Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Alexander Hinz, *Axel Schulz*,* and *Alexander Villinger*

Content

Experimental Details

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. Benzene was dried over Na and freshly distilled prior to use. PC*t*Bu and (Me_2S)AuCl were prepared according to literature procedures.[1,2]

NMR: $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C DEPT, and ^1H NMR spectra were obtained on a Bruker Avance 250, 300 or 500 spectrometer and were referenced internally to the deuterated solvents (^{13}C, C_6D_6: $\delta_{reference}$ = 128.39 ppm) or to protic impurities (^1H, C_6D_5H: $\delta_{reference}$ = 7.16 ppm)[3] or externally (^{31}P: 85 % $H_3PO_{4(aq)}$). C_6D_6 and d^8-toluene were dried over Na/benzophenone and freshly distilled prior to use.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman: Horiba Scientific LabRam HR 800 was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikronalysator TruSpec-932 from Leco were used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

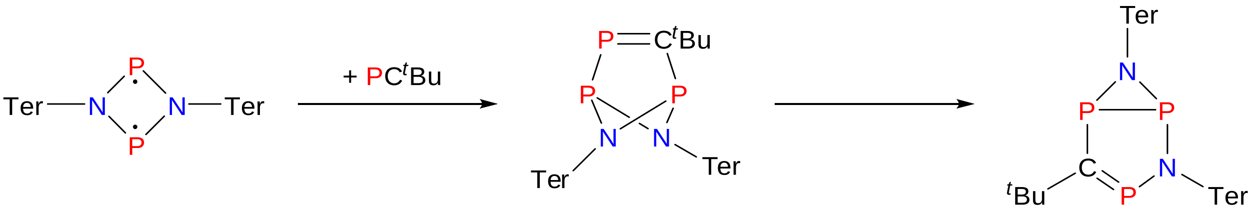
DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min).

MS: Finnigan MAT 95-XP von Thermo Electron.

X-ray Structure Determination: X-ray quality crystals of all compounds were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer or on a Bruker-Nonius Apex X8 CCD diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71073). The structures were solved by direct methods (*SHELXS-2013*)[4] and refined by full-matrix least squares procedures (*SHELXL-2013*).[5] Semi-empirical absorption corrections were applied (SADABS).[6] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model with the exception of the former acetylene protons, whose positions were refined freely.

Synthetic Protocols

Preparation of **3**



[(TerNP)]$_2$ (315 mg, 0.439 mmol) was dissolved in 5 ml benzene. To the orange solution was then treated with neat PCtBu (51 mg, 0.510 mmol), which was added in one shot via syringe. The solution immediately turned red and was then stirred overnight at ambient temperature (18 h). Within time, the solution turned yellow. Volatiles were removed in vacuo (~60 min), affording nearly quantitative amounts of **3** as yellowish powder (348 mg, 0.426 mmol, 97%). The yellowish solid was then redissolved in benzene (5 ml), concentrated to incipient crystallization (~0.5 ml) and then left undisturbed overnight, which lead to the deposition of yellowish crystals. The mother liquor was removed via syringe and the crystals were dried in vacuo, yielding 192 mg (0.235 mmol, 54%) of the product.

Mp: 122 °C (dec.). **EA** found (calc.): C 77.19 (77.92), H 7.10 (7.28), N 3.12 (3.43). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 1.05 (s, 9 H, ^{t}Bu), 1.90 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.21 (s, 9 H, CH_3), 2.22 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.29 (s, 6 H, CH_3), 6.53 (s, 1 H, CH_{Mes}), 6.65 (s, 1 H, CH_{Mes}), 6.73 (d, J_{HP} = 1.3 Hz, 1 H, CH_{Mes}), 6.76 (s, 1 H, CH_{Mes}), 6.79 (s, 2 H, CH_{Mes}), 6.82-6.90 (m, 6 H, CH_{Ar}), 6.95-7.05 (m, 2 H, CH_{Ar}). **^{1}H NMR** intermediate (298 K, C_7D_8, 250.1 MHz): 1.19 (s, 9 H, ^{t}Bu), 2.04 (s, 12 H, o-CH_3), 2.10 (s, 12 H, o-CH_3), 2.37 (s, 12 H, p-CH_3), 6.53, 6.57 (AA'B, J_{HH} = 7.5 Hz), 6.74 (s, 4 H, *m*-C*H*Mes), 6.79 (s, 4 H, *m*-C*H*Mes). **^{13}C{^{1}H}** NMR (298 K, C_6D_6, 62.9 MHz): 20.65 (s, *C*H_3), 21.34 (s, *C*H_3), 21.44 (s, *C*H_3), 21.50 (s, *C*H_3), 21.52 (s, *C*H_3), 21.67 (s, *C*H_3), 22.59 (s, *C*H_3), 23.14 (s, *C*H_3), 33.93 (dd, J_{CP} = 14.8, J_{CP} = 8.4 Hz, C(*C*H3)3), 39.49 (dd, *C*(CH3)3), 118.99 (s, *C*H), 122.61 (d, J_{CP} = 9.2 Hz), 124.87 (s, *C*H), 127.68 (s, *C*H), 128.22 (s, *C*H), 128.92 (s, *C*H), 128.96 (s, *C*H), 129.37 (s, *C*H), 129.26 (s, *C*H), 129.54 (s, *C*H), 129.69 (s, *C*H), 130.22 (s, *C*H), 131.09 (s, *C*H), 131.28 (s, *C*H), 131.84 (s, *C*H), 136.11 (s), 136.25 (s), 136.57 (s), 136.75 (s), 136.78 (s), 136.83 (s), 136.99 (s), 137.09 (s), 137.17 (s), 137.25 (s), 137.41 (s), 137.46 (s), 137.55 (s), 138.17 (s), 137.88 (d, J_{CP} = 2.3 Hz), 142.31 (s), 145.89 (s). **^{31}P NMR (**298 K, C_6D_6, 121.5 MHz): intermediate AMX system: 218.1 (J_{AM} = 23.2, J_{AX} = 18.5 Hz), 259.7 (J_{AM} = 23.2, J_{MX} = 190.1 Hz), 358.4 (J_{MX} = 190.1, J_{AX} = 18.5 Hz). product AMX system: –62.1 (J_{AM} = 125.6, J_{AX} = 13.2 Hz), –23.6 (J_{AM} = 125.6, J_{MX} = 26.2 Hz), –316.2 (J_{MX} = 26.2, J_{AX} = 13.2 Hz). **IR** (ATR, cm^{-1}): 3028 (vw), 2951 (m), 2914 (m), 2854 (w), 2729 (vw), 1610 (m), 1574 (w), 1479 (w), 1450 (s), 1435 (s), 1406 (s), 1375 (m), 1358 (w), 1259 (vw), 1225 (s), 1190 (sh), 1184 (s), 1163 (vw), 1080 (m, 1032 (m), 1007 (w), 987 (vw), 947 (w), 930 (w), 877 (m), 868 (vw), 847 (vs), 800 (m), 781 (w), 768 (w), 748 (m), 714 (w), 673 (s), 596 (w), 577 (vw), 561 (w), 550 (vw), 542 (vw), 528 (vw). **Raman** (632 nm, cm^{-1}): 3043 (12), 3002 (22), 2917 (44), 2856 (13), 2727 (5), 1611 (32), 1583 (34), 1568 (16), 1480 (15), 1435 (30), 1417 (84), 1380 (27), 1376 (28), 1301 (96), 1286 (100), 1266 (24), 1245 (17), 1233 (12), 1187 (7), 1164 (8), 1098 (9), 1085 (40), 1004 (32), 986 (71), 960 (3), 943 (6), 916 (3), 907 (2), 862 (9), 844 (9), 835 (38), 799 (21), 787 (5), 777 (2), 771 (2), 754 (18), 735 (13), 674 (16), 649 (10), 628 (1), 601 (4), 592 (5), 575 (29), 571 (55), 555 (44), 536 (10), 519 (45), 507 (15), 490 (3), 474 (6), 447 (1), 413 (17), 389 (9), 381 (7), 372 (4), 332 (11), 281 (7), 264 (9), 250 (7), 229 (32). **MS** (CI, pos., iso-butane) m/z (%): 330 (14) $[\mathrm{TerNH_3}]^+$, 490 (8) $[\mathrm{M{-}TerN{+}H}]^+$, 716 (13) $[(\mathrm{TerNP})_2]^+$, 817 (100) $[\mathrm{M}]^+$, 873 (8) $[\mathrm{M{+}C_4H_9}]^+$.

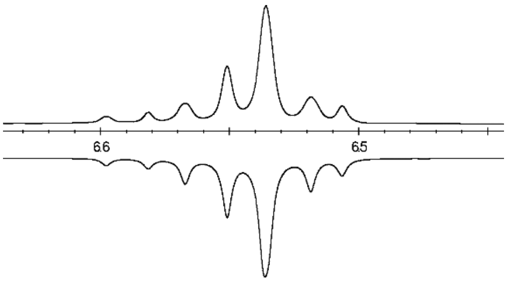


Figure S1. ^{1}H NMR: AA’B pattern of the *m*/*p*-C*H* of **2**

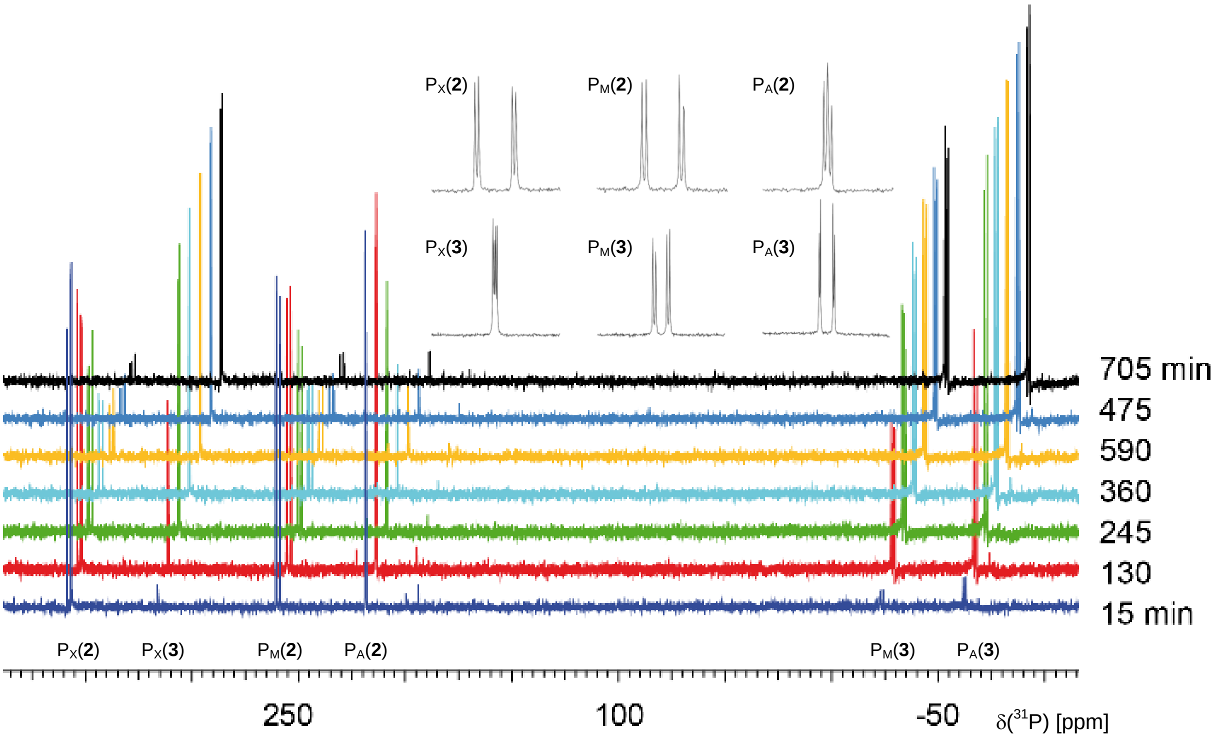


Figure S2. NMR monitoring of the rearrangement reaction (resonance for PC^{t}Bu at –68.6 ppm removed).

NMR experiment for kinetic data: [(TerNP)]$_2$ dissolved in 0.6 ml d^8-toluene. At –80 °C, an excess PC^{t}Bu were added via syringe, which lead to an immediate change in color at the phase contact surface from yellow to red ([(TerNP)]$_2$ is orange at ambient temperature and yellow at –80 °C). The solution was shaken right before NMR data were collected at ambient temperature.

Table S1. NMR data for monitoring the rearrangement from **2** to **3.**

time [min]	A	B	x_A	ln(x_A)
5	96.99	7.09	0.932	-0.07055195
17	197.75	22.29	0.899	-0.10680574
28	243	40	0.859	-0.15238545
39	197.89	42.89	0.822	-0.19617233
51	74.55	20	0.788	-0.23765875
62	199	61.15	0.765	-0.26795356
74	103.33	40	0.721	-0.32722191
85	207.71	91.13	0.695	-0.36376544
96	35.71	17.78	0.668	-0.40406396
108	201.77	115.69	0.636	-0.45322339
119	1.59	1.02	0.609	-0.49561621
131	19.55	14.29	0.578	-0.54866825
142	19.69	15	0.568	-0.56634057
153	19.32	17.4	0.526	-0.64218074
165	27.13	26.37	0.507	-0.67904153
176	21.89	22.98	0.488	-0.71773951
188	28.97	31.24	0.481	-0.73157764
210	6.26	7.97	0.440	-0.82117223
210	6.26	7.97	0.440	-0.82117223
233	0.99	1.53	0.393	-0.93430924
256	19.57	31.95	0.380	-0.9679723
210	6.26	7.97	0.440	-0.82117223
233	0.99	1.53	0.393	-0.93430924
256	19.57	31.95	0.380	-0.9679723
279	19.98	37.53	0.347	-1.05722707
301	20.06	45.65	0.305	-1.18652334
324	19.96	52.57	0.275	-1.29027
347	0.51	1.49	0.255	-1.36649173
370	19.81	61.8	0.243	-1.41576494
392	19.38	69.81	0.217	-1.52652732
415	18.5	73.12	0.202	-1.59987886
438	18.39	77.99	0.191	-1.65649167
461	20.46	100	0.170	-1.77284599
484	18.71	98.73	0.159	-1.83686942
506	18.74	106.92	0.149	-1.90291957
529	20.26	121.95	0.142	-1.94865634
552	19.48	140.15	0.122	-2.10347034
575	1.86	14.98	0.110	-2.20318052
597	19	148.73	0.113	-2.17791656
620	21.13	191.9	0.099	-2.31073917
643	19.69	191.6	0.093	-2.3731207
666	19.68	234.38	0.077	-2.55796757
688	1.22	15	0.075	-2.58739419
711	19.05	256.55	0.069	-2.67188344
734	19.03	272.9	0.065	-2.73049737
757	19.4	275.36	0.066	-2.7208884
780	19.89	311.66	0.060	-2.81356153
802	18.98	360.56	0.050	-2.9955742
825	18.08	343.21	0.050	-2.9948746
848	1.66	37.43	0.042	-3.15904908
871	19.6	419.52	0.045	-3.10924316
893	19.55	638	0.030	-3.51554552
916	16.81	400	0.040	-3.21065654

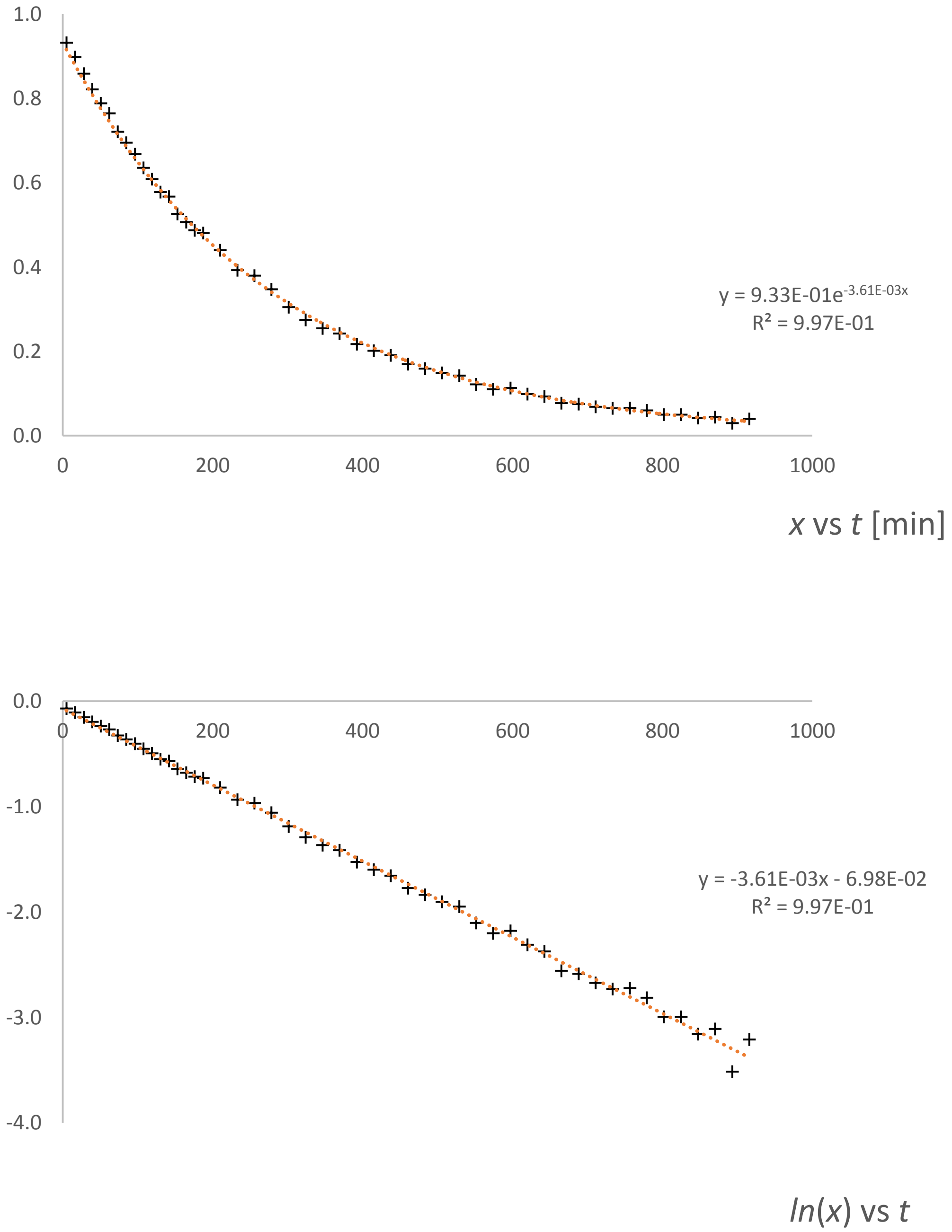
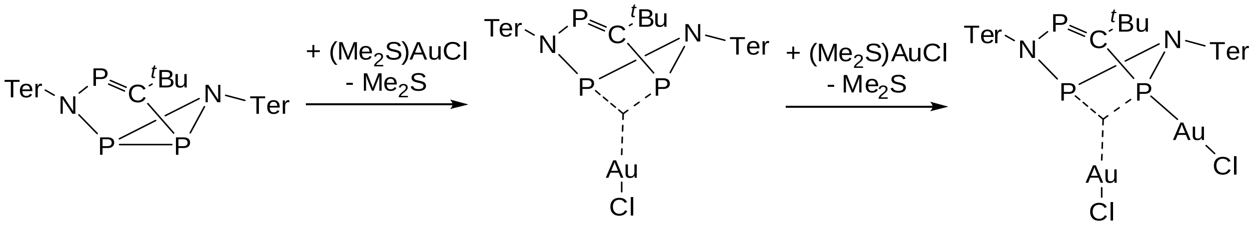


Figure S3. NMR reaction monitoring: 29 mg [(TerNP)$_2$] + 9 mg PC^{t}Bu

NMR Data of in situ generated 2.

The structure of **2** can be derived from the observed NMR data. In the ^{1}H NMR spectra, three singlets (12 H each) are observed for the *ortho* and *para* methyl groups of of the mesityl moieties and two singlets (4 H each) for their *meta* CH protons, indicating the magnetic equivalency of two of the four mesityls. Thus, in solution the molecule possesses averaged C_s symmetry. Moreover, there is only one singlet (9 H) for the *tert*-butyl group, that is why it can be concluded, that the *tert*-butyl group is located on the mirror plane. Moreover, the ^{31}P NMR spectra show an AMX spin system (δ = 218.1, 259.7, 358.4 ppm; $|J_{AB}|$ = 23.2, $|J_{AC}|$ = 18.5, $|J_{BC}|$ = 190.1 Hz), that compares well with the one computed for **2** (δ = 213, 267, 415 ppm; J_{AB} = +6, J_{AC} = +21, J_{BC} = –155 Hz). Comparison with known [2.1.1]heterobicycles confirmes the assigned structure as well ($\delta(\mathrm{Ter_2N_2P_2C_2H_2})$ = 212.3 ppm, A; $\delta(\mathrm{Ter_2N_2P_2P_2Ph_2})$ = 259.5 ppm, B; $\delta(\mathrm{Ter_2N_2PAsPC^{\mathit{t}}Bu})$ = 206.0, 340.2 ppm, A, C).

Synthesis of **4**/**5**



$[\mathrm{Ter_2N_2P_2PC}^t\mathrm{Bu}]$ (101/102 mg, 0.124/0.125 mmol) and $(\mathrm{Me_2S})\mathrm{AuCl}$ (36/73 mg, 0.122/0.248 mmol) are combined as solids. The mixture is then dissolved in benzene (8 ml), which leads to a slightly darker yellow solution than $[\mathrm{Ter_2N_2P_2PC}^t\mathrm{Bu}]$, and stirred for 30 minutes at ambient temperature. The solution is then concentrated to incipient concentration and stored at 4 °C overnight, which leads to the deposition of yellow crystals. The mother liquor is removed via syringe and the crystals are dried in vacuo, yielding 64/109 mg (0.061/0.085 mmol, 49/68%) of the product.

Analytical data for **4**.

Mp: 124 °C (dec.). **EA** found (calc.): C 63.29 (62.85), H 5.81 (5.81), N 2.51 (2.48). **^{1}H** NMR (298 K, $\mathrm{C_6D_6}$, 250.1 MHz): 1.05 (s, 9 H, ^{t}Bu), 1.15 (s, 3 H, $\mathrm{C}H_3$), 1.93 (s, 9 H, $\mathrm{C}H_3$), 2.12 (s, 6 H, $\mathrm{C}H_3$), 2.23 (s, 9 H, $\mathrm{C}H_3$), 2.30 (s, 6 H, $\mathrm{C}H_3$), 2.42 (s, 3 H, $\mathrm{C}H_3$), 6.55 (dd, J_{HH} = 1.3, J_{HH} = 7.2 Hz, 1 H, *p*-C*H*), 6.64 (s, 1 H, *m*-$\mathrm{C}H_{\mathrm{Mes}}$), 6.65 (dd, J_{HH} = 1.8, J_{HH} = 7.3 Hz, 1 H, *p*-C*H*), 6.71-6.77 (m, 4 H, C*H*), 6.85-6.98 (m, 6 H, C*H*), 7.05 (s, 1 H, *m*-$\mathrm{C}H_{\mathrm{Mes}}$). **^{13}C{^{1}H} NMR** (298 K, $\mathrm{C_6D_6}$, 62.9 MHz): 20.65 (s, $C\mathrm{H_3}$), 21.32 (s, $C\mathrm{H_3}$), 21.49 (s, $C\mathrm{H_3}$), 21.99 (s, $C\mathrm{H_3}$), 22.10 (s, $C\mathrm{H_3}$), 22.29 (s, $C\mathrm{H_3}$), 22.44 (s, $C\mathrm{H_3}$), 22.49 (s, $C\mathrm{H_3}$), 34.85 (dd, J_{CP} = 14.2, J_{CP} = 10.5 Hz, $\mathrm{C}(C\mathrm{H_3})_3$), 40.68 (dd, J_{CP} = 22, J_{CP} = 26 Hz, $\mathrm{C}(C\mathrm{H_3})_3$), 124.77 (s, *C*H), 127.77 (s, *C*H), 128.22 (s, *C*H), 128.51 (s, *C*H), 128.92 (s, *C*H), 129.26 (s, *C*H), 129.39 (s, *C*H), 129.80 (d, J_{CP} = 1.8 Hz, *C*H), 129.93 (s, *C*H), 131.26 (s, *C*H), 131.82 (s, *C*H), 131.88 (s, *C*H), 135.72 (d, J_{CP} = 3.2 Hz), 136.03 (s), 136.83 (s), 136.93 (s), 137.39 (s), 137.66 (s), 137.80 (s), 137.83 (d, J_{CP} = 10.4 Hz), 139.40 (d, J_{CP} = 1.1 Hz), 142.26 (s). **^{31}P NMR** (298 K, $\mathrm{C_6D_6}$, 121.5 MHz): AMX pattern –21.15 (dd, J_{PP} = 26.0, J_{PP} = 10.4 Hz, Au*P*C), +9.50 (dd, J_{PP} = 5.5, J_{PP} = 10.4 Hz, N*P*N), 334.22 (dd, J_{PP} = 26.0, J_{PP} = 5.5 Hz, N*P*C). **IR** (ATR, $\mathrm{cm^{-1}}$): 3090 (vw), 3034 (vw), 2951 (m), 2914 (m), 2854 (w), 2729 (vw), 1610 (m), 1574 (w), 1479 (w), 1452 (m), 1437 (m), 1404 (s), 1373 (m), 1362 (w), 1306 (vw), 1271 (vw), 1221 (s), 1180 (s), 1163 (w), 1080 (s), 1032 (m), 1007 (w), 962 (w), 916 (w), 883 (m), 850 (s), 802 (sh), 795 (m), 773 (vw), 754 (w), 737 (vw), 702 (w), 675 (vs), 652 (w), 596 (m), 577 (w), 559 (w), 552 (w), 534 (m). **Raman** (632 nm, $\mathrm{cm^{-1}}$): 3058 (18), 3011 (8), 2944 (15), 2913 (44), 2853 (13), 2730 (4), 1607 (43), 1575 (28), 1479 (12), 1433 (16), 1406 (14), 1376 (23), 1300 (80), 1276 (9), 1226 (9), 1176 (18), 1160 (7), 1089 (23), 1079 (32), 1001 (28), 987 (92), 978 (6), 942 (10), 915 (4), 875 (6), 862 (8), 848 (5), 826 (3) 786 (9), 736 (25), 697 (5), 648 (6), 602 (6), 588 (15), 573 (100), 547 (42), 528 (13), 518 (28), 508 (56), 481 (20), 471 (10), 455 (8), 441 (17), 409 (56), 393 (19), 376 (32), 357 (7), 334 (12), 292 (42), 284 (23), 248 (34), 230 (32), 199 (18).

Analytical data for **5**.

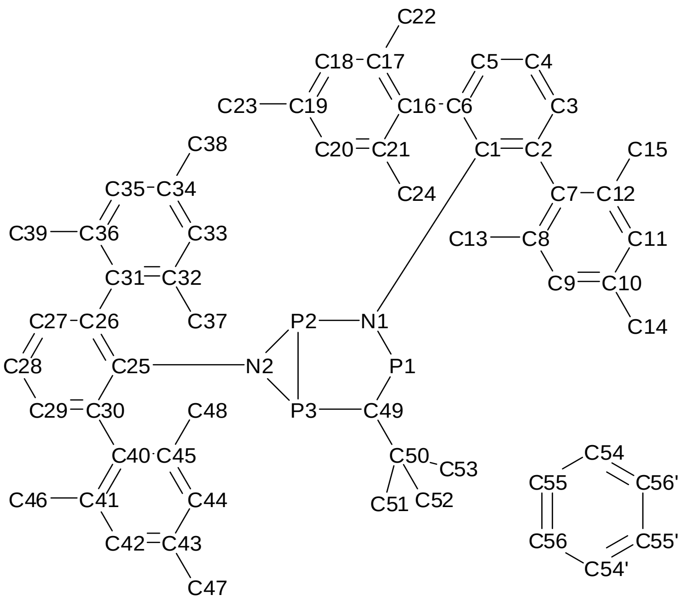
Mp: 137 °C (dec.). **EA** found (calc.): C 58.56 (57.15), H 5.90 (5.18), N 2.32 (1.80). **^{1}H** NMR (298 K, C_6D_6, 250.1 MHz): 0.99 (s, 3 H, CH_3), 1.20 (s, 9 H, ^{t}Bu), 1.54 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.14 (s, 6 H, CH_3), 2.31 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 6.40 (s, 1 H, CH_{Mes}), 6.52 (s, 1 H, CH_{Mes}), 6.54-6.67 (m, 4 H, C*H*), 6.81 (s, 1 H, CH_{Mes}), 6.84-6.93 (m, 6 H, C*H*), 6.99 (s, 1 H, CH_{Mes}). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): poorly resolved due to low solubility in benzene. **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): AMX pattern –11.62 (dd, J_{PP} = 26, J_{PP} = 5 Hz, Au*P*C), +11.15 (dd, J_{PP} = 5, J_{PP} = 20 Hz, N*P*N), 328.74 (dd, J_{PP} = 20, J_{PP} = 26 Hz, N*P*C). **IR** (ATR, cm^{-1}): 2953 (m), 2916 (m), 2854 (w), 2731 (vw), 1610 (m), 1570 (w), 1485 (w), 1452 (m), 1435 (m), 1400 (s), 1375 (m), 1363 (w), 1329 (vw), 1306 (w), 1225 (s), 1207 (m), 1190 (vw), 1173 (m), 1161 (m), 1082 (m), 1070 (m), 1028 (w), 1003 (vw), 991 (vw), 972 (m), 949 (w), 941 (w), 897 (w), 862 (s), 849 (s), 837 (m), 810 (vw), 798 (vs), 773 (vw), 764 (w), 746 (m), 717 (vw), 706 (m), 683 (w), 648 w), 592 (w), 577 (w), 557 (w), 550 (vw), 532 (s). **Raman** (632 nm, cm^{-1}): 3074 (6), 3037 (5), 3004 (4), 2952 (8), 2912 (30), 2888 (17), 2852 (7), 2729 (3), 1609 (4), 1573 (23), 1550 (6), 1481 (4), 1431 (8), 1399 (15), 1377 (13), 1303 (26), 1279 (9), 1227 (22), 1218 (31), 1204 (15), 1186 (7), 1174 (5), 1160 (6), 1093 (14), 1080 (11), 1026 (2), 1002 (8), 964 (2), 941 (100), 864 (6), 790 (7), 770 (1), 735 (12), 728 (4), 679 (1), 659 (2), 647 (5), 590 (15), 575 (36), 567 (23), 554 (41), 529 (20), 510 (39, 503 (4), 497 (6), 485 (8), 467 (4), 448 (15), 524 (2), 414 (4), 401 (11), 373 (6), 346 (3), 329 (5), 322 (5), 295 (9), 283 (12), 256 (8), 233 (15), 215 (8), 198 (5).

Crystallographic Data

Table S2. Crystallographic data of **3**, **4**, and **5**.

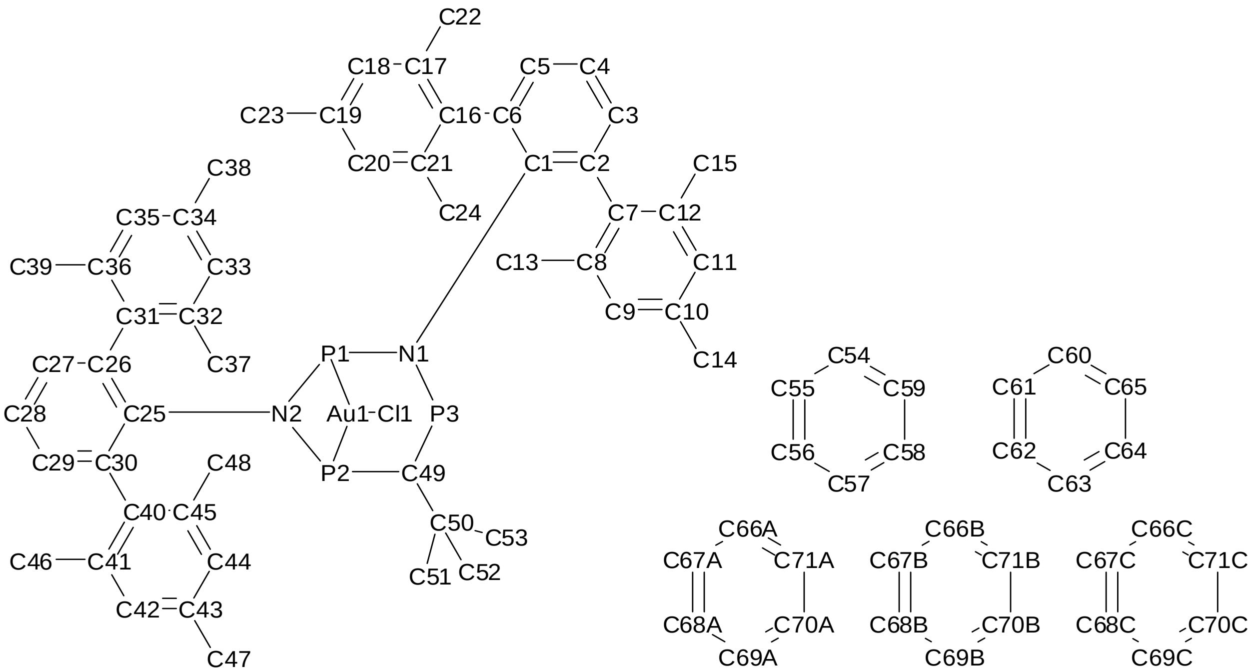
compound	**3 · 0.5 C_6H_6**	**4 · C_6H_6**	**4 · 2.5 C_6H_6**	**5 · 2.25 C_6H_6**
sum formula	$C_{56}H_{62}N_2P_3$	$C_{59}H_{65}AuClN_2P_3$	$C_{68}H_{74}AuClN_2P_3$	$C_{63.5}H_{69.5}Au_2Cl_2N_2P$
formula weight [g·mol^{-1}]	855.98	1127.45	1244.61	1418.45
colour	colourless	yellow	yellow	yellow
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$C2/c$	P-1	P-1
a [Å]	11.3859(3)	19.8747(5)	11.413(1)	12.4677(4)
b [Å]	32.688(1)	12.2909(5)	11.874(1)	21.4096(8)
c [Å]	13.0222(4)	44.936(1)	24.862(3)	22.9115(8)
α [°]	90	90	97.632(3)	75.619(2)
β [°]	96.019(2)	101.502(2)	90.569(3)	89.277(2)
γ [°]	90	90	114.933(3)	82.235(2)
V [Å^3]	4907.0(3)	10756.4(6)	3020.0(5)	5868.4(4)
Z	4	8	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.180	1.392	1.369	1.605
μ [mm^{-1}]	0.162	2.913	2.601	5.207
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
measured reflexes	79076	109237	88244	230798
independent reflexes	14699	12314	17595	47869
reflexes $I > 2\sigma(I)$	9071	9172	13734	30470
$R_{int.}$	0.0574	0.0767	0.0650	0.0676
$2\Theta_{max.}$ [°]	61	55	60	68
$F(000)$	1828	4592	1274	2806
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0525	0.0803	0.0394	0.0440
wR_2 (all data)	0.1472	0.1528	0.0806	0.1006
GooF	1.049	1.253	1.016	1.013
parameter	565	609	686	1343

Numbering scheme of **3**·0.5 C_6H_6



Selected bond lengths [Å] and angles [°] of **3**·0.5 C_6H_6. Symmetry code: ‘ 2-x, 1-y, 2-z.

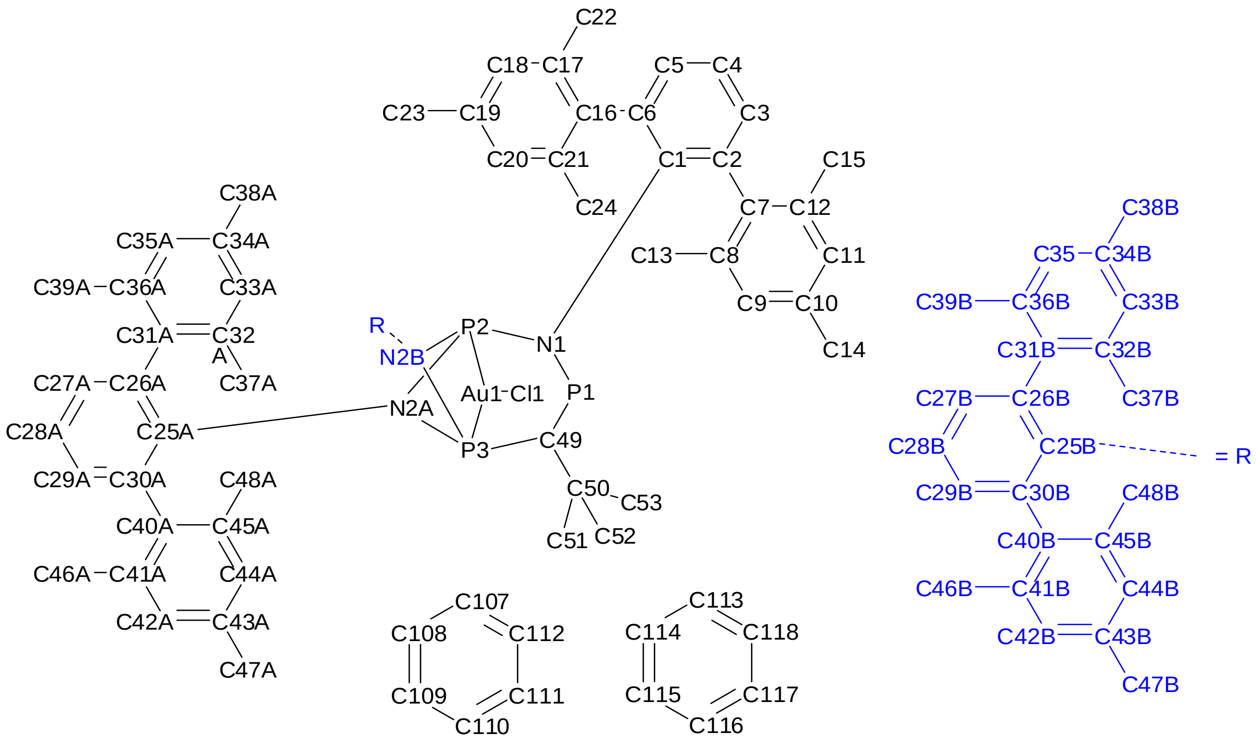
P1–C49	1.6806(19)	N1–P2–P3	97.61(5)
P1–N1	1.7181(15)	N2–P3–C49	99.61(7)
P2–N2	1.7014(14)	N2–P3–P2	49.04(5)
P2–N1	1.7315(15)	C49–P3–P2	96.80(6)
P2–P3	2.2166(7)	C1–N1–P1	112.73(11)
P3–N2	1.7582(14)	C1–N1–P2	120.46(11)
P3–C49	1.8015(18)	P1–N1–P2	121.21(8)
C49–P1–N1	103.02(8)	N2–P2–P3	51.29(5)
N2–P2–N1	100.32(7)		



Numbering scheme of **4**·2.5 C_6H_6

Selected bond lengths [Å] and angles [°] of **4**·2.5 C_6H_6.

Au1–P1	2.3533(8)	P1–Au1–Cl1	171.30(3)
Au1–Cl1	2.3608(8)	P1–Au1–P2	68.66(3)
Au1–P2	2.3657(8)	Cl1–Au1–P2	111.07(3)
P1–N2	1.723(2)	N2–P1–N1	98.30(11)
P1–N1	1.739(2)	N2–P1–Au1	91.68(8)
P1–P2	2.6614(10)	N1–P1–Au1	105.23(8)
P2–N2	1.722(2)	N1–P1–P2	91.71(8)
P2–C49	1.784(3)	Au1–P1–P2	55.89(2)
P3–C49	1.689(3)	N2–P2–C49	101.80(12)
P3–N1	1.697(2)	N2–P2–Au1	91.28(8)
C49–P2–Au1	96.54(9)	C49–P2–P1	89.20(9)
Au1–P2–P1	55.45(2)	C49–P3–N1	105.88(13)
P2–N2–P1	101.18(12)	P3–C49–P2	124.89(16)

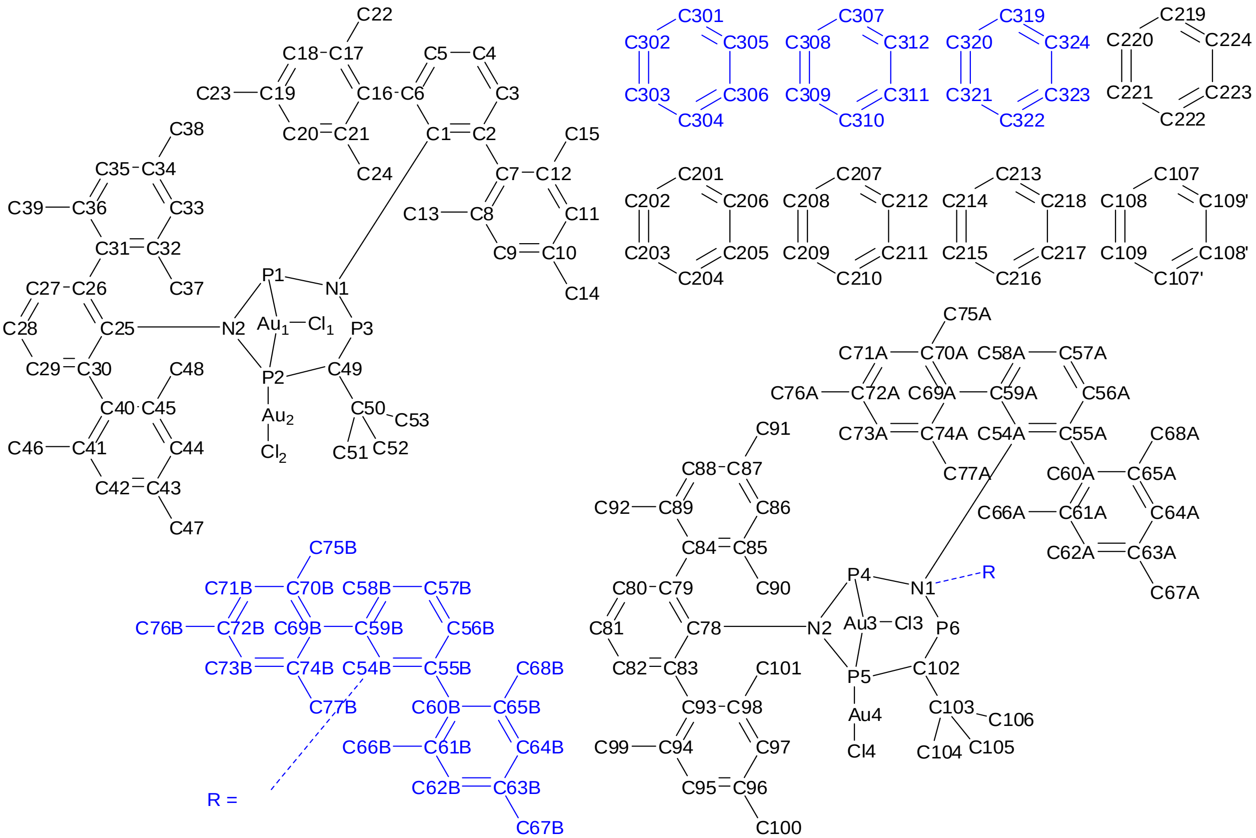


Numbering scheme of **4**·C_6H_6

Selected bond lengths [Å] and angles [°] of **4**·C_6H_6.

Au1–P1	2.359(3)	P1–Au1 P2	68.34(8)
Au1–Cl1	2.368(3)	Cl1–Au1 P2	111.64(9)
Au1–P2	2.368(2)	N1–P1 Au1	107.1(3)
P1–N1	1.743(8)	N1–P1 P2	92.2(2)
P1–P2	2.655(3)	Au1–P1 P2	55.99(7)
P2–C49	1.785(8)	C49–P2 Au1	97.4(3)
P3–C49	1.690(9)	C49–P2 P1	89.1(3)
P3–N1	1.706(7)	C49–P3 --N1	106.0(4)
Au1–P2–P1	55.67(7)	P1–Au1–Cl1	168.87(10)

Numbering scheme of **5**·1.75 C_6H_6



Selected bond lengths [Å] and angles [°] of **5**·1.75 C_6H_6.

Au– P2	2.3470(9)	P2–Au1–P1	68.12(3)
Au1–P1	2.3533(8)	P2–Au1–Cl1	110.36(3)
Au1–Cl1	2.3630(10)	P1–Au1–Cl1	172.36(4)
Au1–C9	2.652(3)	P2–Au1–C9	157.20(8)
Au2–P2	2.2158(8)	P1–Au1–C9	98.26(8)
Au2–Cl2	2.2778(9)	Cl1–Au1–C9	85.49(8)
P1–N2	1.741(3)	P2–Au2–Cl2	178.14(4)
P1–N1	1.744(3)	N2–P1–N1	98.84(13)
P1–P2	2.6324(11)	N2–P1–Au1	90.38(9)
P2–N2	1.684(3)	N1–P1–Au1	105.02(9)
P2–C49	1.781(3)	N2–P1–P2	38.97(9)
P3–C49	1.692(3)	N1–P1–P2	90.42(9)
P3–N1	1.703(3)	Au1–P1–P2	55.83(3)

N2–P2–C49	106.31(14)	Au2–P2–Au1	108.60(4)
N2–P2–Au2	120.89(10)	C49–P2–P1	92.38(11)
C49–P2–Au2	123.17(11)	Au2–P2–P1	144.15(4)
N2–P2–Au1	92.03(10)	Au1–P2–P1	56.06(3)
C49–P2–Au1	98.80(11)	C49–P3–N1	107.21(15)

Computational Details

All calculations were carried out with the Gaussian 09 package of molecular orbital programs.[7] Except from gold a 6-31G(d,p) basis set was utilized at the pbe1pbe level of density functional theory. For gold a ECP60MDF 5 60 pseudo potential was used and a [5s5p4d2f1g] basis set (see below). The optimized structures were checked to be a minimum on the energy hypersurface by frequency analyses. CAS(2,2) calculations were carry out to study the biradical character.

Atomic charges, natural bond orbitals and charge transfer were determined using the NBO analysis for model compounds (phenyl instead of terphenyl and methyl instead of ^{t}Bu).[8]

It should be emphasized that the computation was carried out for a single, isolated (gas-phase) molecule.

Basis set und pseudopotential for gold

```
S 10 1.00
0.36012600E+02 0.19029000E-01
0.22564500E+02 -0.16780000E+00
0.14162000E+02 0.49667700E+00
0.88548700E+01 -0.26625600E+00
0.50607200E+01 -0.69989800E+00
0.14740500E+01 0.87310800E+00
0.70491300E+00 0.50258200E+00
0.21778700E+00 0.32196000E-01
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0.41214000E-01 0.25190000E-02
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0.22564500E+02 0.60008000E-01
0.14162000E+02 -0.18332800E+00
0.88548700E+01 0.11471900E+00
0.50607200E+01 0.24882200E+00
0.14740500E+01 -0.43767100E+00
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0.22564500E+02 0.33760000E-01
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0.70491300E+00 0.56123900E+00
0.21778700E+00 0.18784270E+01
0.97408000E-01 -0.96922900E+00
0.41214000E-01 -0.57563500E+00
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0.88548700E+01 0.17015700E+00
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0.70491300E+00 0.44028320E+01
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S-H
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2 13.523218 426.641867
2 6.264384 36.800668
P-H
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G-H
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```

NBO Data

NBO Charges in e

compound 3	
C 1	-0.24
C 2	-0.27
C 3	-0.26
C 4	0.15
C 5	-0.24
C 6	-0.26
C 7	-0.24
C 8	-0.25
C 9	-0.25
C 10	0.14
C 11	-0.24
C 12	-0.25
H 13	0.25
H 14	0.25
H 15	0.25
H 16	0.26
H 17	0.25
H 18	0.25
N 19	**-1.05**
N 20	**-1.06**
P 21	**0.94**
P 22	**0.71**
C 23	-0.73
C 24	-0.89
P 25	**0.94**
H 26	0.26
H 27	0.26
H 28	0.26
H 29	0.25
H 30	0.26
H 31	0.26
H 32	0.26
sum	0.00

compound4	
Au 1	0.48
Cl 2	-0.62
P 3	**0.84**
P 4	**0.91**
P 5	**0.99**
N 6	**-1.08**
N 7	**-1.03**
C 8	0.14
C 9	-0.26
C 10	-0.26
C 11	-0.23
C 12	0.16
C 13	-0.27
C 14	-0.25
C 15	-0.23
C 16	-0.26
C 17	-0.23
C 18	-0.94
C 19	-0.72
C 20	-0.27
C 21	-0.23
H 22	0.26
H 23	0.26
H 24	0.25
H 25	0.25
H 26	0.26
H 27	0.26
H 28	0.27
H 29	0.26
H 30	0.26
H 31	0.26
H 32	0.26
H 33	0.26
H 34	0.25
sum	0.00

AuCl in 4		**AuCl**	**compound 5**	
Au 1	0.4789	0.49402	Au 1	0.52
Cl 2	-0.6243	-0.49402	Au 2	0.41
charge transfer	**-0.1454**		Cl 3	-0.57

Cl 4	-0.60
P 5	**0.85**
P 6	**0.88**
P 7	**1.03**
N 8	**-1.09**
N 9	**-1.03**
C 10	0.14
C 11	-0.26
C 12	-0.26
C 13	-0.23
C 14	0.15
C 15	-0.26
C 16	-0.25
C 17	-0.23
C 18	-0.25
C 19	-0.23
C 20	-0.93
C 21	-0.72
C 22	-0.25
C 23	-0.23
H 24	0.26
H 25	0.26
H 26	0.26
H 27	0.26
H 28	0.26
H 29	0.26
H 30	0.28
H 31	0.27
H 32	0.26
H 33	0.26
H 34	0.26
H 35	0.26
H 36	0.26
	0.00

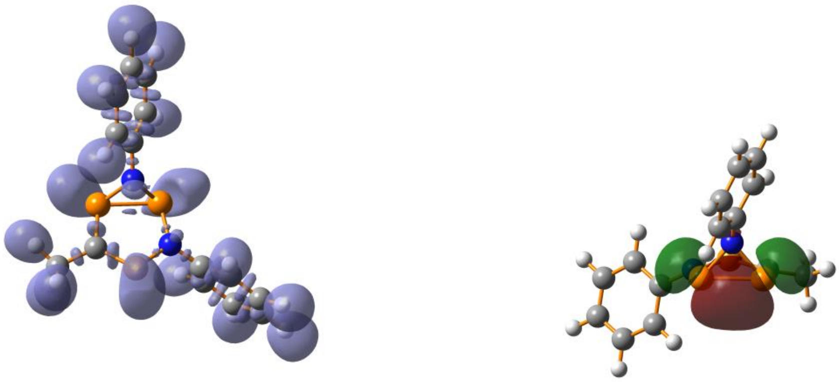
Occupancies of AOs

occ of d AOs	**compound 4**	**compound 5**		
	Au1	Au1	Au2	AuCl
dxy	1.89909	1.81921	1.92309	1.99985
dxy	0.00072	0.00087	0.00071	0
dxy	0.0005	0.00086	0.00023	0.00002
dxy	0.00001	0.00002	0	0
dxz	1.9644	1.9612	1.92646	1.99751
dxz	0.00068	0.00068	0.00076	0
dxz	0.00032	0.00032	0.00021	0.0002
dxz	0	0.00001	0	0
dyz	1.91775	1.92424	1.99783	1.99751

dyz	0.00102		0.00098	0.00035	0
dyz	0.00018		0.00021	0.00015	0.0002
dyz	0.00001		0.00001	0	0
dx2y2	1.9118		1.96107	1.87895	1.99985
dx2y2	0.00094		0.00086	0.00064	0
dx2y2	0.0007		0.00028	0.00062	0.00002
dx2y2	0.00001		0.00001	0.00002	0
dz2	1.94089		1.94897	1.95747	1.87526
dz2	0.00047		0.00055	0.00036	0.00067
dz2	0.00046		0.00044	0.00029	0.00007
dz2	0.00001		0.00001	0.00001	0
sum	9.63996	sum	9.6208	9.68815	9.87116
6s	0.82946		0.80937	0.86142	0.60632

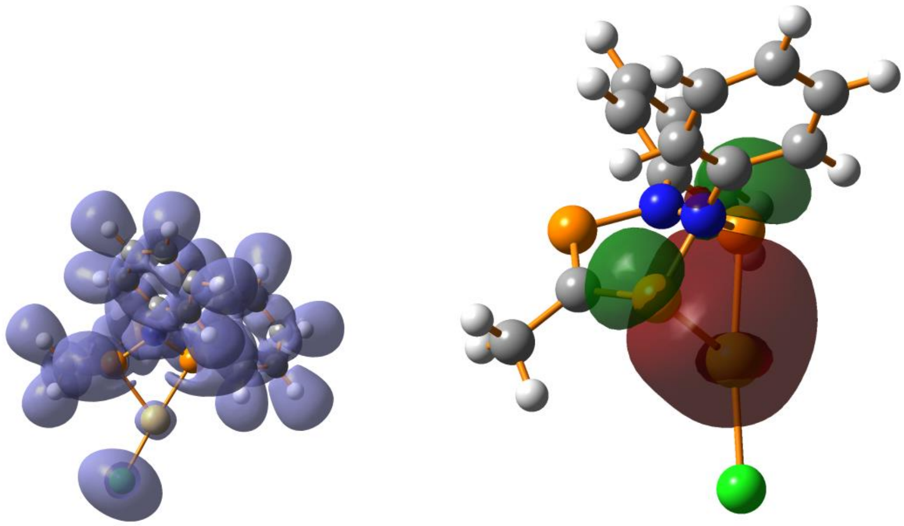
Compound 3

Figure S4. Banana bond - Left: ELF @ 0.87 displaying a tiny disynaptic basin outside the P-P axis, Right: NBO displaying the 2c-2e banana bond for model compound.



Compound 4

Figure S5. ELF @ 0.65 displaying NO disynaptic basin outside the P-P axis, Right: NBO displaying the 3c-2e bond for model compound



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