Electronic Supplementary Information

Imidazoliumyl-Substituted Di- and Iso-Tetraphosphanes and Their Metal-Mediated Fragmentation Reactions

Jannis Fidelius,[a,†] Clemens Taube,[a,†] Kai Schwedtmann,[a] Felix Hennersdorf,[a] Antonio Frontera,[b] Robert Wolf,*[,c] and Jan J. Weigand*[,a]

[†]These authors contributed equally to this work.

[a]Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany
[*] E-mail: jan.weigand@tu-dresden.de

[b]Department of Chemistry, Universitat de Illes Balears, 07122 Palma de Mallorca, Spain

[c]Institute of Inorganic Chemistry, Universität Regensburg, 93040 Regensburg, Germany
[*] E-mail: robert.wolf@ur.de

Table of contents

1. General remarks, materials and methods

Manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified nitrogen or argon, respectively. All glassware was oven-dried at 160 °C prior to use.

Dry, oxygen-free **solvents** (CH_2Cl_2, C_6H_5F, *o*-$C_6H_4F_2$, CH_3CN, $MeNO_2$ $C_2H_4Cl_2$ (distilled from CaH_2), *n*-hexane, *n*-pentane, THF, Et_2O, Toluene, Benzene (distilled from potassium)) were employed. All distilled and deuterated solvents were stored over 4 Å molecular sieves (except CD_3CN and CH_3CN 3 Å molecular sieves). Compounds **2c**[OTf][1] and $(Me_3Si)_2$Pyrazine **4**[2], were synthesized according to literature procedures. Additional reagents were obtained from commercial sources and used as received.

NMR spectra were measured on a Bruker *AVANCE III HD Nanobay 400 MHz UltraSieid* (^{1}H (400.13 MHz), ^{13}C (100.61 MHz), ^{31}P (161.98 MHz) ^{195}Pt (86.01 MHz)) or on a Bruker *AVANCE III HDX, 500 MHz Ascend* (^{1}H (500.13 MHz), ^{13}C (125.75 MHz), ^{31}P (202.45 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 δ_{TMS} = 0.00 ppm (^{1}H, ^{13}C), $\delta_{H3PO4(85\%)}$ = 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.

Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Argon atmosphere or were deducted from STA measurements and are uncorrected.

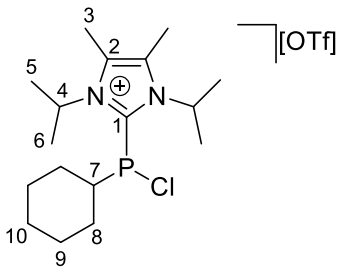
Infrared (IR) and **Raman** spectra were recorded at ambient temperature using a *Bruker Vertex 70* instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was 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.

2. Synthetic Details and Characterization Data

2.1. Synthesis of Imidazoliumyl-substituted Chlorophosphane Salts 2a-c[OTf]

2.1.1. Preparation of [L$_C$P(Cy)Cl][OTf] (**2a**[OTf])



A solution of 345 mg $CyPCl_2$ (1.5 equiv., 1.875 mmol) in 2 mL C_6H_5F is added to a solution of 500 mg **1**[OTf] (1 equiv., 1.24 mmol) in 4 mL C_6H_5F. The colorless solution is stirred three days at 100°C. The volume of the resulting solution is reduced *in vacuo*. Addition of 3 mL *n*-hexane leads to an off-white oil, which is stirred for 16 h. The resulting solid is filtered and washed with 3x1 mL diethyl ether. Drying *in vacuo* affords the product as an off-white powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et_2O into a saturated CH_3CN solution at −30°C.

Yield: 440 mg (74%); **m.p.** 127.0°C (dec.); **Raman** (100 mW, 50 scans, 298 K, [cm^{-1}]): 2972 (45), 2948 (98), 2935 (100), 2901 (36), 2855 (44), 1611 (34), 1445 (53), 1412 (37), 1401 (30), 1388 (18), 1363 (39), 1301 (10), 1276 (97), 1223 (10), 1204 (9), 1143 (16), 1033 (65), 1004 (12), 884 (20), 852 (14), 819 (10), 791 (17), 760 (21), 752 (30), 581 (14), 572 (13), 544 (14), 497 (50), 458 (14), 429 (15), 347 (20), 310 (23), 289 (15), 279 (14), 222 (14); **IR** (ATR, 298 K, [cm^{-1}]): 2991 (vw), 2931 (w), 2855 (vw), 1610 (vw), 1455 (vw), 1411 (w), 1260 (vs), 1220 (m), 1146 (vs), 1114 (w), 1087 (w), 1030 (vs), 1003 (w), 901 (w), 851 (w), 790 (w), 759 (w), 750 (w), 635 (vs); **^{1}H NMR** (CD_3CN, 300 K, in ppm) δ = 1.27 - 1.47 (6H, m, H8/9/10), 1.59 (6H, d, ^3J(HH) = 7.0 Hz, H5/6),1.69 - 1.77 (2H, m, H9/10), 1.81 - 1.9 (2H, m, H9/10), 2.38 (6H, s, H3), 2.70 - 2.80 (1H, m, H7), 5.34 (2H, br, H4); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 11.12 (2C, br. s, C3), 21.46 (4C, br. s, C5/C6), 26.15 (1C, s, C10), 26.38 (1C, s, C9), 26.52 (1C, s, C9), 28.45 (1C, br. s, C8), 28.66 (1C, br. s, C8), 41.93 (1C, d, ^1J(CP) = −27 Hz, C7), 53.95 (1C, s, C4), 54.07 (1C, s, C4), 122.21 (1C, q, ^1J(CF) = –321 Hz, OTf), 133.88 (4C, br. s, C2), 139.25 (1C, d, ^1J(CP) = −86 Hz, C1); **^{19}F{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = −79.27 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ(P) = 55.6 br. s.; **elemental analysis:** calculated for $C_{18}H_{31}ClF_3N_2O_3PS$: N 5.85, C 45.14, H 6.52, S 6.69; found: N 5.90, C 45.18, H 6.286, S 6.882.

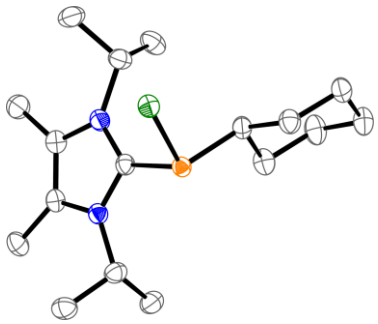


Figure S1: Molecular structure of cation **2a**$^{+}$ in **2a**[OTf] (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

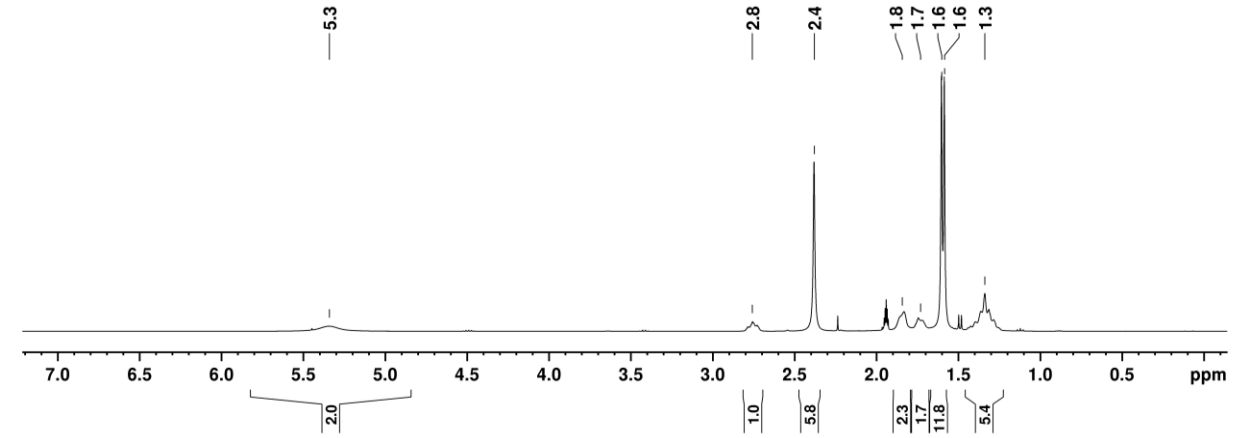


Figure S2: ^{1}H NMR-spectrum of **2a**[OTf] in CD_3CN at 300 K.

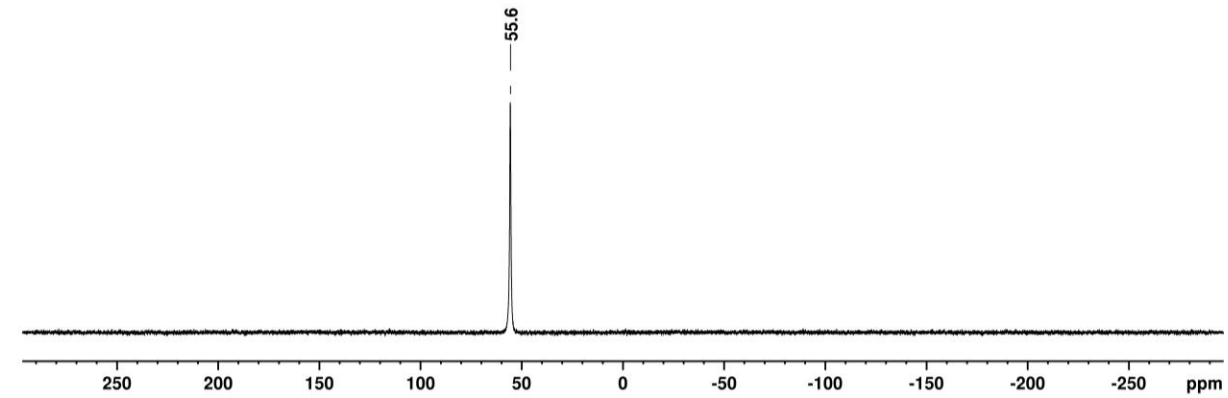


Figure S3: ^{31}P NMR-spectrum of **2a**[OTf] in CD_3CN at 300 K.

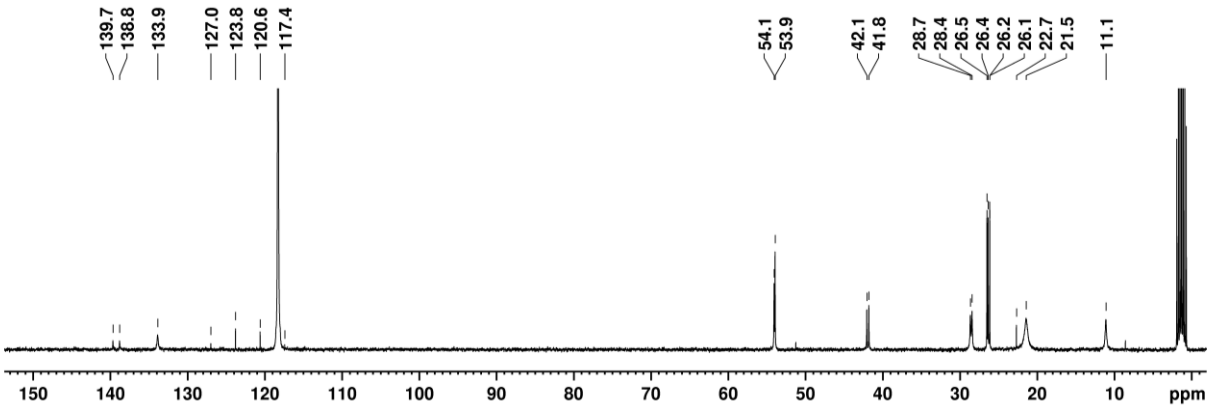


Figure S4: $^{13}C\{^{1}H\}$ NMR-spectrum of **2a**[OTf] in CD_3CN at 300 K.

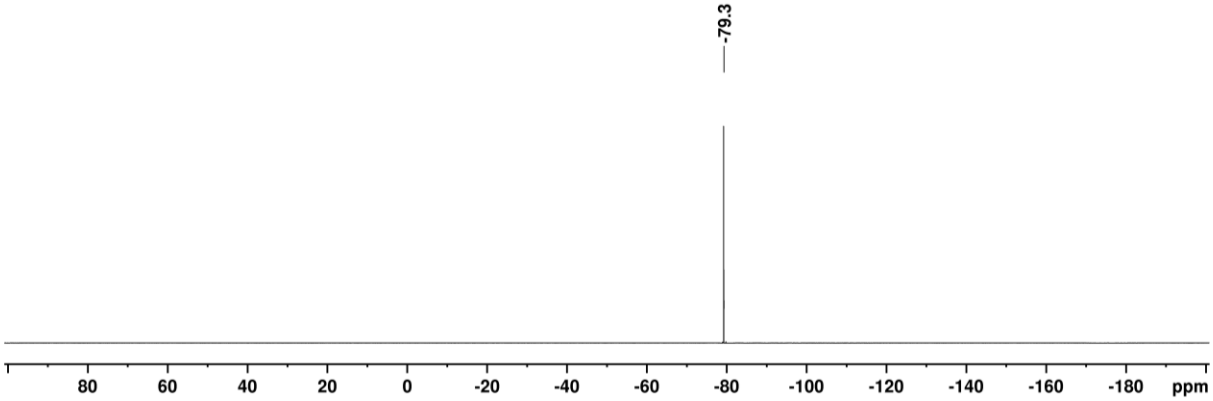
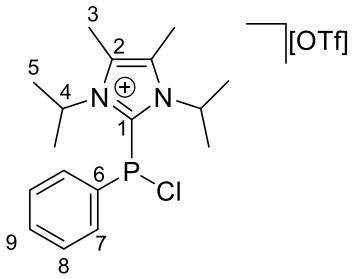


Figure S5: ^{19}F NMR-spectrum of **2a**[OTf] in CD_3CN at 300 K.

2.1.2. Preparation of [L$_C$P(Ph)Cl][OTf] (**2b**[OTf])



0.8 mL $PhPCl_2$ (1 equiv., 5.47 mmol) are added to a solution of 2.2 g **1**[OTf] (1 equiv., 5.47 mmol) in 20 mL C_6H_5F. The colorless solution is stirred overnight at 90°C. Addition of 20 mL *n*-hexane leads to a colorless oil. The supernatant solution is decanted off and the oil is washed with *n*-hexane, resulting in the formation of a colorless solid. After filtration, washing with *n*-hexane and subsequent drying *in vacuo*, the product is obtained as a white powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of *n*-pentane into a saturated CH_2Cl_2 solution at **–**30°C.

Yield: 1.9 g (74%); **m.p.** 67 °C (dec.); **Raman** (100 mW, 200 scans, 298 K, [cm^{-1}]): 3060 (40), 2990 (50), 2946 (74), 2878 (25),1613 (49), 1585 (64), 1574 (25), 1449 (49), 1401 (46), 1364 (32), 1273 (100), 1094 (31), 1032 (91), 997 (57), 753 (40), 500 (65), 347 (42), 312 (47), 276 (53), 169 (43); **IR** (ATR, 298 K, [cm^{-1}]): 2979 (vw), 2942 (vw), 1612 (vw), 1462 (vw), 1435 (vw), 1401 (vw), 1378 (vw), 1262 (vw), 1221 (vw), 1140 (vw),1113 (vw), 1091 (vw), 1070 (vw), 1029 (vw), 747 (vw), 700 (vw), 634 (vw); **^{1}H NMR** (CD_3CN, 298 K, in ppm) δ = 1.28 (6H, s(br), H5), 1.60 (6H, m, H5), 1.80 (2H, m, H4), 2.37 (6H, s, H3), 7.58 (5H, m, Ar-H); **^{13}C{^{1}H} NMR** (CD_3CN, 298 K, in ppm): δ = 11.03 (2C, s, C3), 21.81 (2C, s(br), C5), 26.34 (2C, s, C5), 54.21 (2C, d, ^3J(CP) = 10 Hz, C4), 68.39 (2C, s, C2), 124.59 (1C, q, ^1J(CF) = –320 Hz, OTf), 130.36 (1C, d, ^1J(CP) = 20 Hz, C6), 130.79 (2C, d, ^2J(CP) = 4 Hz, C7), 132.22 (2C, d, ^3J(CP) = 2 Hz, C8), 132.61 (1C, s, C9), 134.16 (1C, s(br), C1); **^{19}F{^{1}H} NMR** (CD_3CN, 298 K, in ppm): δ = **–**75.82 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 298 K, in ppm): δ(P) = 48.8 br. s.; **elemental analysis:** calculated for $C_{18}H_{25}ClF_3N_2O_3PS$: N 5.92, C 45.72, H 5.33, S 6.78; found: N 5.81, C 46.08, H 5.138, S 6.904.

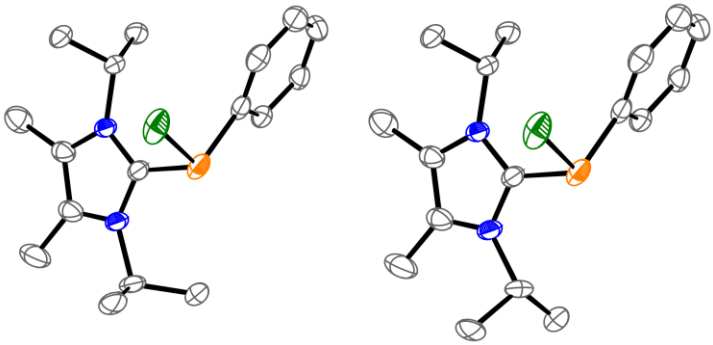


Figure S6: Molecular structure of cation **2b**$^+$ in **2b**[OTf]·C_6H_5F (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability). Herein the two conformers of the molecule are highlighted, which are present in the molecular structure as positional disorder.

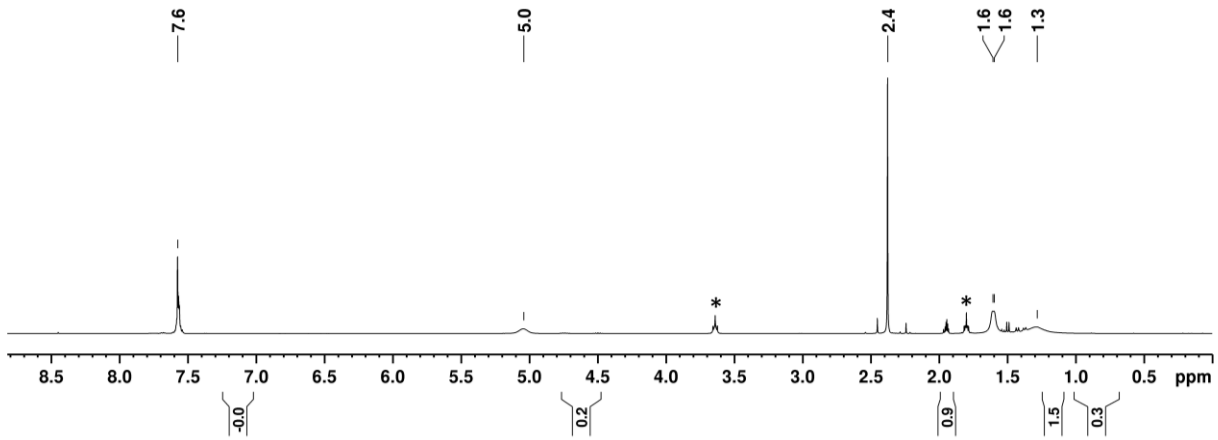


Figure S7: ^{1}H NMR-spectrum of **2b**[OTf] in CD_3CN at 300 K.

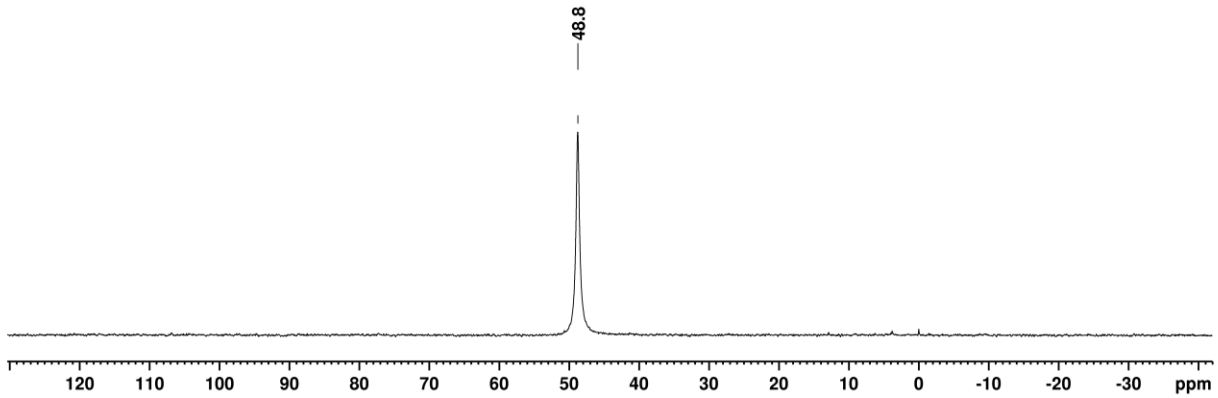


Figure S8: $^{31}P\{^{1}H\}$ NMR-spectrum of **2b**[OTf] in CD_3CN at 300 K

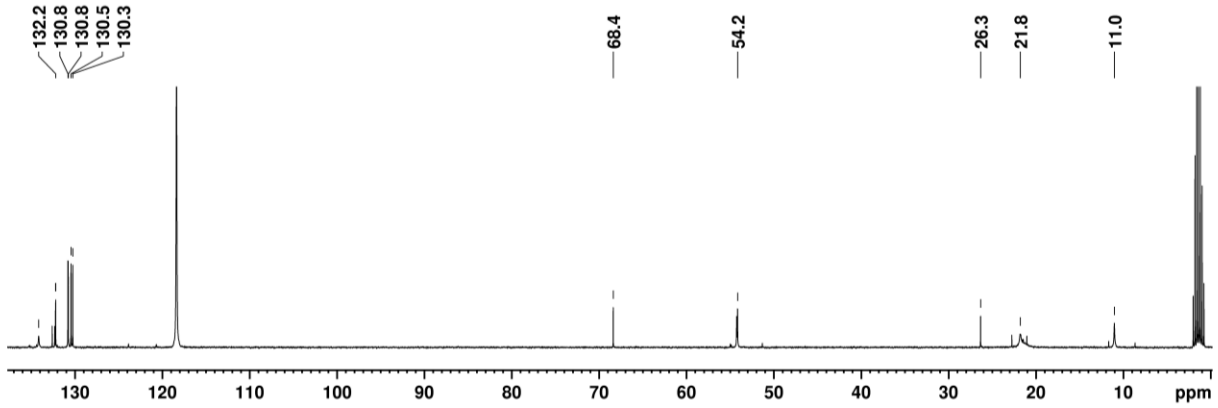


Figure S9: $^{13}C\{^{1}H\}$ NMR-spectrum of **2b**[OTf] in CD_3CN at 300 K

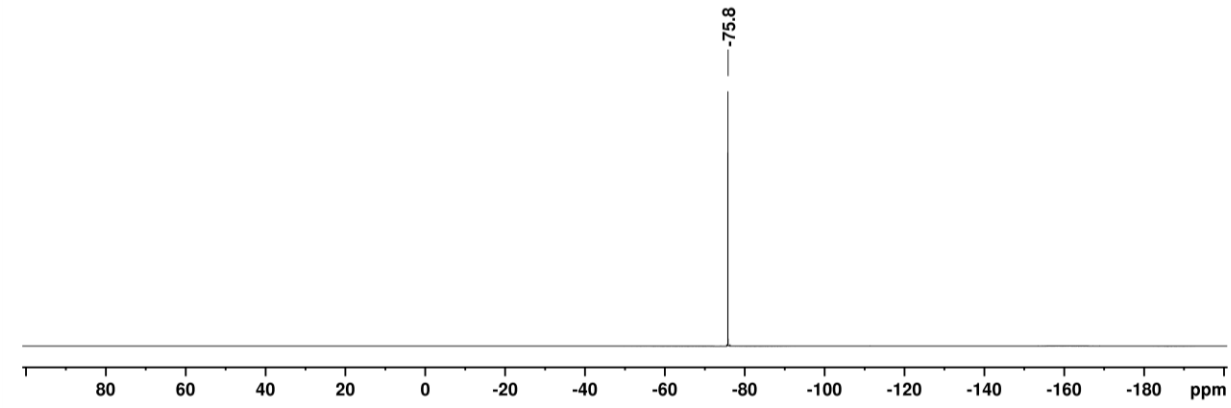


Figure S10: ^{19}F NMR-spectrum of **2b**[OTf] in CD_3CN at 300 K

2.1.3. Variable Temperature NMR Studies

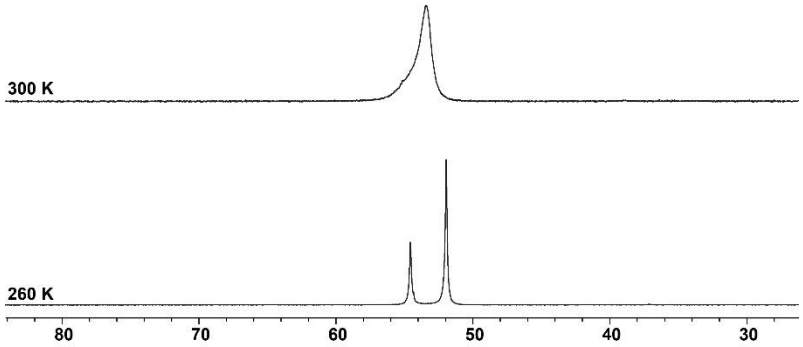


Figure S11: $^{31}P\{^{1}H\}$ NMR-spectra of **2a**[OTf] in CD_2Cl_2 at 300 K (top) and 260 K (bottom).

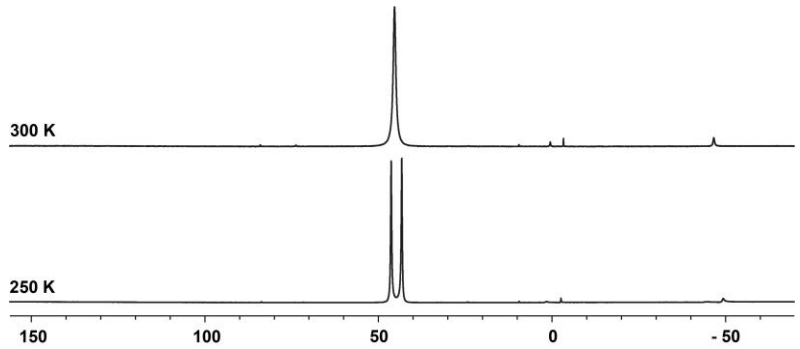


Figure S12: $^{31}P\{^{1}H\}$ NMR-spectra of **2b**[OTf] in CD_2Cl_2 at 300 K (top) and 250 K (bottom).

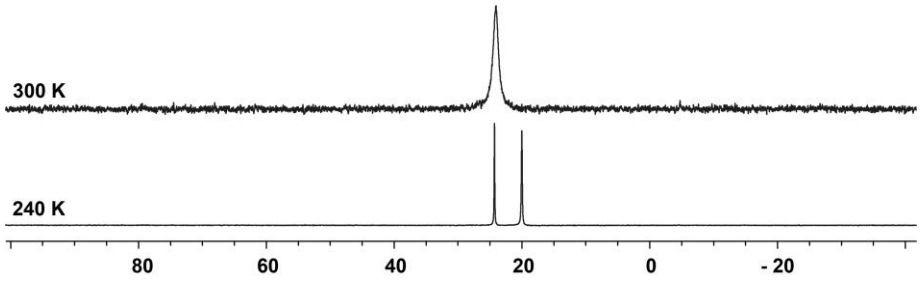
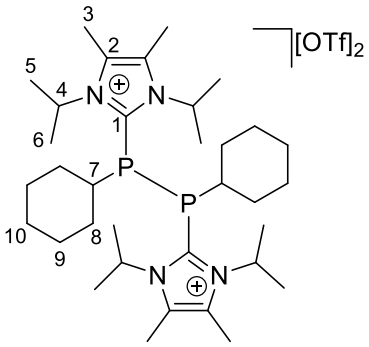


Figure S13: $^{31}P\{^{1}H\}$ NMR-spectra of **2c**[OTf] in CD_2Cl_2 at 300 K (top) and 240 K (bottom).

2.2. Synthesis of Imidazoliumyl-substituted Diphosphane Salts 5a-c[OTf]$_2$

2.2.1. Preparation of [(L$_C$PCy)$_2$][OTf]$_2$ (**5a**[OTf]$_2$)



A solution of 60 mg (Me$_3$Si)$_2$Pyrazine **4** (0.5 equiv., 0.27 mmol) in 2 mL fluorobenzene is dropwise added to a solution of 250 mg L$_C$P(Cy)Cl[OTf] **2a**[OTf] (1 equiv., 0.52 mmol) in 2 mL C$_6$H$_5$F. The color changes immediately to red. After 3 h stirring at room temperature first yellow precipitate is observed After 16 h the orange suspension is filtered and the precipitate washed with 3x1 mL C$_6$H$_5$F, 1x1 mL *o*-C$_6$H$_4$F$_2$ and *n*-pentane. Drying *in vacuo* affords the product as a light-yellow powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et$_2$O into a saturated CH$_3$CN solution at **–**30°C.

Yield: 143 mg (63%); **m.p.** 310.0°C (dec.); **Raman** (100 mW, 500 scans, 298 K, [cm^{-1}]): 2989 (41), 2938 (88), 2856 (40), 1611 (37), 1447 (37), 1410 (41), 1390 (19), 1356 (63), 1300 (16), 1277 (100), 1152 (18), 1033 (48), 886 (16), 792 (16), 753 (21), 742 (18), 505 (35), 348 (20), 312 (20), 170 (24); **IR** (ATR, 298 K, [cm^{-1}]): 2933 (vw), 2855 (vw), 1612 (vw), 1453 (vw), 1395 (w), 1377 (vw), 1263 (vs), 1221 (m), 1171 (vw), 1140 (vs), 1110 (w), 1084 (vw), 1031 (vs), 1000 (vw), 955 (w), 902 (vw), 752 (w), 635 (vs); **^{1}H NMR** (CD$_3$CN, 300 K, in ppm) δ = 0.43 (2H, br, H8), 1.00 (2H, br, H8), 1.12 - 1.31 (10H, m, H8/9), 1.53 - 1.72 (18H, m, H9/H10), 1.66 (6H, d, ^3J(HH) = 7.0 Hz, H6) 1.77 (6H, d, ^3J(HH) = 6.9 Hz, H5), 2.39 (6H, br, H3), 2.44 (6H, s, H3), 2.55 - 2.64 (2H, m, H7), 5.46 (2H, br, H4), 5.70 (2H, br, H4); **^{13}C{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = 11.46 (4C, br. s, C3), 21.30 (4C, br. s, C5), 22.23 (4C, s, C6), 25.90 (2C, s, C10), 26.68 - 27.12 (4C, m, C9), 31.47 - 31.94 (4C, m, C8), 37.63 (2C, br. s., C7), 54.39 - 54.62 (2C, ps. t, C4), 54.92 (2C, br., C4), 122.22 (2C, q, ^1J(CF) = –321 Hz, OTf), 134.80 (4C, br. s, C2), 137.80 (2C, br, C1); **^{19}F{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = **–**79.17 (s); **^{31}P{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ(P) = –50.0 to –38.4 br.; **elemental analysis:** calculated for C$_{36}$H$_{62}$F$_6$N$_4$O$_6$P$_2$S$_2$: N 6.32, C 48.75, H 7.05, S 7.23; found: N 6.30, C 48.74, H 7.013, S 7.665.

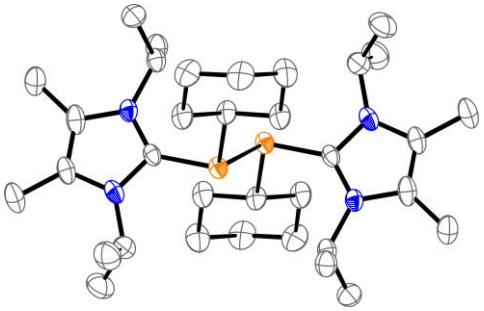


Figure S14: Molecular structure of cation **5a**$^{2+}$ in **5a**[OTf]$_2$·2 CH$_2$Cl$_2$ (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

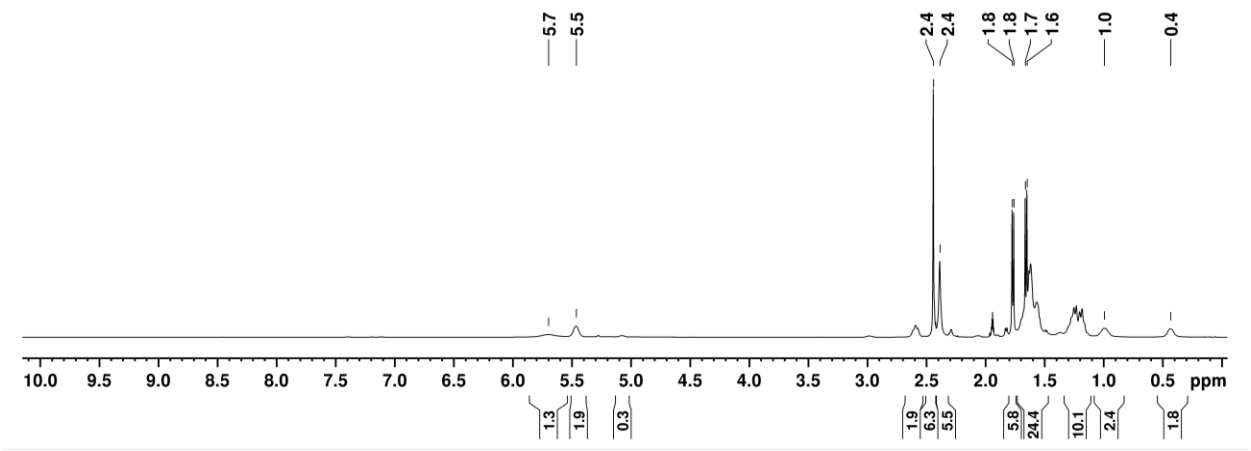


Figure S15: ^{1}H NMR-spectrum of **5a**[OTf]$_2$ in CD_3CN at 300 K.

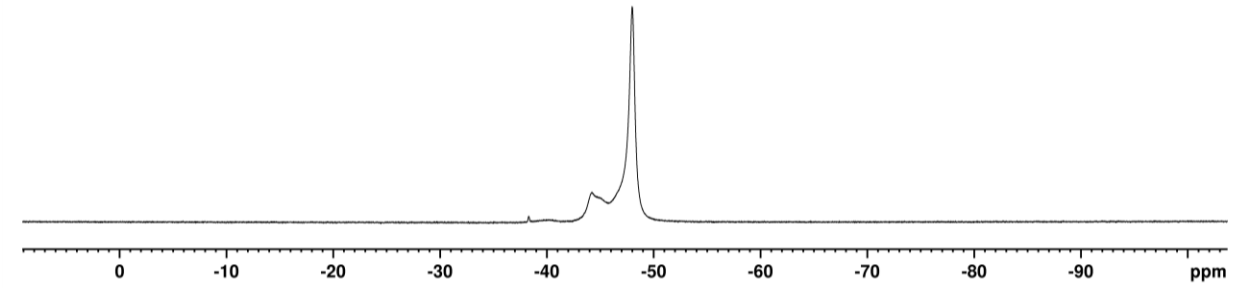


Figure S16: $^{31}P\{^{1}H\}$ NMR-spectrum of **5a**[OTf]$_2$ in CD_3CN at 300 K.

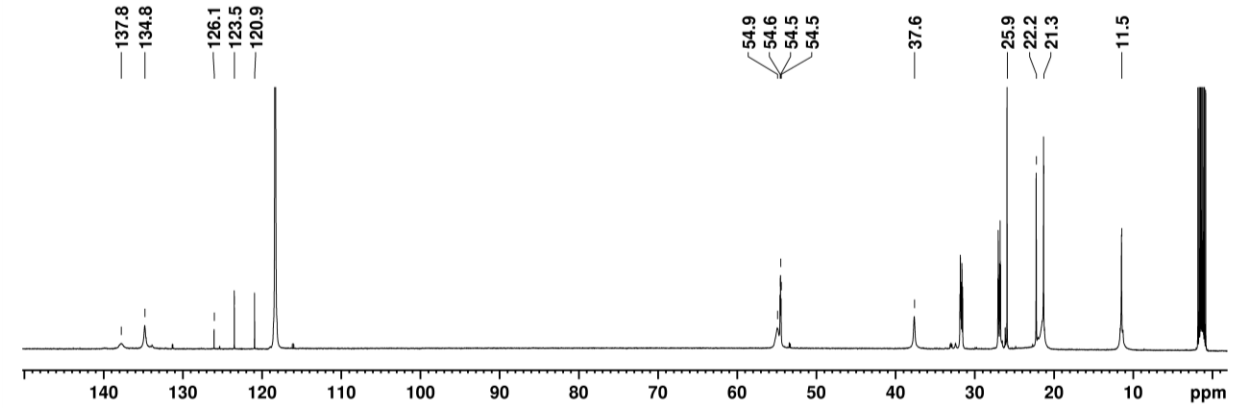


Figure S17: $^{13}C\{^{1}H\}$ NMR-spectrum of **5a**[OTf]$_2$ in CD_3CN at 300 K.

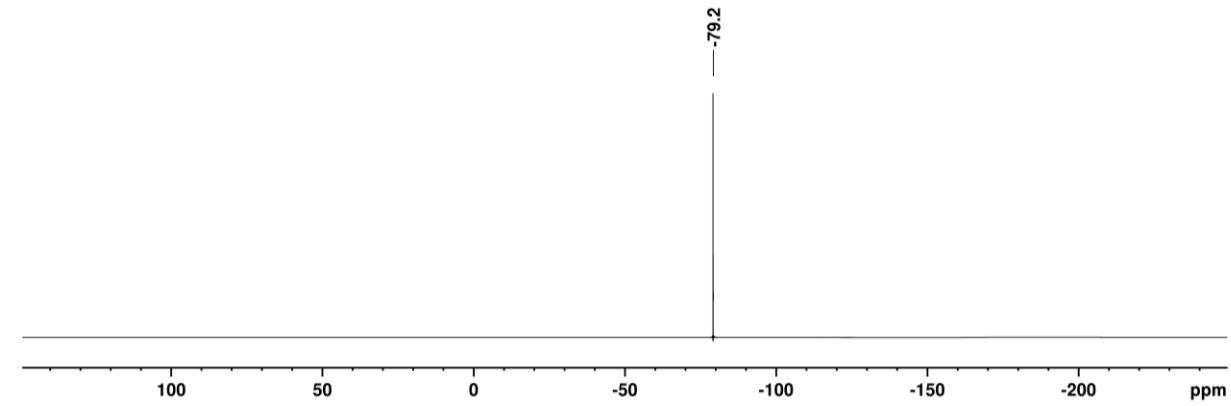
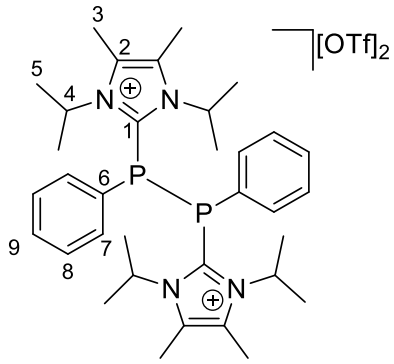


Figure S18: ^{19}F NMR-spectrum of **5a**$[OTf]_2$ in CD_3CN at 300 K.

2.2.2. Preparation of [(L$_C$PPh)$_2$][OTf]$_2$ (**5b**[OTf]$_2$)



A solution of 72 mg (Me$_3$Si)$_2$Pyrazine **4** (0.5 equiv., 0.32 mmol) in 2 mL C_6H_5F is dropwise added to a solution of 300 mg L$_C$P(Ph)Cl[OTf] **2b**[OTf] (1 equiv., 0.52 mmol) in 2 mL fluorobenzene at -30 °C. The color changes immediately from brown to yellow. After 3 h stirring at room temperature first colorless precipitate is observed. After 4 d the suspension is filtered, and the precipitate washed with 3x1 mL C_6H_5F and *n*-pentane. Drying *in vacuo* affords the product as a colorless powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of *n*-pentane into a saturated CH_2Cl_2 solution at **–**30°C.

Yield: 215 mg (78%); **m.p.** 291°C (dec.); **Raman** (90 mW, 100 scans, 298 K, [cm^{-1}]): 3061 (31), 2980 (40), 2938 (70), 1613 (48), 1584 (78), 1446 (43), 1391 (46), 1272 (100), 1091 (40), 1078 (36), 1032 (70), 1025 (61), 998 (61), 887 (30), 791 (28), 753 (33), 708 (28), 573 (30), 532 (31), 505 (52), 494 (39), 473 (33), 415 (39), 348 (34), 312 (37), 247 (33), 214 (34); **IR** (ATR, 298 K, [cm^{-1}]): 2977 (vw), 2938 (vw), 1612 (vw), 1458 (vw), 1437 (vw), 1401 (vw), 1389 (vw), 1373 (vw), 1264 (vs), 1223 (w), 1143 (m), 1111 (w), 1090 (w), 1031 (s), 749 (m), 703 (w), 636 (s); **^{1}H NMR** (CD_3CN, 300K, in ppm) δ = 1.34 (12H, d, ^3J(HH) = 6.60 Hz, H5), 1.54 (12H, d, ^3J(HH) = 6.96 Hz, H5), 2.41 (12H, s, H3), 5.47 (4H, m, H4), 7.50 (10H, m, Ar-H); **^{13}C{^{1}H} NMR** (CD_3CN, 300K, in ppm): δ = 11.56 (4C, s, C3), 21.05 (4C, s(br), C5), 22.23 (4C, s, C5), 55.42 (4C, ps. t, ^3J(CP) = 12 Hz, C4), 122.16 (2C, q, ^1J(CF) = –321 Hz, OTf), 127.91 (2C, s(br), C6), 131.46 (4C, ps. t, ^3J(CP) = 3 Hz, C8), 132.42 (2C, s, C9), 133.06 (4C, ps. t, ^3J(CP) = 11 Hz, C7), 135.44 (2C, s(br), C1); **^{19}F{^{1}H} NMR** (CD_3CN, 300K, in ppm): δ = **–**79.22 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300K, in ppm): δ(P) = –47.9.; **elemental analysis:** calculated for $C_{36}H_{50}F_6N_4O_6P_2S_2$: N 6.40, C 49.42, H 5.76, S 7.33; found: N 6.42, C 49.53, H 5.49, S 7.11.

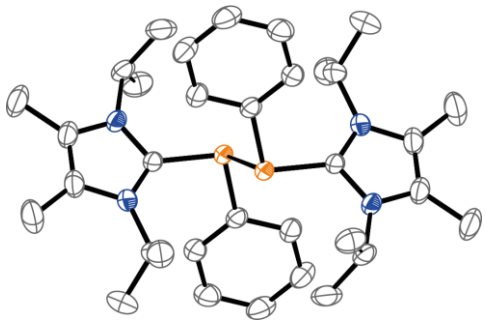


Figure S19: Molecular structure of cation **5b**$^{2+}$ in **5b**[OTf]$_2$ (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

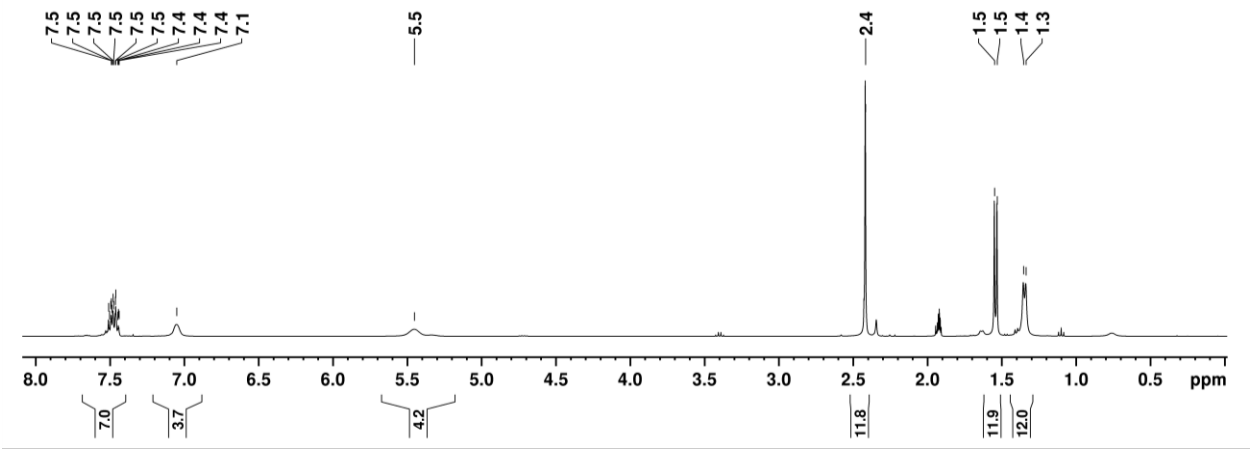


Figure S20: ^{1}H NMR-spectrum of **5b**[OTf]$_2$ in CD_3CN at 300 K.

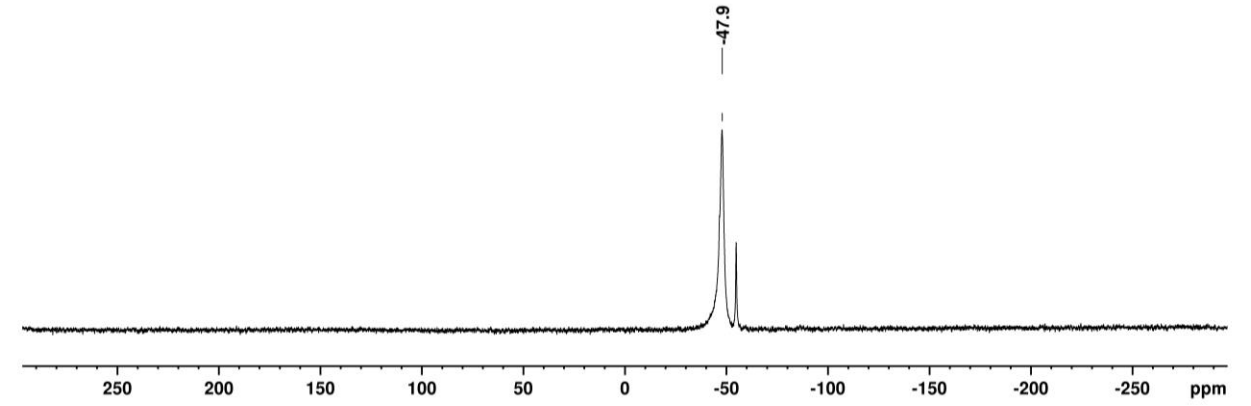


Figure S21: ^{31}P NMR-spectrum of **5b**[OTf]$_2$ in CD_3CN at 300 K.

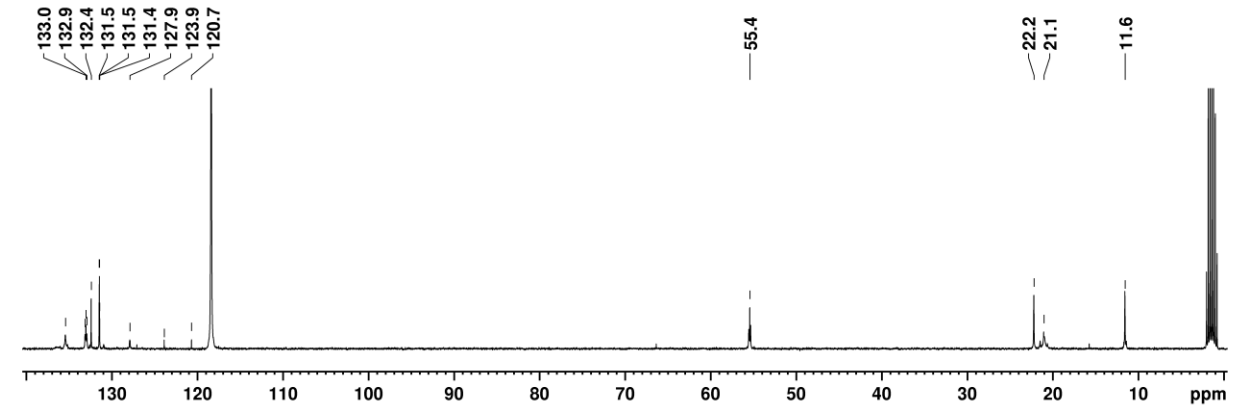


Figure S22: ^{13}C{^{1}H} NMR-spectrum of **5b**[OTf]$_2$ in CD_3CN at 300 K.

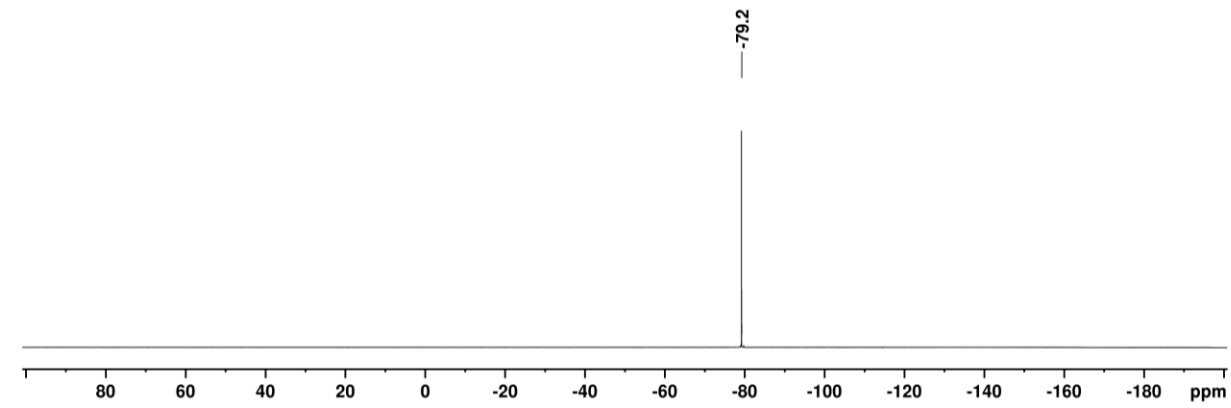
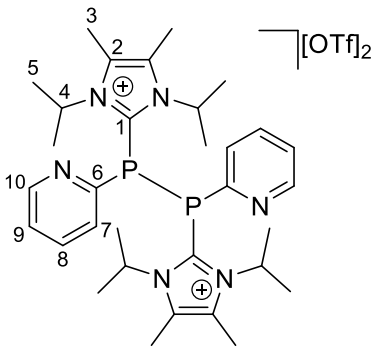


Figure S23: ^{19}F NMR-spectrum of **5b**$[OTf]_2$ in CD_3CN at 300 K.

2.2.3. Preparation of $[(L_CPPy)_2][OTf]_2$ (**5c**$[OTf]_2$)



A solution of 120 mg $(Me_3Si)_2$Pyrazine **4** (0.5 equiv., 0.53 mmol) in 3 mL C_6H_5F is dropwise added to a solution of 500 mg L_CP(Py)Cl[OTf] **2c**[OTf] (1 equiv., 1.06 mmol) in 5 mL C_6H_5F at -30 °C. The color changes immediately from brown to yellow. After 3 h stirring at room temperature first colorless precipitate is observed. After 16 h the suspension is filtered and the precipitate washed with 3x1 mL C_6H_5F and *n*-pentane. Drying *in vacuo* affords the product as a colorless powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of *n*-pentane into a saturated CH_2Cl_2 solution at **–**30°C.

Yield: 402 mg (87%); **m.p.** 269°C (dec.); **Raman** (100 mW, 500 scans, 298 K, [cm^{-1}]): 3054 (16), 2981 (32), 2939 (49), 1618 (31), 1573 (34), 1561 (35), 1453 (32), 1401 (38), 1280 (100), 1125 (34), 1045 (36), 1031 (57), 987 (74), 889 (21), 795 (19), 753 (26), 717 (17), 574 (19), 535 (21), 508 (50), 476 (19), 415 (22), 312 (29), 252 (26), 210 (27); **IR** (ATR, 298 K, [cm^{-1}]): 3046 (vw), 2979 (vw), 2938 (vw), 1616 (vw), 1571 (vw), 1560 (vw), 1450 (w), 1422 (w), 1400 (w), 1378 (w), 1262 (vs), 1223 (m), 1141 (s), 1113 (w), 1090 (w), 1030 (vs), 985 (w), 782 (w), 762 (w), 753 (w), 636 (vs); **^{1}H NMR** (CD_3CN, 300K, in ppm) δ = 1.39 (12H, s(br), H5), 1.59 (12H, s(br), H5), 2.42 (12H, s, H3), 5.61 (4H, s(br), H4), 7.43 (2H, ddd, ^3J(HH) = 7.70 Hz, ^3J(HH) = 7.70 Hz, ^4J(HH) = 2.00 Hz, H9), 7.47 (2H, m, H7), 7.81 (2H, qt, ^3J(HH) = 7.70 Hz, ^4J(HH) = 2.00 Hz, H10), 8.55 (2H, d, ^3J(HH) = 4.64 Hz, H8); **^{13}C{^{1}H} NMR** (CD_3CN, 300K, in ppm): δ = 10.25 (2C, s, C3), 21.08 (4C, s(br), C5), 53.97 (2C, s(br), C4), 121.49 (2C, q, ^1J(CF) = –325 Hz, OTf), 124.72 (1C, s, C9), 129.33 (1C, m, C7), 133.02 (2C, s(br), C2), 137.34 (1C, m, C10), 151.08 (1C, m, C8), 155.45 (1C, m, C6), the C1 resonance could not be detected; **^{19}F{^{1}H} NMR** (CD_3CN, 300K, in ppm): δ = **–**79.27 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300K, in ppm): δ(P) = –43.03 br. s.; **elemental analysis:** calculated for $C_{34}H_{48}F_6N_6O_6P_2S_2$: N 9.58, C 46.57, H 5.52, S 7.31; found: N 9.71, C 46.55, H 5.23, S 7.20.

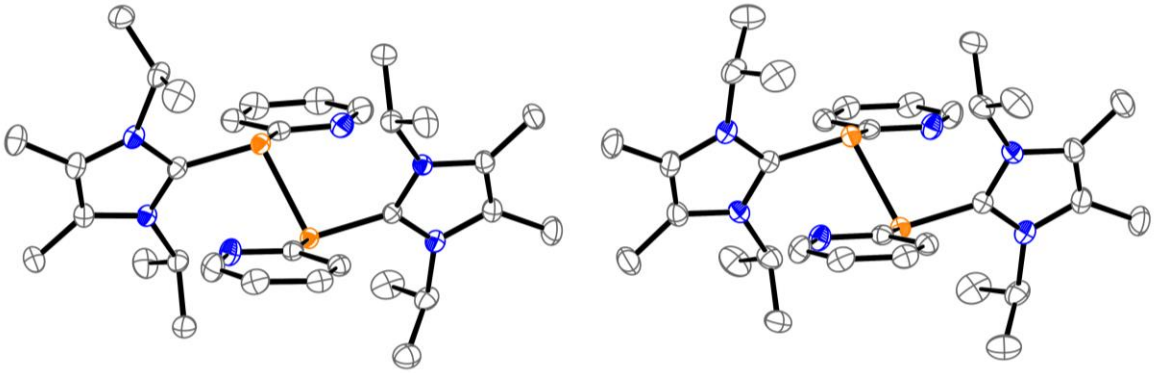


Figure S24: Molecular structure of cation **5c**$^{2+}$ in **5c**$[OTf]_2$ (one of two independent molecules of the asymmetric unit is shown; hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability). Herein two of the three possible conformers of the molecule are highlighted, which are present in the molecular structure as positional disorder.

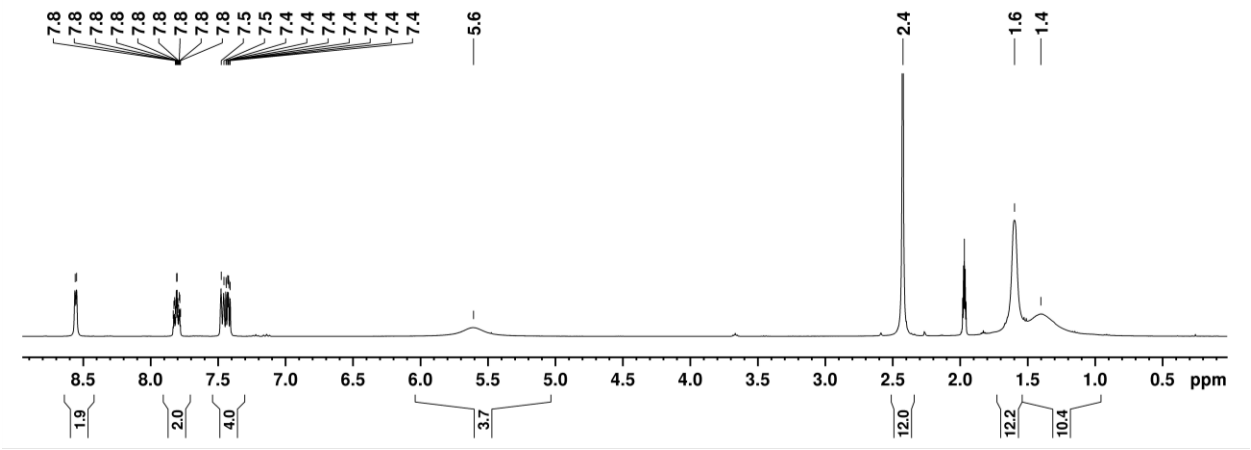


Figure S25: ^{1}H NMR-spectrum of **5c**[OTf]$_2$ in CD_3CN at 300 K.

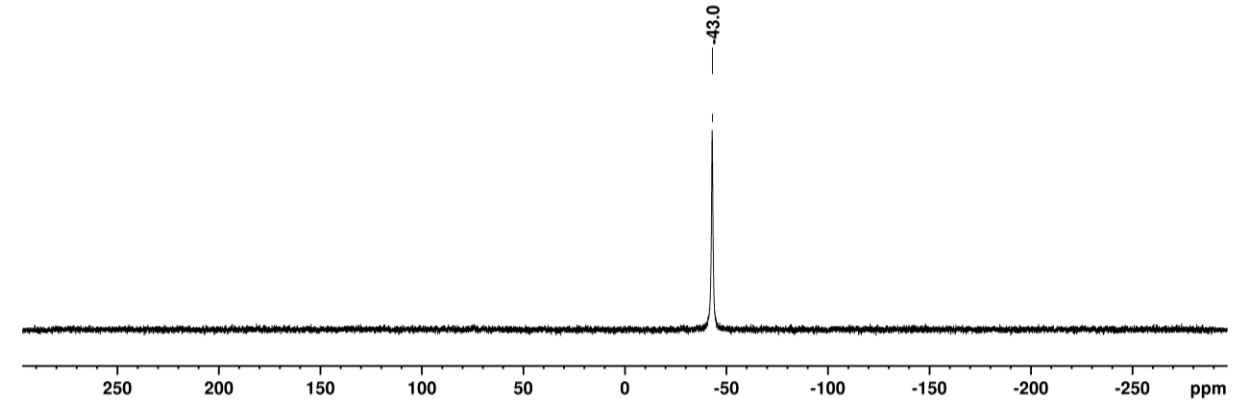


Figure S26: ^{31}P NMR-spectrum of **5c**[OTf]$_2$ in CD_3CN at 300 K.

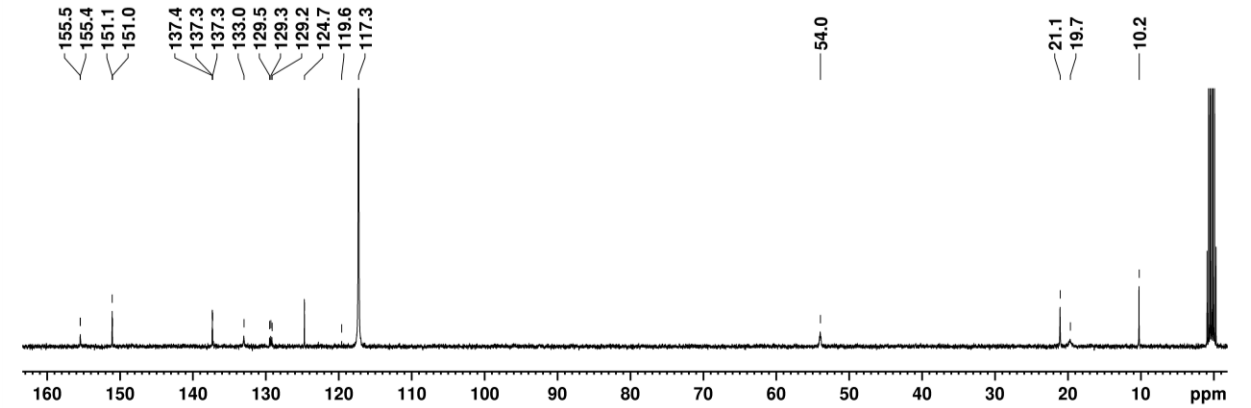


Figure S27: $^{13}C\{^{1}H\}$ NMR-spectrum of **5c**[OTf]$_2$ in CD_3CN at 300 K.

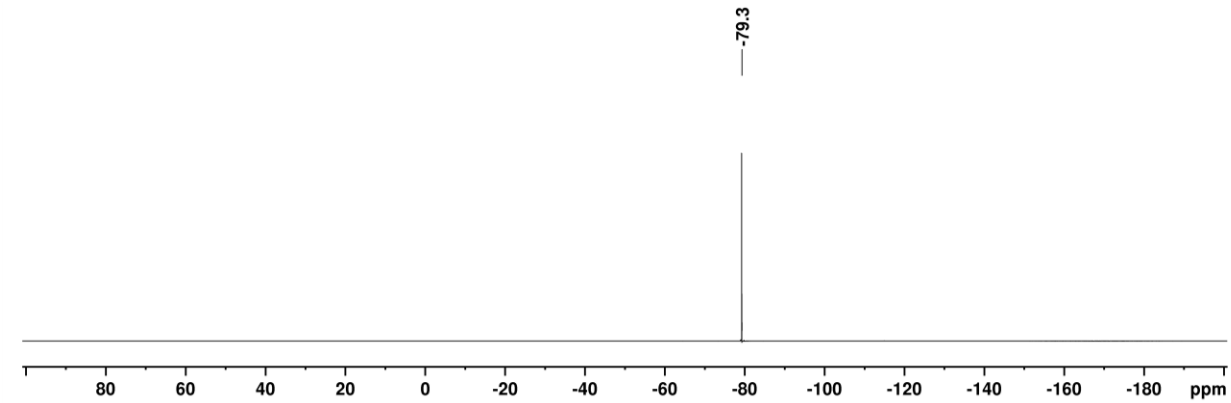


Figure S28: ^{19}F NMR-spectrum of **5c**$[OTf]_2$ in CD_3CN at 300 K.

2.2.4. Variable Temperature NMR Studies

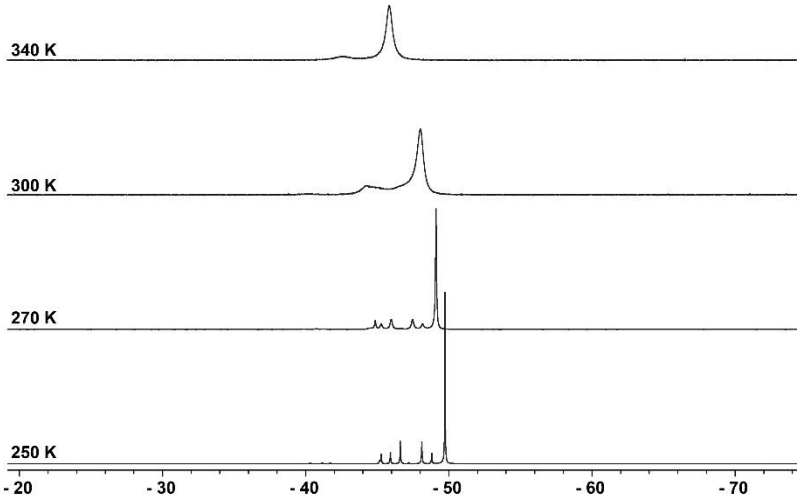


Figure S29: Variable temperature $^{31}P\{^{1}H\}$ NMR-spectra of **5a**$[OTf]_2$ in CD_3CN from 250 K to 340 K. Upon cooling to 250 K the broad resonances resolve into two singlet resonances (**5a**$[OTf]_2$: δ(P)= –49.8 ppm, δ(P)= –45.3 ppm) and an AB spin system (**5a**$[OTf]_2$: AB spin system $\delta(P_A)$= –48.5 ppm $\delta(P_B)$= –46.3 ppm, ^{1}J(PP) = –140 Hz).

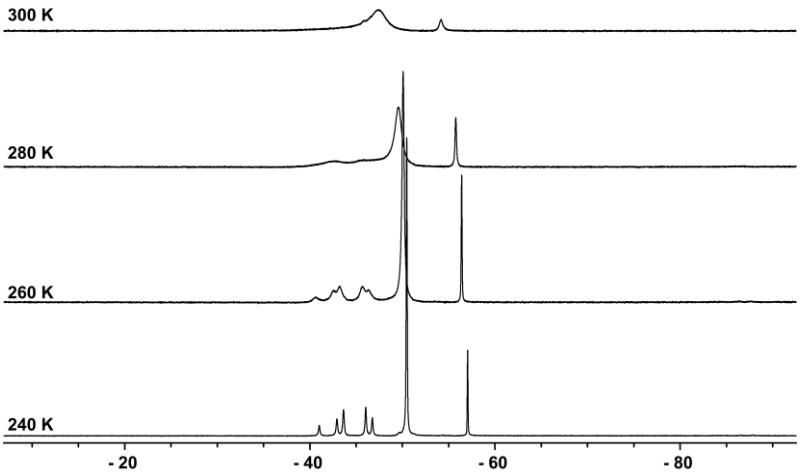


Figure S30: Variable temperature $^{31}P\{^{1}H\}$ NMR-spectra of **5b**$[OTf]_2$ in CD_3CN from 250 K to 340 K. Upon cooling to 250 K the broad resonances resolve into three singlet resonances (**5b**$[OTf]_2$: δ(P)= –57.1 ppm, δ(P)= –50.5 ppm, δ(P)= –41.0 ppm) and an AB spin system (**5b**$[OTf]_2$: AB spin system $\delta(P_A)$= –46.4 ppm $\delta(P_B)$= –43.3 ppm, ^{1}J(PP) = –146 Hz).

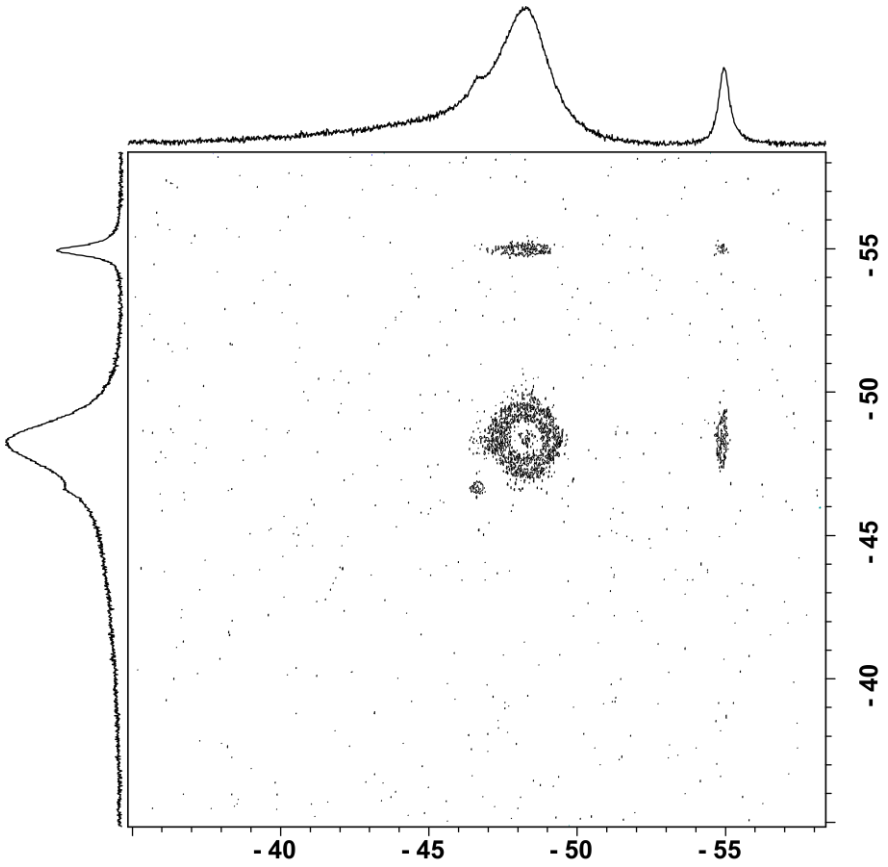


Figure S31: ^{31}P-^{31}P-EXSY NMR spectrum of **5b**$[OTf]_2$ in CD_3CN at 300 K (mixing time 1s).

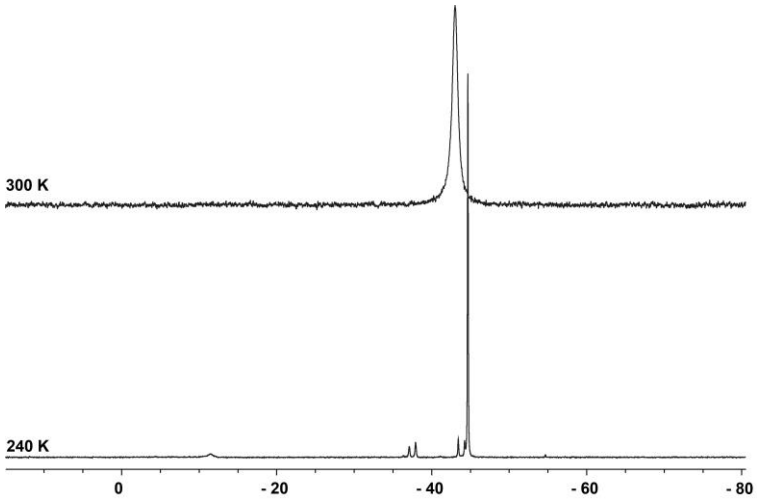
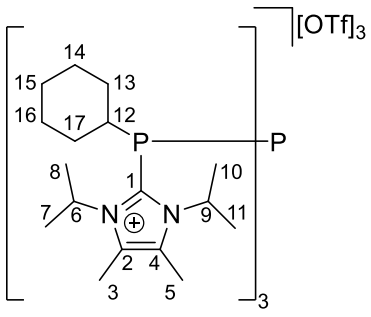


Figure S32: Variable temperature $^{31}P\{^1H\}$ NMR-spectra of **5c**$[OTf]_2$ in CD_3CN from 240 K to 300 K

2.3. Synthesis of Imidazoliumyl-substituted *iso*-Tetraphosphane Salts 6a,b[OTf]$_3$

2.3.1. Preparation of [(L_CPCy)$_3$P][OTf]$_3$ (**6a**[OTf]$_3$)



A solution of 305 mg P(SiMe$_3$)$_3$ (0.53 equiv., 1.22 mmol) in 1.5 mL C_6H_5F is dropwise added to a solution of 1.1 g L_CP(Cy)Cl[OTf] **2a**[OTf] (1 equiv., 2.30 mmol) in 1.5 mL C_6H_5F. The color changes immediately to red. After 3 h stirring at room temperature first precipitate is observed. After 3 d the orange suspension is filtered and the precipitate washed with 3x1 mL C_6H_5F, 2x1 mL *o*-$C_6H_4F_2$ and *n*-pentane. Drying under vacuum affords the product as a white powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et_2O into a saturated CH_3CN solution at –30°C.

Yield: 670 mg (74%); **m.p.** 249.8°C (dec.); **Raman** (100 mW, 100 scans, 298 K, [cm^{-1}]): 2992 (27), 2950 (85), 2880 (24), 2855 (31), 1610 (31), 1449 (38), 1404 (43), 1351 (49), 1272 (100), 1149 (19), 1033 (50), 999 (14), 885 (17), 790 (16), 752 (22), 738 (18), 573 (16), 347 (23), **IR** (ATR, 298 K, [cm^{-1}]): 2992 (vw), 2929 (w), 2855 (vw), 1608 (vw), 1450 (w), 1392 (w), 1351 (vw), 1260 (vs), 1221 (m), 1138 (s), 1028 (vs), 998 (w), 788 (vw), 752 (w), 635 (vs), **^{1}H NMR** (CD_3CN, 300 K, in ppm) δ = 1.03 (9H, d, ^3J(HH) = 6.7 Hz, H11), 1.20 - 1.27 (3H, m, H17), 1.30 - 1.38 (6H, m, H14/H15), 1.42 (9H, d, ^3J(HH) = 6.1 Hz, H10), 1.47 - 1.52 (6H, m, H16/H17), 1.60 (9H, d, ^3J(HH) = 6.5 Hz, H7), 1.62 - 1.65 (3H, m, H13), 1.71 (9H, d, ^3J(HH) = 6.7 Hz, H8), 1.76 - 1.83 (3H, m, H15), 1.83 - 1.89 (3H, m, H14), 1.94 - 1.95 (3H, m, H16), 2.04 - 2.11 (3H, m, H13), 2.34 (9H, s, H5), 2.46 (9H, s, H3), 2.67 - 2.76 (3H, m, H12), 4.05 (3H, br, H9), 5.83 (3H, br, H6); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = 11.43 (3C, s, C5), 11.66 (3C, s, C3), 21.55 (3C, s, C11), 21.94 (3C, s, C7), 22.25 (3C, s, C8), 22.69 (3C, s, C10), 25.88 (3C, s, C15), 26.93 (3C, br, C16), 27.97 (3C, s, C14), 31.24 (3C, s, C17), 33.49 (3C, br, C13), 37.30 (3C, br, C12), 55.20 - 55.84 (6C, m, C6/C9), 122.21 (3C, q, ^1J(CF) = –321 Hz, OTf), 134.64 (3C, s, C4), 135.20 (3C, s, C2), 137.80 (3C, dd, ^1J(CP) = –66 Hz, ^2J(CP) = 23 Hz, C1); **^{19}F{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = **–**79.23 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): AX_3 spin system δ(P_A) = –87.4, δ(P_X) = –57.7, ^1J(PP) = –271 Hz; **elemental analysis:** calculated for $C_{54}H_{93}F_9N_6O_9P_4S_3$: N 6.17, C 47.64, H 6.84, S 7.06; found: N 6.17, C 47.45, H 6.89, S 7.34.

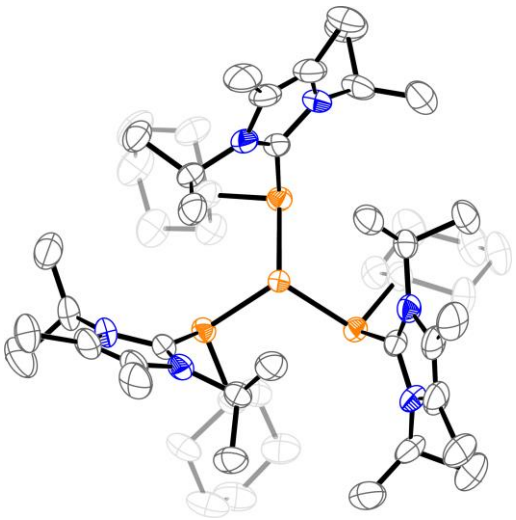


Figure S33: Molecular structure of cation **6a**$^{3+}$ in **6a**[OTf]$_3$·2 CH_3CN (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

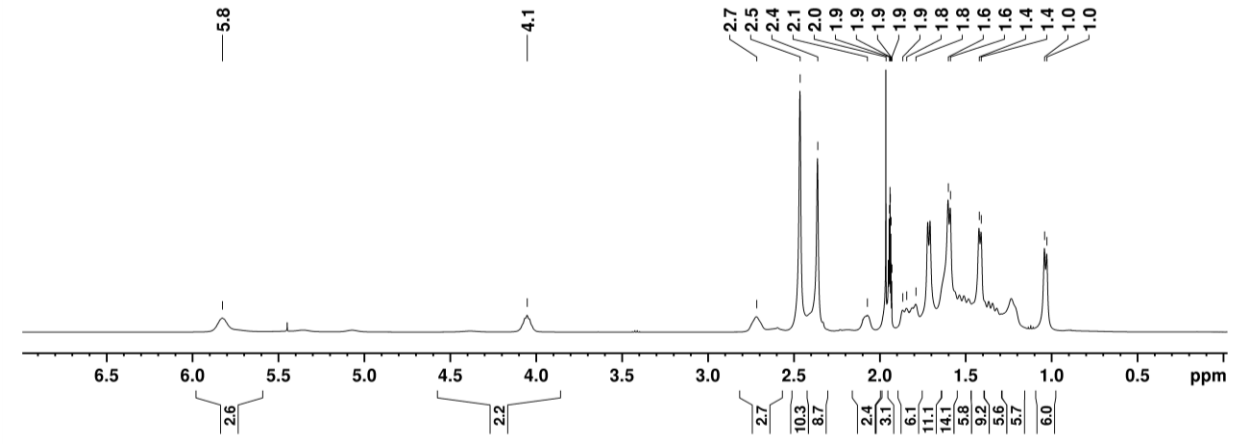


Figure S34: ^1H NMR-spectrum of **6a**[OTf]$_3$ in CD_3CN at 300 K.

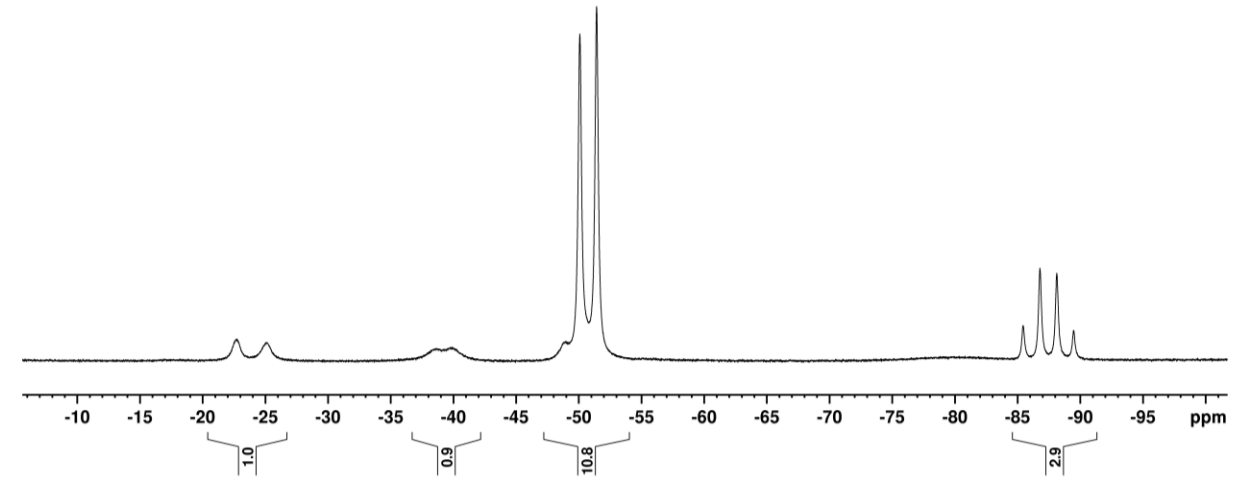


Figure S35: $^{31}P\{^1H\}$ NMR-spectrum of **6a**[OTf]$_3$ in CD_3CN at 300 K.

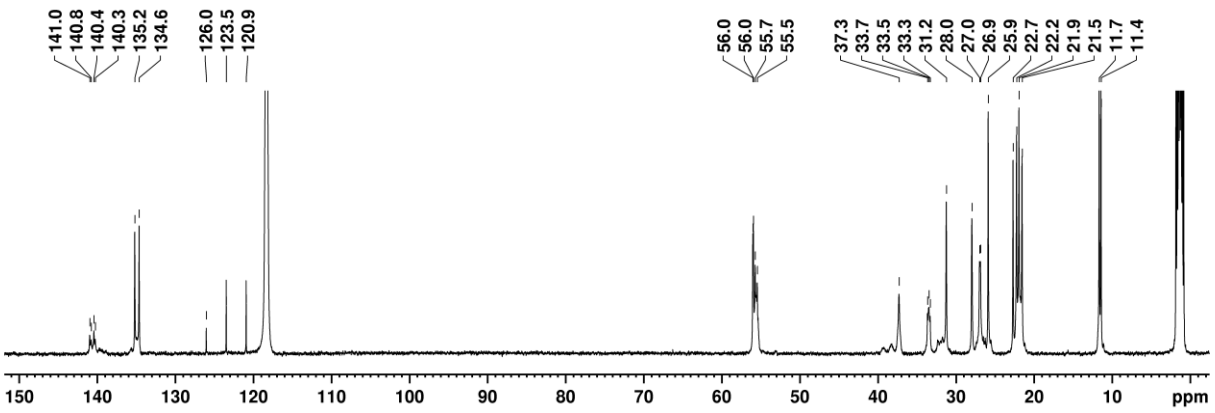


Figure S36: $^{13}C\{^{1}H\}$ NMR-spectrum of **6a**$[OTf]_3$ in CD_3CN at 300 K.

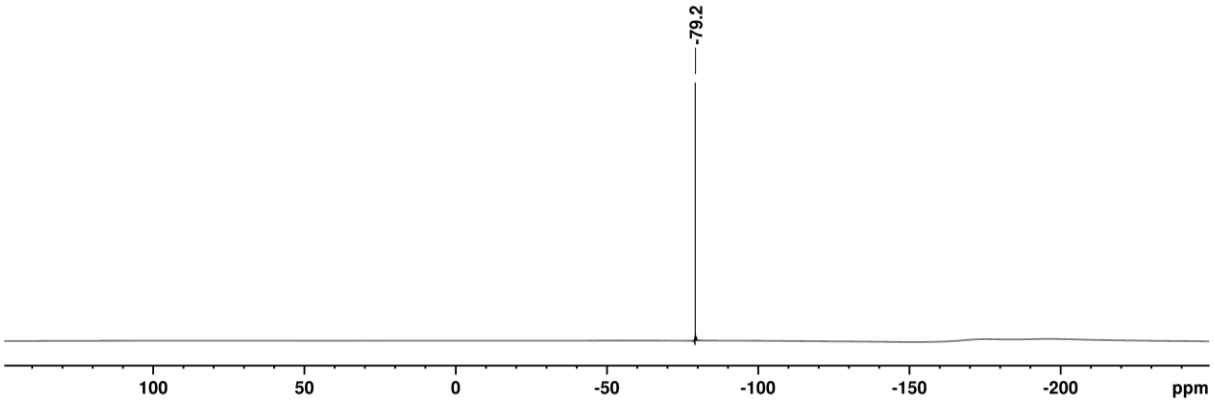
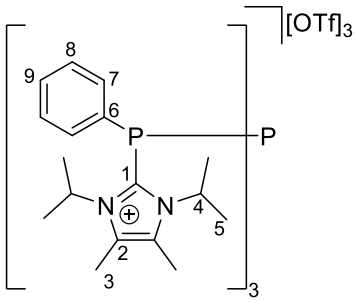


Figure S37: ^{19}F NMR-spectrum of **6a**$[OTf]_3$ in CD_3CN at 300 K.

2.3.2. Preparation of [(L_CPPh)$_3$P][OTf]$_3$ (**6b**[OTf]$_3$)



A solution of 1.1 g P(SiMe$_3$)$_3$ (0.6 equiv., 4.39 mmol) in 15 mL C_6H_5F is dropwise added to a solution of 3.5 g L_CP(Ph)Cl[OTf] **2b**[OTf] (1 equiv., 7.32 mmol) in 5 mL C_6H_5F at room temperature. The color changes immediately to red. After stirring at room temperature overnight. The yellow suspension is filtered and the precipitate washed with C_6H_5F and *n*-pentane. Drying under vacuum affords the product as a colorless powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et_2O into a saturated CH_2Cl_2 solution at –30°C.

Yield: 2.67 g (81 %); **m.p.** 280°C (dec.); **Raman** (80 mW, 200 scans, 298 K, [cm^{-1}]): 3059 (19), 2943 (42), 1607 (30), 1583 (40), 1455 (25), 1404 (38), 1350 (38), 1270 (100), 1149 (23), 1085 (21), 1033 (54), 1001 (53), 884 (14), 789 (15), 754 (21), 573 (15), 348 (25), 312 (24), 282 (21); **IR** (ATR, 298 K, [cm^{-1}]): 2985 (vw), 1605 (vw), 1435 (vw), 1391 (vw), 1260 (m), 1222 (w), 1142 (w), 1029 (m), 745 (w), 703 (vw), 635 (m); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm) δ = 0.25 (6H, s(br), H5), 1.48-2.01 (30H, m, H5), 2.08 (18H, s, H3), 5.22 (3H, s(br), H4), 6.40 (3H, s(br), H4), 7.35-7.60 (9H, m, H8/9), 7.81 (6H, m, H7); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = 10.79 (18C, s(br), C3), 19.77 (3C, s(br), C5), 20.74 (6C, s(br), C5), 22.41 (3C, s(br), C5), 55.48 (3C, s(br), C4), 55.51 (3C, s(br), C4), 56.42 (3C, s, C4), 121.06 (3C, q, ^1J(CF) = –321 Hz, OTf), 129.30 (6C, s, C8), 131.49 (3C, s, C9), 132.71 (3C, s, C2), 133.21 (3C, s, C2), 134.26 (6C, m, C7), 136.50 (3C, d, ^1J(CP) = –49 Hz, C1); **^{19}F{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = **–**79.23 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): AX_3 spin system $\delta(P_A)$ = –47.9 ppm, $\delta(P_X)$= **–**41.8 ppm, ^1J(PP)= –130 Hz; **elemental analysis:** calculated for $C_{54}H_{75}F_9N_6O_9P_4S_3$: N 6.26, C 48.28, H 5.63, S 7.16; found: N 6.08, C 48.11, H 5.58, S 6.98.

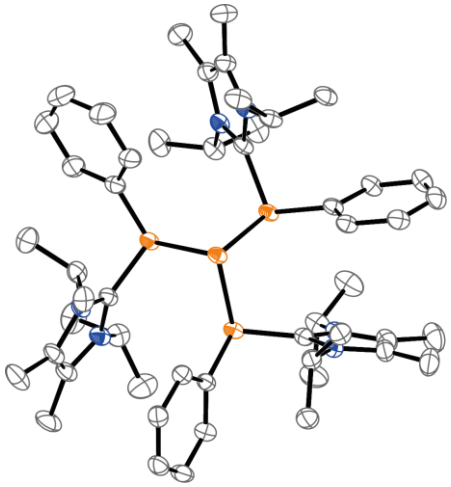


Figure S38: Molecular structure of cation **6b**$^{3+}$ in **6b**[OTf]$_3$·4 CH_2Cl_2 (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

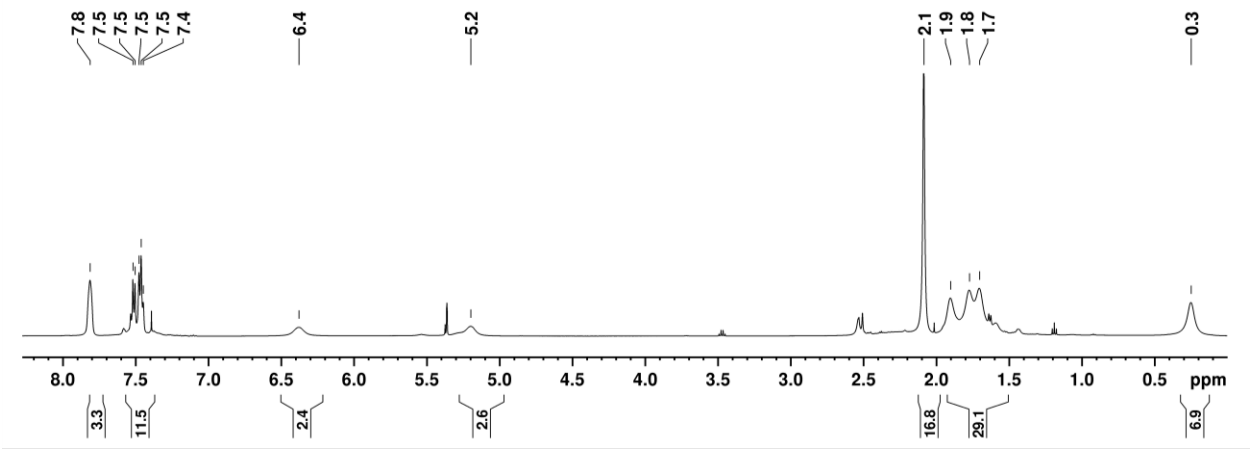


Figure S39: ^{1}H NMR-spectrum of **6b**[OTf]$_3$ in CD_2Cl_2 at 300 K.

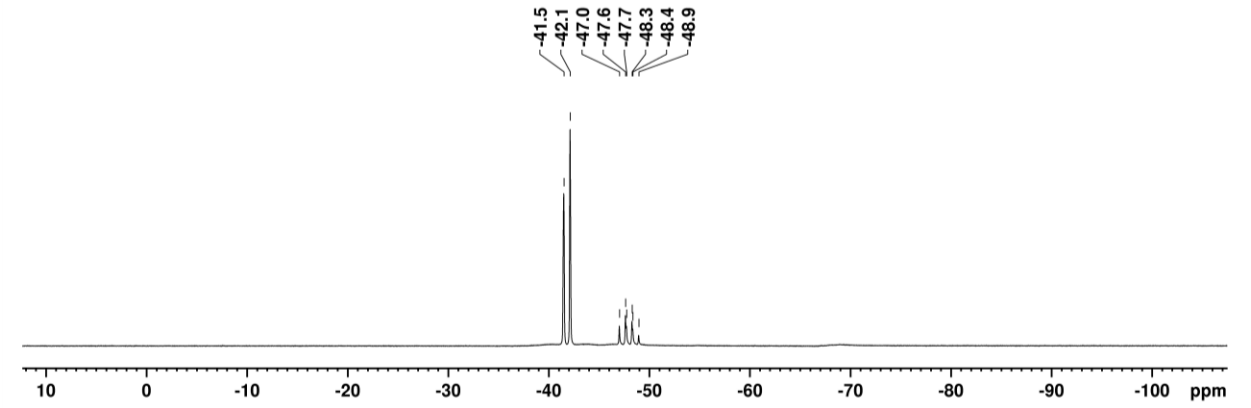


Figure S40: ^{31}P NMR-spectrum of **6b**[OTf]$_3$ in CD_2Cl_2 at 300 K.

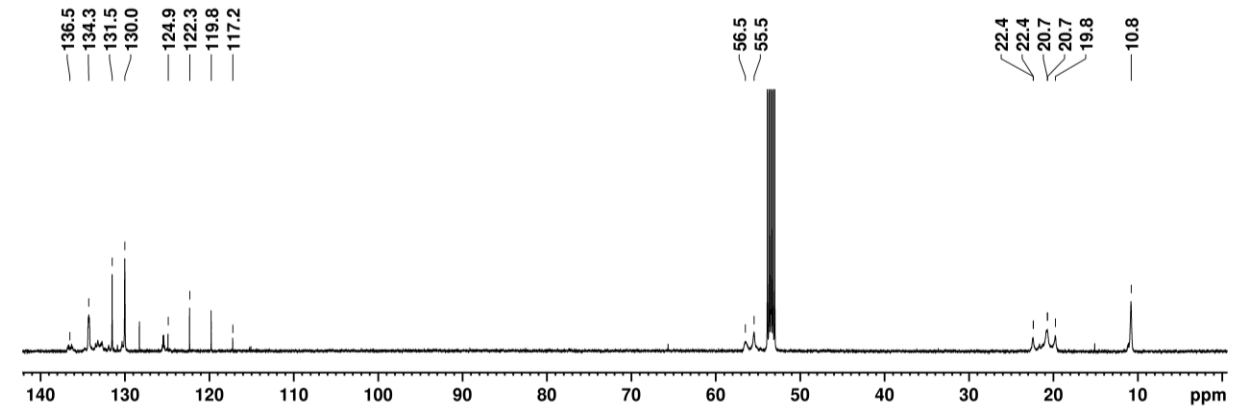


Figure S41: ^{13}C{^{1}H} NMR-spectrum of **6b**[OTf]$_3$ in CD_2Cl_2 at 300 K.

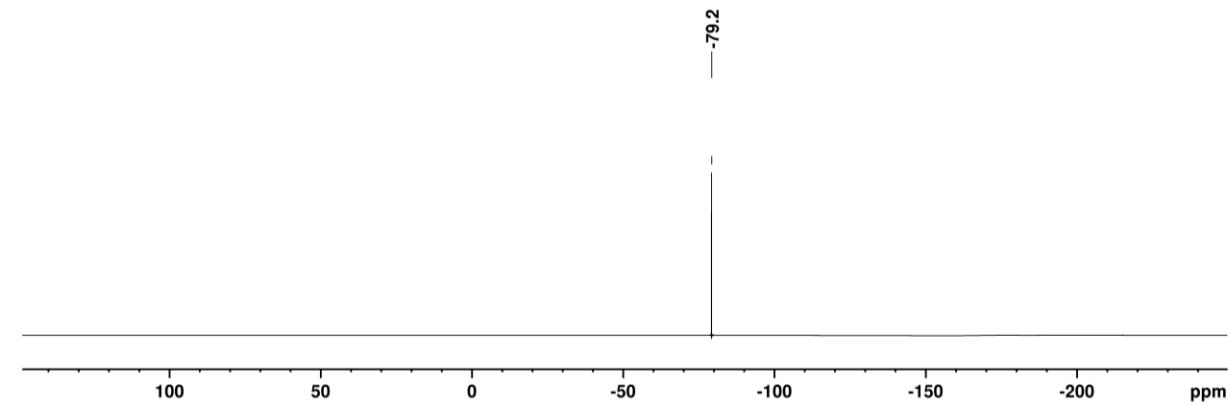
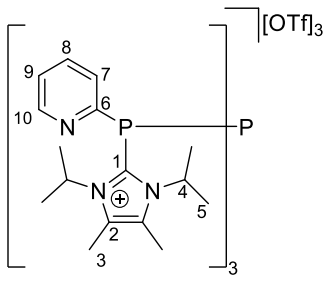


Figure S42: ^{1}H NMR-spectrum of **6b**[OTf]$_3$ in CD_2Cl_2 at 300 K.

2.3.3. Synthesis of crude [(L_CPPy)$_3$P][OTf]$_3$ (**6c**[OTf]$_3$)



A solution of 26.5 mg P(SiMe$_3$)$_3$ (0.5 equiv., 0.11 mmol) in 1.5 mL C_6H_5F is dropwise added to a solution of 100 mg L_CP(Py)Cl[OTf] **2c**[OTf] (1 equiv., 0.21 mmol) in 1.5 mL C_6H_5F at –30 °C. After stirring at room temperature overnight the yellow suspension is filtered, and the precipitate washed with a mixture of *o*-$C_6H_4F_2$ and benzene (2:1) and *n*-pentane yielding a crude product. Further purification was unsuccessful due to the compound's instability in solution.

^{31}P{^{1}H} NMR (CD_3CN, 300 K, in ppm): broadened AX_3 spin system $\delta(P_A)$ = –36.2 $\delta(P_X)$ = –32.6 ^1J(PP) = –101 Hz.

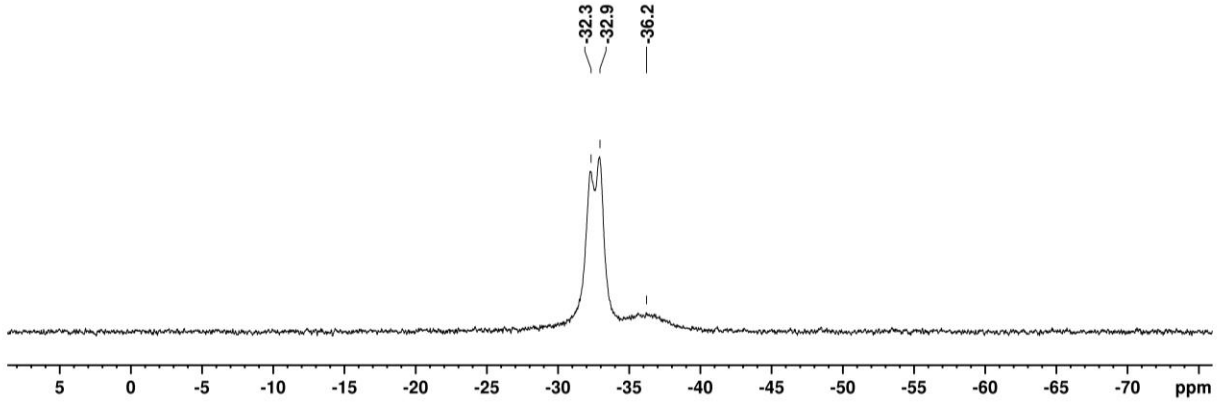


Figure S43: ^{31}P NMR-spectrum of **6c**[OTf]$_3$ in CD_3CN at 300 K.

2.3.4. Variable Temperature NMR Studies

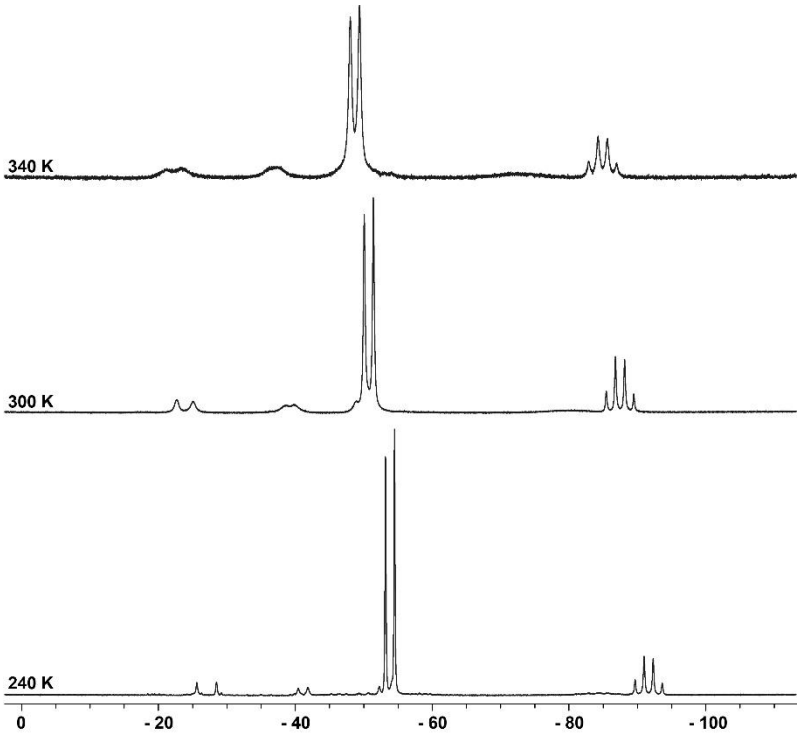


Figure S44: Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **6a**$[OTf]_3$ in CD_3CN from 240 K to 340 K.

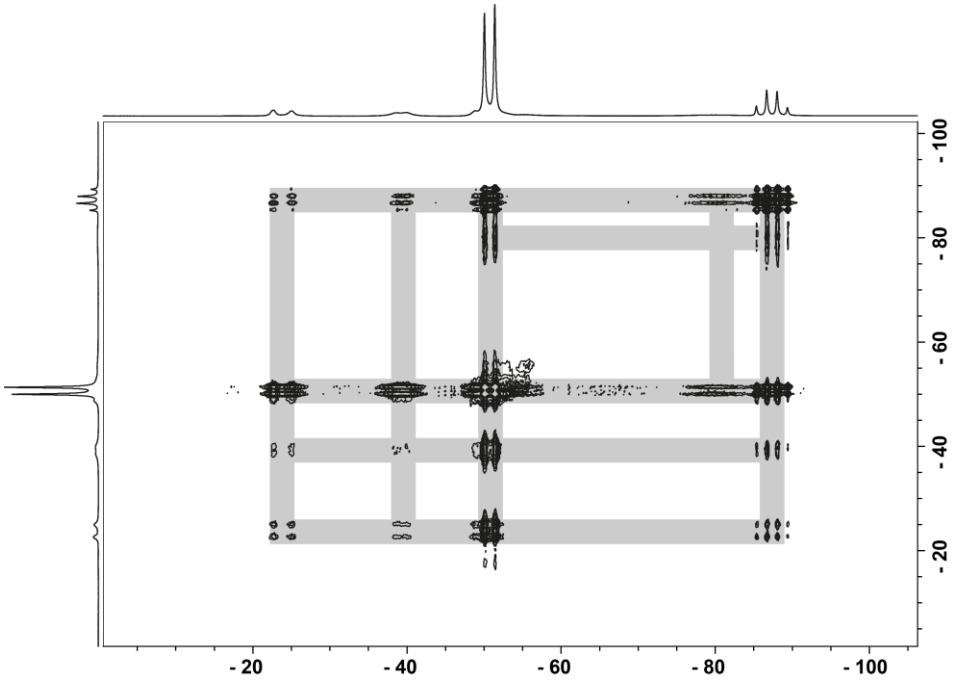


Figure S45: ^{31}P-^{31}P-EXSY NMR spectrum of **6a**$[OTf]_3$ in CD_3CN at 300 K (mixing time 1s).

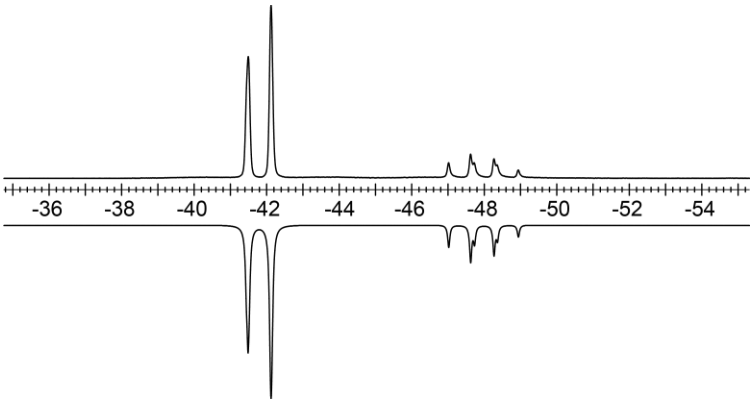
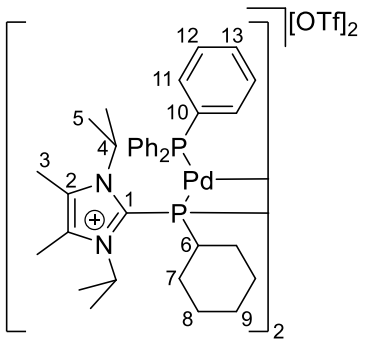


Figure S46: $^{31}P\{^{1}H\}$ NMR spectra of **6b**$[OTf]_3$ in CD_2Cl_2 at 300 K; experimental (upward) and fitted spectra (downward).

2.4. Reactions of Imidazoliumyl-substituted Diphosphanes 5a,b[OTf]$_2$ with Pd(PPh$_3$)$_4$

2.4.1. Preparation of [(L$_C$PCy(PdPPh$_3$))$_2$][OTf]$_2$ (**7a**[OTf]$_2$)



A suspension of 100 mg (L$_C$PCy)$_2$[OTf]$_2$ **5a**[OTf]$_2$ (1 equiv., 0.11 mmol) and 260 mg Pd(PPh$_3$)$_4$ (2 equiv., 0.23 mmol) in 3 mL toluene is stirred at 120°C for 4 d. After cooling to room temperature, the dark precipitate is filtered and dissolved in CH$_3$CN. Drying *in vacuo* affords the product as a dark brown powder. ^{31}P NMR investigations reveal the presence of two isomers A (82%) and B (18%).

Yield: 55 mg (30%); **m.p.** 273.0°C (dec.); **Raman** (100 mW, 50 scans, 298 K, [cm^{-1}]): 3053 (69), 3008 (29), 2948 (68), 2915 (46), 2890 (31), 2870 (28), 2843 (20), 1624 (21), 1586 (47), 1441 (19), 1413 (34), 1356 (88), 1289 (100), 1151 (14), 1094 (23), 1030 (30), 1000 (45), 789 (17), 484 (26); **IR** (ATR, 298 K, [cm^{-1}]): 3069 (vw), 3004 (vw), 2934 (vw), 2912 (w), 2842 (vw), 1622 (vw), 1478 (vw), 1456 (vw), 1436 (w), 1392 (w), 1374 (vw), 1265 (vs), 1222 (w), 1192 (vw), 1142 (s), 1091 (w), 1029 (s), 998 (vw), 759 (w), 747 (w), 696 (m), 636 (m), 571 (vw), 518 (m), 508 (m), 492 (w), 439 (vw); **isomer A (82%): ^{1}H NMR** (CD$_3$CN, 300 K, in ppm) δ = 0.74 (24H, d, ^3J(HH) = 6.95 Hz, H5), 0.86 - 0.96 (4H, m, H9), 1.10 - 1.21 (4H, m, H7), 1.26 - 1.39 (4H, m, H8), 1.55 - 1.65 (8H, m, H7/8), 2.12 (12H, s, H3), 2.52 (2H, br, H6), 5.20 - 5.29 (4H, br, H4), 7.42 (12H, br. t, ^3J(HH) = 7.5 Hz, H12), 7.47 - 7.61 (18H, m, H11/H13); **^{13}C{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = 11.34 (4C, s, C3), 21.56 (8C, s, C5), 26.23 (2C, s, C9), 27.24 (4C, ps. t, C8), 34.31 (4C, ps. t, C7), 42.96 (2C, br, C6), 53.83 (4C, br, C4), 122.21 (2C, q, ^1J(CF) = –321 Hz, OTf), 130.00 (12C, ps. t, C12), 131.29 (4C, s, C2), 132.36 (6C, s, C13), 135.56 (12C, ps. t, C11), 136.79 (6C, ps. t, C10), 143.88 - 144.32 (2C, m, C1); **^{19}F{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = **–**79.31 (s); **^{31}P{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): A$_2$X$_2$ spin system δ(P$_A$) = 26.5 δ(P$_X$) = 141.8, ^2J(PP) = 37 Hz; **isomer B (18%): ^{1}H NMR** (CD$_3$CN, 300 K, in ppm) δ = 0.84 (24H, d, ^3J(HH) = 6.75 Hz, H5), 1.26 - 1.39 (12H, m, H7/H8), 1.40 - 1.50 (4H, m, H9), 1.55 - 1.65 (4H, m, H8), 2.19 (12H, s, H3), 2.33 (2H, br, H6), 5.20 - 5.29 (4H, br, H4), 7.42 (12H, br. t, ^3J(HH) = 7.45 Hz, H12), 7.47 - 7.61 (18H, m, H11/H13); **^{13}C{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = 11.32 (4C, s, C3), 21.78 (8C, s, C5), 25.56 (2C, s, C9), 27.24 (4C, ps. t, C8), 32.61 (4C, ps. t, C7), 43.15 (2C, br, C6), 53.52 (4C, br, C4), 122.21 (2C, q, ^1J(CF) = –321 Hz, OTf), 130.18 (12C, ps. t, C12), 131.29 (4C, s, C2), 132.20 (6C, s, C13), 135.16 (12C, ps. t, C11), 136.12 (6C, ps. t, C10), 143.88 - 144.32 (2C, m, C1); **^{19}F{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = **–**79.32 (s); **^{31}P{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): A$_2$X$_2$ spin system δ(P$_A$) = 25.3 δ(P$_X$) = 132.8, ^2J(PP) = 38 Hz; **elemental analysis:** calculated for C$_{72}$H$_{92}$F$_6$N$_4$O$_6$P$_4$Pd$_2$S$_2$: N 3.45, C 53.24, H 5.71, S 3.95; found: N 3.41, C 53.10, H 5.59, S 3.48.

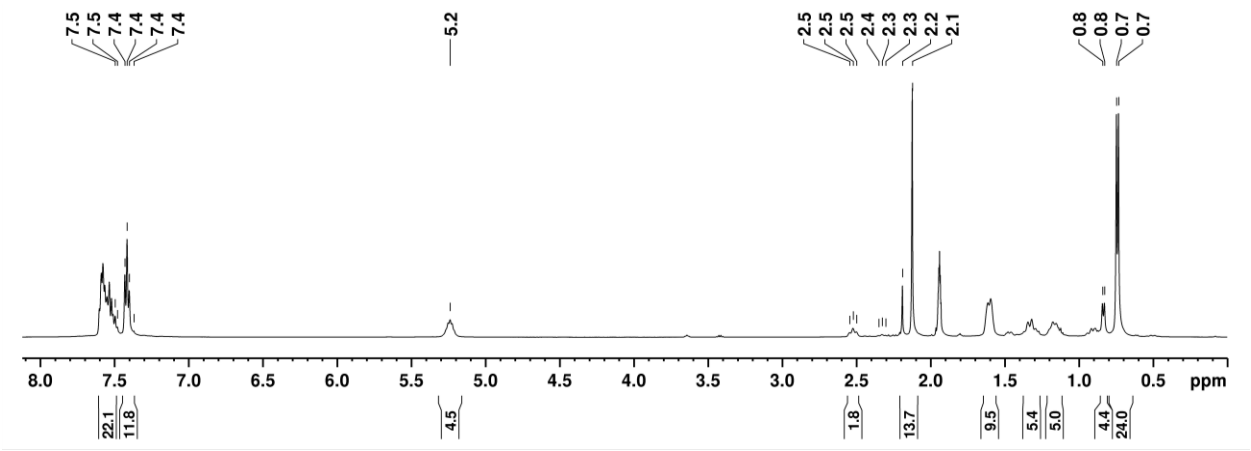


Figure S47: ^{1}H NMR-spectrum of **7a**[OTf]$_2$ in CD_3CN at 300 K.

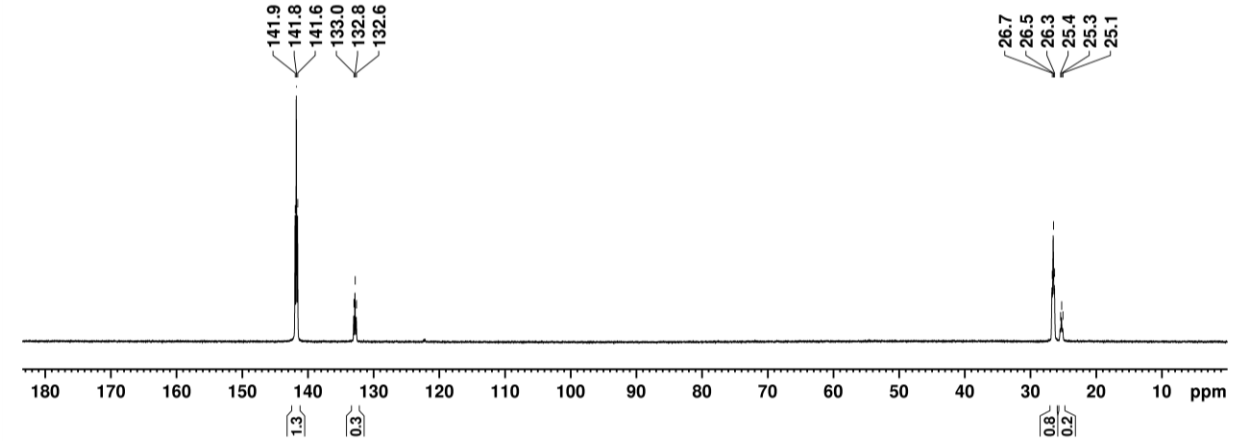


Figure S48: $^{31}P\{^{1}H\}$ NMR-spectrum of **7a**[OTf]$_2$ in CD_3CN at 300 K.

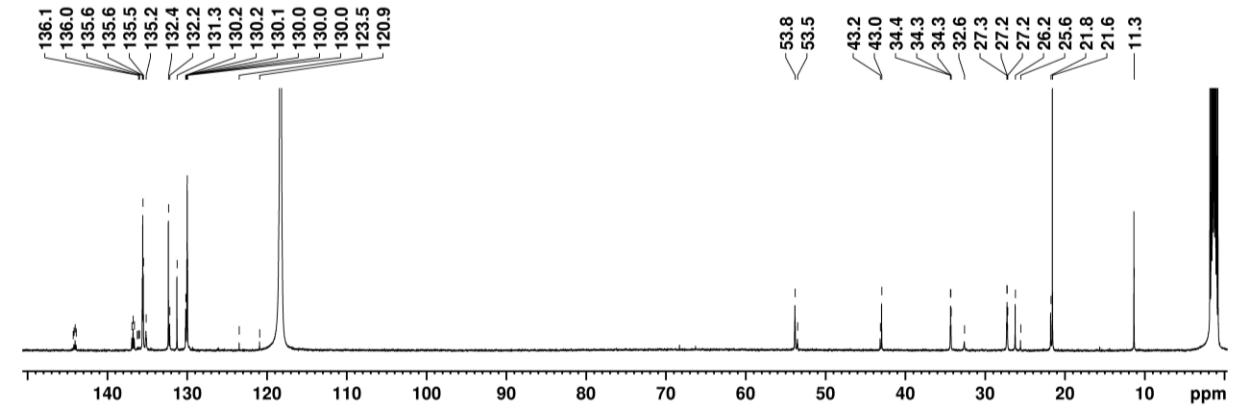


Figure S49: $^{13}C\{^{1}H\}$ NMR-spectrum of **7a**[OTf]$_2$ in CD_3CN at 300 K.

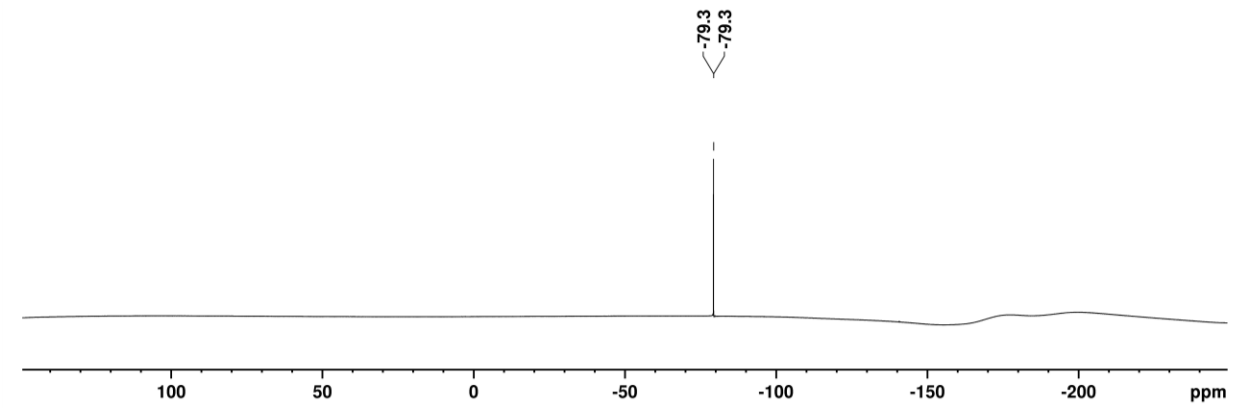
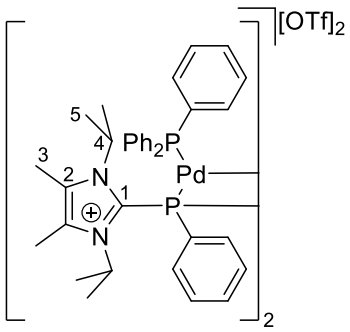


Figure S50: ^{19}F NMR-spectrum of **7a**$[OTf]_2$ in CD_3CN at 300 K.

2.4.2. Preparation of [(L_CPPh(PdPPh$_3$))$_2$][OTf]$_2$ (**7b**[OTf]$_2$)



A solution of 200 mg (*i*PrImPPh)$_2$[OTf]$_2$ **5b**[OTf]$_2$ (1 equiv., 0.23 mmol) and 555 mg Pd(PPh$_3$)$_4$ (2.1 equiv., 0.48 mmol) in 6 mL CH_2Cl_2 is stirred at room temperature overnight. After addition of *n*-pentane a dark precipitate forms. The supernatant solution is decanted off and the remaining solid is washed 3x4 mL with benzene. Washing with *n*-pentane and drying *in vacuo* affords the product as a dark purple powder. ^{31}P NMR investigations reveal the presence of two isomers A (85%) and B (15%). Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of *n*-pentane into a saturated CH_2Cl_2 solution at –30°C.

Yield: 230 mg (63%); **m.p.** 259°C (dec.); **Raman** (80 mW, 300 scans, 298 K, [cm^{-1}]): 3057 (33), 2940 (34), 1619 (29), 1581 (100), 1477 (27), 1438 (26), 1413 (39), 1352 (67), 1284 (91), 1185 (21), 1152 (25), 1084 (91), 1031 (41), 999 (91), 789 (23), 691 (26), 526 (19), 505 (36), 458 (30), 430 (24), 408 (22), 311 (26), 296 (22), 259 (58), 203 (22); **IR** (ATR, 298 K, [cm^{-1}]): 3046 (vw), 2978 (vw), 1617 (vw), 1479 (vw), 1436 (w), 1265 (vs), 1223 (m), 1140 (s), 1096 (w), 1031 (s), 743 (m), 695 (m), 636 (vs); **isomer A (85%): ^{1}H NMR** (CD_2Cl_2, 300K, in ppm) δ = 0.84 (24H, d, ^3J(HH) = 6.96 Hz, H5), 2.33 (12H, s, H3), 5.57 (4H, m, H4), 6.85-7.50 (40H, m, Ar-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): δ = 11.02 (4C, s, C3), 20.86 (8C, s, C5), 53.50 (4C, s, C4), 120.81 (2C, q, ^1J(CF) = –318 Hz, OTf), 128.97 (24C, m, Ar-C), 130.84 (16C, s, Ar-C/C2), 133.67 (12C, s, Ar-C), 141.48 – 141.99 (2C, m, C1); **^{19}F{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): δ = **–**78.8 (s); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): A_2X_2 spin system $\delta(P_A)$ = 24.5 $\delta(P_X)$ = 105.3, ^2J(PP) = 44 Hz; **isomer B (15%): ^{1}H NMR** (CD_2Cl_2, 300K, in ppm) δ = 0.74 (24H, d, ^{3}J(HH) = 7.00 Hz, H5), 2.27 (12H, s, H3), 5.37 (4H, m, H4), 6.85-7.50 (40H, m, Ar-H); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): δ = 10.92 (4C, s, C3), 20.49 (8C, s, C5), 53.50 (4C, s, C4), 120.81 (2C, q, ^1J(CF) = –318 Hz, OTf), 128.97 (24C, m, Ar-C), 130.68 (4C, s, C2), 130.84 (12C, s, Ar-C), 133.67 (12C, s, Ar-C), 141.48 – 141.99 (2C, m, C1); **^{19}F{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): δ = **–**78.8 (s); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300K, in ppm): A_2X_2 spin system $\delta(P_A)$ = 25.9 $\delta(P_X)$ = 111.5, ^2J(PP) = 41 Hz; **elemental analysis:** calculated for **7b**[OTf]·0.5 CH_2Cl_2 $C_{72}H_{92}F_6N_4O_6P_4Pd_2S_2$: N 3.39, C 52.62, H 4.93, S 3.87; found: N 3.51, C 52.69, H 4.92, S 4.00.

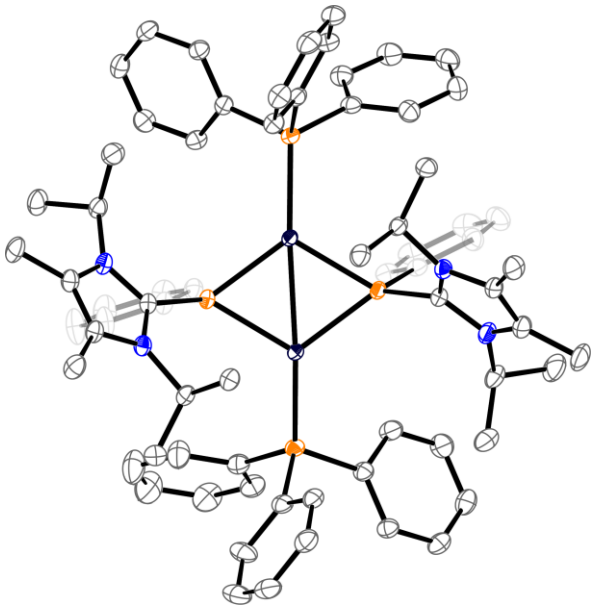


Figure S51: Molecular structure of cation **7b**$^{2+}$ in **7b**[OTf]$_2$·4 CH_2Cl_2 (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

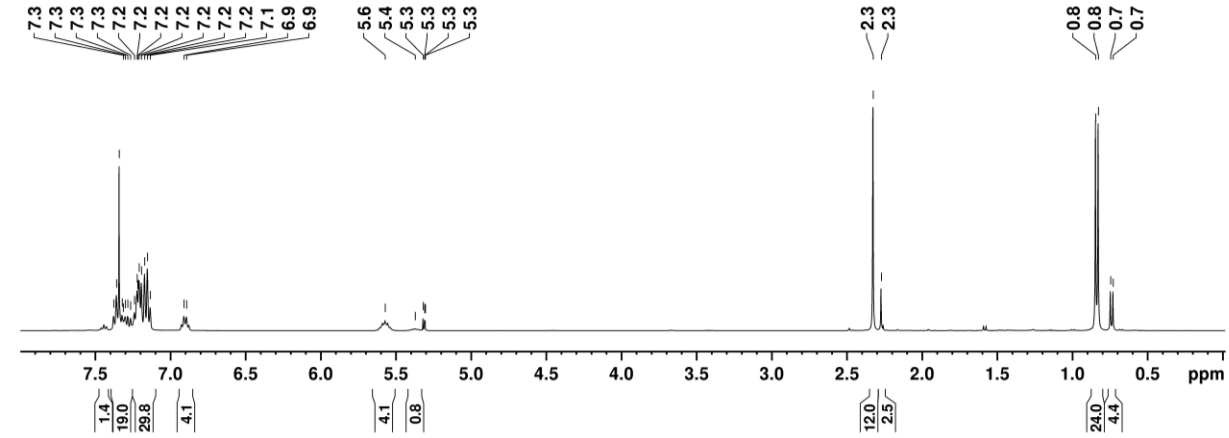


Figure S52: ^{1}H NMR-spectrum of **7b**[OTf]$_2$ in CD_2Cl_2 at 300 K.

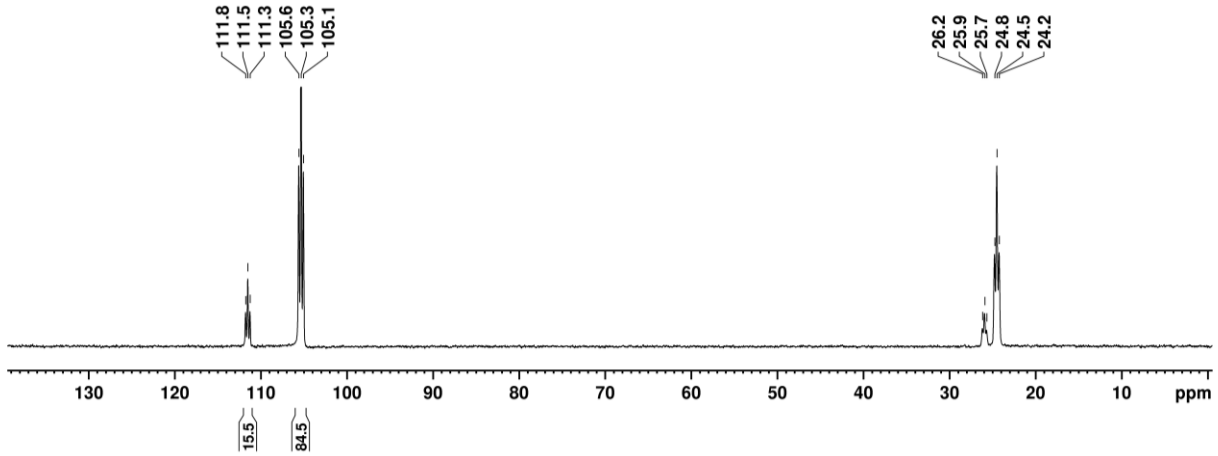


Figure S53: ^{31}P NMR-spectrum of **7b**$[OTf]_2$ in CD_2Cl_2 at 300 K.

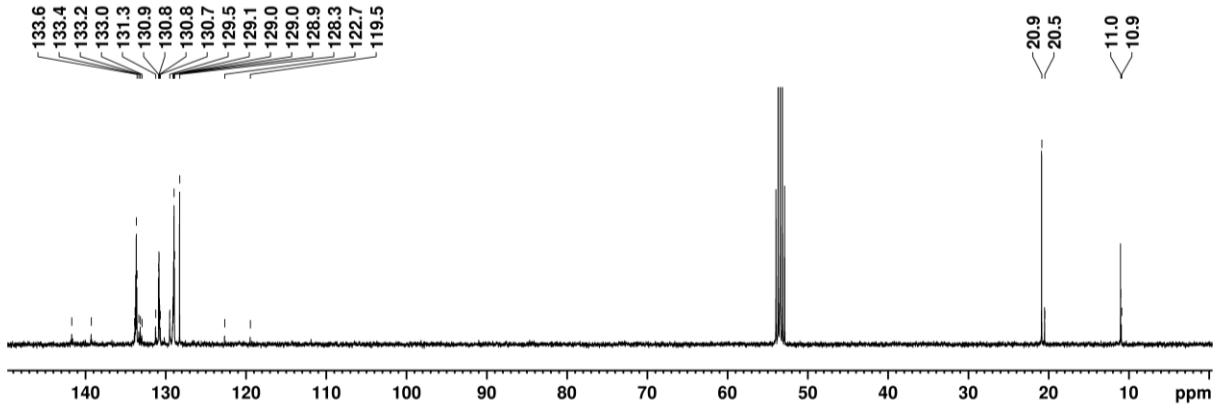


Figure S54: $^{13}C\{^1H\}$ NMR-spectrum of **7b**$[OTf]_2$ in CD_2Cl_2 at 300 K.

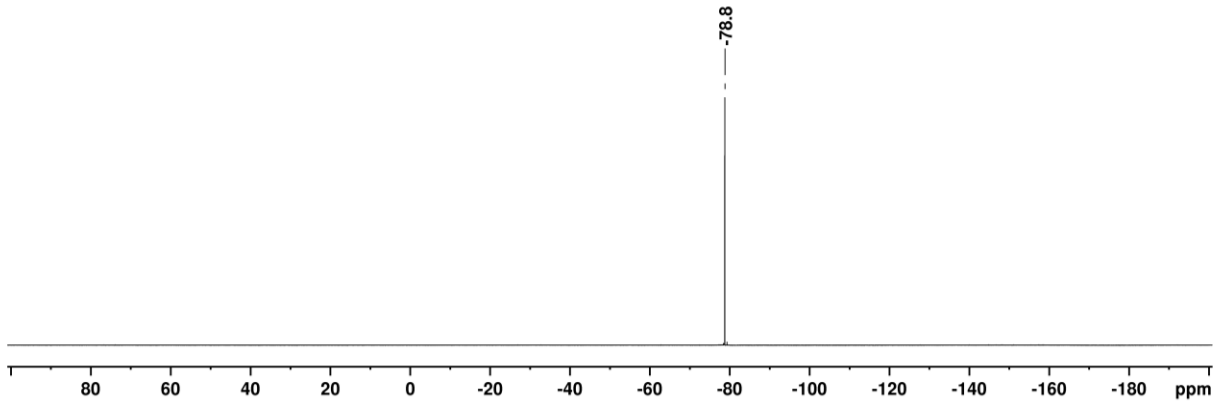
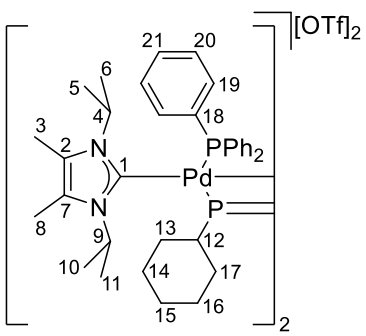


Figure S55: ^{19}F NMR-spectrum of **7b**$[OTf]_2$ in CD_2Cl_2 at 300 K.

2.4.3. Preparation of [(*i*PrIm(PdPPh$_3$)$_2$(CyP=PCy)][OTf]$_2$ (**8**[OTf]$_2$)



A suspension of 100 mg (L$_C$PCy)$_2$[OTf]$_2$ **5a**[OTf]$_2$ (1 equiv., 0.11 mmol) and 260 mg Pd(PPh$_3$)$_4$ (2 equiv., 0.23 mmol) in 3 mL o-C$_6$H$_4$F$_2$ is stirred at 40°C for 14. After cooling to rt the suspension is filtered, and the solution layered with Et$_2$O at –30°C. After filtration and washing with 3x1 mL Et$_2$O of all volatiles are removed and the product is obtained as red crystalline material. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et$_2$O into a saturated *o*-C$_6$H$_4$F$_2$ solution at –30°C.

Yield: 100 mg (54%); **m.p.** 83.5°C (dec.); **Raman** (100 mW, 50 scans, 298 K, [cm^{-1}]): fluorescence; **IR** (ATR, 298 K, [cm^{-1}]): 2970 (w), 2933 (w), 2849 (w), 1592 (vw), 1505 (vw), 1480 (w), 1465 (w), 1435 (w), 1387 (w), 1262 (vs), 1220 (m), 1187 (w), 1156 (s), 1096 (m), 1072 (w), 1025 (s), 997 (w), 904 (w), 804 (w), 751 (s), 694 (m), 633 (vs), 571 (w), 521 (vs), 506 (s), 494 (s), 450 (w), 440 (w), 426 (w),; **^{1}H NMR** (CD$_3$CN, 300 K, in ppm) δ = 0.39 - 0.5 (2H, m, H13), 0.58 (6H, d, ^3J(HH) = 7.1 Hz, H5), 0.94 (6H, d, ^3J(HH) = 7.1 Hz, H11), 1.00 - 1.17 (10H, m, H13/H14/H15/H16/H17), 1.23 (6H, d, ^3J(HH) = 7.2 Hz, H10), 1.35 (6H, d, ^3J(HH) = 7.0 Hz, H16), 1.42 - 1.52 (6H, m, H15/H16/H17), 1.57 - 1.66 (2H, m, H14) 2.09 (6H, s, H3), 2.26 (6H, s, H8), 2.27 - 2.35 (2H, m, H12), 4.92 (2H, sept, ^3J(HH) = 7.1 Hz, H4), 4.98 (2H, sept, ^3J(HH) = 7.2 Hz, H9), 7.28 - 7.34 (12H, m, H19), 7.48 - 7.53 (12H, m, H20), 7.62 (6H, t, ^3J(HH) = 7.35 Hz, H21); **^{13}C{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = 10.80 (2C, s, C3), 10.93 (2C, s, C8), 20.25 (2C, s, C5), 21.03 (2C, s, C10), 22.01 (2C, s, C11), 23.40 (2C, s, C6), 25.07 (2C, s, C15), 27.49 (2C, ps. t, C16), 27.69 (2C, ps. t, C14), 33.45 (2C, ps. t, C13), 35.23 (2C, s, C17), 37.05 - 37.43 (2C, m, C12), 37.23 (2C, dd, ^1J(CP) = –20 Hz, ^2J(CP) = 15 Hz, C12), 56.44 (2C, s, C4) 56.34 (2C, s, C9), 122.21 (2C, q, ^1J(CF) = –321 Hz, OTf), 128.59 (2C, s, C7), 130.10 (2C, s, C2), 130.63 (12C, ps. t, C20), 132.82 (6C, s, C21), 132.84 (12C, d, ^1J(CP) = –43 Hz, C18), 134.31 (12C, ps. t, C19), 159.15 (2C, ps. t, C1); **^{19}F{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = **–**79.32 (s); **^{31}P{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): see below; **elemental analysis:** calculated for C$_{72}$H$_{92}$F$_6$N$_4$O$_6$P$_4$Pd$_2$S$_2$: N 3.45, C 53.24, H 5.71, S 3.95; found: N 3.47, C 53.12, H 5.64, S 3.70.

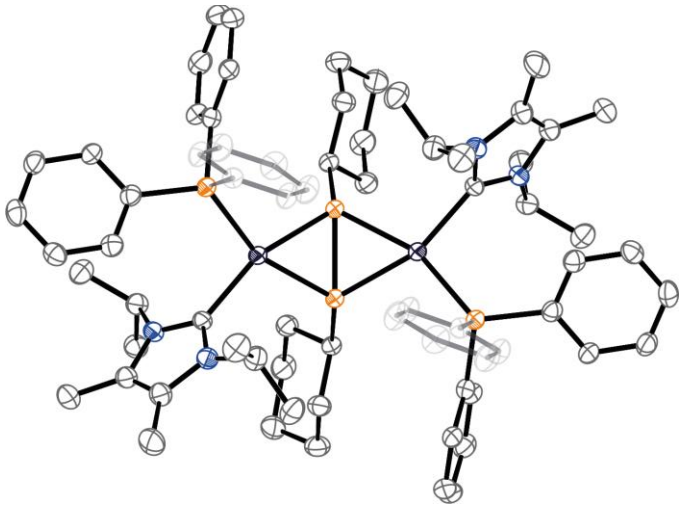


Figure S56: Molecular structure of cation $\mathbf{8}^{2+}$ in $\mathbf{8}[OTf]_2 \cdot 2\ C_6H_4F_2$ (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

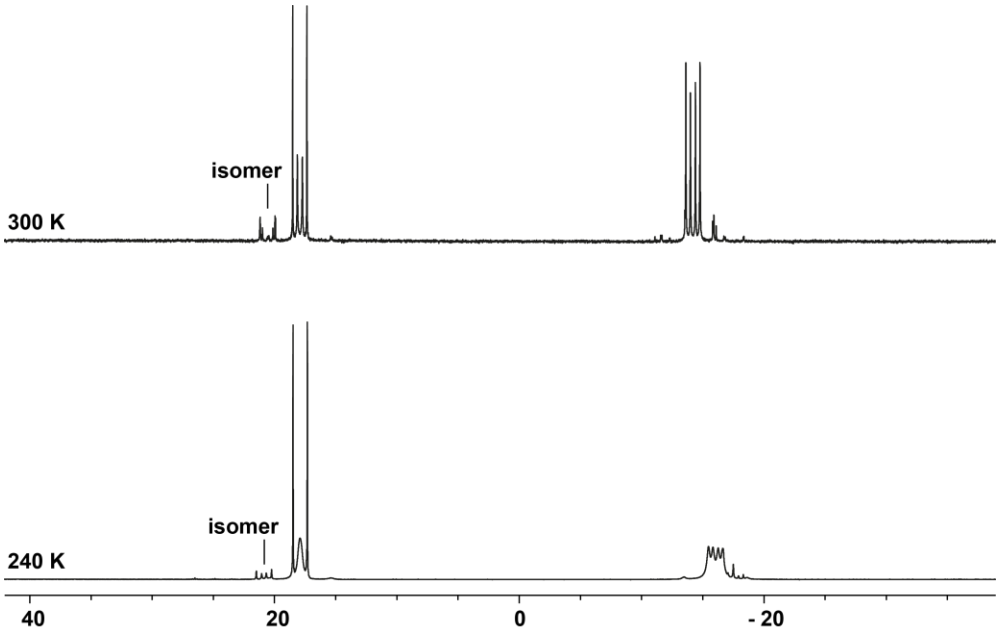


Figure S57: $^{31}P\{^1H\}$ NMR-spectra of $\mathbf{8}[OTf]_2$ at 300 K in CD_3CN (top) and at 240 K in CD_2Cl_2 (bottom).

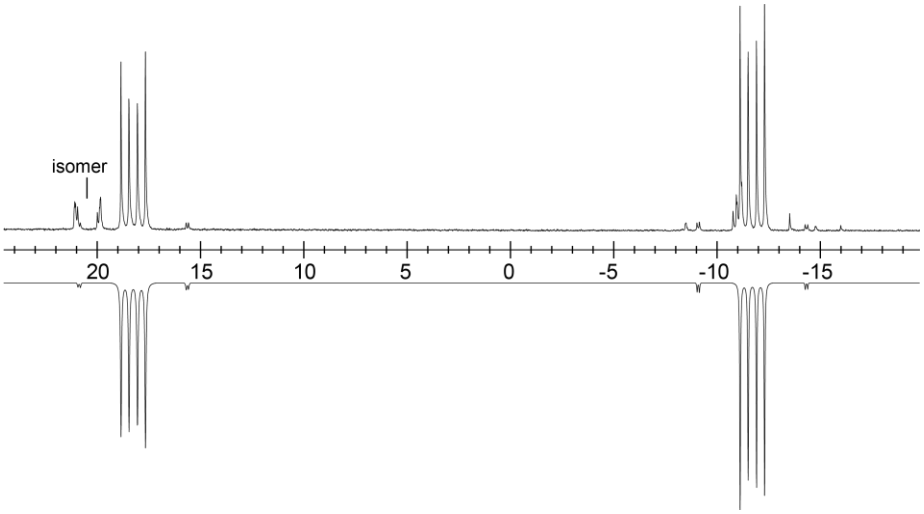


Figure S58: High temperature $^{31}P\{^{1}H\}$ NMR spectra of **8**$[OTf]_2$ in *o*-$C_6H_4F_2$ and toluene-d^8 at 340 K; experimental (upward) and fitted spectra (downward); parameters of the spin systems are given in **Table S 1**.

Table S 1: Iteratively generated parameters for the $^{31}P\{^{1}H\}$ NMR resonances of **8**$[OTf]_2$.

	Iterated parameter	Value
chemical shift	$\delta(P_A)$	-11.70 ppm
	$\delta(P_X)$	18.23 ppm
line width	ν_A	12.3 Hz
	ν_X	8.6 Hz
coupling constants	$^1J(P_AP_A)$	-489.4 Hz
	$^2J(P_AP_X) = {}^2J(P_{A'}P_{X'})$	267.6 Hz
	$^2J(P_AP_{X'}) = {}^2J(P_{A'}P_X)$	-27.7 Hz
	$^4J(P_XP_{X'})$	12.4 Hz

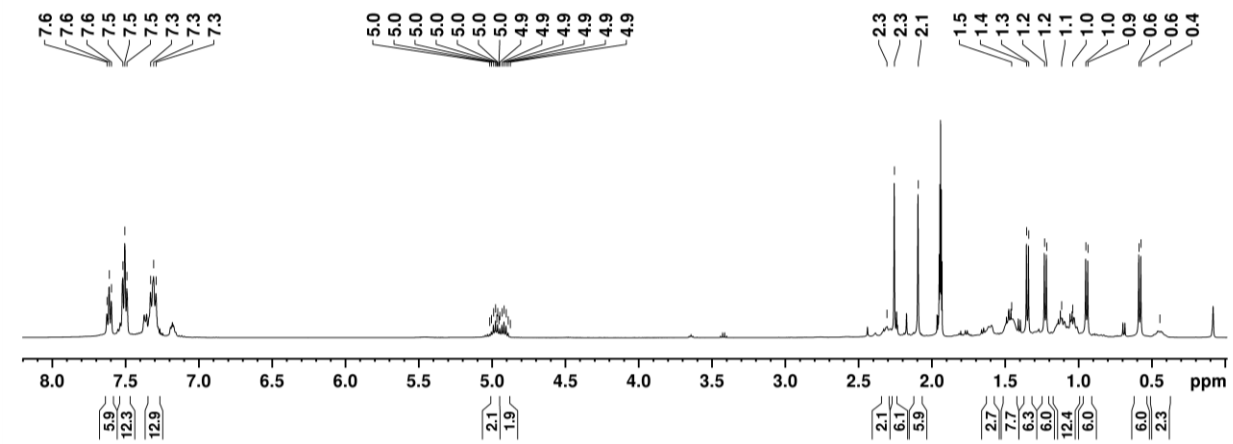


Figure S59: ^{1}H NMR-spectrum of **8**[OTf]$_2$ in CD_3CN at 300 K.

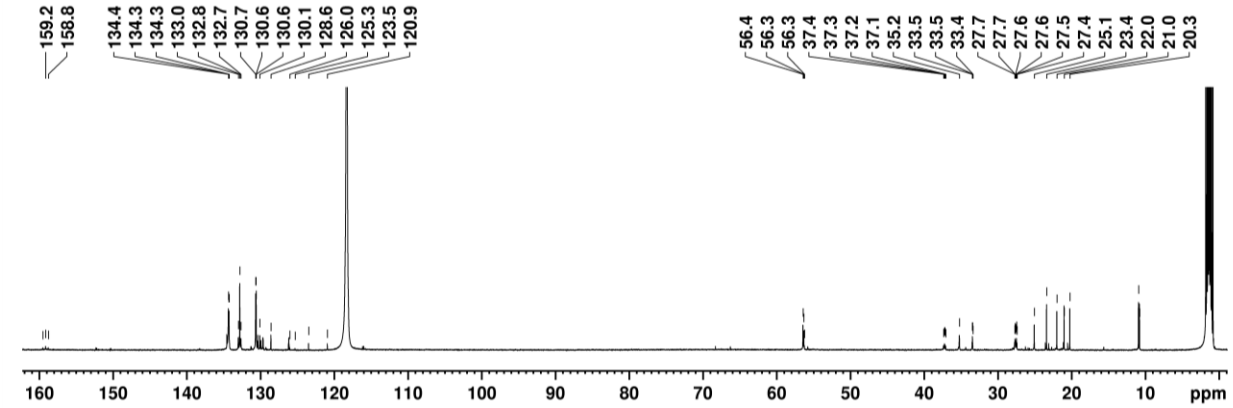


Figure S60: $^{13}C\{^{1}H\}$ NMR-spectrum of **8**[OTf]$_2$ in CD_3CN at 300 K.

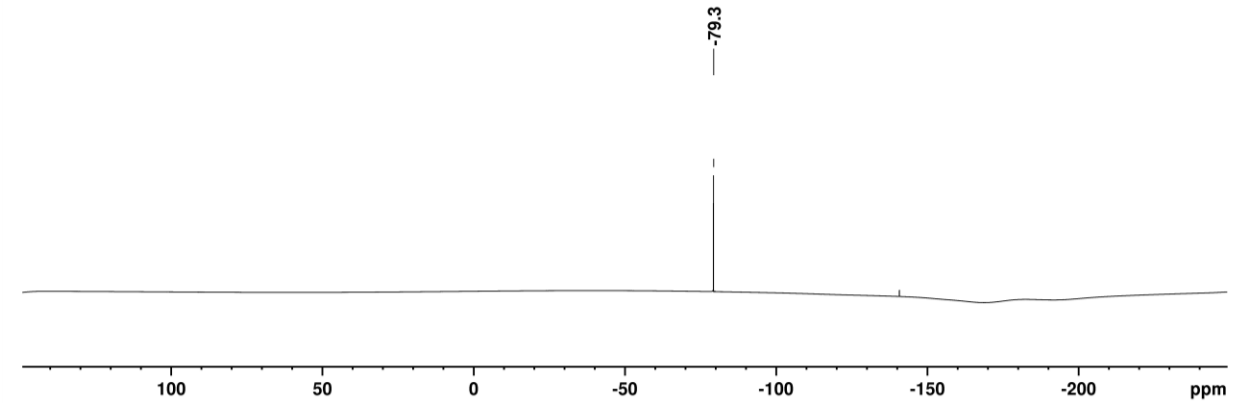
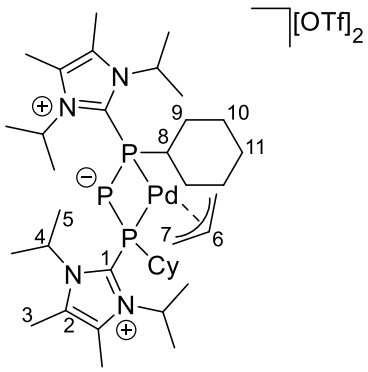


Figure S61: ^{19}F NMR-spectrum of **8**[OTf]$_2$ in CD_3CN at 300 K.

2.5. Reactions of Imidazoliumyl-substituted iso-Tetraphosphanes 6a,b[OTf]$_3$ with Nucleophiles

2.5.1. Preparation of [(L$_C$PCy)$_2$PPd(η^3-C$_3$H$_5$)][OTf]$_2$ (**9**[OTf]$_2$)



A solution of ((η^3-C$_3$H$_5$)PdCl)$_2$ (0.45 equiv., 26 mg, 0.07 mmol) in 1 mL CH$_3$CN is added to a solution of (L$_C$PCy)$_3$P[OTf]$_3$ **6a**[OTf]$_3$ (1 equiv., 200 mg, 0.15 mmol) in 2 mL CH$_3$CN at –30°C. A color change to orange is observed. After 30 min stirring, all volatiles are removed and the residue is dissolved in o-C$_6$H$_4$F$_2$. After filtration the solution is layered with *n*-hexane. The resulting oil is stirred with toluene for 16 h and subsequently washed with 3x2 mL toluene. Washing with *n*-pentane and removal of all volatiles affords the product as an orange powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of *n*-pentane into a saturated *o*-C$_6$H$_4$F$_2$/THF (v/v = 1:1) solution at –30°C. In the molecular structure, the allyl substituent of the palladium complex **8**[OTf]$_2$ is disordered over two positions, of which the major one is displayed in **Figure 4**.

Yield: 90 mg (59%); **m.p.** 144.3°C (dec.); **Raman** (80 mW, 50 scans, 298 K, [cm^{-1}]): 2940 (100), 2874 (30), 2857 (37), 1622 (27), 1447 (43), 1413 (40), 1387 (18), 1361 (45), 1285 (74), 1153 (15), 1032 (63), 885 (16), 753 (21), 738 (16), 479 (21), 460 (18); **IR** (ATR, 298 K, [cm^{-1}]): 2983 (vw), 2928 (w), 2852 (w), 1620 (vw), 1449 (w), 1396 (w), 1376 (w), 1260 (vs), 1220 (m), 1141 (s), 1029 (vs), 904 (w), 884 (w), 850 (w), 786 (w), 753 (w), 735 (w), 635 (vs), 571 (m), 559 (w), 516 (s), 492 (m), 455 (w); **isomer A (56%): ^{1}H NMR** (CD$_2$Cl$_2$, 300 K, in ppm) δ = 0.86 - 1.01 (2H, m, H9), 1.09 - 1.43 (8H, m, H9/H10/H11) 1.50 - 1.75 (24H, m, H5), 1.75 - 1.88 (4H, m, H10/H11), 1.93 - 2.06 (6H, m, H8/H10), 2.53 - 2.60 (1H, br, H9), 2.36 (6H, s, H3), 2.38 (6H, s, H3), 2.76 - 2.84 (1H, br, H9), 3.60 - 3.68 (2H, m, H7), 4.46 - 4.55 (2H, br, H4), 4.56 - 4.60 (2H, m, H7), 5.73 - 5.97 (3H, m, H4/H6); **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, 300 K, in ppm) δ = 10.62 - 11.77 (4C, m, C3), 20.83 - 22.00 (8C, m, C5), 25.91 (2C, s, C11), 26.63 - 27.00 (4C, m, C10), 30.26 - 30.43 (1C, m, C9), 30.61 - 30.78 (2C, br, C9), 31.10 (1C, s, C9), 42.35 - 42.75 (2C, m, C8), 52.43 - 55.00 (4C, m, C4), 70.37 - 70.81 (2C, m, C7) 119.66 (1C, t, ^2J(CP) = 8.7 Hz, C6), 121.29 (2C, q, ^1J(CF) = –321 Hz, OTf), 130.61 (4C, s, C3), 140.30 - 140.89 (2C, m, C1);); **^{19}F{^{1}H} NMR** (CD$_3$CN, 300 K, in ppm): δ = **–**78.77 (s); **^{31}P{^{1}H} NMR** (CD$_2$Cl$_2$, 300 K, in ppm) AX$_2$ spin system δ(P$_A$) = –61.3 ppm, δ(P$_X$) = –16.1 ppm, ^1J(PP) = –323 Hz; **isomer B (44%): ^{1}H NMR** (CD$_2$Cl$_2$, 300 K, in ppm) δ = 0.86 - 1.01 (2H, m, H9), 1.09 - 1.43 (8H, m, H9/H10/H11) 1.50 - 1.75 (24H, m, H5), 1.75 - 1.88 (4H, m, H10/H11), 1.93 - 2.06 (6H, m, H8/H10), 2.53 - 2.60 (1H, br, H9), 2.36 (6H, s, H3), 2.38 (6H, s, H3), 2.76 - 2.84 (1H, br, H9), 3.32 - 3.40 (2H, m, H7), 4.46 - 4.55 (2H, br, H4), 5.05 - 5.11 (2H, m, H7), 5.73 - 5.97 (3H, m, H4/H6), **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, 300 K, in ppm) δ = 10.62 - 11.77 (4C, m, C3), 20.83 - 22.00 (8C, m, C5), 26.00 (2C, s, C11), 26.63 - 27.00 (4C, m, C10),

30.26 - 30.43 (1C, m, C9), 30.61 - 30.78 (2C, br, C9), 31.10 (1C, s, C9), 42.82 - 43.20 (2C, m, C8), 52.43 - 55.00 (4C, m, C4), 69.90 - 70.33 (2C, m, C7), 121.29 (2C, q, ^{1}J(CF) = –321 Hz, OTf), 122.17 (1C, t, ^{2}J(CP) = 9.0 Hz, C6), 131.12 - 131.43 (4C, m, C3), 140.30 - 140.89 (2C, m, C1);); **^{19}F{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = **–**78.77 (s); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm) AX_2 spin system $\delta(P_A)$ = –57.6 ppm, $\delta(P_X)$ = –25.1 ppm, ^{1}J(PP) = –321 Hz; **elemental analysis:** calculated for **9**[OTf]$_2$·0.5 CH_2Cl_2 $C_{39.5}H_{68}F_6ClN_4O_6P_3PdS_2$: N 5.06, C 42.82, H 6.19, S 5.79; found: N 4.83, C 42.86, H 6.13, S 5.50.

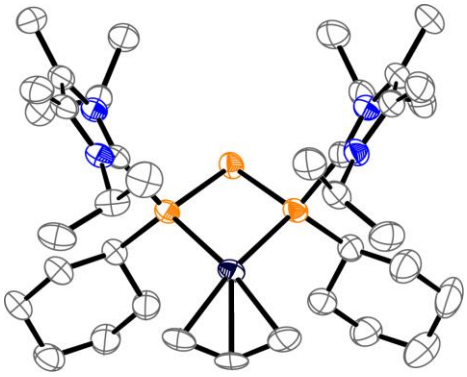


Figure S62: Molecular structure of cation **9**$^{2+}$ in **9**[OTf]$_2$·C_6H_5F·0.5 THF (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

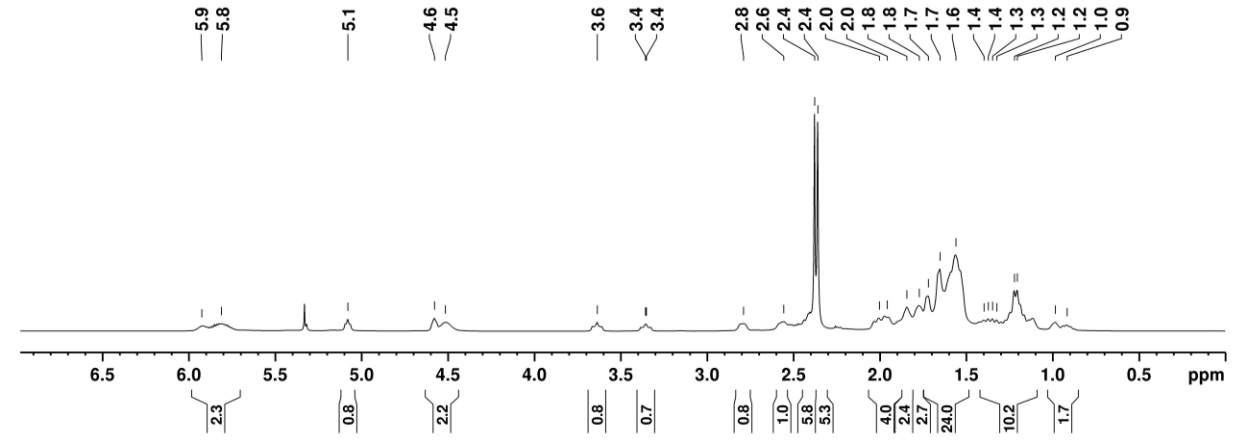


Figure S63: ^{1}H NMR-spectrum of **9**[OTf]$_2$ in CD_2Cl_2 at 300 K.

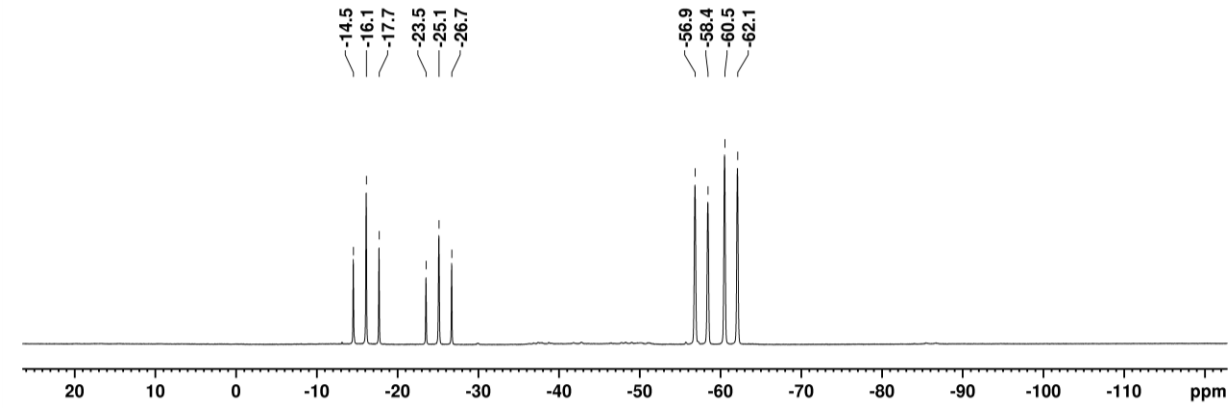


Figure S64: $^{31}P\{^{1}H\}$ NMR-spectrum of **9**$[OTf]_2$ in CD_2Cl_2 at 300 K.

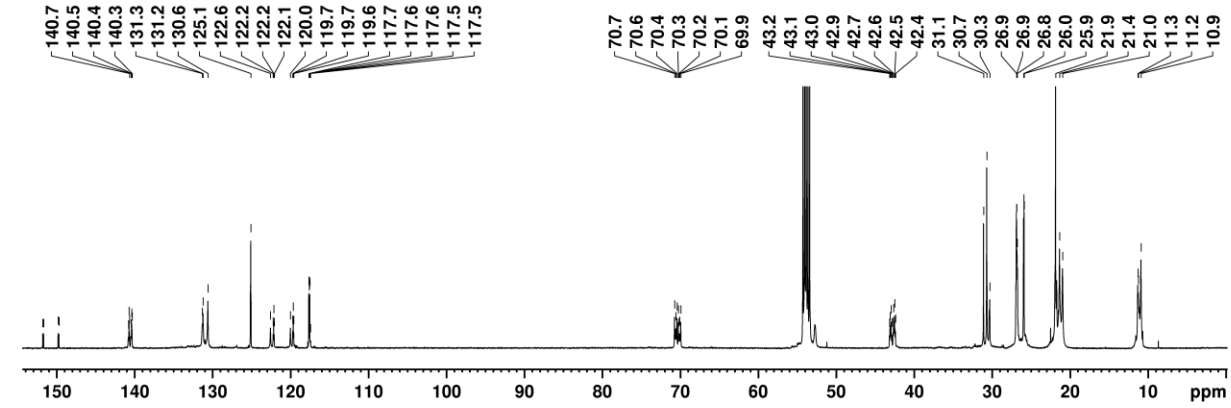


Figure S65: $^{13}C\{^{1}H\}$ NMR-spectrum of **9**$[OTf]_2$ in CD_2Cl_2 at 300 K.

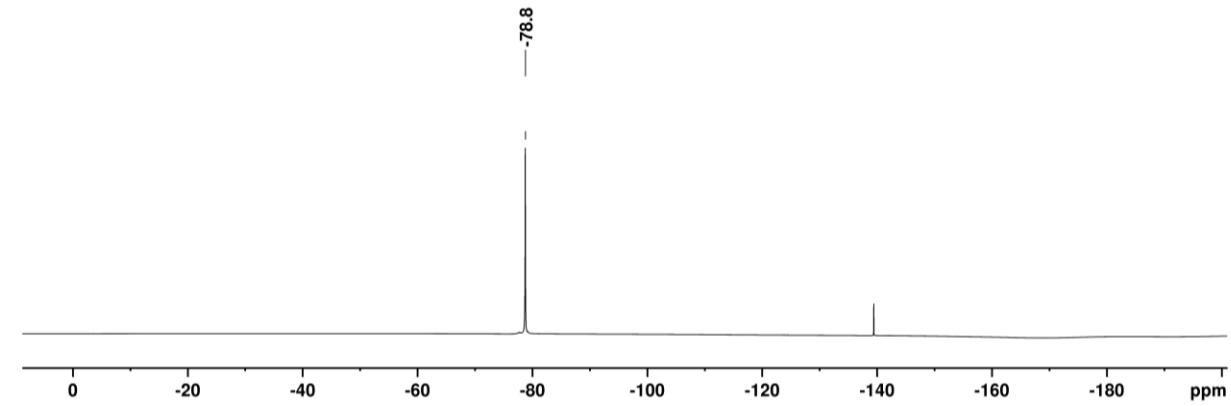
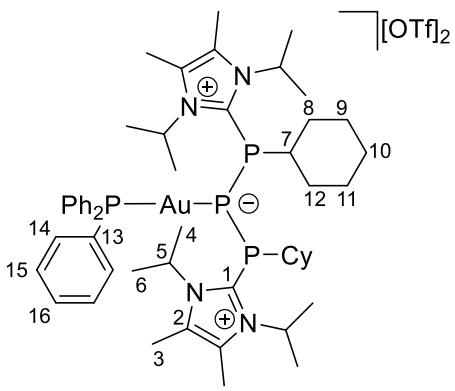


Figure S66: ^{19}F NMR-spectrum of **9**$[OTf]_2$ in CD_2Cl_2 at 300 K; some residual C_6H_5F is observed at ~-140 ppm.

2.5.2. Preparation of $[(L_CPCy)_2PAu(PPh_3)][OTf]_2$ (**10**$[OTf]_2$)



A solution of PPh_3AuCl (0.98 equiv., 90 mg, 0.18 mmol) in 1 mL CH_3CN is added to a solution of $(L_CPCy)_3P[OTf]_3$ **6a**$[OTf]_3$ (1 equiv., 250 mg, 0.18 mmol) in 2 mL CH_3CN at –30°C. After 30 min stirring, all volatiles are removed and the residue is dissolved in *o*-$C_6H_4F_2$. After filtration the solution is overlayed with *n*-hexane. The resulting oil is stirred with toluene for 16 h and subsequently washed with 3x2 mL toluene. Washing with *n*-pentane and removal of all volatiles affords the product as white powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et_2O and *n*-hexane into a saturated CH_2Cl_2/CH_3CN solution at –30°C.

Yield: 223 mg (88%); **m.p.** 231.3°C (dec.); **Raman** (100 mW, 50 scans, 298 K, [cm^{-1}]): 3058 (32), 2940 (80), 2898 (31), 2880 (29), 2851 (37), 1619 (23), 1585 (46), 1573 (18), 1445 (49), 1412 (34), 1359 (43), 1345 (23), 1285 (63), 1185 (30), 1100 (32), 1031 (88), 999 (100), 886 (19), 848 (19), 789 (19), 752 (30), 740 (28), 618 (19), 572 (20), 499 (22), 460 (21); **IR** (ATR, 298 K, [cm^{-1}]): 2979 (vw), 2923 (vw), 2849 (vw), 1619 (vw), 1440 (w), 1396 (w), 1378 (vw), 1267 (vs), 1221 (m), 1142 (s), 1114 (vw), 1099 (w), 1030 (vs), 997 (vw), 905 (vw), 787 (vw), 752 (m), 711 (w), 696 (m), 636 (vs), 571 (w), 546 (vw), 532 (m), 512 (s), 496 (m), 481 (w), 449 (w); **^{1}H NMR** (CD_3CN, 300 K, in ppm) δ = 0.85 - 0.98 (1H, br, H9), 1.11 - 1.39 (10H, br, H8/H9/H10/H11/H12), 1.44 (12H, d, ^3J(HH) = 7.6 Hz, H4), 1.51 - 1.62 (2H, m, H10), 1.65 (12H, d, ^3J(HH) = 6.9 Hz, H6), 1.70 - 1.82 (2H, m, H11), 2.27 (2H, br, H7), 2.31 (12H, s, H3), 2.37 - 2.50 (2H, m, H8), 2.90 - 2.97 (1H, m, H12), 5.24 - 5.36 (1H, m, H5), 5.38 - 5.48 (1H, m, H5), 5.52 - 5.80 (2H, br, H5), 7.31 - 7.40 (3H, m, H14), 7.52 - 7.62 (9H, m, H14/H15), 7.63 - 7.69 (3H, m, H16); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm) δ = 10.80 - 11.30 (4C, m, C3), 21.20 (2C, s, C4), 21.36 (2C, s, C4), 21.89 - 22.53 (4C, m, C6), 26.28 (1C, s, C7), 26.34 (1C, s, C10), 26.94 - 27.34 (4C, m, C9/C11), 31.08 - 31.44 (2C, m, C8), 32.27 - 32.60 (2C, m, C12), 43.00 - 43.40 (2C, m, C7), 53.88 - 54.86 (4C, m, C5), 122.22 (2C, q, ^1J(CF) = –321 Hz, OTf), 130.84 (6C, d, ^3J(CP) = 11 Hz, C15), 131.92 (2C, s, C2), 132.30 (2C, br, C2), 133.48 (3C, br, C16), 134.46 - 135.00 (6C, m, C13/C14), 145.46 - 146.00 (2C, m, C1); **^{19}F{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = **–**79.23 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): see below; **elemental analysis:** calculated for $C_{54}H_{77}AuF_6N_4O_6P_4S_2$: N 4.07, C 47.10, H 5.64, S 4.66; found: N 4.11, C 46.92, H 5.56, S 4.82.

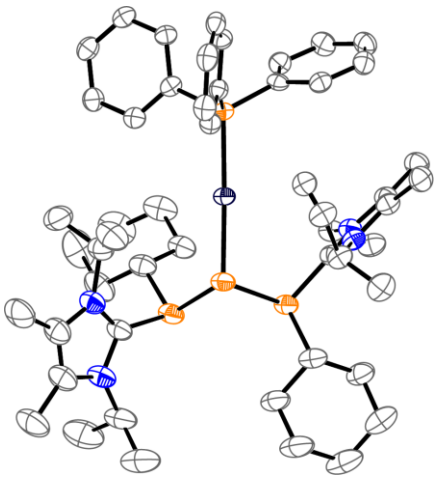


Figure S67: Molecular structure of cation $\mathbf{10}^{2+}$ in $\mathbf{10}[OTf]_2 \cdot 1.5\ CH_2Cl_2 \cdot 2\ MeCN$ (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

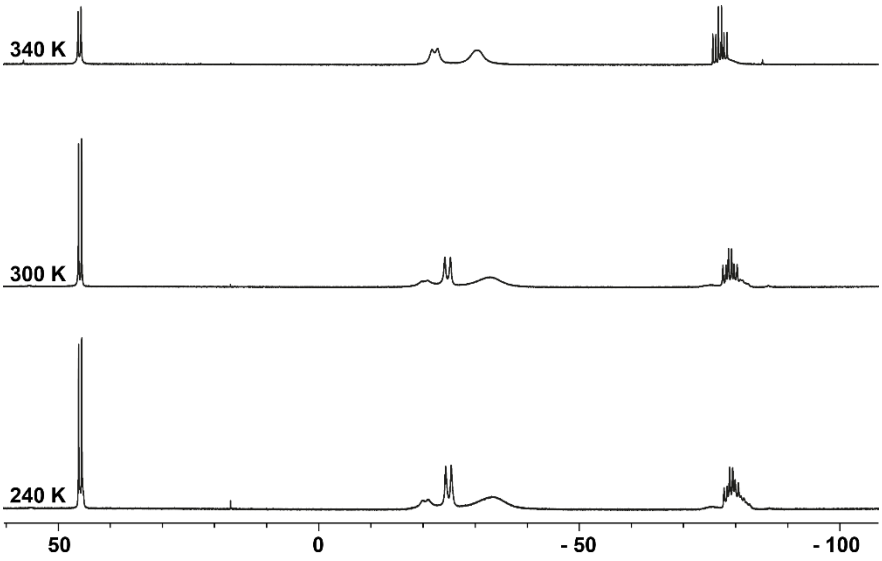


Figure S68: $^{31}P\{^{1}H\}$ NMR-spectra of $\mathbf{10}[OTf]_2$ in CD_3CN at 340 K (top), 300 K (middle) and 240 K (bottom).

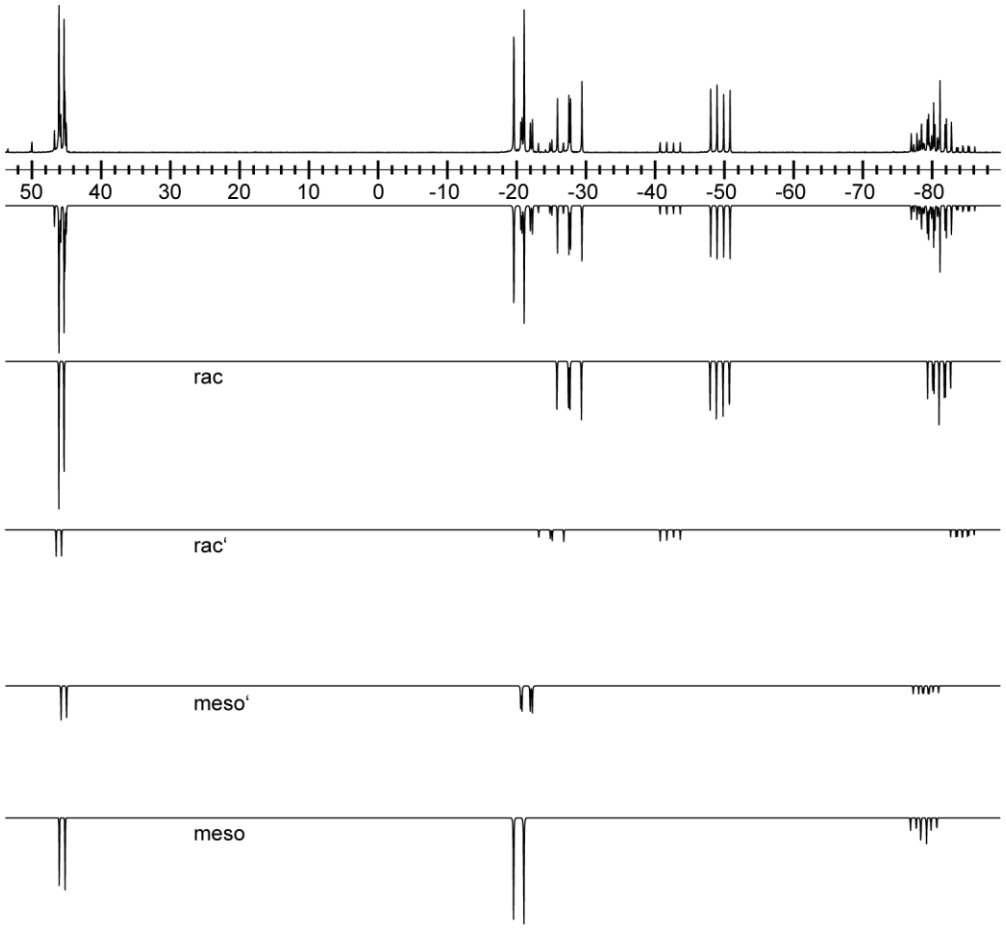


Figure S69: $^{31}P\{^{1}H\}$ NMR-spectra of **10**$[OTf]_2$ in CD_2Cl_2 190 K; experimental (upward) and fitted spectra of the *rac* and *meso* isomers (downward); parameters of the spin systems are given in **Table S 2**.

Table S 2: Iteratively generated parameters for the $^{31}P\{^{1}H\}$ NMR resonances of **10**$[OTf]_2$.

Isomer		Iterated parameter	Value
rac	chemical shift	$\delta(P_A)$	-81.14 ppm
		$\delta(P_M)$	-49.42 ppm
		$\delta(P_N)$	-27.32 ppm
		$\delta(P_X)$	45.71 ppm
	line width	ν_A	5.5 Hz
		ν_M	7.6 Hz
		ν_N	7.6 Hz
		ν_X	4.6 Hz
	coupling constants	$^1J(P_AP_M)$	-148.5 Hz
		$^1J(P_AP_N)$	-269.4 Hz
		$^2J(P_AP_X)$	120.3 Hz
		$^2J(P_MP_N)$	303.3 Hz
		$^3J(P_MP_X)$	1.5 Hz
		$^3J(P_NP_X)$	2.8 Hz
rac'	chemical shift	$\delta(P_A)$	-84.46 ppm
		$\delta(P_M)$	-42.14 ppm
		$\delta(P_N)$	-25.04 ppm
		$\delta(P_X)$	46.33 ppm
	line width	ν_A	6.5 Hz
		ν_M	8.9 Hz
		ν_N	9.8 Hz
		ν_X	6.2 Hz
	coupling constants	$^1J(P_AP_M)$	-156.1 Hz
		$^1J(P_AP_N)$	-269.7 Hz
		$^2J(P_AP_X)$	125.1 Hz
		$^2J(P_MP_N)$	315.1 Hz
		$^3J(P_MP_X)$	0 Hz
		$^3J(P_NP_X)$	0 Hz
meso'	chemical shift	$\delta(P_A)$	-79.18 ppm
		$\delta(P_M)$	-21.56 ppm
		$\delta(P_N)$	-21.33 ppm
		$\delta(P_X)$	45.42 ppm
	line width	ν_A	9.4 Hz
		ν_M	11.2 Hz
		ν_N	10.2 Hz
		ν_X	6.9 Hz
	coupling constants	$^1J(P_AP_M)$	-244.3 Hz
		$^1J(P_AP_N)$	-220.6 Hz
		$^2J(P_AP_X)$	128.6 Hz
		$^2J(P_MP_N)$	0 Hz
		$^3J(P_MP_X)$	0 Hz
		$^3J(P_NP_X)$	3.8 Hz
meso	chemical shift	$\delta(P_A)$	-78.88 ppm
		$\delta(P_M)$	-20.37 ppm
		$\delta(P_X)$	45.63 ppm
	line width	ν_A	10.8 Hz
		ν_M	9.2 Hz
		ν_X	4.0 Hz
	coupling constants	$^1J(P_AP_M)$	-240.0 Hz
		$^2J(P_AP_X)$	134.9 Hz
		$^3J(P_MP_X)$	4.1 Hz

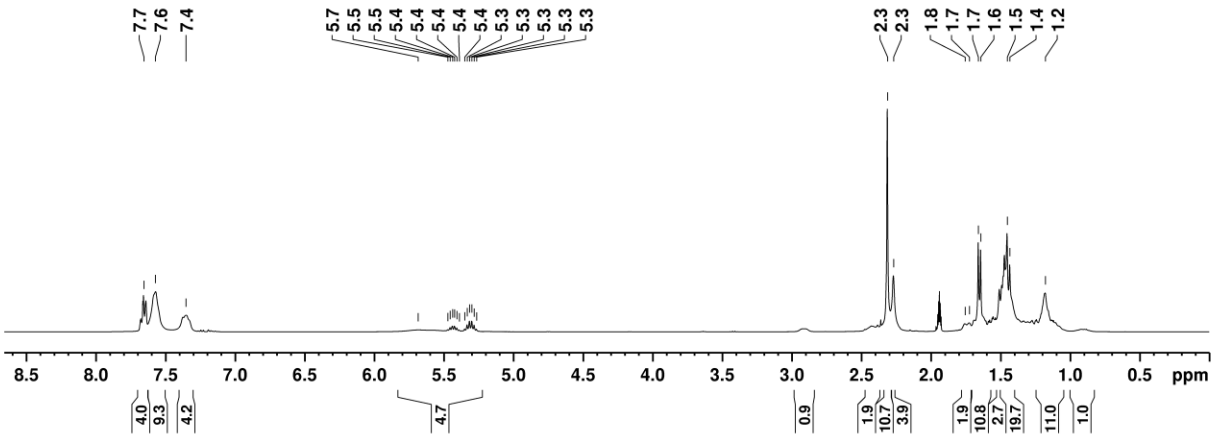


Figure S70: ^{1}H NMR-spectrum of **10**$[OTf]_2$ in CD_3CN at 300 K.

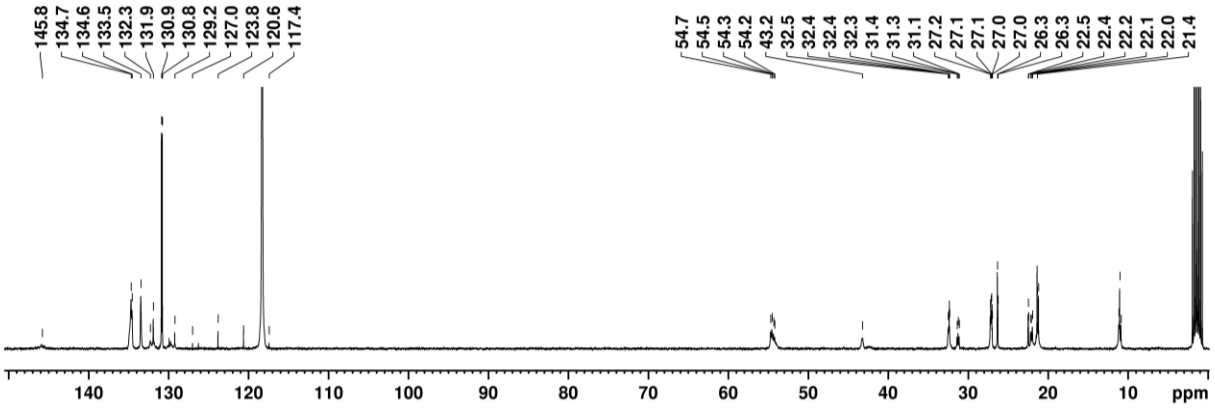


Figure S71: $^{13}C\{^{1}H\}$ NMR-spectrum of **10**$[OTf]_2$ in CD_3CN at 300 K.

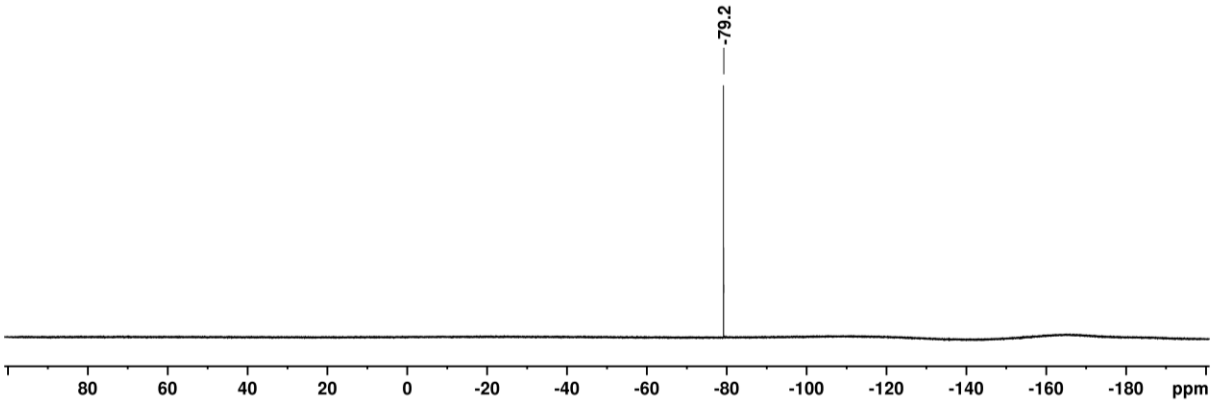
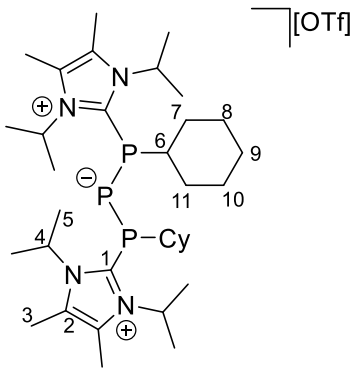


Figure S72: ^{19}F NMR-spectrum of **10**$[OTf]_2$ in CD_3CN at 300 K.

2.5.3. Preparation of [(L_CPCy)$_2$P][OTf] (**11**[OTf])



A solution of **IPr** (1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2-ylidene) (0.9 equiv., 30 mg, 0.17 mmol) in 1 mL *o*-$C_6H_4F_2$ is slowly added to a suspension of (L_CPCy)$_3$P[OTf]$_3$ **6a**[OTf]$_3$ (1 equiv., 310 mg, 0.19 mmol) in 2 mL *o*-$C_6H_4F_2$. The resulting suspension is stirred for 60 min. Subsequently, the mixture is filtered and all volatiles are removed *in vacuo*. The residue is dissolved in 2 mL C_6H_5F and the suspension is filtered again to remove **12**[OTf]$_2$. Addition of *n*-pentane leads to precipitation of a red oil and yellow crystalline solid, which are stirred in cold (**–**30°C) THF. The suspension is filtered and the yellow residue washed with 2x0.5 mL cold (–30°C) THF and 2x0.5 mL Et_2O. Removal of all volatiles affords the product as a yellow crystalline solid. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of *n*-pentane into a saturated CH_2Cl_2/C_6H_5F (v/v= 1:1) solution at –30°C.

Yield: 115 mg (81%); **Raman** (100 mW, 100 scans, 298 K, [cm^{-1}]): 2969 (60), 2939 (98), 2889 (44), 2847 (59), 1626 (25), 1444 (70), 1420 (53), 1401 (31), 1355 (68), 1293 (100), 1265 (25), 1191 (19), 1170 (12), 1152 (19), 1135 (15), 1084 (14), 1033 (40), 999 (15), 886 (23), 850 (15), 816 (15), 783 (21), 751 (19), 733 (31), 705 (18), 583 (16), 573 (18), 508 (26), 483 (18), 459 (20), 429 (18); **IR** (ATR, 298 K, [cm^{-1}]): 2976 (vw), 2920 (w), 2847 (w), 1625 (vw), 1449 (w), 1393 (w), 1375 (w), 1338 (vw), 1269 (vs), 1222 (m), 1169 (w), 1137 (s), 1112 (w), 1070 (vw), 1031 (s), 999 (w), 904 (w), 882 (vw), 849 (vw), 781 (vw), 751 (w), 733 (w), 703 (vw), 636 (vs), 571 (w), 547 (vw), 516 (m), 482 (m), 445 (w), 417 (w); **^{1}H NMR** (CD_2Cl_2, 300 K, in ppm) δ = 0.84 - 0.95 (1H, br, H11), 1.00 - 1.30 (9H, m, H7/H9/H11), 1.45 - 1.62 (24H, m, H5), 1.63 - 1.90 (10H, br, H6/H8/H10), 2.05 - 2.12 (1H, br, H11), 2.27 (6H, s, H3), 2.32 (6H, s, H3), 2.40 - 2.49 (1H, br, H6), 5.36 (2H, br, H4), 5.95 (2H, br, H4); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm) δ = 10.69 (4C, s, C3), 21.48 (8C, s, C5), 26.63 (1C, s, C9), 26.67 (1C, s, C9), 26.97 - 27.33 (4C, m, C8/C10), 29.78 - 30.50 (2C, m, C11), 32.62 - 33.00 (2C, br. C7), 41.16 - 42.20 (2C, br, C6), 52.00 - 53.21 (4C, br, C4), 121.41 (1C, q, ^1J(CF) = –321 Hz, OTf), 127.50 - 129.00 (4C, br, C2) 153.00 - 154.44 (2C, br, C1); **^{19}F{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): δ = **–**79.92 (s); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 300 K, in ppm): AX_2 spin systems: *meso* isomer: $\delta(P_A)$ = –135.2 ppm, $\delta(P_X)$ = –3.2 ppm, ^1J(PP) = –316 Hz; *rac* isomer: $\delta(P_A)$ = –130.6 ppm, $\delta(P_X)$ = –6.9 ppm, ^1J(PP) = –315 Hz at room temperature, low temperature see below; **elemental analysis:** calculated for **11**[OTf]·0.33 CH_2Cl_2 $C_{35.33}H_{62.66}F_3N_4O_3P_3Cl_{0.66}S$: N 7.03, C 53.24, H 7.92, S 4.02; found: N 6.64, C 53.54, H 7.94, S 3.76.

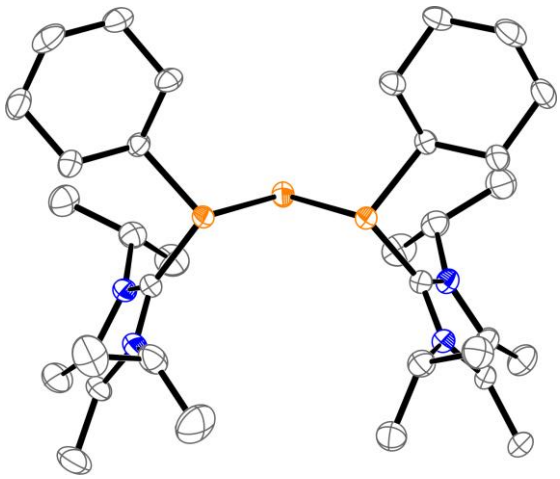


Figure S73: Molecular structure of cation **11**$^{+}$ in **11**[OTf]·CH_2Cl_2 (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability).

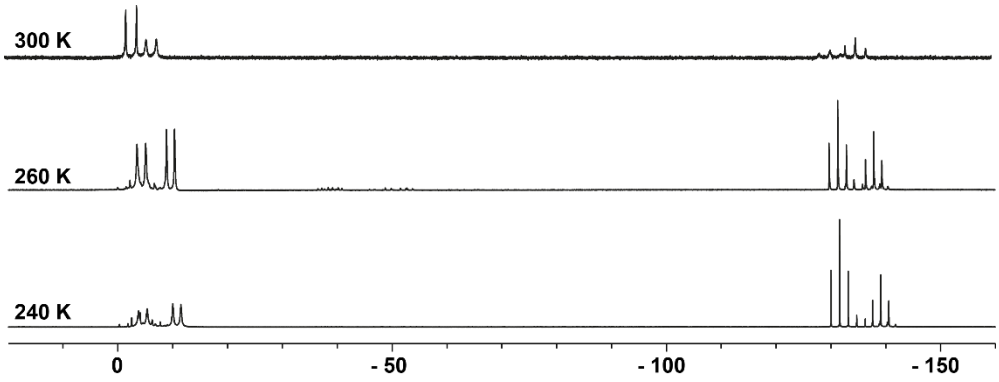


Figure S74: $^{31}P\{^{1}H\}$ NMR-spectra of **11**[OTf] in CD_2Cl_2 at 300 K (top), 260 K (middle) and 240 K (bottom).

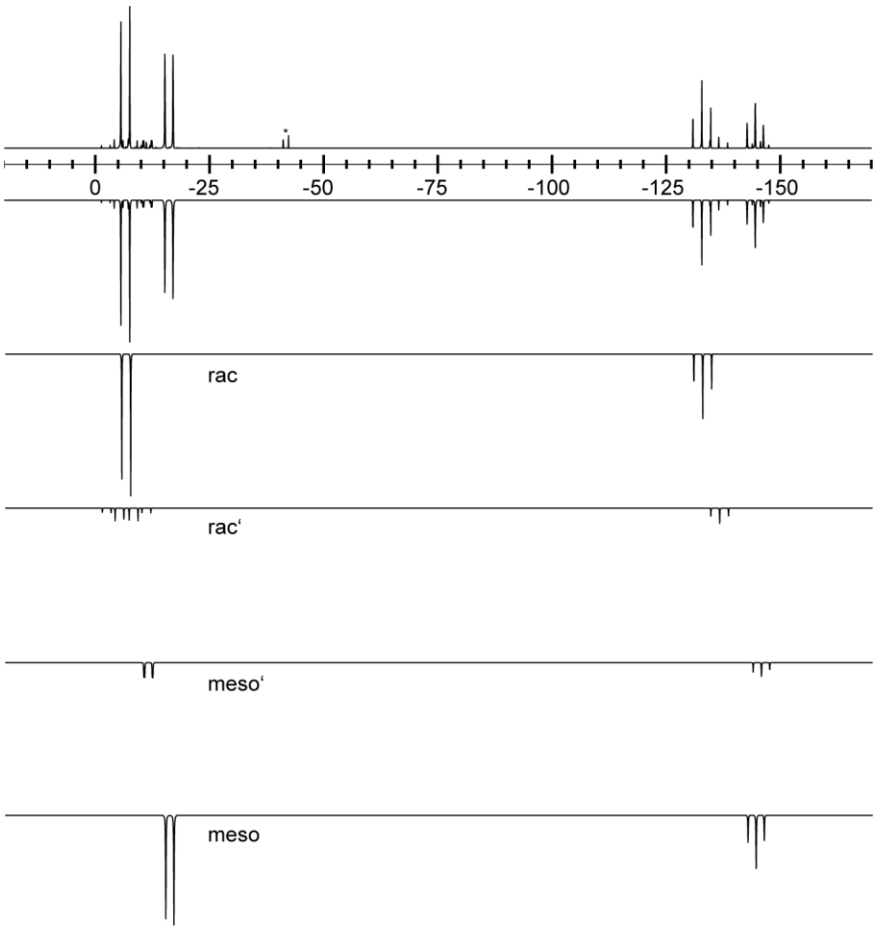


Figure S75: $^{31}P\{^{1}H\}$ NMR-spectra of **11**[OTf] in CD_2Cl_2 190 K; experimental (upward) and fitted spectra of the *rac* and *meso* isomers (downward); parameters of the spin systems are given in **Table S 3**.

Table S 3: Iteratively generated parameters for the $^{31}P\{^{1}H\}$ NMR resonances of **11**[OTf].

Isomer		Iterated parameter	Value
rac	chemical shift	$\delta(P_A)$	-132.82 ppm
		$\delta(P_X)$	-6.60 ppm
	line width	ν_A	8.7 Hz
		ν_X	8.7 Hz
	coupling constants	$^{1}J(P_AP_X)$	-315.8 Hz
rac'	chemical shift	$\delta(P_A)$	-136.5 ppm
		$\delta(P_X)$	-9.26 ppm
		$\delta(P_Y)$	-4.08 ppm
	line width	ν_A	8.2 Hz
		ν_X	8.2 Hz
		ν_Y	8.2 Hz
	coupling constants	$^{1}J(P_AP_X)$	-313.9 Hz
		$^{1}J(P_AP_Y)$	-310.8 Hz
		$^{2}J(P_YP_X)$	454.0 Hz
meso'	chemical shift	$\delta(P_A)$	-145.7 ppm
		$\delta(P_X)$	-11.5 ppm
		$\delta(P_Y)$	-11.4 ppm
	line width	ν_A	8.2 Hz
		ν_X	8.2 Hz
		ν_Y	8.2 Hz
	coupling constants	$^{1}J(P_AP_X)$	-289.0 Hz
		$^{1}J(P_AP_Y)$	-297.7 Hz
		$^{2}J(P_YP_X)$	6.2 Hz
meso	chemical shift	$\delta(P_A)$	-144.5 ppm
		$\delta(P_X)$	-.16.2 ppm
	line width	ν_A	16.1 Hz
		ν_X	16.1 Hz
	coupling constants	$^{1}J(P_AP_M)$	-288.1 Hz

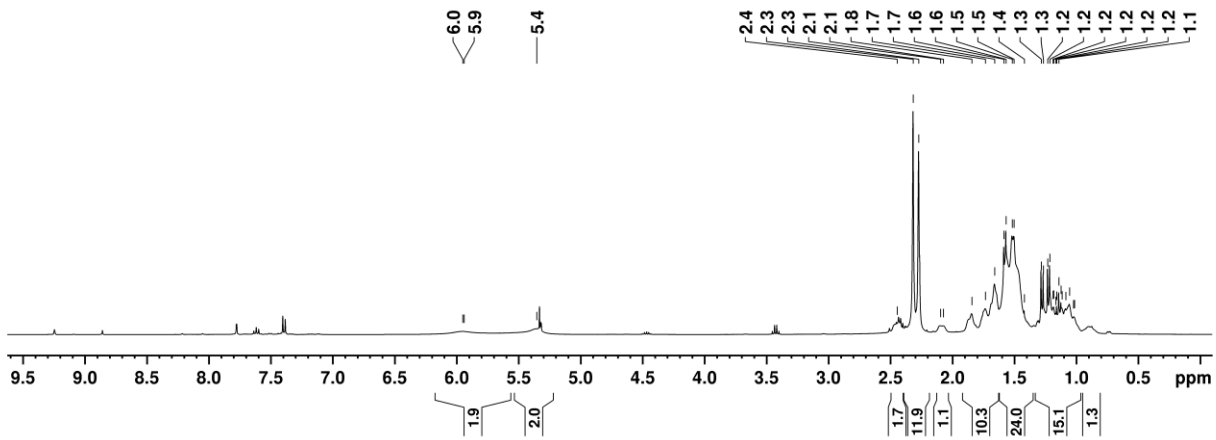


Figure S76: ^{1}H NMR-spectrum of **11**[OTf] in CD_2Cl_2 at 300 K.

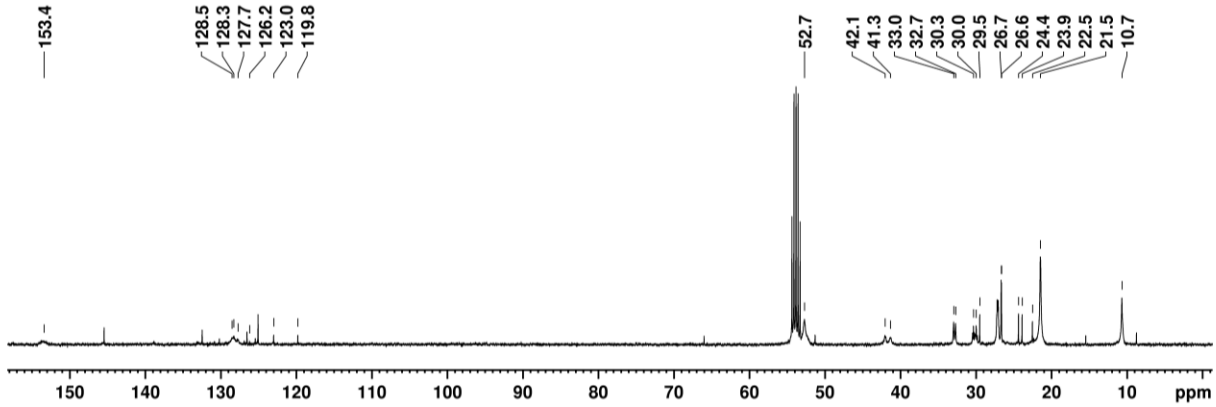


Figure S77: $^{13}C\{^{1}H\}$ NMR-spectrum of **11**[OTf] in CD_2Cl_2 at 300 K.

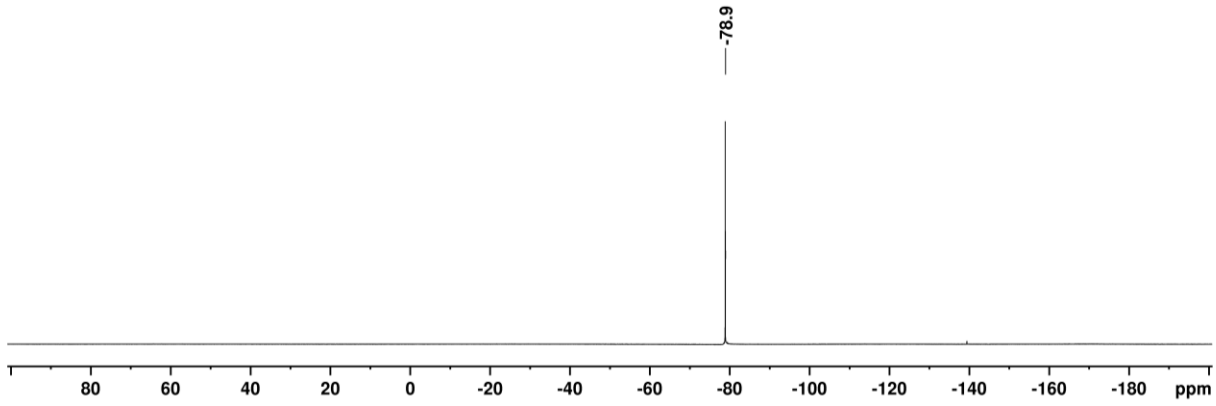
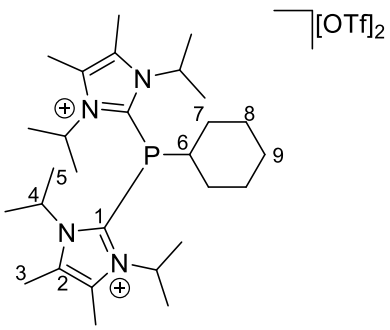


Figure S78: ^{19}F NMR-spectrum of **11**[OTf] in CD_2Cl_2 at 300 K.

2.5.4. Preparation of $[(L_C)_2PCy][OTf]_2$ (**12**$[OTf]_2$)



A solution of 50 mg $CyPCl_2$ (1 equiv., 0.27 mmol) in 2 mL C_6H_5F is added to a solution of 217 mg L_CSiMe_3OTf (**1**[OTf], 2 equiv., 0.55 mmol) in 4 mL C_6H_5F. The colorless solution is stirred 16 h days at 80°C. Upon cooling to room temperature, a white precipitate is formed, which is filtered and washed with 3x1 mL C_6H_5F. Drying *in vacuo* affords the product as an off-white powder. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et_2O into a saturated CH_3CN solution at –30°C.

Yield: 149 mg (71%); **m.p.** 231.5°C (dec.); **Raman** (100 mW, 100 scans, 298 K, [cm^{-1}]): 3064 (12), 2991 (44), 2950 (100), 2862 (30), 1614 (28), 1449 (43), 1407 (46), 1349 (46), 1276 (78), 1224 (15), 1153 (25), 1032 (70), 1001 (17), 884 (20), 785 (15), 752 (28), 584 (15), 572 (18), 545 (16), 463 (16), **IR** (ATR, 298 K, [cm^{-1}]): 2986 (vw), 2935 (vw), 2860 (vw), 1610 (vw), 1490 (vw), 1454 (vw), 1392 (w), 1380 (w), 1358 (vw), 1261 (vs), 1222 (m), 1138 (s), 1115 (m), 1085 (w), 1030 (vs), 999 (w), 979 (vw), 903 (vw), 805 (vw), 791 (vw), 766 (w), 752 (w), 691 (vw), 635 (vs), 571 (w), 543 (w), 516 (m), 476 (w), 456 (w), 436 (vw); **^{1}H NMR** (CD_3CN, 300 K, in ppm) δ = 1.34 - 1.44 (1H, m, H9), 1.49 (24H, d, ^3J(HH) = 6.8 Hz, H5), 1.53 - 1.61 (4H, m, H7/H8), 1.68 - 1.81 (3H, m, H7/H9), 1.81 - 1.89 (2H, m, H9), 2.42 (12H, s, H3), 3.28 - 3.38 (1H, m, H6), 4.97 (4H, br, H4); **^{13}C{^{1}H} NMR** (CD_3CN, 300 K, in ppm) δ = 11.64 (4C, s, C3), 21.19 (4C, s, C5), 21.50 (4C, s, C4), 25.92 (1C, d, ^4J(CP) = 2 Hz, C9), 26.19 (1C, d, ^3J(CP) = 16 Hz, C8), 31.52 (1C, d, ^2J(CP) = 21 Hz, C7), 36.46 (1C, d, ^1J(CP) = –17 Hz, C6), 54.57 (2C, s, C4), 54.70 (2C, s, C4), 122.20 (1C, q, ^1J(CF) = –321 Hz, OTf), 134.65 (4C, s, C2), 136.13 (2C, d, ^1J(CP) = –53 Hz, C1); **^{19}F{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = -79.20 (s); **^{31}P{^{1}H} NMR** (CD_3CN, 300 K, in ppm): δ = –38.2; **elemental analysis:** calculated for **12**$[OTf]_2$·0.33 C_6H_5F $C_{32}H_{52.66}F_{6.33}N_4O_6PS_2$: N 6.96, C 47.55, H 6.60, S 7.97; found: N 6.92, C 47.73, H 6.53, S 7.70.

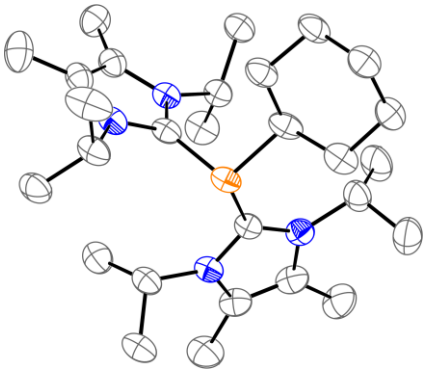


Figure S79: Molecular structure of cation **12**$^{2+}$ in **12**$[OTf]_2$·CH_3CN (hydrogen atoms, solvate molecules, and anions are omitted for clarity and ellipsoids are set at 50% probability). Selected bond lengths [Å] and angles [°]: P1–C1 1.837(3), P1–C2 1.840(3), P1–C3 1.860(4), C1-P1-C3 100.94(16).

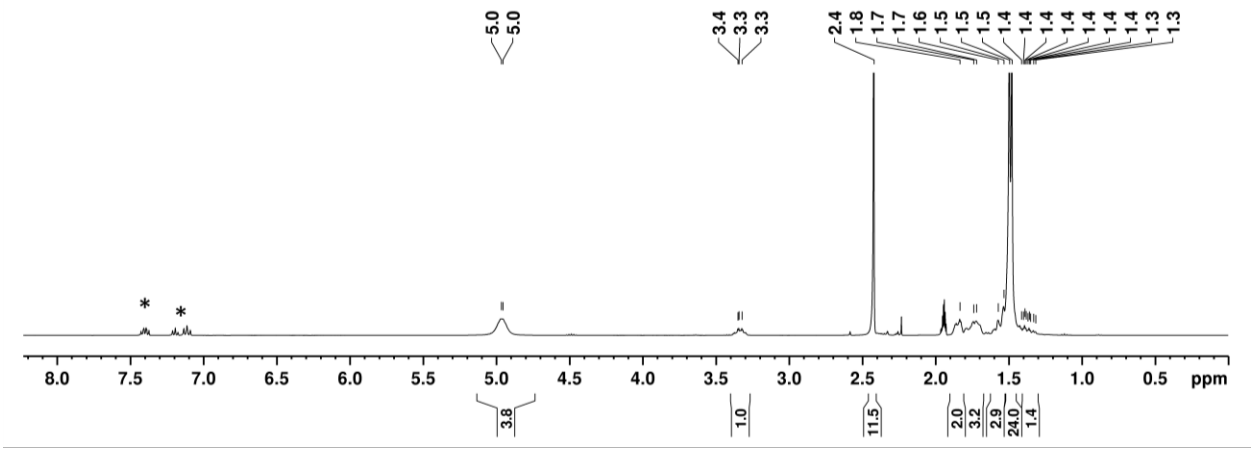


Figure S80: ^{1}H NMR-spectrum of **12**[OTf]$_2$ in CD_3CN at 300 K; signals of residual C_6H_5F between 7 and 7.5 ppm.

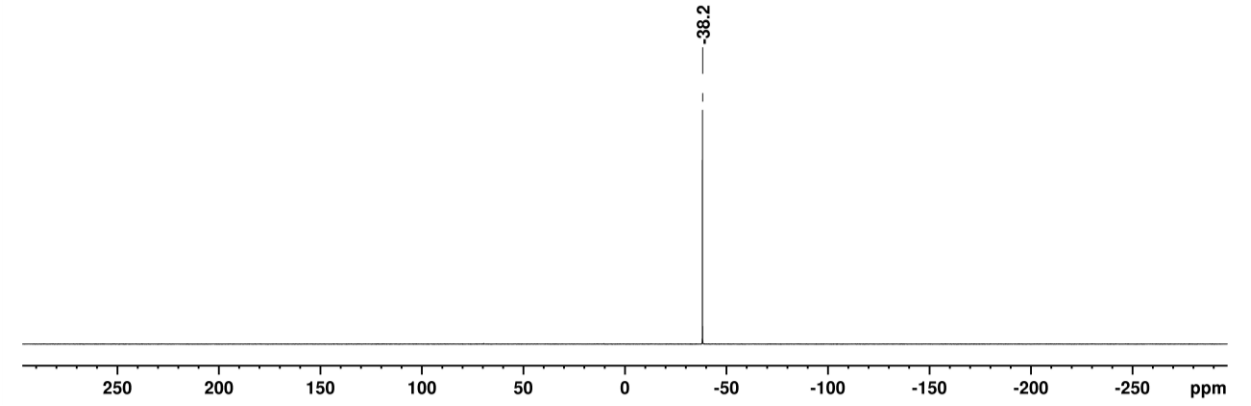


Figure S81: $^{31}P\{^{1}H\}$ NMR-spectrum of **12**[OTf]$_2$ in CD_3CN at 300 K.

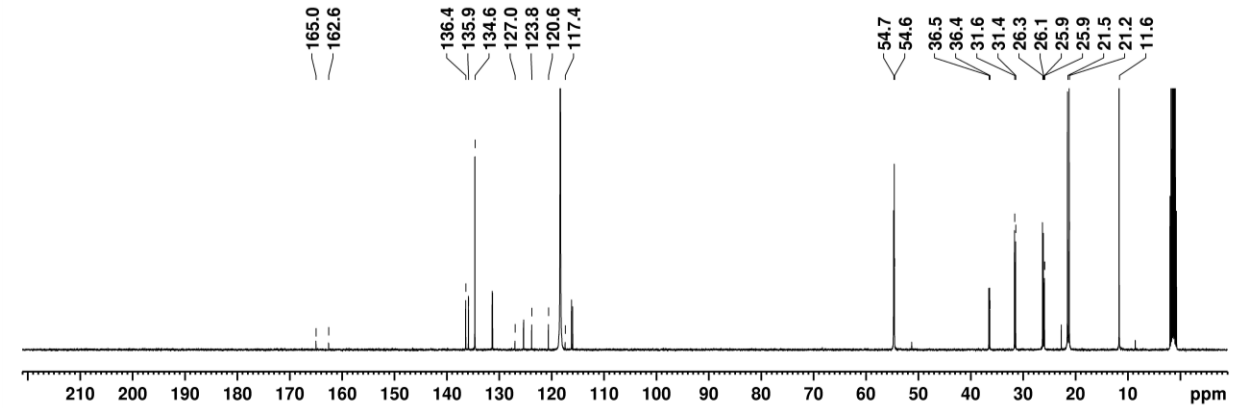


Figure S82: $^{13}C\{^{1}H\}$ NMR-spectrum of **12**[OTf] in CD_3CN at 300 K.

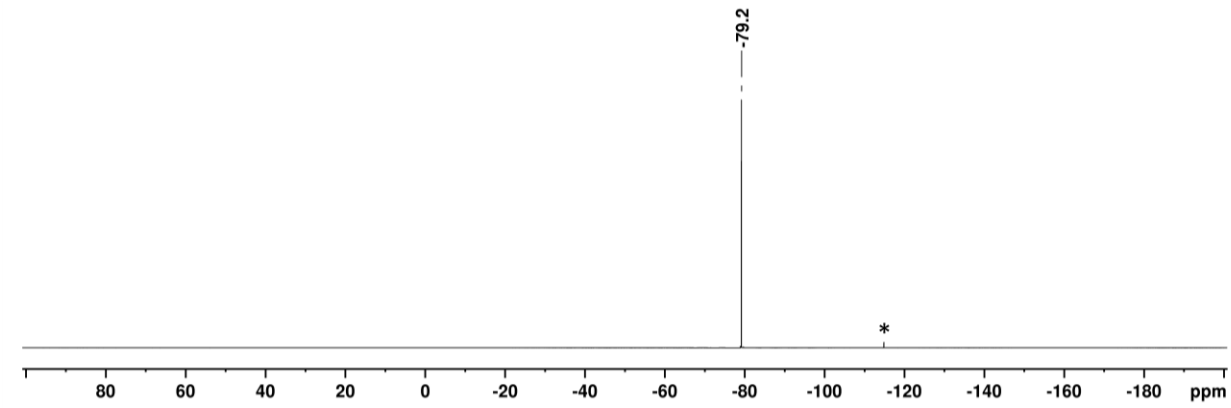


Figure S83: ^{19}F NMR-spectrum of **12**$[OTf]_2$ in CD_3CN at 300 K; signals of residual C_6H_5F at -114.9 ppm.

2.5.5. Reaction of **6a**[OTf]$_3$ with Ph_4PCl

6a[OTf]$_3$ (300 mg, 1 equiv., 0.19 mmol) and Ph_4PCl (80 mg, 1 equiv. 0.19 mmol) were dissolved in 5 mL of cold (-30°C) acetonitrile. The mixture was allowed to warm to room temperature and subsequently stirred for 1 h. After evaporating to dryness, the solids were washed with 2 mL of toluene and dried *in vacuo*. The remaining colorless residue was taken up in 1 mL of C_6H_5F and the so obtained yellow solution was used for NMR studies.

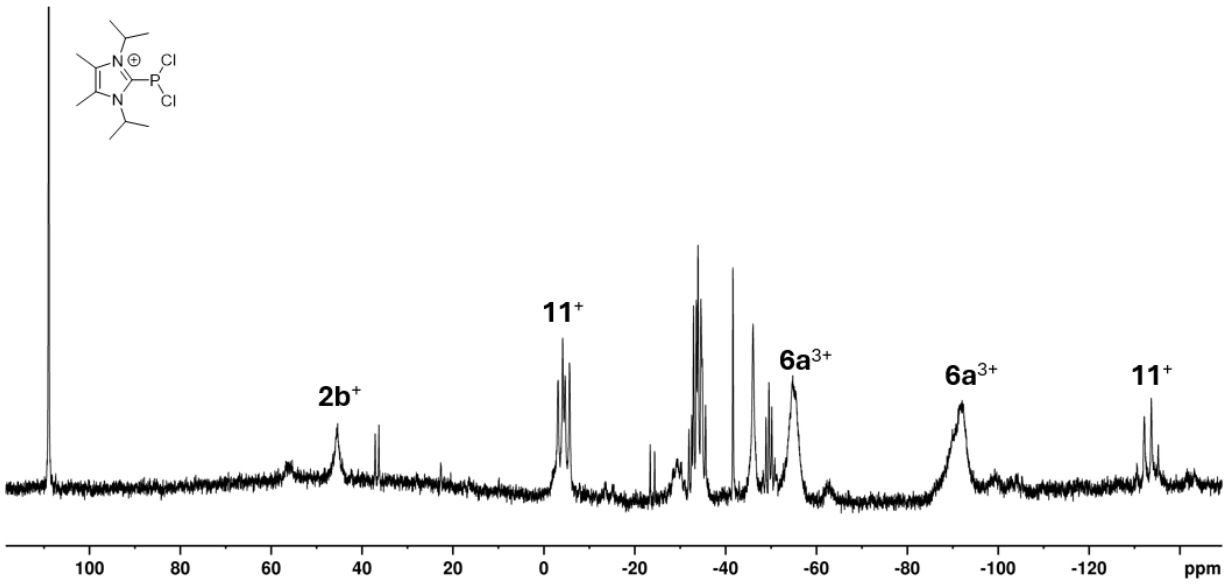


Figure S 84: ^{31}P NMR spectrum (300K) of the reaction mixture of **6a**[OTf]$_3$ with Ph_4PCl in C_6H_5F (C_6D_6 ref.).

3. Computational Investigations

The geometries and energies of all systems included in this study were fully optimized at the RI-BP86-D4/def2-TZVP level of theory without symmetry constrains. The calculations have been performed by using the program TURBOMOLE version 7.0.[3] For the calculations we have used the BP86 functional[4] with the D4 correction[5] for dispersion. In order to reproduce solvent effects, we have used the conductor-like screening model COSMO[6], which is a variant of the dielectric continuum solvation models. The minimum nature of the complexes and compounds have been confirmed by doing frequency calculations. The NMR spectra were computed using the GIAO method as implemented in ORCA 5.0[7]. The conformational searches of the rotamers were computed using the conformer-rotamer ensemble sorting tool[8] (CREST).

3.1. Conformer Search for 2b[OTf]

Initially, a conformer search for compound **2b**$^+$ was conducted using the Conformer-Rotamer Ensemble Sampling Tool (CREST), a tool based on the xTB method developed by Grimme[8]. Forty rotamers were identified by CREST, with energies ranging from 0 to 6 kcal/mol. These rotamers were subsequently optimized at the BP86-D4/def2-TZVP level of theory, resulting in convergence from the initial 40 structures down to only 4 distinct rotamers, depicted in **Figure S85**. This reduction indicates that only four conformations represent true energy minima. Notably, two of these rotamers are isoenergetic, exhibiting the lowest energies and aligning with those observed in the solid state. The remaining two isomers, with energies ≥ 5 kcal/mol higher, are not detected in the ^{31}P-NMR spectrum due to their negligible population (< 0.1%). The analysis revealed that rotation of the isopropyl groups, highlighted in yellow in **Figure S85**, marginally affects stabilization energy, whereas rotation of the isopropyl groups marked in green significantly influences their relative energy

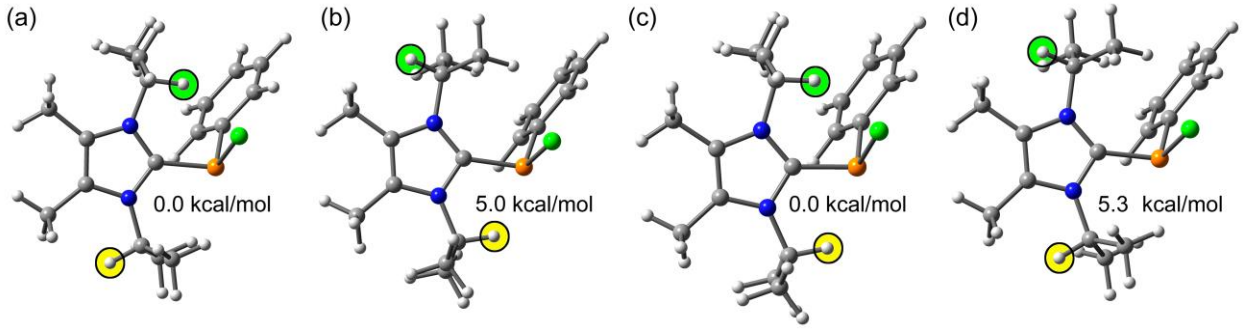


Figure S85: Optimized geometries of the four rotamers of compound **2b**$^+$ and their relative energies

The rotation barrier to interconvert the isoenergetic isomers has been computed in CH_2Cl_2, and it is 10.2 kcal/mol, that is consistent with a rapid interconversion at 300 K compared to the NMR scale. The ^{31}P NMR spectrum of **2b**$^+$ exhibits two singlet resonances at 240 K and a broad singlet resonance at 300 K. The Gutowsky–Holm equation[9] allows a rough estimation of $\Delta G^{\neq}$.

k_B Boltzmann constant $1.38064852 \cdot 10^{-23}$ $m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$

h Planck constant $6.62607004 \cdot 10^{-34}$ $m^2 \cdot kg \cdot s^{-1}$

$$k_{T_c} = \Delta\nu \cdot \frac{\pi}{\sqrt{2}}$$

$$\Delta G^{\neq} = RT \cdot \ln\left(\frac{k_B T}{k_{T_c} h}\right)$$

Coalescence occurs at 280 K and the signals are separated by 618.3 Hz at low temperature. Therefore an energy barrier $\Delta G^{\neq}$ of 51.6 $kJ \cdot mol^{-1}$ or 12.3 $kcal \cdot mol^{-1}$ can be attributed to the process, which is in close agreement to the theoretical value of 10.2·kcal mol^{-1}. Remarkably, the chemical shift difference between both isomers Δδ(P) is 3.0 ppm, that strongly agrees with the experimental difference (3.1 ppm).

3.2. Frontier Molecular Orbitals and WBI of 7b[OTf]$_2$

In order to gain a better understanding of the bonding situation in **7b**[OTf]$_2$, we conducted DFT calculations at the RI-BP86-D4/def2-TZVP level of theory.

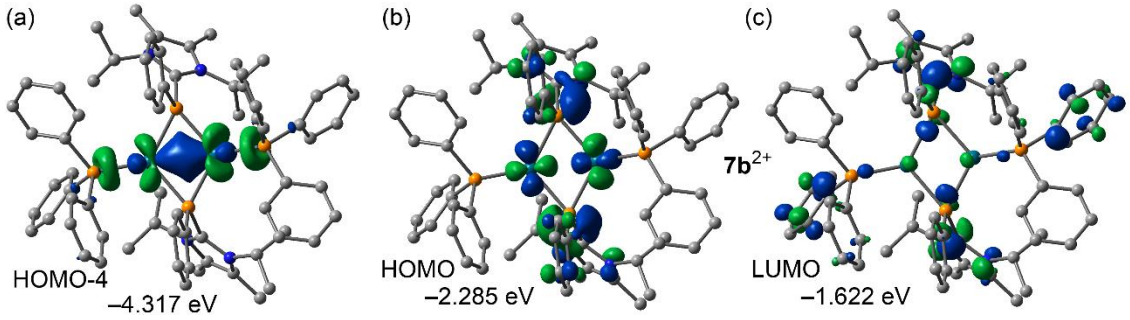


Figure S86: Frontier molecular orbitals of **7b**$^{2+}$.

The frontier molecular orbitals of **7b**$^{2+}$ are depicted in **Figure S86**. In the HOMO, there is a significant contribution of the d-atomic orbitals of the metal centers but in anti-bonding phase. Interestingly, we have found the bonding phase of such orbitals in the HOMO-4. Additionally, the LUMO is predominantly located at the aromatic rings. The calculated Wiberg Bond Index of the PdPd bond is 0.24, indicating only a weak interaction.

3.3. Cartesian Coordinates

2b_anti

Cl	6.8946705	3.3373640	11.9872396
P	5.9015051	4.2927192	10.4250781
N	7.3076066	6.7506462	11.1324634
N	5.1243927	6.8994698	11.1601756
C	6.1594966	6.0500733	10.9192642
C	6.9972750	8.0480791	11.5043695
C	5.6180865	8.1403989	11.5174262
C	8.6721164	6.1537111	11.0101903
H	8.4747257	5.1008873	10.7905212
C	9.4391436	6.7354626	9.8247482
H	8.8425620	6.6877222	8.9058909
H	10.3436969	6.1332772	9.6686696
H	9.7593392	7.7710758	9.9896938
C	9.4256113	6.2125900	12.3375725
H	9.7609776	7.2253824	12.5896712
H	10.3199561	5.5814994	12.2562551
H	8.8126586	5.8215918	13.1599174
C	7.9824972	9.1099347	11.8526304
H	8.3674646	8.9866368	12.8749551
H	7.4989707	10.0916850	11.7984870
H	8.8376614	9.1256621	11.1689132
C	4.7596930	9.3094814	11.8501612
H	4.1035162	9.5912302	11.0141971
H	5.3876739	10.1759430	12.0833910
H	4.1280966	9.1181841	12.7296490
C	7.0806858	4.1789480	9.0317370
C	8.0479511	3.1721369	8.9270857
H	8.2128851	2.4798503	9.7531494
C	8.8094884	3.0613637	7.7619113
H	9.5655149	2.2794477	7.6868244
C	8.6016974	3.9397070	6.6969399
H	9.1960976	3.8462912	5.7880955
C	7.6237856	4.9336152	6.7928918
H	7.4529528	5.6175465	5.9611907
C	6.8614536	5.0533908	7.9537666
H	6.0968073	5.8310970	8.0159794
C	3.6623598	6.5925569	11.0926838
H	3.1933699	7.5458704	11.3630632
C	3.2620212	5.5583954	12.1452310
H	3.6495051	4.5599425	11.9055693
H	2.1667926	5.4924445	12.1801124
H	3.6181047	5.8465780	13.1428392
C	3.2229583	6.2441502	9.6702449
H	3.5551592	7.0054051	8.9516397
H	2.1262819	6.2034640	9.6370000
H	3.6012335	5.2626913	9.3562137

2b_syn

Cl	6.8025146	3.3381423	11.9038157
P	5.8526960	4.3884184	10.3772163
N	7.3548159	6.7641814	11.1714289
N	5.1745918	6.9851217	11.1969641
C	6.1860942	6.1125230	10.9306170
C	7.0825121	8.0561247	11.5850567
C	5.7055357	8.1983572	11.5952286
C	8.6985872	6.1244362	11.0357391
H	8.4656400	5.0867840	10.7805752

C	9.4904528	6.7173792	9.8723879
H	8.8985954	6.7136021	8.9491400
H	10.3782230	6.0940167	9.7041357
H	9.8389277	7.7384496	10.0687068
C	9.4450908	6.1137846	12.3682262
H	9.8084792	7.1062636	12.6589411
H	10.3208514	5.4592810	12.2701714
H	8.8149630	5.7126477	13.1725347
C	8.0980596	9.0699569	11.9827730
H	8.4295636	8.9225744	13.0209462
H	7.6623135	10.0735650	11.9183598
H	8.9829613	9.0502269	11.3388890
C	4.9207252	9.4010987	11.9886495
H	4.0621811	9.5733794	11.3307094
H	5.5595794	10.2902293	11.9380739
H	4.5481981	9.3233609	13.0201110
C	7.0277540	4.2736398	8.9801235
C	7.9665236	3.2440908	8.8473238
H	8.1065110	2.5198986	9.6502712
C	8.7313661	3.1510422	7.6825745
H	9.4649887	2.3505590	7.5846945
C	8.5549721	4.0702987	6.6470495
H	9.1519803	3.9907833	5.7385826
C	7.6041148	5.0872381	6.7708832
H	7.4571140	5.8028278	5.9615468
C	6.8381480	5.1884272	7.9309753
H	6.0937309	5.9837540	8.0154415
C	3.7289061	6.6366563	11.0461808
H	3.7486285	5.5559293	10.8452016
C	3.1218903	7.3248445	9.8246345
H	3.0580035	8.4141602	9.9397218
H	2.1015983	6.9479756	9.6752608
H	3.6997101	7.1047904	8.9171565
C	2.9547292	6.8540685	12.3444752
H	3.4697375	6.3932293	13.1975804
H	1.9725373	6.3739300	12.2471167
H	2.7805997	7.9139045	12.5637443

$5b^{2+}$, Figure 3 (a)

P	1.3104429	5.6813718	10.4281340
N	3.1829746	4.0071683	8.9166455
N	1.7563359	5.1709651	7.7249602
C	2.1400429	4.8828484	9.0032795
C	3.4652055	3.7558205	7.5848719
C	2.5653348	4.4927050	6.8329577
C	3.8975161	3.4431838	10.1013549
H	3.3014661	3.7999997	10.9501356
C	3.8656913	1.9160636	10.1200363
H	2.8514823	1.5303395	9.9622118
H	4.2003034	1.5755879	11.1084832
H	4.5369830	1.4710886	9.3777447
C	5.3063779	4.0221173	10.2228286
H	5.9855322	3.6407143	9.4510032
H	5.7235712	3.7326090	11.1960439
H	5.3019980	5.1183717	10.1705834
C	0.6041529	6.0658304	7.3900643
H	0.1572483	6.2708063	8.3740603
C	-0.4429371	5.3455398	6.5429774
H	-0.1289651	5.2073707	5.5023675
H	-1.3559873	5.9545806	6.5297155
H	-0.7002411	4.3670620	6.9695024

C	1.0840048	7.3957261	6.8137458
H	1.7783572	7.8972526	7.5005457
H	0.2154787	8.0509139	6.6663686
H	1.5766526	7.2847986	5.8398941
C	4.5071126	2.8205248	7.0788342
H	5.4470772	2.8940193	7.6354238
H	4.7261046	3.0458530	6.0290597
H	4.1664511	1.7760040	7.1230496
C	2.4395203	4.5245473	5.3494390
H	1.6709544	3.8236873	4.9932002
H	3.3898020	4.2261339	4.8918072
H	2.1897180	5.5211304	4.9712609
C	0.7538099	4.2433645	11.4126433
C	0.5446887	2.9860671	10.8235765
H	0.8183823	2.8138201	9.7826292
C	-0.0386553	1.9509224	11.5539850
H	-0.2001927	0.9817566	11.0812824
C	-0.4217644	2.1548192	12.8809593
H	-0.8766623	1.3445684	13.4502999
C	-0.2382525	3.4086747	13.4681142
H	-0.5585926	3.5811719	14.4960638
C	0.3345379	4.4497246	12.7388619
H	0.4378777	5.4278475	13.2080866
P	3.1436952	6.3943518	11.5919694
N	1.2728296	8.0452359	13.1152519
N	2.6371932	6.8168753	14.3106418
C	2.2993479	7.1468706	13.0322500
C	0.9588230	8.2716872	14.4456460
C	1.8216830	7.4947282	15.1973573
C	0.6023525	8.6565560	11.9269884
H	1.2021612	8.2977432	11.0820990
C	0.6880479	10.1815656	11.9458489
H	1.7114149	10.5262145	12.1353969
H	0.3880438	10.5566371	10.9588575
H	0.0153597	10.6322164	12.6837562
C	-0.8239075	8.1331248	11.7610873
H	-1.5067822	8.5184462	12.5274175
H	-1.2063273	8.4653233	10.7874431
H	-0.8620285	7.0364911	11.7799202
C	3.7642199	5.9392699	14.7618737
H	3.7089423	6.0069336	15.8544535
C	3.5493878	4.4755372	14.3802360
H	3.6427715	4.3208035	13.2986542
H	4.3152082	3.8684575	14.8806008
H	2.5646356	4.1151403	14.7017018
C	5.1144861	6.5121711	14.3310217
H	5.2202377	7.5611651	14.6372017
H	5.9148511	5.9380288	14.8158604
H	5.2609338	6.4417919	13.2451565
C	-0.0791963	9.2148265	14.9465605
H	-1.0139462	9.1524408	14.3798137
H	-0.3131505	8.9826447	15.9913028
H	0.2707322	10.2563059	14.9117697
C	1.9307364	7.3808588	16.6772507
H	2.8934176	7.7613626	17.0491414
H	1.1434572	7.9726811	17.1559566
H	1.8190980	6.3429587	17.0208646
C	3.6690682	7.8650003	10.6426210
C	3.9841060	9.0696628	11.2927917
H	3.7981927	9.1830052	12.3612222
C	4.5555610	10.1256110	10.5835377

H	4.7987839	11.0540091	11.1010681
C	4.8219953	9.9948514	9.2188289
H	5.2676291	10.8220848	8.6668464
C	4.5312623	8.7934719	8.5691752
H	4.7562637	8.6789136	7.5085287
C	3.9678563	7.7307979	9.2755918
H	3.7804931	6.7913750	8.7560380

$5b^{2+}$, Figure 3 (b)

P	1.1539893	5.3295382	10.5994785
N	3.2691057	4.1583926	8.9484718
N	1.9398167	5.5685463	7.9251082
C	2.2089956	4.9950349	9.1321458
C	3.6590345	4.1932597	7.6212873
C	2.8181391	5.0834103	6.9751288
C	3.8608406	3.3171392	10.0293782
H	3.3770857	3.6902095	10.9369982
C	3.4732066	1.8494031	9.8577124
H	2.3860267	1.7349079	9.7682535
H	3.8011621	1.2908785	10.7438190
H	3.9487232	1.3883575	8.9835304
C	5.3613252	3.5512765	10.1889601
H	5.9541142	3.1037414	9.3842378
H	5.6843239	3.0865058	11.1295616
H	5.5956425	4.6220987	10.2491246
C	0.8039941	6.5131351	7.6973324
H	0.4949338	6.7888498	8.7145928
C	-0.3611649	5.7870215	7.0276391
H	-0.1116796	5.4419025	6.0164540
H	-1.2134146	6.4734497	6.9429499
H	-0.6805525	4.9187731	7.6199217
C	1.2421572	7.7888335	6.9832478
H	2.1657061	8.1910369	7.4161323
H	0.4547987	8.5427247	7.1120649
H	1.3813746	7.6469219	5.9060274
C	4.7888459	3.4238358	7.0309944
H	4.8322396	2.3943089	7.4019344
H	5.7580589	3.9009858	7.2358449
H	4.6737612	3.3761352	5.9425727
C	2.8366558	5.4679094	5.5369314
H	1.8323460	5.4890558	5.0982575
H	3.4275011	4.7406972	4.9689755
H	3.2953110	6.4548615	5.3838153
C	0.8943840	3.6673122	11.3224822
C	-0.0590691	2.8541910	10.6878027
H	-0.5595659	3.2005628	9.7812072
C	-0.3736216	1.6011420	11.2140886
H	-1.1072433	0.9713646	10.7106921
C	0.2405008	1.1614905	12.3901338
H	-0.0112866	0.1849990	12.8037905
C	1.1711215	1.9764625	13.0393263
H	1.6470569	1.6365566	13.9595437
C	1.4986168	3.2243130	12.5076775
H	2.2446681	3.8422682	13.0139767
P	2.8317093	6.1979475	11.8203343
N	2.8689433	7.9063024	14.0002686
N	0.8310929	7.1333207	13.8115686
C	2.0717468	7.0892766	13.2566841
C	2.1230129	8.4966984	15.0097937
C	0.8396414	8.0055652	14.8968018
C	4.3344395	8.0639087	13.7591940
H	4.5178317	7.4523426	12.8631499

C	5.1512720	7.4428249	14.8916436
H	4.8402087	6.4074237	15.0830764
H	6.2090313	7.4322940	14.5984054
H	5.0799547	8.0075410	15.8284277
C	4.7045203	9.5039633	13.4168824
H	4.6460407	10.1672743	14.2874512
H	5.7414599	9.5258011	13.0579892
H	4.0611793	9.9013288	12.6216074
C	-0.3273961	6.3124774	13.3653340
H	0.0531470	5.7881880	12.4819582
C	-0.6971452	5.2426422	14.3915850
H	-1.2117271	5.6535005	15.2676120
H	-1.3784621	4.5235875	13.9183677
H	0.1897071	4.6932272	14.7295622
C	-1.4963442	7.1739854	12.8975534
H	-1.1702511	7.9255726	12.1663984
H	-2.2361395	6.5267474	12.4089028
H	-2.0025142	7.6831278	13.7251257
C	2.6291301	9.5100714	15.9761663
H	2.7217219	10.5010526	15.5091777
H	1.9258649	9.6076943	16.8102438
H	3.6033926	9.2425632	16.3981378
C	-0.3454357	8.3633475	15.7246465
H	-0.9495908	7.4925355	15.9992602
H	-0.0123620	8.8353949	16.6552856
H	-0.9990213	9.0823231	15.2097661
C	3.0880440	7.6381284	10.7028458
C	2.1964898	8.7196093	10.6285166
H	1.2783804	8.7156249	11.2180164
C	2.4904394	9.8135150	9.8153434
H	1.8020351	10.6578672	9.7707144
C	3.6686846	9.8307535	9.0615842
H	3.9015489	10.6921793	8.4354132
C	4.5497500	8.7481004	9.1158023
H	5.4715097	8.7627263	8.5337092
C	4.2640887	7.6570838	9.9390566
H	4.9709159	6.8281644	10.0066037

5b^{2+}, Figure 3 (c)

P	1.3104866	5.6784783	10.4505066
N	3.1848672	4.0094315	8.9401690
N	1.7655188	5.1800841	7.7457494
C	2.1455842	4.8893286	9.0246018
C	3.4686477	3.7577064	7.6090462
C	2.5720569	4.4969408	6.8553298
C	3.8954649	3.4424052	10.1265469
H	3.3011432	3.8010747	10.9757297
C	3.8569846	1.9153548	10.1422528
H	2.8408258	1.5350754	9.9833149
H	4.1891079	1.5720253	11.1304185
H	4.5266808	1.4682435	9.3995440
C	5.3067067	4.0158099	10.2489385
H	5.9842062	3.6338931	9.4758831
H	5.7229525	3.7226565	11.2213597
H	5.3068543	5.1123772	10.1994945
C	0.6200977	6.0824770	7.4083431
H	0.1805762	6.3026340	8.3924090
C	-0.4378643	5.3607112	6.5760392
H	-0.1259748	5.1973035	5.5384265
H	-1.3426855	5.9815200	6.5505064
H	-0.7077131	4.3944442	7.0224146

C	1.1088937	7.4013730	6.8139589
H	1.8153203	7.9022540	7.4889501
H	0.2460356	8.0643895	6.6682423
H	1.5904281	7.2753446	5.8364446
C	4.5099864	2.8213233	7.1042338
H	5.4448768	2.8849918	7.6703336
H	4.7398129	3.0556562	6.0587741
H	4.1634227	1.7782785	7.1358462
C	2.4448871	4.5202774	5.3717052
H	1.6823214	3.8098948	5.0211093
H	3.3970174	4.2268907	4.9146173
H	2.1858270	5.5116314	4.9869698
C	0.7652536	4.2312799	11.4264421
C	0.5309758	2.9860256	10.8210046
H	0.7792251	2.8293329	9.7711250
C	-0.0435870	1.9437880	11.5480588
H	-0.2245378	0.9838728	11.0635998
C	-0.3926009	2.1285473	12.8874297
H	-0.8415648	1.3127188	13.4534440
C	-0.1828175	3.3699114	13.4916588
H	-0.4734257	3.5269241	14.5307255
C	0.3818536	4.4187190	12.7661023
H	0.5029900	5.3885822	13.2480204
P	3.1339200	6.3982007	11.6244702
N	1.2575080	8.0703963	13.1231514
N	2.6312663	6.8573188	14.3289637
C	2.2828598	7.1733957	13.0474227
C	0.9516620	8.3087563	14.4517976
C	1.8187230	7.5418694	15.2126324
C	0.5814456	8.6665226	11.9306507
H	1.1797374	8.2998593	11.0877827
C	0.6625108	10.1917557	11.9316920
H	1.6880624	10.5402703	12.1022683
H	0.3474397	10.5550632	10.9450387
H	0.0001598	10.6493692	12.6747755
C	-0.8424281	8.1328315	11.7781875
H	-1.5237567	8.5247913	12.5426578
H	-1.2324032	8.4477237	10.8017813
H	-0.8726173	7.0362054	11.8146028
C	3.7540461	5.9305324	14.6760272
H	4.2098062	5.7176210	13.6977422
C	4.8065983	6.6221482	15.5402353
H	4.4755418	6.7772488	16.5731504
H	5.6996196	5.9849622	15.5765244
H	5.1028574	7.5892098	15.1130479
C	3.2314155	4.6117358	15.2407656
H	2.5263517	4.1357608	14.5467162
H	4.0795379	3.9306884	15.3897026
H	2.7364796	4.7312568	16.2124236
C	-0.0799642	9.2592148	14.9500673
H	-1.0035927	9.2259568	14.3635176
H	-0.3370304	9.0131613	15.9864671
H	0.2901671	10.2946152	14.9431757
C	1.9142801	7.4944464	16.6980595
H	2.6780561	8.1897381	17.0754893
H	0.9565259	7.7929490	17.1398217
H	2.1530731	6.4941562	17.0725986
C	3.6709312	7.8583791	10.6634931
C	3.9756762	9.0702196	11.3050415
H	3.7824945	9.1921956	12.3712807
C	4.5468251	10.1227157	10.5905268

H	4.7821062	11.0567087	11.1016274
C	4.8230885	9.9812683	9.2288174
H	5.2692559	10.8053922	8.6727005
C	4.5424075	8.7728633	8.5879981
H	4.7745818	8.6498477	7.5298199
C	3.9795296	7.7135284	9.3000131
H	3.8000456	6.7689120	8.7874997

6a^{3+}

P	0.0015848	8.0973924	36.2421549
P	0.6987790	6.1993891	37.2293033
N	2.1701071	4.4929498	35.5861175
N	0.2816160	4.9800281	34.5915215
C	0.9931637	5.1652010	35.7382717
C	2.2184010	3.9129144	34.3286544
C	1.0267501	4.2217164	33.6981814
C	3.3390294	3.0858375	33.7979794
H	4.3185312	3.4517415	34.1219602
H	3.3289159	3.1027404	32.7022396
H	3.2519071	2.0358084	34.1115515
C	0.6083194	3.8416575	32.3201478
H	-0.3844698	3.3769934	32.2906401
H	1.3139667	3.1111499	31.9104179
H	0.5958019	4.7073865	31.6430520
C	3.1584156	4.3145917	36.6983441
H	2.6522637	4.7793878	37.5568021
C	4.4429881	5.0966188	36.4510192
H	4.9981809	4.7455060	35.5722317
H	5.1024042	4.9812599	37.3205020
H	4.2300924	6.1667074	36.3307515
C	3.3681291	2.8366414	37.0227702
H	2.4105270	2.3096432	37.1242796
H	3.8960336	2.7621123	37.9822314
H	3.9792301	2.3184585	36.2753673
C	-1.1506144	5.3606681	34.4569124
H	-1.3370485	5.9774966	35.3465576
C	-1.4254041	6.2214315	33.2280485
H	-0.7228376	7.0613096	33.1721203
H	-2.4410807	6.6309482	33.3089550
H	-1.3754433	5.6523903	32.2931453
C	-2.0390076	4.1182047	34.5351851
H	-1.8572439	3.4264348	33.7050466
H	-3.0911948	4.4216778	34.4783517
H	-1.8885537	3.5734932	35.4749419
C	-0.7803412	5.3954233	38.0421564
H	-1.6931205	5.6085262	37.4596783
C	-0.5729917	3.8731756	38.1249256
H	0.3490103	3.6611403	38.6934133
H	-0.4363488	3.4353250	37.1243135
C	-1.7692335	3.2166881	38.8312843
H	-2.6709434	3.3497010	38.2083597
H	-1.5997870	2.1331611	38.9060745
C	-2.0085528	3.8203026	40.2190674
H	-1.1636420	3.5626978	40.8793769
H	-2.9023484	3.3733187	40.6756546
C	-2.1516035	5.3445032	40.1534633
H	-3.0727308	5.6091950	39.6051265
H	-2.2562354	5.7655655	41.1635422
C	-0.9503341	5.9884946	39.4490401
H	-0.0326952	5.8022107	40.0320909
H	-1.0807473	7.0801548	39.3999807

P	1.2952468	9.6509852	37.2322330
N	2.0370581	11.7804127	35.5924829
N	2.5509701	9.9030283	34.5908278
C	2.0420238	10.4247170	35.7415573
C	2.5089450	12.1144470	34.3333049
C	2.8315383	10.9290484	33.6979599
C	2.6638246	13.4998221	33.8058005
H	1.8681738	14.1695566	34.1483969
H	2.6326563	13.4882141	32.7102668
H	3.6259431	13.9415371	34.1028108
C	3.3611969	10.7582356	32.3163281
H	4.2624188	10.1349364	32.2811088
H	3.6330382	11.7357730	31.9044923
H	2.6152652	10.3107847	31.6441561
C	1.7014202	12.7227694	36.7080890
H	1.5582397	12.0501348	37.5660119
C	0.3787890	13.4412812	36.4685597
H	0.4019314	14.1052359	35.5956141
H	0.1474045	14.0618746	37.3439301
H	-0.4383437	12.7198168	36.3412698
C	2.8755376	13.6464118	37.0284762
H	3.8129631	13.0837144	37.1262295
H	2.6778131	14.1391500	37.9893030
H	3.0131462	14.4356111	36.2812188
C	2.9380185	8.4727533	34.4504761
H	2.5033407	8.0004423	35.3422663
C	2.3225904	7.8059201	33.2249488
H	1.2441762	7.9956738	33.1751820
H	2.4750354	6.7211047	33.3050359
H	2.7859072	8.1332222	32.2878159
C	4.4590694	8.3277067	34.5185699
H	4.9617976	8.8406226	33.6908195
H	4.7244963	7.2662129	34.4495828
H	4.8591938	8.7226764	35.4601577
C	2.7321901	8.7693168	38.0422663
H	2.9995318	7.8702649	37.4603488
C	3.9511350	9.7053105	38.1191320
H	3.6804966	10.6122570	38.6875919
H	4.2596458	10.0399702	37.1171506
C	5.1172757	8.9919171	38.8215146
H	5.4447737	8.1410365	38.1985719
H	5.9752726	9.6754954	38.8904758
C	4.7176796	8.4886397	40.2124189
H	4.5253834	9.3518072	40.8709280
H	5.5511957	7.9351659	40.6667770
C	3.4645816	7.6091058	40.1547383
H	3.6885988	6.6750091	39.6093230
H	3.1545163	7.3134904	41.1669046
C	2.3069245	8.3300995	39.4514913
H	2.0130280	9.2208069	40.0328114
H	1.4246402	7.6736884	39.4072984
P	-1.9943598	8.4432912	37.2215651
N	-4.2103429	8.0341168	35.5795215
N	-2.8343743	9.4117976	34.5789110
C	-3.0352424	8.7103806	35.7292992
C	-4.7333725	8.2779845	34.3199369
C	-3.8640502	9.1467349	33.6856156
C	-6.0118891	7.7242499	33.7906254
H	-6.1934374	6.6974855	34.1249993
H	-5.9879966	7.7118392	32.6952451
H	-6.8745899	8.3343101	34.0942735

C	-3.9786019	9.6915285	32.3041683
H	-3.8850377	10.7836593	32.2692261
H	-4.9621240	9.4429546	31.8912312
H	-3.2196684	9.2664772	31.6320789
C	-4.8660189	7.2786250	36.6951254
H	-4.2146122	7.4906518	37.5552417
C	-4.8329910	5.7731396	36.4600127
H	-5.4057986	5.4638214	35.5768458
H	-5.2739315	5.2666583	37.3282088
H	-3.7994141	5.4185868	36.3535460
C	-6.2518285	7.8404384	37.0078535
H	-6.2300958	8.9343259	37.0964415
H	-6.5826893	7.4323901	37.9715124
H	-7.0037860	7.5606025	36.2618459
C	-1.7856357	10.4582191	34.4392639
H	-1.1591369	10.3149307	35.3302019
C	-0.9026309	10.2575155	33.2118807
H	-0.5323884	9.2274435	33.1586074
H	-0.0364511	10.9276621	33.2922568
H	-1.4184833	10.4996775	32.2762332
C	-2.4163436	11.8498773	34.5087326
H	-3.1096139	12.0328325	33.6799403
H	-1.6278047	12.6093626	34.4418344
H	-2.9598407	11.9988649	35.4496618
C	-1.9458218	10.1251807	38.0379083
H	-1.2974713	10.8056533	37.4599858
C	-3.3644670	10.7171294	38.1151825
H	-4.0179075	10.0276229	38.6766659
H	-3.8040249	10.8246362	37.1121024
C	-3.3284871	12.0787851	38.8279214
H	-2.7539225	12.7911316	38.2110474
H	-4.3493911	12.4801707	38.8992576
C	-2.6937624	11.9745035	40.2190696
H	-3.3462218	11.3735288	40.8736769
H	-2.6295957	12.9702116	40.6793818
C	-1.3057937	11.3273116	40.1578481
H	-0.6087154	11.9896436	39.6155912
H	-0.8952846	11.2003331	41.1696589
C	-1.3543837	9.9675141	39.4475487
H	-1.9817446	9.2674646	40.0245155
H	-0.3461118	9.5286577	39.4016612

7b^{2+}

Pd	2.1451176	2.6116209	4.1167959
Pd	4.8725006	2.5786358	4.2237178
P	3.5464424	4.4924578	3.6751626
P	3.4787096	0.6633554	4.5258659
P	7.0123797	2.2478807	3.6091659
P	0.0492267	2.6030410	3.2952233
N	4.6929706	6.9103155	4.6987454
N	2.8532573	6.2780325	5.7278147
N	4.0772391	-0.1744951	7.1399529
N	2.2814581	-1.1818371	6.3618697
C	3.6858981	5.9677467	4.6746603
C	5.9580238	6.7038453	3.9566572
H	5.7062080	5.9341178	3.2188013
C	7.0114146	6.1106396	4.8883986
H	7.3070995	6.8072557	5.6853683
H	7.9056676	5.8427821	4.3121918
H	6.6100348	5.1936521	5.3396532
C	6.4322988	7.9417592	3.2014970

H	5.6206512	8.3818461	2.6084323
H	7.2274074	7.6364589	2.5091697
H	6.8458076	8.7112887	3.8657848
C	4.4971145	7.7783147	5.7722703
C	5.3591011	8.9545637	6.0749471
H	6.4202378	8.6873597	6.1734294
H	5.0434205	9.4119002	7.0206208
H	5.2842915	9.7265375	5.2945314
C	3.3580968	7.3767851	6.4215389
C	2.7186064	7.9871144	7.6211837
H	1.8359257	8.5927826	7.3668899
H	3.4350462	8.6439794	8.1291881
H	2.3995425	7.2251576	8.3442336
C	1.5903422	5.5570918	5.9799236
H	1.4846021	4.9241658	5.0802185
C	1.7159803	4.6054029	7.1678264
H	2.5248798	3.8852416	6.9845957
H	0.7797828	4.0421616	7.2764516
H	1.9104309	5.1312916	8.1139304
C	0.3802984	6.4849472	6.0449158
H	0.3124583	7.0430700	6.9879083
H	-0.5300882	5.8789382	5.9541601
H	0.3907628	7.2005458	5.2111291
C	3.6975166	5.0999615	1.9856276
C	3.7519459	4.1128747	0.9731045
H	3.7375512	3.0621035	1.2665643
C	3.8223539	4.4612684	-0.3708805
H	3.8585813	3.6744082	-1.1260845
C	3.8491102	5.8063399	-0.7576300
H	3.9104181	6.0799427	-1.8111253
C	3.7708520	6.7948943	0.2313058
H	3.7676163	7.8497234	-0.0521071
C	3.6815280	6.4503064	1.5778758
H	3.5814498	7.2395046	2.3242626
C	3.2924458	-0.3089893	6.0142972
C	5.3303177	0.6054605	7.1469934
H	5.4670079	0.8619725	6.0804035
C	6.5367116	-0.2178917	7.5911246
H	6.5667875	-0.3912617	8.6748962
H	7.4508851	0.3241864	7.3182411
H	6.5558068	-1.1887624	7.0781433
C	5.1644431	1.9280382	7.8921720
H	4.3532073	2.5142343	7.4400056
H	6.0923653	2.5072887	7.8019934
H	4.9516983	1.7897695	8.9621069
C	3.5391567	-0.9255452	8.1841406
C	4.1273211	-1.0214585	9.5498563
H	5.0223717	-1.6603674	9.5791814
H	3.3915434	-1.4506055	10.2407229
H	4.4126117	-0.0366556	9.9417645
C	2.4271473	-1.5618481	7.6954899
C	1.5481408	-2.5392561	8.3962147
H	0.4852618	-2.2663334	8.3427055
H	1.8248131	-2.5899060	9.4558216
H	1.6503638	-3.5522056	7.9791820
C	1.0492240	-1.2934364	5.5476545
H	1.3376457	-0.8759018	4.5755132
C	0.5915295	-2.7317169	5.3242194
H	1.4209916	-3.3676788	4.9897075
H	-0.1693174	-2.7285843	4.5326564
H	0.1397360	-3.1770528	6.2196201

C	-0.0350834	-0.3868628	6.1259689
H	-0.3771013	-0.7208907	7.1158093
H	-0.8988784	-0.3660757	5.4495746
H	0.3612735	0.6340407	6.2055400
C	3.4147175	-0.5532445	3.1973358
C	3.3981125	-1.9557958	3.3405618
H	3.4270467	-2.3985410	4.3369927
C	3.3641539	-2.7912363	2.2263421
H	3.3401823	-3.8738226	2.3702116
C	3.3737989	-2.2590146	0.9314580
H	3.3537869	-2.9160928	0.0618185
C	3.4365167	-0.8696505	0.7734747
H	3.4694899	-0.4337264	-0.2263523
C	3.4521699	-0.0316813	1.8824046
H	3.4911939	1.0511593	1.7518656
C	7.8810085	3.5431535	2.6461535
C	7.1125517	4.2492760	1.7071443
H	6.0585814	4.0011863	1.5833897
C	7.6762930	5.2695425	0.9430041
H	7.0574173	5.7959279	0.2146722
C	9.0172080	5.6202842	1.1306841
H	9.4611013	6.4288358	0.5477321
C	9.7890314	4.9282721	2.0697815
H	10.8372904	5.1945572	2.2167129
C	9.2300152	3.8874934	2.8154295
H	9.8440498	3.3477638	3.5368187
C	8.2507277	1.8640727	4.9093711
C	8.2961778	2.7096009	6.0314602
H	7.5952048	3.5420955	6.0950402
C	9.2173044	2.4935683	7.0552521
H	9.2400283	3.1643503	7.9157509
C	10.0990677	1.4104079	6.9868127
H	10.8134794	1.2312241	7.7914165
C	10.0561389	0.5573920	5.8802844
H	10.7429808	-0.2881156	5.8158840
C	9.1447752	0.7850432	4.8471194
H	9.1266412	0.1206593	3.9836667
C	7.1127787	0.7896715	2.5067984
C	7.4991785	0.8680897	1.1623910
H	7.8197399	1.8218975	0.7436067
C	7.4684062	-0.2693821	0.3525092
H	7.7584451	-0.1911872	-0.6966031
C	7.0728477	-1.4993572	0.8806402
H	7.0404113	-2.3853527	0.2455603
C	6.6989702	-1.5873476	2.2240814
H	6.3668089	-2.5390592	2.6379031
C	6.7008016	-0.4499349	3.0259823
H	6.3488488	-0.5100864	4.0565107
C	-0.0241063	3.4483767	1.6716967
C	-0.4626185	2.8242810	0.4965342
H	-0.8242549	1.7968176	0.5284428
C	-0.4318442	3.5109989	-0.7195158
H	-0.7645230	3.0092022	-1.6298637
C	0.0169367	4.8317685	-0.7713175
H	0.0468384	5.3648780	-1.7225951
C	0.4439184	5.4642352	0.3994410
H	0.8204478	6.4861155	0.3646368
C	0.4383206	4.7737612	1.6076607
H	0.8280191	5.2478703	2.5097362
C	-0.7798689	1.0054914	2.9455730
C	-2.1353966	0.7452870	3.1941565

H	-2.7761761	1.5303470	3.5965176
C	-2.6679837	-0.5200350	2.9349909
H	-3.7218526	-0.7149402	3.1417380
C	-1.8620035	-1.5301279	2.4007338
H	-2.2843987	-2.5148188	2.1942777
C	-0.5137658	-1.2715556	2.1326004
H	0.1315763	-2.0461570	1.7155877
C	0.0238991	-0.0178479	2.4188301
H	1.0816579	0.1713665	2.2379328
C	-1.2345417	3.4844879	4.2684525
C	-2.0744302	4.4761720	3.7411799
H	-1.9899526	4.7512255	2.6901035
C	-3.0184421	5.1115831	4.5510823
H	-3.6616332	5.8830724	4.1243596
C	-3.1497563	4.7578651	5.8967834
H	-3.8902367	5.2534694	6.5259527
C	-2.3211608	3.7655914	6.4307394
H	-2.4128612	3.4820462	7.4806058
C	-1.3660096	3.1465424	5.6266788
H	-0.7074758	2.3871498	6.0489358

4. X-ray Diffraction Refinements

4.1. General Remarks

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 100 K on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu K_α radiation (λ = 1.54184 Å) generated by a micro-focus source. The data reduction and absorption correction was performed using CrysAlisPro[10], respectively. Using Olex2[11], the structures were solved with SHELXT[12] by direct methods and refined with SHELXL[13] 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 the Olex2 software.

4.2. Crystallographic data

Compound	**2a**[OTf]	**2b**[OTf]·C_6H_5F	**5a**$[OTf]_2$·CH_2Cl_2	**5b**$[OTf]_2$	**5c**$[OTf]_2$
Empirical formula	$C_{18}H_{31}ClF_3N_2O_3PS$	$C_{24}H_{30}ClF_4N_2O_3PS$	$C_{38}H_{66}Cl_4F_6N_4O_6P_2S_2$	$C_{36}H_{50}F_6N_4O_6P_2S_2$	$C_{34}H_{48}F_6N_6O_6P_2S_2$
Formula weight [g/mol]	478.93	568.98	1056.80	874.86	876.84
Temperature [K]	100.01(10)	100.01(10)	100.00(10)	200.00(10)	100.01(10)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a [Å]	12.93012(14)	10.5631(2)	9.6285(3)	7.96005(6)	7.88912(4)
b [Å]	10.76679(12)	9.37960(10)	24.5346(7)	12.02181(9)	35.09855(17)
c [Å]	16.9595(2)	27.2987(4)	11.7235(3)	22.34595(15)	22.64824(12)
a [°]	90	90	90	90	90
β [°]	90	96.6200(10)	112.159(3)	99.1657(6)	98.2437(5)
γ [°]	90	90	90	90	90
Volume [$Å^3$]	2361.03(5)	2686.66(7)	2564.91(14)	2111.08(3)	6206.43(6)
Z	4	4	2	2	6
ρ_{calc} [g/cm^3]	1.347	1.407	1.368	1.376	1.408
μ [mm^{-1}]	3.300	3.055	4.025	2.508	2.575
F(000)	1008.0	1184.0	1108.0	916.0	2748.0
Crystal size [mm^3]	0.19 × 0.164 × 0.102	0.331 × 0.225 × 0.198	0.164 × 0.1 × 0.079	0.252 × 0.176 × 0.112	0.187 × 0.14 × 0.081
Radiation (λ in Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection [°]	9.73 to 153.624	6.52 to 153.134	7.206 to 153.502	8.016 to 153.128	4.678 to 153.49
Index ranges	$-16 \le h \le 16$, $-13 \le k \le 11$, $-21 \le l \le 21$	$-13 \le h \le 9$, $-7 \le k \le 11$, $-34 \le l \le 29$	$-11 \le h \le 12$, $-28 \le k \le 30$, $-14 \le l \le 13$	$-9 \le h \le 6$, $-14 \le k \le 15$, $-27 \le l \le 27$	$-9 \le h \le 9$, $-42 \le k \le 43$, $-28 \le l \le 28$
Reflections collected	23232	14240	20967	11092	68320
Independent reflections	4871 [R_{int} = 0.0435, R_{sigma} = 0.0247]	5587 [R_{int} = 0.0332, R_{sigma} = 0.0395]	5355 [R_{int} = 0.0493, R_{sigma} = 0.0339]	4372 [R_{int} = 0.0120, R_{sigma} = 0.0129]	12985 [R_{int} = 0.0276, R_{sigma} = 0.0196]
Data/restraints/parameters	4871/1/277	5587/0/361	5355/48/386	4372/253/332	12985/224/863
Goodness-of-fit on F^2	1.043	1.021	1.052	1.026	1.020
Final R indexes (I>=2σ (I))	R_1 = 0.0400, wR_2 = 0.1074	R_1 = 0.0445, wR_2 = 0.1163	R_1 = 0.0689, wR_2 = 0.1840	R_1 = 0.0385, wR_2 = 0.1056	R_1 = 0.0487, wR_2 = 0.1248
Final R indexes (all data)	R_1 = 0.0405, wR_2 = 0.1081	R_1 = 0.0532, wR_2 = 0.1245	R_1 = 0.0740, wR_2 = 0.1890	R_1 = 0.0395, wR_2 = 0.1066	R_1 = 0.0511, wR_2 = 0.1268
Largest diff. peak/hole [$e/Å^3$]	0.51/-0.23	0.55/-0.70	0.75/-0.61	0.52/-0.32	0.51/-0.58
Flack Parameter	0.002(17)	---	---	---	---
CCDC Number	2524562	2524560	2524561	2524563	2524566

Compound	**6a**$[OTf]_3 \cdot CH_3CN$	**6b**$[OTf]_3 \cdot 4CH_2Cl_2$	**7b**$[OTf]_2 \cdot 4CH_2Cl_2$	**8**$[OTf]_2 \cdot 4C_6H_4F_2 \cdot Et_2O$	**9**$[OTf]_2 \cdot 4C_6H_4F_2 \cdot 0{,}5THF$
Empirical formula	$C_{60}H_{102}F_9N_9O_9P_4S_3$	$C_{58}H_{83}Cl_8F_9N_6O_9P_4S_3$	$C_{76}H_{88}Cl_8F_6N_4O_6P_4Pd_2S_2$	$C_{88}H_{110}F_{10}N_4O_7P_4Pd_2S_2$	$C_{47}H_{75}F_8N_4O_{6.5}P_3PdS_2$
Formula weight [g/mol]	1484.56	1682.96	1951.90	1926.59	1215.54
Temperature [K]	100.01(10)	100.01(10)	100.01(10)	100.01(10)	100.00(10)
Crystal system	trigonal	triclinic	triclinic	monoclinic	monoclinic
Space group	R3c	P-1	P-1	I2/a	$P2_1/c$
a [Å]	14.02799(8)	14.3379(3)	14.2227(2)	26.0433(3)	16.6307(4)
b [Å]	14.02799(8)	16.0023(3)	17.67070(10)	16.79110(10)	14.8734(2)
c [Å]	68.3806(5)	19.1242(4)	18.94390(10)	23.4811(2)	23.4810(4)
a [°]	90	74.3662(18)	100.7730(10)	90	90
β [°]	90	85.3052(17)	96.8500(10)	121.4210(10)	106.231(2)
γ [°]	120	68.1297(18)	108.2840(10)	90	90
Volume [$Å^3$]	11653.45(16)	3920.54(15)	4359.50(8)	8762.45(16)	5576.65(19)
Z	6	2	2	4	4
ρ_{calc} [g/cm^3]	1.269	1.426	1.487	1.460	1.448
μ [mm^{-1}]	2.300	4.789	7.257	5.096	4.856
F(000)	4716.0	1740.0	1988.0	3984.0	2528.0
Crystal size [mm^3]	0.315 × 0.254 × 0.102	0.55 × 0.335 × 0.109	0.213 × 0.178 × 0.111	0.144 × 0.09 × 0.06	0.173 × 0.035 × 0.019
Radiation (λ in Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	7.722 to 152.074	4.8 to 153.67	4.838 to 153.464	6.598 to 153.606	5.534 to 136.49
Index ranges	$-14 \le h \le 17$, $-16 \le k \le 17$, $-85 \le l \le 85$	$-17 \le h \le 17$, $-20 \le k \le 14$, $-23 \le l \le 23$	$-17 \le h \le 17$, $-22 \le k \le 21$, $-23 \le l \le 20$	$-31 \le h \le 32$, $-21 \le k \le 20$, $-27 \le l \le 29$	$-18 \le h \le 20$, $-12 \le k \le 17$, $-28 \le l \le 27$
Reflections collected	33073	42231	50554	40986	25258
Independent reflections	5261 [R_{int} = 0.0246, R_{sigma} = 0.0154]	16256 [R_{int} = 0.0513, R_{sigma} = 0.0513]	18157 [R_{int} = 0.0283, R_{sigma} = 0.0338]	9092 [R_{int} = 0.0446, R_{sigma} = 0.0301]	9837 [R_{int} = 0.0428, R_{sigma} = 0.0456]
Data/restraints/parameters	5261/433/477	16256/1069/1178	18157/480/1067	9092/911/617	9837/1140/883
Goodness-of-fit on F^2	1.083	1.019	1.028	1.054	1.020
Final R indexes ($I>=2\sigma$ (I))	R_1 = 0.0696, wR_2 = 0.1896	R_1 = 0.0642, wR_2 = 0.1749	R_1 = 0.0392, wR_2 = 0.1077	R_1 = 0.0431, wR_2 = 0.1158	R_1 = 0.0531, wR_2 = 0.1413
Final R indexes (all data)	R_1 = 0.0701, wR_2 = 0.1913	R_1 = 0.0696, wR_2 = 0.1817	R_1 = 0.0412, wR_2 = 0.1098	R_1 = 0.0458, wR_2 = 0.1188	R_1 = 0.0636, wR_2 = 0.1512
Largest diff. peak/hole [$e/Å^3$]	0.97/-0.48	0.82/-0.88	1.42/-1.53	0.86/-0.88	1.41/-0.76
Flack parameter	0.07(4)	----	----	----	----
CCDC Number	2524564	2524565	2524569	2524568	2524567

Compound	**10**$[OTf]_2 \cdot 1{,}5CH_2Cl_2 \cdot 0{,}5MeCN$	**11**$[OTf] \cdot CH_2Cl_2$	**12**$[OTf]_2 \cdot MeCN$
Empirical formula	$C_{56.5}H_{81.5}AuCl_3F_6N_{4.5}O_6P_4S_2$	$C_{36}H_{64}Cl_2F_3N_4O_3P_3S$	$C_{32}H_{54}F_6N_5O_6PS_2$
Formula weight [g/mol]	1525.07	853.78	813.89
Temperature [K]	100.01(10)	100.01(10)	100.01(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a [Å]	25.5676(7)	17.24000(10)	11.1951(5)
b [Å]	16.6234(3)	14.58910(10)	11.9364(7)
c [Å]	17.3590(4)	17.7842(2)	17.3601(11)
a [°]	90	90	88.986(5)
β [°]	109.614(3)	96.1790(10)	73.486(5)
γ [°]	90	90	62.793(5)
Volume [$Å^3$]	6949.8(3)	4447.03(6)	1960.8(2)
Z	4	4	2
ρ_{calc} [g/cm^3]	1.458	1.275	1.378
μ [mm^{-1}]	7.010	3.190	2.286
F(000)	3104.0	1816.0	860.0
Crystal size [mm^3]	0.241 × 0.139 × 0.021	0.169 × 0.147 × 0.136	0.266 × 0.045 × 0.024
Radiation (λ in Å)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection [°]	6.46 to 136.502	5.156 to 153.612	5.356 to 144.248
Index ranges	-30 ≤ h ≤ 24, -20 ≤ k ≤ 20, -14 ≤ l ≤ 20	-21 ≤ h ≤ 18, -18 ≤ k ≤ 17, -22 ≤ l ≤ 22	-9 ≤ h ≤ 13, -14 ≤ k ≤ 14, -19 ≤ l ≤ 21
Reflections collected	72425	51699	19200
Independent reflections	12719 [R_{int} = 0.0656, R_{sigma} = 0.0430]	9329 [R_{int} = 0.0370, R_{sigma} = 0.0216]	7718 [R_{int} = 0.0420, R_{sigma} = 0.0511]
Data/restraints/parameters	12719/346/861	9329/50/567	7718/1374/757
Goodness-of-fit on F^2	1.066	1.030	1.025
Final R indexes (I>=2σ (I))	R_1 = 0.0502, wR_2 = 0.1281	R_1 = 0.0530, wR_2 = 0.1423	R_1 = 0.0703, wR_2 = 0.1909
Final R indexes (all data)	R_1 = 0.0571, wR_2 = 0.1331	R_1 = 0.0546, wR_2 = 0.1442	R_1 = 0.0843, wR_2 = 0.2070
Largest diff. peak/hole [$e/Å^3$]	2.39/-2.03	1.14/-0.73	1.07/-0.58
CCDC Number	2524572	2524571	2524570

5. References

1 J. Fidelius, K. Schwedtmann, S. Schellhammer, J. Haberstroh, S. Schulz, R. Huang, M. C. Klotzsche, A. Bauzá, A. Frontera, S. Reineke and J. J. Weigand, *Chem*, 2024, **10**, 644.
2 W. Kaim, *J. Am. Chem. Soc.*, 1983, **105**, 707.
3 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
4 a) A. D. Becke, *J. Chem. Phys.*, 1996, **104**, 1040; b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822;
5 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
6 A. Klamt, *WIREs Comput Mol Sci*, 2011, **1**, 699.
7 F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108.
8 P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169.
9 K. C. Ramey, D. J. Louick, P. W. Whitehurst, W. B. Wise, R. Mukherjee and R. M. Moriarty, *Org. Magn. Reson.*, 1971, **3**, 201.
10 Oxford Diffraction / Agilent Technologies UK Ltd, CrysAlisPRO.
11 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr*, 2009, **42**, 339.
12 G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3.
13 G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3.