619(18), 572(13), 549(16), 538(20), 515(46), 459(16), 421(16), ; **IR** (ATR, in cm^{-1}): ν = 3055(vw), 2982(vw), 2936(vw), 2879(vw), 1620(w), 1587(vw), 1573(w), 1480(w), 1463(w), 1436(m), 1388(w), 1376(w), 1262(vs), 1220(w), 1189(w), 1140(m), 1113(s), 1095(m), 1029(s), 999(m), 988(w), 931(w), 902(w), 849(vw), 784(m), 750(s), 649(s), 635(vs), 571(m), 536(m), 517(vs), 495(m), 455(m), 422(m), 392(m), 374(w), 363(w); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm): δ = 1.34 (12H, s, H5), 1.40 (12H, s, H6), 2.37 (12H, s(br), H3), 5.63 (4H, s(br), H4) 7.13-7.19 (12H, m, H8), 7.26 (12H, t(br), $^3J_{\mathrm{HH}}$ = 7.31 Hz, H9), 7.46 (6H, t(br), $^3J_{\mathrm{HH}}$ = 7.31 Hz, H10); **^{13}C{^{1}H}** NMR (CD_2Cl_2, 300 K, in ppm): δ = 10.91 (4C, s, C3), 21.01 (4C, s, C5), 21.72 (4C, s, C6), 53.10 (4C, s(br), C4), 121.22 (2C, q, $^1J_{\mathrm{CF}}$ = 321 Hz, -CF_3), 128.95 (12C, d, $^3J_{\mathrm{CP}}$ = 10 Hz, C9), 130.53 (4C, s, C2), 131.63 (6C, d, $^1J_{\mathrm{CP}}$ = 52 Hz, C7), 131.81 (6C, s, C10), 133.63 (12C, d, $^2J_{\mathrm{CP}}$ = 12 Hz, C8), 140.66-142.12 (2C, m, C1); **^{19}F NMR** (CD_2Cl_2, 300 K, in ppm): δ = –79.0 (6F, s, -CF_3); **^{31}P NMR** (CD_2Cl_2, 260 K, in ppm): $\delta(P_A)$ = –42.7 (2P, dd, $^2J_{\mathrm{PP}}$ = 40 Hz, $^2J_{\mathrm{PP}}$ = 29 Hz, $^1J_{\mathrm{PPt}}$ = 236 Hz), $\delta(P_X)$ = 25.1 (2P, $^2J_{\mathrm{PP}}$ = 40 Hz, $^2J_{\mathrm{PP}}$ = 29 Hz, $^1J_{\mathrm{PPt}}$ = 3280 Hz); **^{195}Pt NMR** (CD_2Cl_2, 260 K, in ppm): δ = –5016.0 (tt, $^1J_{\mathrm{PtP}}$ = 3280 Hz, $^1J_{\mathrm{PtP}}$ = 236 Hz); **elemental analysis**: calculated for $C_{60}H_{70}F_6N_4O_64_2S_2Pt$: C: 50.0, N: 3.9, H: 4.9, S: 4.5; found: C: 49.7, N: 3.8, H: 4.7, S: 4.2.

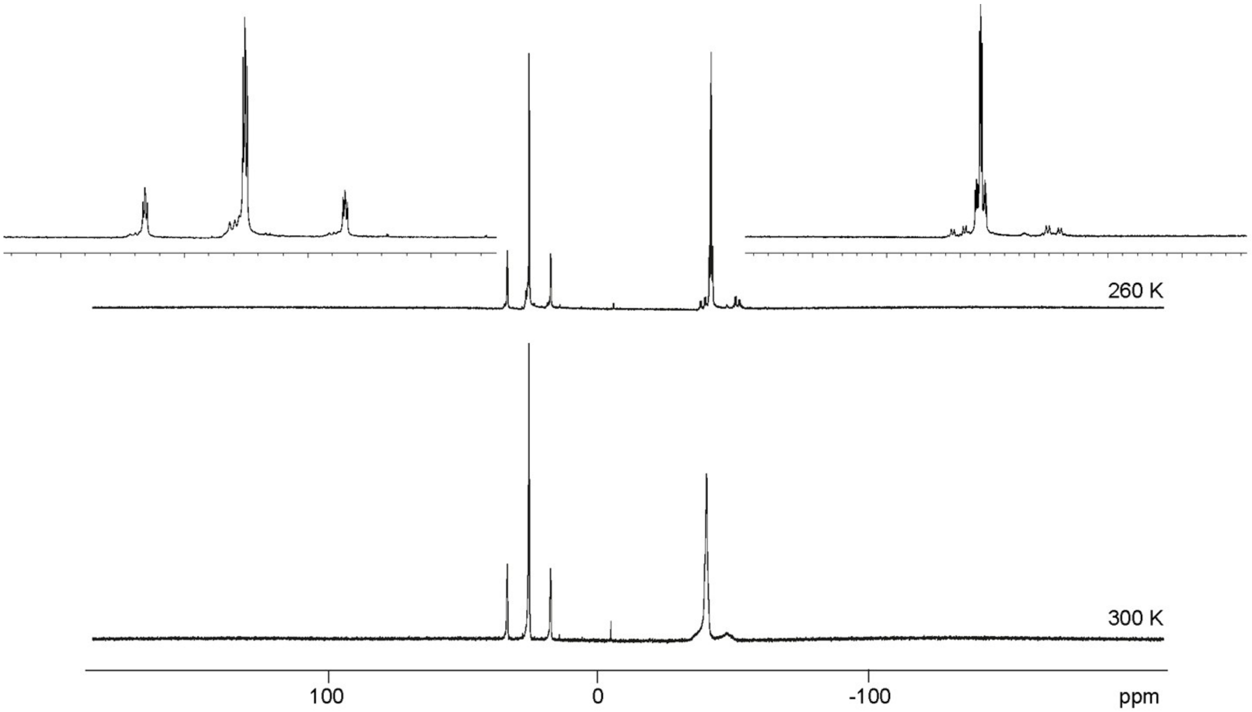


Figure S7. Variable temperature ^{31}P NMR spectra of **14**[OTf]$_2$ (CD$_3$CN). The extension at 260 K reveals the spin system of higher order which we attribute to a rotational isomer of **14**[OTf]$_2$.

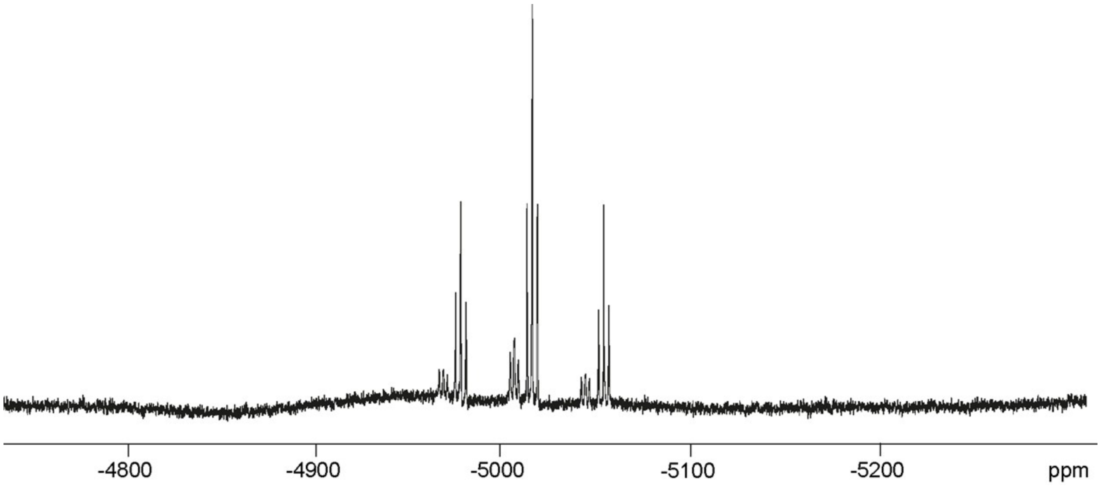
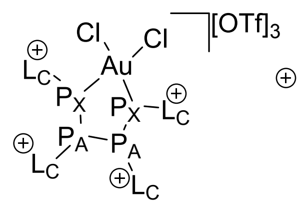
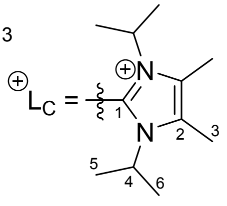


Figure S8. ^{195}Pt NMR spectrum of **14**[OTf]$_2$ (260 K, CD$_3$CN). The low intensity triplet of triplet resonance is attributet to a rotational isomer of **14**[OTf]$_2$.

S2.8. Preparation of [((L$_C$)$_4$P$_4$)AuCl$_2$][OTf]$_3$ (15[OTf]$_3$)





3[OTf]$_4$ (160.0 mg, 0.11 mmol) was dissolved in CH$_3$CN/THF (1 ml/1.5 ml) and a colorless suspension of AuCl(tht) (25 mg, 0.44 mmol) in THF (2 ml) was slowly added in portions at room temperature accompanied by a color change to yellow. The reaction mixture was stirred for 8 h. A grey residue was filtered off and the solvent was removed *in vacuo*. The remaining orange-colored oil was suspended in THF, filtered and a yellow precipitate was obtained after 10 minutes. The recrystallization step was repeated for 4 more times. The obtained yellow precipitate was combined, filtered and dried *in vacuo*. The five-membered P$_4$Au-complex **15**[OTf]$_3$ was obtained as yellow, air and moisture sensitive powder.

Yield: 92 mg, (57%); **m.p.**: 115 °C – 117 °C; **Raman (**60 mW, in cm^{-1}): v = 2946(33), 1607(39), 1453(9), 1405(28), 1355(48), 1272(100), 1149(19), 1085(7), 1032(15), 978(5), 884(6), 790(10), 754(6), 573(5), 492(5), 445(8), 429(5), 393(10), 347(5), 312(50), 294(5); **IR** (ATR, in cm^{-1}): v = 2939(vw), 1606(vw), 1456(vw), 1395(w), 1376(vw), 1259(vs), 1220(w), 1145(s), 1113(vw), 1085(vw), 1028(vs), 978(vw), 901(vw), 788(vw), 751(w), 694(vw), 635(vs), 571(w), 543(vw), 516(m), 442(vw), 419(vw); **^{1}H NMR** (CD$_2$Cl$_2$, 260 K, in ppm): δ = 0.76 (6H, d, $^3J_{HH}$ = 6.94 Hz, H18), 1.08 (6H, s(br), H21), 1.67 (6H, s(br), H22), 1.69 (6H, d, $^3J_{HH}$ = 6.94 Hz, H19), 1.87 (6H, d, $^3J_{HH}$ = 6.87 Hz, H7), 1.92 (6H, d, $^3J_{HH}$ = 6.87 Hz, H10), 1.99 (6H, $^3J_{HH}$ = 6.97 Hz, H8), 2.02 (6H, $^3J_{HH}$ = 6.97 Hz, H11), 2.39 (6H, s, H15), 2.48 (6H, s, H4), 2.52 (6H, s, H5), 2.61 (6H, s, H16), 5.24 (2H, sept, $^3J_{HH}$ = 6.94 Hz, H17), 5.52 (2H, s(br), H20), 5.95 (4H, sept, $^3J_{HH}$ = 6.97 Hz, H6/H9); **^{13}C{^{1}H}** NMR (CD$_2$Cl$_2$, 260 K, in ppm): δ = 10.93 (4C, s, C4/C5), 11.15 (4C, s, C15/C16), 19.53 (2C, s, C19), 20.52 (2C, s(br), C22), 20.71 (2C, s, C10), 20.87 (2C, s, C7), 21.24 (2C, s(br), C21), 21.61 (2C, s, C11), 21.83 (2C, s, C18), 22.22 (2C, s, C8), 54.64 (2C, dd, $^3J_{CP}$ = 13 Hz, C6), 55.28 (2C, *pseudo* t, $^3J_{CP}$ = 15 Hz, C17), 55.95 (2C, d, $^3J_{CP}$ = 52 Hz, C20), 56.36 (2C, s(br), C9), 120.84 (3C, q, $^1J_{CF}$ = 321 Hz, -CF$_3$), 132.95 (2C, s, C2), 133.03 (2C, dd, $^1J_{CP}$ = 71 Hz, $^3J_{CP}$ = 22 Hz C12), 134.24 (2C, s, C14), 134.47 (2C, s, C3), 135.39 (2C, s, C13), 137.95 (2C, d *pseudo* t, $^1J_{CP}$ = 78 Hz, $^3J_{CP}$ = 14 Hz C1); **^{19}F NMR** (CD$_2$Cl$_2$, 260 K, in ppm): δ = –79.1 (9F, s, -CF$_3$);

^{31}P NMR (CD_2Cl_2, 260 K, in ppm): AA´BB´ spin system $\delta(P_A)$ = –49.9 (2P), $\delta(P_B)$ = –24.7 (2P); **elemental analysis**: calculated for $C_{47}H_{80}Cl_2F_9N_8O_9P_4S_3Au$: C: 36.2, N: 7.2, H: 5.2, S: 6.2; found: C: 35.9, N: 6.2, H: 4.9, S: 6.6.

Table S2: Parameter of the iteratively fitted ^{31}P NMR spectrum of the AA´XX´ spin system of **15**$^{3+}$.

	iterated parameter	value
chemical shift	δ_A	-52.4 ppm
	δ_X	-21.7 ppm
line widths	$\nu_{1/2}(A)$	11.0 Hz
	$\nu_{1/2}(X)$	11.0 Hz
coupling constants	$^1J(AX) = {}^1J(A'X')$	-107.7 Hz
	$^1J(AA')$	-171.2 Hz
	$^2J(AB) = {}^2J(A'B)$	107.6 Hz
	$^3J(BB')$	8.0 Hz

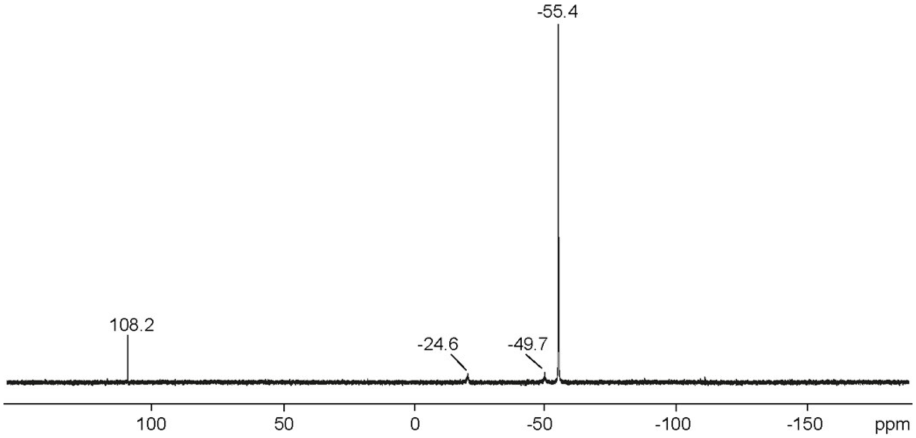


Figure S9. ^{31}P NMR spectrum of the reaction of **3**[OTf]$_4$ with 1 equivalent AuCl(tht) after 12 h (300 K, C_6D_6 capillary). The resonances can be assigned as follows: δ(P) = 1078.2 ppm to **1**$^+$; AA´BB´ spin system $\delta(P_A)$ = –49.9 ppm, $\delta(P_B)$ = –24.7 ppm to **15**$^{3+}$ and δ(P) = –55.4 ppm to **3**$^{4+}$.

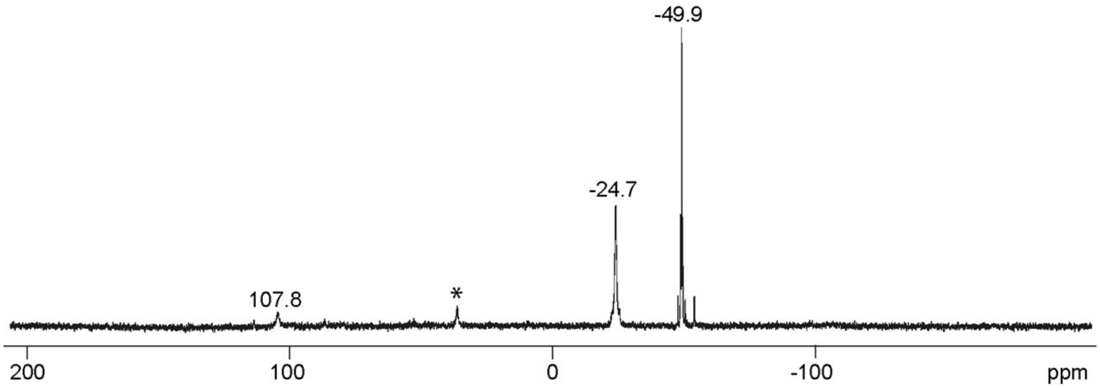


Figure S10. ^{31}P NMR spectrum of the reaction of **3**[OTf]$_4$ with 4 equivalents AuCl(tht) after 8 h (300 K, C_6D_6 capillary). The resonances can be assigned as follows: δ(P) = 107.8 ppm to **1**$^+$; and AA´BB´ spin system $\delta(P_A)$ = –49.9 ppm, $\delta(P_B)$ = –24.7 ppm to **15**$^{3+}$; and asterisk is assigned to an unidentified side product.

Alternative procedure to the formation of **15**[OTf]$_3$

3[OTf]$_4$ (50.0 mg, 0.03 mmol) was dissolved in CH_3CN/THF (1 ml/1.5 ml) and a colorless suspension of AuCl(tht) (14 mg, 0.04 mmol) and *n*Bu$_4$N[Cl] (10 mg, 0.03 mmol) in THF (2 ml) was slowly added in portions at room temperature accompanied by a color change to yellow. The reaction mixture was stirred for 12 h. The solvent was reduced to 1 ml *in vacuo* and ^{31}P NMR experiments of the crude material revealed the complete consumption of **3**[OTf]$_4$ and the formation of **15**[OTf]$_3$ in 70 % yield (see figure S11).

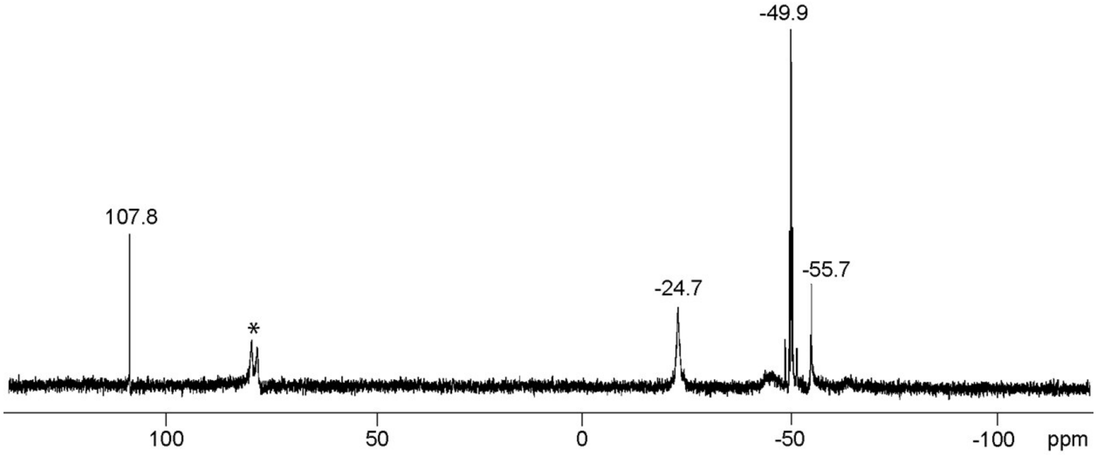


Figure S11. ^{31}P NMR spectrum of the reaction of **3**[OTf]$_4$ with 1 eq. AuCl(tht) and 1 eq. nBu$_4$N[Cl] after 12 h (300 K, C_6D_6 capillary). The resonances can be assigned as follows: δ(P) = 107.8 ppm to **1**$^+$; and AA´BB´ spin system $\delta(P_A)$ = –49.9 ppm, $\delta(P_B)$ = –24.7 ppm to **15**$^{3+}$; δ(P) = –55.4 ppm to **3**$^{4+}$. and asterisk is assigned to an unidentified side product.

S3. Crystallographic Details

S3.1 Structure solution and refinement

Suitable single crystals were coated with Paratone-N oil or Fomblin Y25 PFPE oil, mounted using a glass fiber and frozen in the cold nitrogen stream. X-ray diffraction data were collected at low temperature as indicated in tables S3, S4 and S5 on a Rigaku Oxford Diffraction SuperNova diffractometer using either Cu K_α radiation (λ = 1.54184 Å) or Mo K_α radiation (λ = 0.71073 Å) generated by micro-focus sources. The data reduction and absorption correction was performed using CrysaAlisPro,[S7] respectively. For further crystal and data collection details see tables S3, S4 and S5. Using Olex2[S8], the structures were solved with SHELXS/T[S9] by direct methods and refined with SHELXL[S10] by least-square minimization against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions using the riding model. Images of the structures were produced with Olex2[S11] software.

Crystals of **5**[OTf]·CH_2Cl_2 were measured and refined as inversion twin. The ratio of the twin components was refined to 62:38. The structure of **3**$[OTf]_4$·$2CH_3CN$ exhibits disorder of two triflat anions and one isopropyl group. They were restrained using the SIMU command. The C-C bond distances of the disordered isopropyl group are constrained using DFIX. **9**$[OTf]_3$·$0.8CH_3CN$·$1.7CH_2Cl_2$ was crystallized from a mixture of acetonitrile and dichloromethane. Both solvents are present in the crystal lattice. To account for the disorder of solvent molecules and triflat anions and to obtain a meaningful converging structure model SADI and SUMP restraints as well as several SIMU restraints were applied. The trications are not disordered and well resolved. Crystals of **9**$[OTf]_2$ exhibit one triflat anion disordered over two positions. The minor component was restrained using SIMU. **13**$[OTf]_2$·$3C_6H_5F$ and **14**$[OTf]_2$·$3C_6H_5F$ crystallized isostructural with fluorobenzene in the crystal lattice. All solvent molecules and one or two anions are disordered over two positions, respectively. SADI and SIMU restraints were applied to obtain a meaningful converging structure model. **15**$[OTf]_3$·$3CH_2Cl_2$ was crystalized from a mixture of dichloromethane and pentane. Two triflate ions and one dichloromethane molecule is disordered on a special position. To achieve a stable refinement these moieties were restrained using SIMU. The relatively high R_{int} is due to sample wobbeling during measurement.

Table S3. Crystallographic data and details of the structure refinements of compounds **5**[OTf]$\cdot$CH$_2$Cl$_2$, **3**[OTf]$_4$$\cdot$2CH$_3$CN and **8**[OTf]$_3$.

	3[OTf]$_4$$\cdot$2CH$_3$CN	**5**[OTf]$\cdot$CH$_2$Cl$_2$	**8**[OTf]$_3$
formula	$C_{52}H_{85}F_{12}N_{10}O_{12}P_4S_4$	$C_{24}H_{42}Cl_5F_3N_4O_3P_2S$	$C_{36}H_{60}F_9N_6O_9P_3S_3$
M_r / g mol^{-1}	1522.41	762.86	1080.99
color, habit	colorless block	colorless block	colorless block
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Pca2_1$	$P2_1/n$
a / Å	19.31294(18)	11.51562(4)	23.0670(2)
b / Å	16.76136(17)	10.67077(3)	12.77419(14)
c / Å	23.1443(2)	29.25903(9)	16.55090(19)
α / °	90	90	90
β / °	105.4253(10)	90	103.7111(10)
γ / °	90	90	90
V / Å^3	7222.20(13)	3595.366(18)	4737.94(9)
Z	4	4	4
T / K	104.6(7)	102(1)	100.0(10)
crystal size / mm^3	0.313x0.273x0.124	0.296x0.206x0.075	0.189x0.127x0.087
ρ_c / g cm^{-3}	1.400	1.409	1.515
F(000)	3180	1584	2256
$\lambda_{XK\alpha}$ / Å	1.54184 (X = Cu)	1.54184 (X = Cu)	0.71073 (X = Mo)
θ_{min} / °	3.2810	3.021	2.349
θ_{max} / °	76.4770	76.739	28.700
index range	$-24 \le h \le 24$ $-21 \le k \le 15$ $-28 \le l \le 27$	$-13 \le h \le 14$ $-9 \le k \le 13$ $-36 \le l \le 35$	$-31 \le h \le 31$ $-15 \le k \le 17$ $-22 \le l \le 21$
μ / mm^{-1}	2.851	5.475	0.350
absorption correction	multi-scan	gaussian	gaussian
refl. collected	45993	38748	56620
refl. unique	15049	7366	12235
R_{int}	0.0372	0.0579	0.0310
reflection obs. [F>2σ(F)]	13385	7373	10099
residual density min / max / e Å^{-3}	1.26/ –0.64	0.25 / –0.30	0.72/ –0.53
parameters	1040	392	613
GOOF	1.026	1.050	1.026
R_1 [I>2σ(I)]	0.0559	0.0210	0.0393
wR_2	0.1621	0.0579	0.0962
CCDC	1884157	1884156	1884161

Table S4. Crystallographic data and details of the structure refinements of compounds **9**[OTf]$_3$·0.8CH$_3$CN·1.7CH$_2$Cl$_2$, **12**[OTf]$_2$ and **13**[OTf]$_2$·3C$_6$H$_5$F

	9[OTf]$_3$·0.8CH$_3$CN·1.7CH$_2$Cl$_2$	**12**[OTf]$_2$	**13**[OTf]$_2$·3C$_6$H$_5$F
formula	$C_{39.44}H_{66.01}Cl_{3.37}F_9N_{6.88}N_9P_7S_3$	$C_{28}H_{40}F_6N_4O_{10}P_2S_2Fe$	$C_{78}H_{85}F_9N_4O_6P_4S_2Pd$
M$_r$ / g mol^{-1}	1384.11	888.55	1639.90
color, habit	colorless block	orange prism	yellow needle
crystal system	triclinic	monoclinic	monoclinic
space group	*P*-1	*P*2$_1$/*n*	*P*2$_1$/*n*
a / Å	13.83853(13)	14.4005(3)	15.02480(18)
b / Å	17.90754(17)	15.3233(3)	19.8179(3)
c / Å	27.2960(2)	17.8619(3)	25.7120(4)
α / °	101.3965(7)	90	90
β / °	103.3332(8)	100.9141(17)	91.3090(12)
γ / °	104.3661(8)	90	90
V / Å^3	6138.77(10)	3870.18(12)	7654.00(19)
Z	4	4	4
T / K	101(10)	100.0(4)	100.1(7)
crystal size / mm^3	0.45x0.24x0.104	0.402x0.066x0.051	0.18x0.043x0.031
ρ_c / g cm^{-3}	1.498	1.525	1.423
F(000)	2857	1832	3392
$\lambda_{XK\alpha}$ / Å	1.54184 (X = Cu)	0.71073 (X = Mo)	1.54184 (X = Cu)
θ_{min} / °	2.646	2.322	2.7980
θ_{max} / °	76.878	28.700	76.0720
index range	$-17 \leq h \leq 17$	$-19 \leq h \leq 14$	$-18 \leq h \leq 18$
	$-22 \leq k \leq 20$	$-15 \leq k \leq 20$	$-24 \leq k \leq 24$
	$-34 \leq l \leq 34$	$-24 \leq l \leq 22$	$-32 \leq l \leq 32$
μ / mm^{-1}	4.894	0.665	3.905
absorption correction	gaussian	gaussian	gaussian
refl. collected	145167	27061	44109
refl. unique	25653	10001	15851
R$_{int}$	0.0279	0.0363	0.0458
reflection obs. [F>2σ(F)]	24333	8508	12830
residual density min / max / e Å^{-3}	0.84 / –0.74	0.79/ –0.54	1.24/ –1.07
parameters	1645	523	1081
GOOF	1.078	1.061	1.015
R$_1$ [I>2σ(I)]	0.0449	0.0453	0.0501
wR$_2$	0.1262	0.1186	0.1328
CCDC	1884162	1884158	1884160

Table S5. Crystallographic data and details of the structure refinements of compound **14**[OTf]$_2$·3C_6H_5F and **15**[OTf]$_3$·3CH_2Cl_2.

	14[OTf]$_2$·3C_6H_5F	**15**[OTf]$_3$·3CH_2Cl_2
formula	$C_{78}H_{85}F_9N_4O_6P_4S_2Pt$	$C_{49}H_{85}Cl_7F_9N_8O_9P_4S_3Au$
M_r / g mol^{-1}	1728.58	1772.43
color, habit	yellow needle	yellow plate
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a / Å	14.98968(8)	30.6491(6)
b / Å	19.89396(13)	11.9065(2)
c / Å	25.71449(16)	20.2311(5)
α / °	90	90
β / °	91.6799(5)	91.738(2)
γ / °	90	90
V / Å^3	7664.88(8)	7379.4(3)
Z	4	4
T / K	100.0(2)	100.0(2)
crystal size / mm^3	0.263x0.043x0.034	0.372x0.192x0.061
ρ_c / g cm^{-3}	1.498	1.595
F(000)	3520	3588
$\lambda_{XK\alpha}$ / Å	1.54184 (X = Cu)	1.54184 (X = Cu)
θ_{min} / °	2.7940	2.885
θ_{max} / °	76.4240	74.531
index range	$-16 \leq h \leq 18$ $-24 \leq k \leq 25$ $-32 \leq l \leq 32$	$-31 \leq h \leq 38$ $-14 \leq k \leq 14$ $-25 \leq l \leq 25$
μ / mm^{-1}	5.371	8.354
absorption correction	gaussian	gaussian
refl. collected	57628	79611
refl. unique	15980	15093
R_{int}	0.0295	0.1157
reflection obs. [F>2σ(F)]	14507	13873
residual density min / max / e Å^{-3}	1.25/ –1.24	1.76/ –4.38
parameters	1149	998
GOOF	1.021	1.039
R_1 [I>2σ(I)]	0.0323	0.0613
wR_2	0.0875	0.1647
CCDC	1884159	1904570

S4. Computational Methods

S4.1 General Considerations

The geometry optimization has been performed at the PBE0-D3/def2-TZVP level of theory without symmetry constrains by means of the Turbomole version 7.0 program.[S12] The minimum nature of the complexes has been checked by using frequency analysis. The orbital analysis and NBO calculations[S13] have been performed at the same level of theory using the Gaussian-09 and the GaussView program to represent the molecular orbitals.[S14] For the theoretical NMR studies we used the DFT/GIAO (Gauge Including Atomic Orbitals) approach as implemented in the Gaussian 09 program to estimate the ^{31}P NMR chemical shifts. The level of theory used was PBE0/def2-TZVP and the molecular systems were completely optimized in acetonitrile. The primary result of a quantum chemical calculation of NMR shifts is the absolute magnetic shielding (σ) (i.e., with respect to a naked nucleus). The chemical shift of a substance S with respect to a reference compound is then given as: $\delta(S) = \sigma(\text{ref}) - \sigma(S)$. We have used phosphoric acid as reference to estimate the chemical shift. At our level of theory, the absolute shielding of phosphoric acid is 293 ppm, which is in quite good agreement with that previously reported in the literature at the B3LYP/6-311G level (295 ppm).[S15] It should be kept in mind that the experimental reference compound for ^{31}P NMR is 85% aqueous phosphoric acid, for which one can hardly obtain an accurate theoretical magnetic shielding.

S4.2 Additional discussion, Figures and Tables (see also main text)

Table S6: GIAO-NMR absolute magnetic shieldings (s, ppm) and chemical shifts (d, ppm) at the PBE0/def2-TZVP level of theory in acetonitrile.

Compound	Absolute shielding (σ)	Chemical shift (δ)
H_3PO_4	293.0	0.0
7^{2+} [(L$_C$P(Cl)-P(Cl)Lc)]$^{2+}$	326.4	-33.4

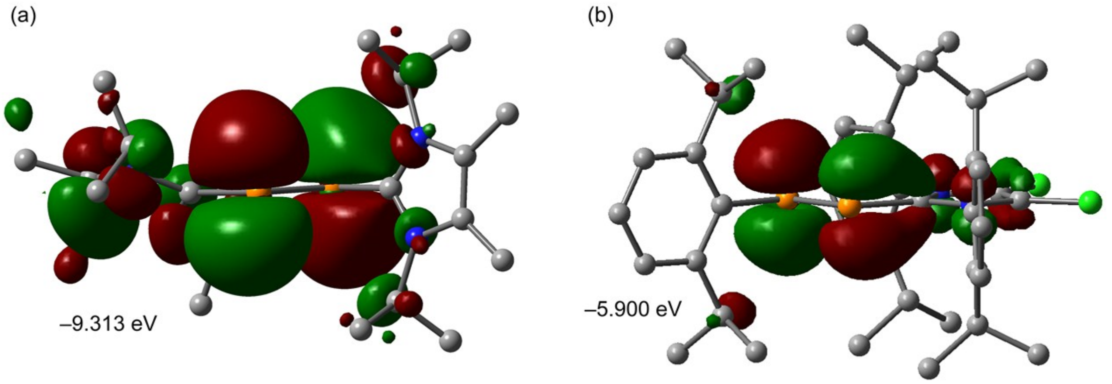


Figure S12. LUMO plots of the dicationic ligand [L$_C$P=PL$_C$]$^{2+}$ (left, a) and cationic diphosphene [L$_C$-P=P-Dipp]$^+$ (right, b) using 0.04 a.u. isosurface at the PBE0/def2-TZVP functional. H-atoms omitted for clarity. LUMO energy for [L$_C$P=PL$_C$]$^{2+}$: –9.313 eV and for [L$_C$-P=P-Dipp]$^+$ = –5.900 eV.

The π-accepting property is related to the LUMO energy of the ligand and also its shape (ability to overlap with the d orbitals of Fe). That is, if the energy of the LUMO is low, its electron accepting ability increases. In Figure S10 we represent the LUMO of [L$_C$P=PL$_C$]$^{2+}$ (left) [L$_C$-P-L$_C$]$^+$ (right). For ([L$_C$P=PL$_C$]$^{2+}$ the caclulations reveal that the LUMO is very low in energy ([L$_C$P=PL$_C$]$^{2+}$: –9.313 eV; due to the dicationic nature) and the orbital clearly corresponds to the π-antibonding P=P orbital, perfectly pre-organized to interact with the d atomic orbitals of the Fe(0) metal atom. In case of the cationic diphosphene [L$_C$-P=P-Dipp]$^+$, the shape of the LUMO orbital is adequate comparable, however, not as low in energy (–5.900 eV) compared to [L$_C$P=PL$_C$]$^{2+}$ which we attribute to the dicationic charge in [L$_C$P=PL$_C$]$^{2+}$.

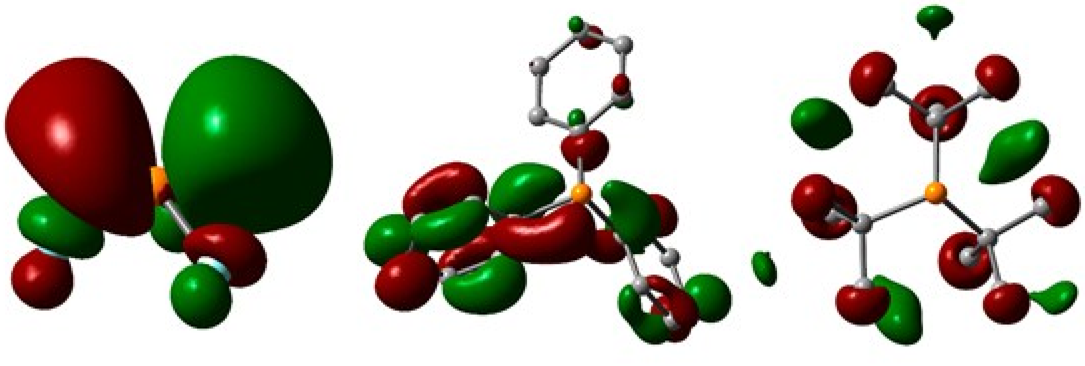


Figure S13. LUMO plots of the ligand PF_3 (left), PPh_3 (middle) and $^tBu_3P$ (right) using 0.04 a.u. isosurface at the PBE0/def2-TZVP level of theory. H-atoms omitted for clarity. LUMO energy for PF_3: –0.146 eV, for PPh_3: –0.729 eV and for $^tBu_3P$: 1.021 eV.

Also the PF_3 ligand presents an adequate shape to act as a π-acceptor, in agreement with the CO stretching frequencies ($[(PF_3)Fe(CO)_4]$: 2101 cm^{-1}, 2022 cm^{-1}, 2018 cm^{-1}, 1999 cm^{-1}).[S16] The other two ligands Ph_3P and tBu_3P are not good π-acceptors taking into consideration this orbital analysis. To further analyze this particular point, we have also computed the natural bond orbital (NBO) analysis of the complexes **12**$^+$ and $[(PF_3)Fe(CO)_4]$. We have focused our attention to the second order perturbation analysis, since it is very convenient to study donor-acceptor orbital interactions. We summarize in Table S6 the back-bonding donation from Fe(0) d atomic orbitals to the P-ligand in complexes **12**$^+$ and $[(PF_3)Fe(CO)_4]$. It is clear that the $[L_{\mathbf{C}}P{=}PL_{\mathbf{C}}]^{2+}$ ligands is significantly more stabilized due to back-donation than the PF_3 ligand..

Table S7: Second order stabilization energy ($E^{(2)}$, kcal/mol) due to back-bonding donation from d orbitals Fe(0) to antibonding P–C or P–F orbitals or unfilled Rydberg atomic orbitals of P

Complex	Accepting orbital of ligand	$E^{(2)}$
12$^+$	BD* (P–C)	35.77
$[(PF_3)Fe(CO)_4]$	BD* (P–F)	9.16
	Ry* (P)	7.69

The optimized complexes of **12**$^+$ and $[(PF_3)Fe(CO)_4]$ are given in figure S11. The theoretical distances are in good agreement (slightly shorter) with the experimental ones, giving reliability to the level of theory.

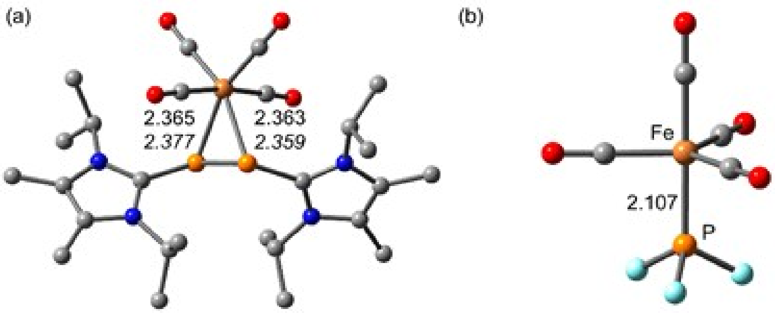


Figure S14. Optimized complexes **12**$^+$ (left, a) and [(PF_3)Fe$(CO)_4$] (left, b). Distances in Å. Experimental distances in italics. H-atoms omitted for clarity.

S.4.3 Cartesian coordinates

S.4.3.1 [L_CP=PL_C]$^{2+}$ (Figure S12, left)

P	-0.63927172	0.58535637	-0.99229755
P	0.43549005	-0.29175828	0.50465865
N	-3.05950293	-0.83173471	-0.72537344
N	-2.99797833	0.90148933	0.58307924
N	2.89357982	0.90754048	-0.53458161
N	3.09462503	-0.93494122	0.61691085
C	-2.28574323	0.17810594	-0.29595798
C	-4.27773016	-0.77132940	-0.08615434
C	-4.23958496	0.32399897	0.73920850
C	-2.59878747	-1.81605077	-1.73164097
H	-1.66696987	-1.37682520	-2.10914901
C	-3.54985140	-1.93024339	-2.90888864
H	-4.45469409	-2.48390913	-2.66235574
H	-3.04589486	-2.47510366	-3.70858393
H	-3.82922277	-0.94944629	-3.29720240
C	-2.25478532	-3.14473268	-1.08387758
H	-1.52169885	-3.01953381	-0.28400806
H	-1.83198357	-3.81097127	-1.83742904
H	-3.13294837	-3.63814739	-0.66623751
C	-5.40250532	-1.71528096	-0.29471687
H	-5.95957396	-1.48298989	-1.20539856
H	-6.09919881	-1.64545835	0.53929472
H	-5.06912508	-2.75019207	-0.35555485
C	-5.31786913	0.83489707	1.62034947
H	-4.93828566	1.19002400	2.57676309
H	-6.03046631	0.03798773	1.82796181
H	-5.86978391	1.65111746	1.14836329
C	-2.47714641	2.13160553	1.22345476
H	-1.54741779	2.32533920	0.67866021
C	-3.38788231	3.32589430	1.00094806
H	-3.67220778	3.42432487	-0.04809087
H	-2.84892276	4.23010496	1.28802542
H	-4.29073868	3.28331096	1.60836738
C	-2.12184051	1.89020203	2.67918144
H	-3.00012537	1.67837354	3.28971165
H	-1.65162584	2.78726893	3.08526763
H	-1.42407079	1.05690985	2.78709931

C	2.18879440	-0.04997296	0.11974538
C	4.22612591	0.61810967	-0.46249655
C	4.35244305	-0.54721401	0.26718278
C	2.29578990	2.10600397	-1.17085867
H	1.26864897	2.10683798	-0.80349624
C	2.93120379	3.39862601	-0.68704588
H	3.01985074	3.42227001	0.40059290
H	2.28534277	4.22561909	-0.98654846
H	3.90963956	3.58446887	-1.12584312
C	2.25704153	1.96535914	-2.68280737
H	3.25230326	1.98694039	-3.12734382
H	1.69405379	2.80114374	-3.10145182
H	1.76552229	1.04038021	-2.98965430
C	5.32872282	1.40347551	-1.06732577
H	5.05725019	1.82207050	-2.03397563
H	6.19096143	0.75640857	-1.22274686
H	5.64318211	2.22401457	-0.41711233
C	5.61323264	-1.26104719	0.58364437
H	5.59888961	-1.71207722	1.57299349
H	6.44658584	-0.56040716	0.55655965
H	5.81792364	-2.04998555	-0.14495368
C	2.73062558	-2.12837350	1.42681983
H	1.63995000	-2.16284435	1.36821310
C	3.10247375	-1.93513098	2.88632900
H	4.17990691	-1.90947127	3.04881352
H	2.70777024	-2.77412417	3.46156895
H	2.67121305	-1.01707994	3.28965044
C	3.24993349	-3.41668858	0.81275001
H	3.00947343	-3.48198136	-0.24989803
H	2.76781600	-4.25538835	1.31730538
H	4.32436739	-3.54070970	0.93910263

S.4.3.1 [L_CP=PDipp]$^+$ (Figure S12, right)

P	0.9841	1.3302	0.6494
P	-0.6061	0.0662	1.5068
N	3.5695	0.3780	0.3275
N	2.1628	-1.0639	-0.5175
N	-3.0829	-0.7309	0.5462
N	-2.6029	1.2335	-0.2805
C	2.2276	0.1357	0.1427
C	4.3246	-0.6457	-0.2323
C	3.4461	-1.5569	-0.7424
C	4.0448	1.5798	1.0106
H	3.1273	1.9307	1.5230
C	4.4513	2.6638	0.0207
H	5.3321	2.3764	-0.5760
H	4.6976	3.5926	0.5578
H	3.6202	2.8809	-0.6665
C	5.0914	1.3059	2.0827
H	4.7936	0.4575	2.7166
H	5.1703	2.1919	2.7304
H	6.0957	1.1106	1.6803
C	5.8116	-0.7012	-0.2322
H	6.2560	0.2534	-0.5500
H	6.1556	-1.4717	-0.9347
H	6.2295	-0.9470	0.7571
C	3.7547	-2.8721	-1.3665
H	3.4688	-3.7136	-0.7148
H	4.8346	-2.9525	-1.5469
H	3.2491	-3.0177	-2.3322
C	0.9304	-1.5380	-1.1493
H	0.1583	-0.8955	-0.7009
C	0.9433	-1.2796	-2.6513
H	1.1560	-0.2190	-2.8525
H	-0.0447	-1.5139	-3.0766
H	1.6876	-1.8885	-3.1876

C	0.5715	-2.9653	-0.7642
H	1.2401	-3.7200	-1.2022
H	-0.4471	-3.1872	-1.1172
H	0.5778	-3.0716	0.3306
C	-2.0915	0.2259	0.4980
C	-4.1941	-0.3119	-0.1762
C	-3.8853	0.9018	-0.7156
C	-2.9339	-1.9459	1.3448
H	-1.8394	-1.9955	1.4985
C	-3.5751	-1.7910	2.7183
H	-3.1665	-0.9058	3.2274
H	-3.3552	-2.6717	3.3409
H	-4.6702	-1.6880	2.6532
C	-3.3526	-3.2185	0.6195
H	-4.4417	-3.3617	0.5788
H	-2.9339	-4.0838	1.1549
H	-2.9585	-3.2396	-0.4077
C	-5.4603	-1.0814	-0.3179
H	-5.3473	-1.9795	-0.9457
H	-6.2283	-0.4482	-0.7805
H	-5.8540	-1.4074	0.6565
C	-4.7263	1.7378	-1.6172
H	-5.2001	2.5860	-1.0978
H	-5.5294	1.1263	-2.0490
H	-4.1456	2.1485	-2.4553
C	-1.9337	2.5243	-0.4540
H	-1.0911	2.4714	0.2504
C	-2.7976	3.7037	-0.0209
H	-3.5815	3.9616	-0.7469
H	-2.1545	4.5893	0.0907
H	-3.2689	3.5081	0.9538
C	-1.3311	2.6844	-1.8419
H	-0.6209	1.8677	-2.0357
H	-0.7677	3.6282	-1.8925
H	-2.0938	2.7017	-2.6360

S.4.3.3 PF_3 (Figure S13, left)

P	0.00002796	-0.00009052	0.50060407
F	-1.23571592	-0.58060593	-0.27812174
F	0.11489558	1.36036451	-0.27805770
F	1.12077373	-0.77960772	-0.27816069

S.4.3.4 PPh_3 (Figure S13, middle)

C	0.19739474	1.64266674	-0.40680203
C	-0.54894934	2.69851765	-0.93415400
C	-0.44648396	3.97440397	-0.40407298
C	0.42380167	4.22165524	0.64915502
C	1.18254687	3.18481225	1.16969599
C	1.06776845	1.90268401	0.64900797
C	1.32389376	-0.99228223	-0.40680203
C	1.11388846	-1.87605661	0.64900797
C	2.16685488	-2.61652175	1.16969599
C	3.44415985	-2.47785063	0.64915502
C	3.66517678	-1.60053553	-0.40407298
C	2.61145950	-0.87385475	-0.93415400
C	-1.52128849	-0.65038451	-0.40680203
C	-2.18165691	-0.02662740	0.64900797
C	-3.34940175	-0.56829050	1.16969599
C	-3.86796152	-1.74380461	0.64915502
C	-3.21869282	-2.37386843	-0.40407298
C	-2.06251017	-1.82466289	-0.93415400
H	-1.21505254	2.51572003	-1.77180300
H	-1.03818367	4.78104186	-0.82237397
H	0.51403224	5.22181064	1.05771803

H	1.86707709	3.37117674	1.98993799
H	1.66119317	1.09858411	1.06832496
H	0.12080516	-1.98792754	1.06832496
H	1.98598615	-3.30252457	1.98993799
H	4.26520455	-3.05607029	1.05771803
H	4.65959554	-1.49142750	-0.82237397
H	2.78620373	-0.20559365	-1.77180300
H	-1.78199833	0.88934343	1.06832496
H	-3.85306325	-0.06865218	1.98993799
H	-4.77923678	-2.16574034	1.05771803
H	-3.62141187	-3.28961436	-0.82237397
H	-1.57115119	-2.31012638	-1.77180300
P	0.00000000	-0.00000000	-1.20274705

S.4.3.5 $^{t}Bu_3P$ (Figure S13, right)

P	-0.00087361	-0.00023691	-0.69784585
C	-1.69917005	-0.54917054	-0.00078374
C	0.37357773	1.74481192	-0.00118432
C	1.32543775	-1.19513532	-0.00157474
C	-2.18419806	-1.70730971	-0.88495341
H	-3.21693584	-1.95197654	-0.61214748
H	-2.17154404	-1.42362312	-1.93979339
H	-1.59503326	-2.61439635	-0.77483739
C	2.57031162	-1.03807265	-0.88688462
H	3.06206828	-0.07456632	-0.77801062
H	3.29806228	-1.81005095	-0.61270145
H	2.31850427	-1.17090444	-1.94153405
C	1.72847715	-1.04163779	1.46389398
H	0.88523618	-1.16659957	2.14363187
H	2.46928263	-1.81022056	1.71533491
H	2.18925731	-0.07602408	1.67186929
C	0.86341226	-2.63803619	-0.22265869
H	0.55177501	-2.80891139	-1.25567151
H	1.70751815	-3.30584290	-0.01934897
H	0.05207540	-2.93411763	0.44106720
C	-2.71760305	0.57198383	-0.22522691
H	-3.71847516	0.17312566	-0.02748975
H	-2.57322516	1.42227186	0.43999707
H	-2.70500988	0.92902547	-1.25764440
C	-1.76855155	-0.97214855	1.46522677
H	-1.44744282	-0.18008725	2.14194932
H	-2.80569822	-1.22194482	1.71936122
H	-1.16794613	-1.85738872	1.67313029
C	-0.38871627	2.74550813	-0.88256912
H	-1.46827668	2.69019353	-0.76597728
H	-0.08142465	3.76182895	-0.61155250
H	-0.15503975	2.59253003	-1.93859618
C	1.85362515	2.06640477	-0.22735789
H	2.01057433	3.13119277	-0.02403498
H	2.51856083	1.51152457	0.43358783
H	2.15426616	1.88292559	-1.26143515
C	0.04447241	2.01377051	1.46582062
H	0.35141439	3.03467571	1.72285476
H	-1.02279488	1.94007905	1.67470365
H	0.56690482	1.33502472	2.14048782

S.4.3.6 ***12***$^{+}$ *(Figure S14, left)*

Fe	-0.7722361	0.0939918	-2.4961274
P	-0.8028972	-0.7974937	-0.3072420
P	0.5325035	0.8627960	-0.6795849
O	-2.6613124	2.1785626	-1.6146474
O	1.1958651	-2.0525895	-2.9474880
O	-2.8425304	-1.4278753	-3.9091080

O	0.1341302	1.7820624	-4.7179651
N	-2.1714465	0.8021384	1.6984040
N	-3.4574487	-0.4389579	0.4704255
N	3.1732861	0.4322925	-1.5140572
N	2.7293108	-0.8025120	0.2136585
C	3.1784627	0.9090001	-3.9568613
H	4.2164214	0.6647599	-4.1761082
H	2.8656148	1.6671904	-4.6753434
H	2.5793643	0.0128684	-4.1207184
C	-2.1824717	-0.0389049	0.6445970
C	-3.4593509	0.9566214	2.1727238
C	-4.2678380	0.1728993	1.4002736
C	-0.9585432	1.4100613	2.2835699
H	-0.1427218	0.9348708	1.7426350
C	-0.8814157	2.8982996	1.9993088
H	-0.9867441	3.1017243	0.9325844
H	0.0950480	3.2650272	2.3196878
H	-1.6405925	3.4645848	2.5372787
C	-0.7922966	1.0500213	3.7490028
H	-1.4833148	1.5879261	4.3950841
H	0.2194435	1.3229123	4.0537010
H	-0.9205488	-0.0220000	3.9096042
C	-3.8491494	-1.4912084	-0.4867132
H	-2.9543401	-1.6343787	-1.0960353
C	-4.9723414	-1.0531566	-1.4072456
H	-5.9347205	-1.0283504	-0.8997231
H	-5.0520157	-1.7724403	-2.2230459
H	-4.7810701	-0.0681522	-1.8374792
C	-4.1172774	-2.8008073	0.2331216
H	-3.2623849	-3.0913116	0.8464098
H	-4.2894979	-3.5821146	-0.5084446
H	-4.9993719	-2.7445455	0.8706551
C	-3.8604885	1.8030228	3.3217722
H	-3.6859661	1.2960503	4.2733062
H	-4.9246225	2.0223263	3.2526319
H	-3.3334744	2.7542462	3.3400043
C	-5.7363579	0.0048791	1.5005766
H	-6.2551715	0.5391090	0.7019715
H	-6.0822729	0.4055811	2.4512071
H	-6.0350766	-1.0417523	1.4604053
C	2.1866316	0.0539217	-0.6768006
C	4.3436784	-0.2098099	-1.1726294
C	4.0633009	-0.9898191	-0.0873374
C	3.0037133	1.4652175	-2.5554794
H	1.9649277	1.7857347	-2.4411415
C	3.8774712	2.6741383	-2.2771871
H	3.7500045	3.0250651	-1.2517651
H	3.5819942	3.4783293	-2.9524721
H	4.9321515	2.4657621	-2.4519607
C	2.0240240	-1.3775377	1.3782260
H	1.0563756	-0.8812518	1.3662655
C	1.7714579	-2.8636124	1.2082300
H	1.2760350	-3.0721468	0.2587679
H	1.1168679	-3.2009021	2.0135403
H	2.6876332	-3.4499644	1.2588115
C	2.6967261	-1.0080537	2.6881242
H	3.6192815	-1.5597634	2.8582190
H	2.0141181	-1.2544161	3.5030819
H	2.9113530	0.0612487	2.7344063
C	5.6561585	-0.0336057	-1.8372185
H	5.5748662	0.0031380	-2.9207084
H	6.3024286	-0.8724738	-1.5845057
H	6.1551112	0.8775751	-1.4998706
C	5.0067832	-1.8497429	0.6658378
H	5.4118438	-1.3310773	1.5375956
H	5.8448976	-2.1128067	0.0221560
H	4.5490875	-2.7768048	1.0028151
C	-1.9384391	1.3883206	-1.9704173
C	0.4380953	-1.2294145	-2.7981909
C	-2.0549490	-0.8358711	-3.3571510

C	-0.1937706	1.1233488	-3.8619039

S.4.3.7 [(PF$_3$)Fe(CO)$_4$] (Figure S14, right)

C	-0.60308800	-0.33477500	1.75677900
O	-0.62590700	-0.55242000	2.87488700
C	-0.59496000	-1.36317800	-1.15467000
O	-0.61301100	-2.23170000	-1.89195500
C	-0.59269500	1.68874800	-0.58367400
O	-0.60947900	2.76679200	-0.95224700
C	-2.38843700	0.00618700	-0.01228600
O	-3.52332100	0.01123500	-0.02333300
P	1.50865100	0.00118500	-0.00097100
Fe	-0.59834000	-0.00002400	0.00141800
F	2.25257100	-0.15877100	-1.35314500
F	2.25941200	1.25045500	0.53122700
F	2.26311800	-1.08616100	0.80880600

*S.4.3.8 **3**$^{4+}$ (Figure 3)*

P	0.0089362	-1.4815646	0.5109907
P	-1.5048450	0.1600778	0.3902371
P	-0.0715216	0.9079918	-1.1506161
P	1.4090041	0.2524520	0.3801545
N	-0.1491554	-3.4075291	2.4477849
N	-0.0738121	-1.4594093	3.4168590
N	-3.0898632	-1.3197951	-1.5448958
N	-4.1691452	-0.4040328	0.1091666
N	0.2929901	3.3791693	-2.2613943
N	-0.0472048	3.6322762	-0.1260770
N	3.0926803	-0.9886734	-1.6445643
N	4.0581837	0.4036720	-0.2789902
C	-0.0437544	-2.0767007	2.2157825
C	-0.2496321	-3.6292169	3.7907750
C	-0.1959301	-2.3957143	4.4065183
C	-0.2414511	-4.4227683	1.3691957
H	0.0456056	-3.8741511	0.4698658
C	0.7567292	-5.5503219	1.5374222
H	1.7586977	-5.1683340	1.7406259
H	0.7893398	-6.1097192	0.6014708
H	0.4761010	-6.2479388	2.3232997
C	-1.6776738	-4.8779769	1.1930843
H	-2.0400566	-5.4453022	2.0499895
H	-1.7378819	-5.5266076	0.3181806
H	-2.3468434	-4.0272828	1.0387150
C	0.0976307	-0.0028990	3.5953722
H	0.0150636	0.3922639	2.5834916
C	1.4906600	0.3139249	4.1049045
H	1.6592448	-0.0686297	5.1107397
H	1.6219174	1.3961905	4.1390007
H	2.2535368	-0.1100126	3.4484189
C	-1.0202248	0.6200381	4.4085645
H	-2.0009667	0.2884003	4.0621752
H	-0.9670476	1.7039640	4.2963754
H	-0.9344241	0.4093478	5.4721131
C	-0.3800654	-4.9545096	4.4346362
H	-1.1842257	-5.5445030	3.9956642
H	-0.6050789	-4.8255653	5.4906313
H	0.5470947	-5.5240251	4.3589772
C	-0.2593251	-2.1084510	5.8558410
H	0.5664390	-1.4778340	6.1843841
H	-0.2030977	-3.0401527	6.4133368

H	-1.1962164	-1.6182698	6.1247813
C	-2.9390818	-0.5586219	-0.4385555
C	-4.4094161	-1.6363959	-1.7023054
C	-5.0919632	-1.0595481	-0.6510143
C	-1.9847154	-1.6853973	-2.4544249
H	-1.0919676	-1.3777168	-1.9112203
C	-1.8832625	-3.1842971	-2.6608632
H	-1.9042721	-3.7185200	-1.7095861
H	-0.9349987	-3.4033555	-3.1539819
H	-2.6710033	-3.5768633	-3.2996822
C	-2.0495427	-0.8748718	-3.7352460
H	-2.9110888	-1.1351335	-4.3482852
H	-1.1543477	-1.0694469	-4.3270058
H	-2.0987495	0.1940110	-3.5179984
C	-4.4331677	0.3838132	1.3384857
H	-3.4370247	0.6623316	1.6885143
C	-5.0716286	-0.4624345	2.4212982
H	-6.0979488	-0.7395005	2.1878538
H	-5.0911259	0.1200368	3.3434735
H	-4.4977643	-1.3738110	2.6038017
C	-5.1700306	1.6695050	1.0167215
H	-4.6773715	2.2106318	0.2070332
H	-5.1679839	2.3015340	1.9056323
H	-6.2085547	1.5014294	0.7348373
C	-4.9762269	-2.4673926	-2.7864943
H	-4.5183750	-2.2612891	-3.7513711
H	-6.0422514	-2.2666879	-2.8760209
H	-4.8573151	-3.5314228	-2.5691645
C	-6.5407239	-1.1560631	-0.3671859
H	-6.7459195	-1.9555088	0.3481842
H	-7.0757265	-1.3904887	-1.2858696
H	-6.9496329	-0.2296179	0.0278075
C	0.0182385	2.7125735	-1.1135809
C	0.4070661	4.7126866	-1.9972190
C	0.1735461	4.8760483	-0.6479887
C	0.5378322	2.7060550	-3.5604083
C	2.0308840	2.5797535	-3.8033960
H	2.5257452	3.5505331	-3.8367840
H	2.1994348	2.0861635	-4.7612152
H	2.5067671	1.9826699	-3.0198133
C	-0.2335771	3.3308484	-4.7057520
H	-1.2814678	3.4833567	-4.4421611
H	-0.1926061	2.6401419	-5.5489450
H	0.1910568	4.2752063	-5.0385119
C	0.7259520	3.8303237	2.2230771
H	1.7190453	3.5062102	1.9069493
H	0.5372937	3.4306865	3.2204526
H	0.7251697	4.9142774	2.3105124
C	-0.3449518	3.3101742	1.2844954
H	-0.2968747	2.2225114	1.3160275
C	-1.7604312	3.7166705	1.6490902
H	-1.8854565	4.7975640	1.6925789
H	-2.0031569	3.3180683	2.6351969
H	-2.4786370	3.3231455	0.9271753
C	0.7218248	5.7707549	-2.9820877
H	1.5638929	5.4990481	-3.6176305
H	0.9869858	6.6851088	-2.4552241
H	-0.1357837	5.9855584	-3.6221395
C	0.1660110	6.1517561	0.1034335
H	-0.5267913	6.1374949	0.9404315
H	-0.1379578	6.9598556	-0.5600474
H	1.1617441	6.3878375	0.4869738
C	2.8783139	-0.1934798	-0.5737803
C	4.4053948	-0.9048480	-2.0183765
C	5.0118659	-0.0086886	-1.1636064
C	2.0571926	-1.8519993	-2.2475814
H	1.1298064	-1.4825377	-1.8116246
C	1.9465231	-1.6664150	-3.7481025
H	1.8729514	-0.6108636	-4.0164732
H	1.0406779	-2.1688985	-4.0901983

H	2.7764409	-2.1099627	-4.2924490
C	2.2386707	-3.2928399	-1.8091479
H	3.1374542	-3.7410895	-2.2310677
H	1.3852498	-3.8817231	-2.1489912
H	2.3040567	-3.3672353	-0.7210777
C	4.2144484	1.4328018	0.7786317
H	3.3246283	1.3067519	1.3988321
C	4.1672615	2.8182487	0.1612622
H	4.9985997	2.9902184	-0.5224741
H	4.2275259	3.5664237	0.9529657
H	3.2351169	2.9724369	-0.3898681
C	5.4157292	1.1863227	1.6706672
H	5.5004629	0.1333517	1.9434072
H	5.2760934	1.7622745	2.5863757
H	6.3495004	1.5144632	1.2191218
C	5.0362016	-1.6488055	-3.1309956
H	4.7114549	-2.6872842	-3.1641820
H	6.1161433	-1.6474393	-2.9995681
H	4.8149652	-1.1874329	-4.0957925
C	6.4224794	0.4368061	-1.1799323
H	6.5079701	1.5198380	-1.0957725
H	6.8848425	0.1431049	-2.1199601
H	6.9909774	-0.0171238	-0.3662990
H	0.1329726	1.7017559	-3.4177884

S.4.3.9 Intermediate 7^{2+} (scheme 2; Table S6)

P	0.6380	-0.5757	0.7808
P	-0.6023	0.4658	-0.8113
N	3.3155	-0.8908	0.1316
N	2.8205	1.2399	0.0607
N	-3.2730	0.9192	-0.2183
N	-2.8610	-1.2209	-0.0248
C	2.3091	0.0072	0.2994
C	4.4574	-0.2285	-0.2306
C	4.1471	1.1230	-0.2650
C	3.1637	-2.3637	0.3003
H	2.1638	-2.4687	0.7477
C	4.1575	-2.9323	1.3017
H	5.1779	-3.0039	0.9047
H	3.8419	-3.9532	1.5601
H	4.1766	-2.3452	2.2314
C	3.1397	-3.0714	-1.0464
H	2.3629	-2.6535	-1.7033
H	2.9156	-4.1357	-0.8856
H	4.1027	-3.0189	-1.5728
C	5.7795	-0.8489	-0.5110
H	6.3321	-1.0608	0.4177
H	6.3901	-0.1637	-1.1114
H	5.6911	-1.7851	-1.0747
C	5.0639	2.2381	-0.6207
H	4.9578	2.5227	-1.6796
H	6.1042	1.9281	-0.4637
H	4.8959	3.1324	-0.0106
C	2.0561	2.5076	0.1982
H	1.0300	2.1723	0.3913
C	2.5010	3.2988	1.4208
H	2.4701	2.6806	2.3287
H	1.8106	4.1423	1.5642
H	3.5094	3.7214	1.3179
C	2.0362	3.2985	-1.1010
H	3.0023	3.7620	-1.3386
H	1.3057	4.1143	-1.0027
H	1.7282	2.6700	-1.9498
C	-2.2957	-0.0214	-0.3033
C	-4.4531	0.3163	0.1258
C	-4.1943	-1.0419	0.2402

C	-3.0568	2.3764	-0.4387
H	-2.0357	2.4253	-0.8463
C	-3.9839	2.9443	-1.5026
H	-3.9871	2.3230	-2.4099
H	-3.6167	3.9415	-1.7845
H	-5.0165	3.0703	-1.1539
C	-3.0597	3.1336	0.8814
H	-4.0443	3.1349	1.3694
H	-2.7899	4.1825	0.6924
H	-2.3269	2.7117	1.5850
C	-5.7624	0.9967	0.3048
H	-5.6683	1.9628	0.8142
H	-6.4267	0.3684	0.9111
H	-6.2640	1.1663	-0.6608
C	-5.1774	-2.1138	0.5448
H	-5.5610	-2.5777	-0.3777
H	-6.0378	-1.6879	1.0759
H	-4.7602	-2.9064	1.1758
C	-2.1215	-2.5100	0.0039
H	-1.1199	-2.2431	-0.3548
C	-2.6875	-3.5149	-0.9882
H	-3.6574	-3.9257	-0.6802
H	-1.9893	-4.3606	-1.0647
H	-2.7879	-3.0736	-1.9901
C	-1.9770	-3.0301	1.4275
H	-1.5650	-2.2604	2.0971
H	-1.2842	-3.8840	1.4246
H	-2.9241	-3.3856	1.8551
Cl	-0.1529	-0.8769	-2.3317
Cl	0.0995	0.6825	2.3445

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