Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

1. Experimental Details

All manipulations regarding the preparation of air-sensitive compounds were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 and internally referenced to the residual solvent resonances (CD_2Cl_2: ^{1}H δ 5.32 ppm, $^{13}C\{^{1}H\}$ δ 53.84 ppm; $CDCl_3$: ^{1}H δ 7.26 ppm, $^{13}C\{^{1}H\}$ δ 77.16 ppm; THF-d_8: δ ^{1}H δ 3.58, 1.72 ppm, $^{13}C\{^{1}H\}$ δ 67.21, 25.31 ppm). $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85% H_3PO_4). ^{19}F NMR spectra were recorded on a Bruker Avance 250 and externally referenced ($CFCl_3$). Melting points were measured on samples in sealed capillaries and are uncorrected. ESI Mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer in positive (capillary potential of 4500 V) ion mode.

White phosphorus was sublimed prior to use (40 ^{o}C, 1 x 10^{-3} mbar), $Li[Al(OC(CF_3)_3)_4]$[1] and 2,6-dimesitylphenyl lithium[2] (DmpLi) were prepared according to literature procedures and 2,4,6-trimethylphenyl lithium (MesLi) was prepared according to a modified literature procedure (see below).[3] All other reagents were purchased from commercial resources and used without further purification.

Preparation of MesLi·$(OEt_2)_{0.12}$:

n-BuLi (1.6 M in hexanes, 27.62 mL, 44.2 mmol, 1.1 equiv.) was added to a solution of MesBr (8 g, 6.15 mL, 40.2 mmol, 1 equiv.) in diethyl ether (80 mL) at room temperature, over a period of 30 minutes. The resulting bright yellow solution was stirred for 16 hours during which a white solid precipitated. The solvent was removed *in vacuo* after which the residue was washed with *n*-hexane (3 x 10 mL) to give analytically pure **MesLi·$(OEt_2)_{0.12}$** as a white powder in 93% yield (5.05 g, 37.4 mmol).

^{1}H NMR (400.1 MHz, THF-d_8, 293 K): δ 6.46 (s, 2H; *m*-C_6H_2), 2.35 (s, 6H; *o*-CH_3), 2.07 (s, 3H; *p*-CH_3).

Preparation of [IPrCu(η^2–P_4)][$Al(OC(CF_3)_3)_4$] (1a):

A solution of IPrCuCl (0.200 g, 0.410 mmol, 1.0 equiv.) in DCM (15 mL) was added dropwise to a suspension of $Li[Al(OC(CF_3)_3)_4]$ (0.399 g, 0.410 mmol, 1 equiv.) and P_4 (0.056 g, 0.451 mmol, 1.1 equiv.) in DCM (20 mL) at 0 °C. The turbid solution was stirred for 1 hour at 0 °C, and then allowed to warm to room temperature after which it was filtered through a cannula. Removal of the solvent *in vacuo* and subsequent washing of the residue with *n*-pentane (3 x 10 mL) gave **1a** as a white solid in 92% (0.580 g, 0.376 mmol).

Mp. (nitrogen, sealed capillary): 100–228 ^{o}C (decomposition).

^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K): δ 7.61 (t, $^{3}J_{H,H}$ = 7.6 Hz, 2H; *p*-C_6H_3), 7.39 (d, $^{3}J_{H,H}$ = 8.0 Hz, 4H; *m*-C_6H_3), 7.30 (s, 2H; $C(NCH)_2$), 2.46 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 4H; $CH(CH_3)_2$), 1.26 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H; $CH(CH_3)_2$), 1.21 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H; $CH(CH_3)_2$).

$^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 293 K): δ 176.1 (only observed in the HMBC spectrum, $^3J_{C,H}$ coupling with C(NC*H*)$_2$; *C*(NCH)$_2$), 146.1 (s; *o*-*C*$_6$H$_3$), 134.0 (s; *ipso*-*C*$_6$H$_3$), 131.8 (s; *p*-*C*$_6$H$_3$), 125.1 (s; *m*-*C*$_6$H$_3$), 124.8 (s; C(N*C*H)$_2$), 121.7 (q, $^1J_{C,F}$ = 293.5 Hz; C(*C*F$_3$)$_3$), 29.2 (s; *C*H(CH$_3$)$_2$), 25.2 (s; CH(*C*H$_3$)$_2$), 24.2 (s; CH(*C*H$_3$)$_2$), not observed (*C*(CF$_3$)$_3$).

^{19}F NMR (235.4 MHz, $CDCl_3$, 293 K): δ –75.4 (s).

$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 293 K): δ –483.1 (s).

HR–MS (ESI): 389.2920 $[M + H - CuP_4]^+$. Calcd.: for $C_{27}H_{37}N_2$ 389.2956.

Preparation of [IPrAu(η^2–P$_4$)][Al(OC(CF$_3$)$_3$)$_4$] (1b):

A solution of IPrAuCl (0.204 g, 0.328 mmol, 1.0 equiv.) in DCM (15 mL) was added dropwise to a suspension of Li[Al(OC(CF$_3$)$_3$)$_4$] (0.319 g, 0.328 mmol, 1 equiv.) and P$_4$ (0.045 g, 0.361 mmol, 1.1 equiv.) in DCM (15 mL) at 0 °C. The turbid solution was stirred for 1 hour at 0 °C, and then allowed to warm to room temperature after which it was filtered through a cannula. Removal of the solvent *in vacuo* and subsequent washing of the residue with *n*-pentane (3 x 10 mL) gave **1b** as a white solid in 87% (0.478 g, 0.285 mmol). X-ray quality crystals were grown by cooling a saturated solution of **1b** in a DCM/*n*-pentane solvent mixture to –20 °C.

Mp. (nitrogen, sealed capillary): 160–175 °C (trajectory).

^1H NMR (400.1 MHz, $CDCl_3$, 293 K): δ 7.62 (t, $^3J_{H,H}$ = 8.0 Hz, 2H; *p*-C$_6$*H*$_3$), 7.38 (d, $^3J_{H,H}$ = 8.0 Hz, 4H; *m*-C$_6$*H*$_3$), 7.36 (s, 2H; C(NC*H*)$_2$), 2.46 (sept, $^3J_{H,H}$ = 8.0 Hz, 4H; C*H*(CH$_3$)$_2$), 1.28 (d, $^3J_{H,H}$ = 8.0 Hz, 12H; CH(C*H*$_3$)$_2$), 1.27 (d, $^3J_{H,H}$ = 8.0 Hz, 12H; CH(C*H*$_3$)$_2$).

$^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 291 K): δ 191.1 (only observed in the HMBC spectrum, $^3J_{C,H}$ coupling with C(NC*H*)$_2$; *C*(NCH)$_2$), 146.1 (s; *o*-*C*$_6$H$_3$), 133.0 (s; *ipso*-*C*$_6$H$_3$), 132.1 (s; *p*-*C*$_6$H$_3$), 125.1 (s; *m*-*C*$_6$H$_3$), 125.0 (s; C(N*C*H)$_2$), 121.6 (q, $^1J_{C,F}$ = 291.3 Hz; C(*C*F$_3$)$_3$), 29.3 (s; *C*H(CH$_3$)$_2$), 25.0 (s; CH(*C*H$_3$)$_2$), 24.3 (s; CH(*C*H$_3$)$_2$), not observed (*C*(CF$_3$)$_3$).

^{19}F NMR (235.4 MHz, CD_2Cl_2, 293 K): δ –75.8 (s).

$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 293 K): δ –464.4 (br. s).

HR–MS (ESI): 709.1489 $[M]^+$. Calcd.: for $C_{27}H_{36}AuN_2P_4$ 709.1494.

Preparation of [DmpP$_4$·(IPrAu)$_2$][Al(OC(CF$_3$)$_3$)$_4$] (3):

A solution of DmpLi (0.024 g, 0.075 mmol, 1 equiv.) in toluene (2.5 mL) was slowly added to a solution of **1b** (0.251 g, 0.150 mmol, 2 equiv.) in toluene (10 mL) at –78 °C. The resulting yellow suspension was allowed to warm to room temperature and stirred for 30 min. after which the solvent was removed *in vacuo* to give a yellow solid. The product was extracted into DCM (10 mL), evaporated to dryness and subsequently washed with *n*-pentane (2 x 10 mL) to give a pale yellow powder. Cooling a saturated solution of the crude product in a mixture of DCM/*n*-pentane to –80 °C resulted in the precipitation of a yellow oil, which was removed by filtration over neutral Al_2O_3. The filtrate was evaporated to dryness to give **3** as a white powder in 67% (0.129 g, 0.050 mmol). X-ray quality crystals were grown at 0 °C from a saturated solution of **3** in DCM layered with *n*-pentane.

Mp. (nitrogen, sealed capillary): 219–256 °C (decomposition).

^{1}H NMR (400.1 MHz, CD_2Cl_2, 297 K): δ 7.54 (t, $^{3}J_{H,H}$ = 7.9 Hz, 2H; *p*-dipp*H*), 7.51 (t, $^{3}J_{H,H}$ = 7.9 Hz, 2H; *p*-dipp*H*), 7.28 (d, $^{3}J_{H,H}$ = 7.9 Hz, 4H; *m*-dipp*H*), 7.25 (buried, 1H; *p*-C_6H_3), 7.23 (d, $^{3}J_{H,H}$ = 7.9 Hz, 4H; *m*-dipp*H*), 7.16 (s, 2H; C(NC*H*)$_2$), 7.11 (s, 2H; C(NC*H*)$_2$), 6.89 (s, 4H; *m*-mes*H*), 6.85 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H; *m*-C_6H_3), 2.38 (s, 6H; *p*-CH_3), 2.33 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 2.32 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 1.88 (s, 12H; *o*-CH_3), 1.18 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12H; CH(CH_3)$_2$), 1.15 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12H; CH(CH_3)$_2$), 1.14 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12H; CH(CH_3)$_2$), 0.98 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12H; CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 297 K): δ 191.9 (only observed in the HMBC spectrum, $^{3}J_{C,H}$ coupling with C(NC*H*)$_2$; *C*(NCH)$_2$), 190.5 (only observed in the HMBC spectrum, $^{3}J_{C,H}$ coupling with C(NC*H*)$_2$; *C*(NCH)$_2$), 146.0 (s; *o*-dipp*C*), 145.9 (s; *o*-dipp*C*), 145.4 (d, $^{2}J_{C,P}$ = 9.0 Hz; *o*-C_6H_3), 139.0 (s; *ipso*-mes*C*), 137.6 (s; *p*-mes*C*), 136.4 (s; *o*-mes*C*), 133.8 (s; *ipso*-dipp*C*), 133.7 (s; *ipso*-dipp*C*), 131.3 (s; *p*-dipp*C*), 131.2 (s; *p*-dipp*C*), 129.7 (s; *p*-C_6H_3), 129.3 (s; *m*-C_6H_3), 129.1 (s; *m*-mes*C*), 124.6 (s; *m*-dipp*C*), 124.5 (s; *m*-dipp*C*), 124.3 (s; C(N*C*H)$_2$), 124.2 (s; C(N*C*H)$_2$), 121.7 (q, $^{1}J_{C,F}$ = 293.1 Hz; C(*C*F$_3$)$_3$), 29.1 (s; *C*H(CH$_3$)$_2$), 29.0 (s; *C*H(CH$_3$)$_2$), 25.0 (s; CH(*C*H$_3$)$_2$), 24.9 (s; CH(*C*H$_3$)$_2$), 24.1 (s; CH(*C*H$_3$)$_2$), 23.9 (s; CH(*C*H$_3$)$_2$), 21.6 (s; *o*-*C*H$_3$), 21.4 (s; *p*-*C*H$_3$), not observed (*C*(CF$_3$)$_3$), not observed (*ipso*-C_6H_3).

^{19}F NMR (235.4 MHz, CD_2Cl_2, 292 K): δ –78.9 (s).

^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 297 K): δ –105.5 (td, $^{1}J_{P,P}$ = –185.9 Hz, $^{2}J_{P,P}$ = 117.7 Hz, 1P; *P*-Dmp), –118.7 (td, $^{1}J_{P,P}$ = –201.1 Hz, $^{2}J_{P,P}$ = 117.7 Hz, 1P; *P*-(AuIPr)$_2$), –327.9 (dd, $^{1}J_{P,P}$ = –202.0 Hz, $^{1}J_{P,P}$ = –186.8 Hz, 2P; *P*-bridgehead).

HR–MS (ESI): 1023.3488 [M + H – IPrAu]$^{+}$. Calcd.: for $C_{51}H_{62}AuN_2P_4$ 1023.3523.

Preparation of [MesP$_4$·(IPrAu)$_2$][Al(OC(CF$_3$)$_3$)$_4$] (4):

Cold toluene (10 mL, –78 °C) was added to a pre-cooled Schlenk flask (–78 °C) containing a mixture of MesLi (0.014 g, 0.104 mmol, 1 equiv.) and **1b** (0.350 g, 0.209 mmol, 2 equiv.). The resulting yellow suspension was allowed to warm to room temperature and stirred for 60 min. after which the solvent was removed *in vacuo* to give a yellow solid. The product was extracted into DCM (10 mL), evaporated to dryness and subsequently washed with *n*-pentane (2 x 10 mL) to give a pale yellow powder. Cooling a saturated solution of the crude product in a mixture of DCM/*n*-pentane to –80 °C resulted in the precipitation of a yellow oil, which was removed by filtration over neutral Al_2O_3. The filtrate was evaporated to dryness to give **4** as a pale yellow powder in 62% (0.154 g, 0.065 mmol).

Mp. (nitrogen, sealed capillary): 166–226 °C (decomposition).

^{1}H NMR (400.1 MHz, CD_2Cl_2, 293 K): δ 7.56 (t, $^{3}J_{H,H}$ = 7.8 Hz, 2H; *p*-dipp*H*), 7.32 (d, $^{3}J_{H,H}$ = 7.8 Hz, 4H; *m*-dipp*H*), 7.23-7.19 (multiple signals, 10H; *m*-dipp*H*, *p*-dipp*H*, C(NC*H*)$_2$), 6.73 (s, 2H; *m*-mes*H*), 2.43 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 4H; C*H*(CH$_3$)$_2$), 2.39 (s, 6H; *o*-CH_3), 2.36 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 4H; C*H*(CH$_3$)$_2$), 2.23 (s, 3H; *p*-CH_3), 1.23 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H; CH(CH_3)$_2$), 1.21 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H; CH(CH_3)$_2$), 1.20 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H; CH(CH_3)$_2$), 1.14 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H; CH(CH_3)$_2$).

^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 294 K): δ 192.3 (s; *C*(NCH)$_2$), 191.1 (*C*(NCH)$_2$), 146.1 (s; *o*-dipp*C*), 146.0 (s; *o*-dipp*C*), 140.4 (d, $^{2}J_{C,P}$ = 9.1 Hz; *o*-mes*C*), 139.3 (s; *p*-mes*C*), 133.9 (s; *ipso*-dipp*C*), 133.6 (s; *ipso*-dipp*C*), 131.3 (s; *p*-dipp*C*), 131.2 (s; *p*-dipp*C*), 129.2 (s; *m*-mes*C*), 124.6 (s; *m*-dipp*C*), 124.4 (s; *m*-dipp*C*), 124.3 (d, $^{4}J_{C,P}$ = 2.6

Hz; C(NCH)$_2$), 124.2 (d, $^4J_{C,P}$ = 2.1 Hz; C(NCH)$_2$), 121.7 (q, $^1J_{C,F}$ = 293.5 Hz; C(CF_3)$_3$), 29.1 (s; $CH(CH_3)_2$), 25.1 (s; $CH(CH_3)_2$), 24.9 (s; $CH(CH_3)_2$), 24.1 (s; *o*-CH_3), 24.0 (s; $CH(CH_3)_2$), 21.0 (s; *p*-CH_3), not observed ($C(CF_3)_3$), not observed (*ipso*-mes*C*).

^{19}F NMR (235.4 MHz, CD_2Cl_2, 293 K): δ –76.2 (s).

^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 294 K): δ –110.6 (td, $^1J_{P,P}$ = –181.9 Hz, $^2J_{P,P}$ = 133.1 Hz, 1P; *P*-Mes), –119.9 (td, $^1J_{P,P}$ = –193.4 Hz, $^2J_{P,P}$ = 132.4 Hz, 1P; *P*-(AuIPr)$_2$), –314.5 (dd, $^1J_{P,P}$ = –180.6 Hz, $^1J_{P,P}$ = –193.1 Hz, 2P; *P*–bridgehead).

HR–MS (ESI): 829.2432 (M + H – IPrAu)$^+$. Calcd.: for $C_{36}H_{48}AuN_2P_4$ 829.2428.

Reaction of MesLi with P_4 and BPh_3:

To a solution of P_4 (0.098 g, 0.791 mmol, 1 equiv.) and BPh_3 (0.192 g, 0.791 mmol, 1 equiv.) in toluene at 0 °C was added a suspension of MesLi (0.100 g, 0.791 mmol, 1 equiv.) in toluene (15 mL). The resulting suspension was stirred for 1 h at room temperature and analyzed using ^{11}B and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum only showed a sharp signal originating from P_4 at –519.8 ppm, and in the ^{11}B NMR spectrum one new product was observed resonating at –6.9 ppm, corresponding to $Li^+MesBPh_3^-$. Formation of the latter was confirmed in a control experiment, in which MesLi (0.010 g, 0.079 mmol, 1 equiv.) was reacted with BPh_3 (0.019 g, 0.079 mmol, 1 equiv.) in THF-d_8 (0.6 mL) to give a clear colorless solution which was analyzed using ^{1}H and ^{11}B NMR spectroscopy.

^{1}H NMR (400.1 MHz, THF-d_8, 293 K): δ 7.38 (br. s, 6H; *o*-B(C_6H_5)$_3$), 6.79 (t, $^3J_{H,H}$ = 7.3 Hz, 6H; *m*-B(C_6H_5)$_3$), 6.65 (t, $^3J_{H,H}$ = 7.3 Hz, 3H; *p*-B(C_6H_5)$_3$), 6.39 (s, 2H; *m*-C_6H_2), 2.11 (s, 3H; *p*-CH_3), 1.58 (s, 6H; *o*-CH_3).

^{11}B NMR (128.4 MHz, THF-d_8, 293 K): δ –8.69 (s; Mes*B*Ph_3).

VT NMR Spectroscopy:

[IPrM(η^2–P_4)][Al(OC(CF_3)$_3$)$_4$] (M = Cu, Au; 0.06 mmol) was dissolved in CD_2Cl_2 (0.6 mL) and loaded into an NMR tube. The samples were used to record the $^{31}P\{^1H\}$ NMR spectra using a Bruker Avance 400 in the temperature range of –90 °C to 0 °C (Figure S1).

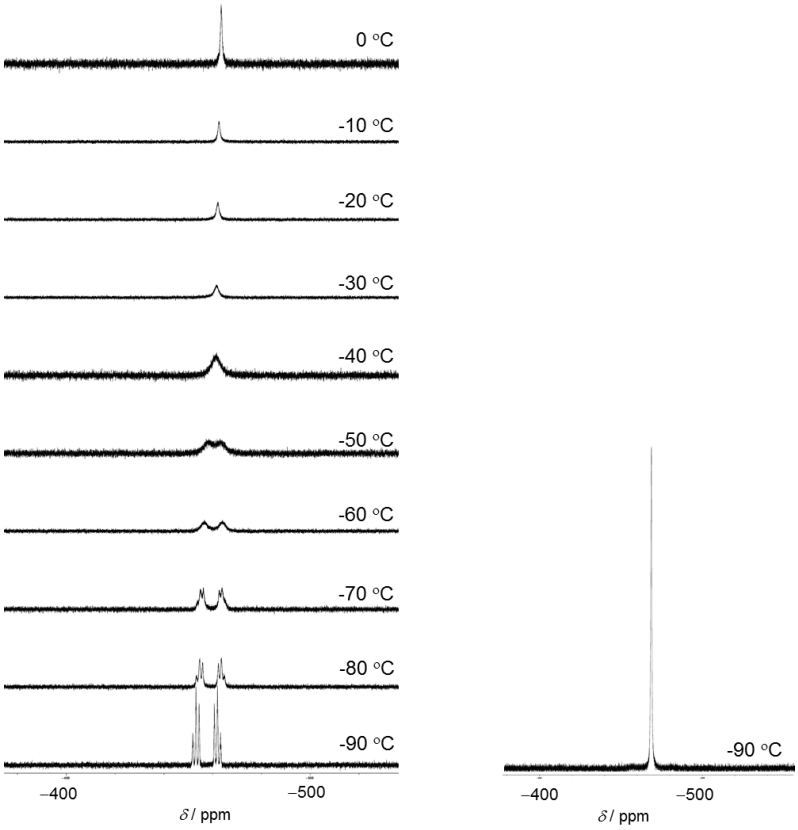


Figure S1. VT $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2) spectra recorded of [IPrAu(η^2–P_4)][Al(OC(CF_3)$_3$)$_4$] **1b** (left) and [IPrCu(η^2–P_4)][Al(OC(CF_3)$_3$)$_4$] **1a** (right).

Calculation of the estimated free enthalpy of activation $\Delta G^{\ddagger}$ for **1b** at the coalescence temperature (T_C = –40 °C) was performed using the Eyring equation (1), with the corresponding rate constant k_C defined by equation (2).[4]

$$\Delta G^{\ddagger}_C = 4.58\ T_C\,(10.32 + \log\,(T_C / k_C))\ \text{cal mol}^{-1} \quad (1)$$

$$k_C = (\pi\ \Delta\nu / \sqrt{2}) = 2.22\ \Delta\nu \quad (2)$$

($\Delta\nu$ is the separation in Hz between the two signals at the low–temperature limit)

k_{233K} = 2.22 · 1424.72 Hz = 3162.88 s^{-1}

$\Delta G^{\ddagger}_{233K}$ = 4.58 · 233 K · (10.32 + log (233 K / 3162.88 s^{-1})) = 9804.11 cal mol^{-1} = 9.8 kcal mol^{-1}

2. Computational Details

Density functional calculations were performed at the ωB97X-D[5] level of theory using Gaussian09, revision D.01.[6] Geometry optimizations of **1a**$^+$ and **1b**$^+$ were performed using the 6-31+G(2d,p)[7] basis set for atoms C, H, N, P in combination with the LANL2DZ[8] basis set for Cu and Au. All other geometry optimizations were performed using the 6-31G(d) basis set for atoms C, H, N, P in combination with the LANL2DZ basis set for Au, and uncorrected energies were obtained from single point calculations (SPE) using 6-311+G(2d,p) for atoms C, H, N, P and the LANL2DZ basis set for Au. The nature of each stationary point was confirmed by frequency calculations. The ETS-NOCV[9] and AIM[10] analyses were performed at the ZORA-BP86-D3/TZ2P[11] level of theory using ADF2013.01.[12]

[IPrCu(η^2–P_4)]$^+$ (1a$^+$)

E: -2721.209026 a.u.

ZPE: 0.585241 a.u.

G: -2720.697589 a.u.

Cartesian coordinates:

C	-1.052134000	-3.035818000	-0.325289000
C	0.296110000	-3.175033000	-0.389038000
H	-1.847280000	-3.760788000	-0.387909000
H	0.918294000	-4.046045000	-0.515958000
N	0.825054000	-1.909408000	-0.246602000
N	-1.298170000	-1.689599000	-0.155220000
C	-0.149211000	-0.990950000	-0.103356000
C	2.218223000	-1.562808000	-0.229648000
C	2.903891000	-1.649351000	0.989755000
C	2.802573000	-1.099931000	-1.414321000
C	4.241173000	-1.255261000	0.995282000
C	4.142872000	-0.714713000	-1.352801000
C	4.854061000	-0.792609000	-0.163222000
H	4.811840000	-1.304803000	1.916256000
H	4.636850000	-0.349075000	-2.247295000
H	5.896681000	-0.492915000	-0.137464000
C	-2.589795000	-1.075551000	-0.032789000
C	-3.282941000	-0.753358000	-1.207690000
C	-3.069990000	-0.791429000	1.250734000
C	-4.522248000	-0.131958000	-1.063098000
C	-4.315886000	-0.168207000	1.339268000
C	-5.035138000	0.154493000	0.196788000
H	-5.094952000	0.136242000	-1.944264000
H	-4.730630000	0.065591000	2.314595000
H	-6.003748000	0.634852000	0.287900000
P	-0.685743000	3.154307000	0.044534000

P	0.455807000	4.391077000	1.446085000
P	1.564888000	2.733232000	0.540627000
P	0.937859000	4.407264000	-0.726688000
Cu	0.084857000	0.919555000	0.122058000
C	2.027084000	-0.978449000	-2.716450000
C	2.712426000	-1.732292000	-3.863093000
C	1.810860000	0.497533000	-3.079521000
H	1.039631000	-1.429376000	-2.576091000
H	2.876256000	-2.783046000	-3.606406000
H	2.092363000	-1.693650000	-4.764154000
H	3.682980000	-1.291799000	-4.112750000
H	1.276403000	1.028433000	-2.281506000
H	2.766155000	1.009094000	-3.237812000
H	1.221541000	0.587732000	-3.997169000
C	2.210009000	-2.084456000	2.271170000
C	1.762075000	-0.852127000	3.072002000
C	3.072699000	-3.013006000	3.132441000
H	1.308243000	-2.643637000	2.002129000
H	1.088553000	-0.219357000	2.483134000
H	1.232149000	-1.155082000	3.980861000
H	2.625249000	-0.245657000	3.367845000
H	3.437340000	-3.868633000	2.556477000
H	3.939522000	-2.494202000	3.554039000
H	2.484660000	-3.393450000	3.973051000
C	-2.280372000	-1.108630000	2.510572000
C	-3.068315000	-2.019019000	3.460877000
C	-1.844459000	0.184396000	3.213754000
H	-1.370013000	-1.646310000	2.227050000
H	-3.376947000	-2.941295000	2.959697000
H	-2.451985000	-2.289205000	4.324177000
H	-3.968943000	-1.525608000	3.840038000
H	-1.240784000	0.814831000	2.548036000
H	-2.709173000	0.774866000	3.534169000
H	-1.243281000	-0.042362000	4.099697000
C	-2.682709000	-0.998153000	-2.583321000
C	-2.000110000	0.281143000	-3.091577000
C	-3.704923000	-1.517262000	-3.599965000
H	-1.908259000	-1.766003000	-2.489067000
H	-1.222407000	0.618195000	-2.397022000
H	-1.531719000	0.108128000	-4.065892000
H	-2.729530000	1.090910000	-3.202748000
H	-4.230004000	-2.399747000	-3.222803000
H	-4.452990000	-0.759340000	-3.853192000
H	-3.198219000	-1.792902000	-4.529708000

[IPrAu(η^2–P_4)]$^+$ ($1b^+$)

E: -2660.51528746 a.u.

ZPE: 0.584799 a.u.

G: -2660.005308 a.u.

Cartesian coordinates:

C	-0.731644000	-3.301440000	-0.085633000
C	0.625020000	-3.322214000	-0.119903000
H	-1.460351000	-4.095323000	-0.093696000
H	1.328158000	-4.138008000	-0.158758000
N	1.038290000	-2.008218000	-0.087848000
N	-1.102891000	-1.975519000	-0.037111000
C	-0.019532000	-1.180236000	-0.038315000
C	2.397311000	-1.543343000	-0.078736000
C	3.034225000	-1.403716000	1.160499000
C	2.985992000	-1.195729000	-1.300054000
C	4.327698000	-0.883022000	1.150764000
C	4.281928000	-0.681714000	-1.252279000
C	4.943845000	-0.524422000	-0.041576000
H	4.858913000	-0.751529000	2.087788000
H	4.780012000	-0.398201000	-2.173962000
H	5.950318000	-0.119182000	-0.026853000
C	-2.447564000	-1.473041000	0.005187000
C	-3.099250000	-1.234866000	-1.210713000
C	-3.010397000	-1.198211000	1.257049000
C	-4.382732000	-0.693653000	-1.143664000
C	-4.297447000	-0.660720000	1.266447000
C	-4.975271000	-0.410321000	0.080341000
H	-4.925675000	-0.487966000	-2.060578000
H	-4.776201000	-0.433614000	2.213594000
H	-5.974940000	0.010524000	0.110462000
P	-0.475305000	3.107507000	-0.998443000
P	-0.916868000	4.542349000	0.598958000
P	0.586501000	3.036363000	1.136863000
P	1.078553000	4.531646000	-0.390441000
Au	0.014850000	0.855858000	0.013975000
C	2.264730000	-1.347091000	-2.629417000
C	3.028328000	-2.284977000	-3.573679000
C	2.015286000	0.018940000	-3.282577000
H	1.286039000	-1.800834000	-2.444229000
H	3.192870000	-3.263659000	-3.112636000
H	2.464952000	-2.432980000	-4.500123000
H	4.006054000	-1.872976000	-3.843511000
H	1.427497000	0.670223000	-2.625951000
H	2.956710000	0.530597000	-3.507992000
H	1.466136000	-0.102040000	-4.221528000
C	2.354170000	-1.764039000	2.471785000

C	1.997869000	-0.500642000	3.267632000
C	3.204923000	-2.726063000	3.310300000
H	1.415144000	-2.279024000	2.246136000
H	1.334395000	0.154254000	2.693397000
H	1.489107000	-0.766296000	4.199706000
H	2.897178000	0.069475000	3.524495000
H	3.470979000	-3.622387000	2.741703000
H	4.133323000	-2.255433000	3.649192000
H	2.651932000	-3.038164000	4.201569000
C	-2.268941000	-1.443874000	2.561166000
C	-3.037496000	-2.412310000	3.469575000
C	-1.971973000	-0.121965000	3.282158000
H	-1.306056000	-1.911274000	2.332128000
H	-3.240825000	-3.358977000	2.959822000
H	-2.456419000	-2.627871000	4.371651000
H	-3.996030000	-1.989885000	3.787781000
H	-1.382062000	0.550356000	2.649075000
H	-2.896119000	0.398196000	3.554627000
H	-1.406874000	-0.306606000	4.201107000
C	-2.445368000	-1.513696000	-2.554474000
C	-2.120015000	-0.204172000	-3.285924000
C	-3.307276000	-2.437205000	-3.424339000
H	-1.496289000	-2.029336000	-2.377532000
H	-1.457459000	0.428869000	-2.686550000
H	-1.622460000	-0.411227000	-4.238602000
H	-3.030825000	0.365680000	-3.498400000
H	-3.538413000	-3.372184000	-2.904938000
H	-4.254860000	-1.963244000	-3.699700000
H	-2.780554000	-2.682171000	-4.351732000

$[NHC^{Ph}Au(\eta^2–P_4)]^+$

E: -2188.72572027 a.u.

ZPE: 0.245533 a.u.

G: -2188.535713 a.u.

SPE: -2189.03893801 a.u.

Cartesian coordinates:

C	-1.604149000	-3.530408000	-0.011158000
C	-0.290021000	-3.858086000	-0.031216000
H	-2.492741000	-4.141219000	0.002018000
H	0.206872000	-4.814637000	-0.059449000
N	0.415780000	-2.669253000	-0.027427000
N	-1.668539000	-2.148902000	0.009484000
C	-0.428464000	-1.616373000	-0.001618000
C	1.846896000	-2.562134000	-0.042373000
C	2.572859000	-3.061352000	1.033296000

C	2.473501000	-1.954204000	-1.126485000
C	3.959461000	-2.943026000	1.021917000
H	2.058521000	-3.522722000	1.870757000
C	3.859591000	-1.831260000	-1.120899000
H	1.882428000	-1.598011000	-1.964868000
C	4.600692000	-2.325026000	-0.049408000
H	4.537137000	-3.327842000	1.855615000
H	4.360049000	-1.362986000	-1.961992000
H	5.681780000	-2.232279000	-0.051596000
C	-2.881209000	-1.382073000	0.035465000
C	-3.766289000	-1.480339000	-1.032449000
C	-3.140698000	-0.554502000	1.124338000
C	-4.936374000	-0.727461000	-1.007697000
H	-3.534431000	-2.126038000	-1.874013000
C	-4.308025000	0.202802000	1.131777000
H	-2.443988000	-0.519636000	1.956483000
C	-5.204506000	0.115289000	0.068835000
H	-5.635918000	-0.794859000	-1.834157000
H	-4.524110000	0.848741000	1.976345000
H	-6.118024000	0.700707000	0.081836000
P	0.211635000	2.635229000	-1.106254000
P	0.085541000	4.202706000	0.418336000
P	1.121435000	2.398603000	1.107487000
P	2.050219000	3.629880000	-0.449232000
Au	0.078983000	0.362918000	0.007843000

[AuNHC^{Ph}]$^{+}$

E: -823.325658148 a.u.

ZPE: 0.23811 a.u.

G: -823.13484 a.u.

SPE: -823.505925964 a.u.

Cartesian coordinates:

Au	-0.000079000	-1.359270000	-0.000187000
C	0.000029000	0.623413000	-0.000137000
N	-1.079577000	1.426375000	-0.008617000
N	1.079699000	1.426294000	0.008320000
C	-0.677518000	2.749591000	-0.004493000
C	-2.446957000	0.978804000	-0.022861000
C	0.677726000	2.749539000	0.004204000
C	2.447045000	0.978657000	0.022915000
H	-1.393708000	3.555597000	-0.016540000
C	-3.222627000	1.154016000	1.117527000
C	-2.954069000	0.385226000	-1.174696000
H	1.393974000	3.555494000	0.016217000
C	3.223228000	1.154338000	-1.117048000

C	2.953654000	0.384600000	1.174732000
C	-4.544099000	0.718167000	1.100561000
C	-4.274744000	-0.053230000	-1.175137000
C	4.544695000	0.718482000	-1.099666000
C	4.274319000	-0.053869000	1.175584000
C	-5.066792000	0.114217000	-0.041088000
H	-5.162456000	0.846440000	1.982464000
H	-4.687092000	-0.515088000	-2.065832000
C	5.066878000	0.114053000	0.041959000
H	5.163454000	0.847132000	-1.981233000
H	4.686272000	-0.516090000	2.066274000
H	-6.097371000	-0.225037000	-0.048144000
H	6.097455000	-0.225202000	0.049340000
H	-2.795347000	1.614409000	2.002923000
H	-2.328228000	0.282924000	-2.056023000
H	2.796347000	1.615077000	-2.002457000
H	2.327429000	0.281973000	2.055750000

[PhP_4AuNHC^{Ph}]

E: -2420.49290947 a.u.

ZPE: 0.33725 a.u.

G: -2420.218916 a.u.

SPE: -2420.8662849 a.u.

Cartesian coordinates:

P	2.448554000	0.170284000	-0.882943000
P	2.126664000	-1.556167000	0.406329000
P	0.950714000	-1.379887000	-1.488890000
P	3.869889000	-1.550108000	-0.987055000
C	5.223683000	-0.956658000	0.129824000
C	6.096757000	0.044181000	-0.315264000
C	5.462486000	-1.545089000	1.377550000
C	7.168929000	0.455568000	0.470917000
C	6.536041000	-1.135068000	2.163810000
C	7.391084000	-0.133082000	1.713623000
H	7.833381000	1.236511000	0.111874000
H	6.702914000	-1.600349000	3.131200000
C	-4.487222000	1.337478000	1.285112000
C	-3.721349000	2.448234000	1.215441000
H	-5.482040000	1.180028000	1.669589000
H	-3.896609000	3.458370000	1.548880000
N	-2.534862000	2.073021000	0.606907000
N	-3.750674000	0.312530000	0.711804000
C	-2.540620000	0.754428000	0.288380000
C	-1.457626000	2.974948000	0.325557000
C	-1.721089000	4.119335000	-0.420498000

C	-0.174229000	2.692738000	0.784151000
C	-0.679147000	4.993098000	-0.714225000
C	0.864439000	3.561161000	0.465132000
C	0.613226000	4.711322000	-0.278654000
H	-0.876465000	5.885345000	-1.299904000
H	1.870904000	3.328175000	0.796067000
H	1.426827000	5.385977000	-0.525398000
C	-4.215861000	-1.034981000	0.594733000
C	-4.698936000	-1.682817000	1.727288000
C	-4.185857000	-1.672937000	-0.641485000
C	-5.160495000	-2.990803000	1.617782000
C	-4.633454000	-2.986234000	-0.736073000
C	-5.124106000	-3.644381000	0.388973000
H	-5.534707000	-3.502294000	2.498786000
H	-4.601238000	-3.492460000	-1.695191000
H	-5.475700000	-4.668036000	0.308027000
H	5.933629000	0.509865000	-1.284321000
H	4.802380000	-2.327908000	1.741758000
H	8.228166000	0.186927000	2.327471000
Au	-0.961976000	-0.293514000	-0.565561000
H	-4.691365000	-1.174615000	2.686842000
H	-3.810728000	-1.147093000	-1.513071000
H	-2.725526000	4.306814000	-0.788291000
H	0.013752000	1.798986000	1.369945000

$[PhP_4{\cdot}(AuNHC^{Ph})_2]^+$

E: -3243.95399755 a.u.

ZPE: 0.577794 a.u.

G: -3243.460129 a.u.

SPE: -3244.50716908 a.u.

Cartesian coordinates:

P	-1.009625000	-2.807592000	-0.764312000
P	-1.090535000	-2.469094000	1.409008000
P	-0.108108000	-0.985148000	0.100241000
P	-2.860500000	-1.948284000	0.145309000
C	-3.950805000	-3.415413000	0.356250000
C	-4.338147000	-4.190531000	-0.742589000
C	-4.541866000	-3.657764000	1.602525000
C	-5.287546000	-5.197947000	-0.593522000
C	-5.491222000	-4.664339000	1.749043000
C	-5.866179000	-5.434996000	0.650584000
H	-5.575406000	-5.798384000	-1.451153000
H	-5.937835000	-4.848204000	2.721458000
C	6.095288000	0.752304000	0.766815000
C	6.474575000	-0.384065000	0.137939000

H	6.668196000	1.584420000	1.143509000
H	7.448898000	-0.761497000	-0.128173000
N	5.317063000	-1.096757000	-0.128497000
N	4.715334000	0.709000000	0.863026000
C	4.229113000	-0.430693000	0.315882000
C	5.280133000	-2.372759000	-0.779618000
C	5.861673000	-2.508762000	-2.035706000
C	4.667230000	-3.448466000	-0.144097000
C	5.824074000	-3.747778000	-2.667677000
C	4.622454000	-4.678374000	-0.791936000
C	5.201164000	-4.829516000	-2.049894000
H	6.274293000	-3.863896000	-3.647989000
H	4.143671000	-5.522181000	-0.306246000
H	5.168348000	-5.792580000	-2.548650000
C	3.899879000	1.696669000	1.508003000
C	4.129631000	1.985273000	2.848905000
C	2.867962000	2.311030000	0.803414000
C	3.302150000	2.897171000	3.496911000
C	2.028641000	3.198674000	1.467983000
C	2.246265000	3.493485000	2.811655000
H	3.471858000	3.123462000	4.544409000
H	1.207455000	3.659120000	0.929282000
H	1.591396000	4.188686000	3.327106000
H	-3.896947000	-4.010876000	-1.719722000
H	-4.259303000	-3.057433000	2.464121000
H	-6.607993000	-6.219362000	0.764441000
Au	2.229211000	-0.890781000	0.199962000
Au	-1.365814000	0.996264000	-0.239537000
C	-2.503097000	2.670247000	-0.589541000
N	-3.855281000	2.677627000	-0.567086000
N	-2.155850000	3.938398000	-0.914794000
C	-4.352929000	3.931638000	-0.872265000
C	-4.664386000	1.530264000	-0.255756000
C	-3.282535000	4.728322000	-1.090365000
C	-0.816783000	4.423079000	-1.054904000
H	-5.411861000	4.130958000	-0.908334000
C	-4.883726000	1.195797000	1.075510000
C	-5.193371000	0.770889000	-1.293023000
H	-3.211903000	5.766248000	-1.373526000
C	0.081265000	3.762230000	-1.889101000
C	-0.444647000	5.575316000	-0.367422000
C	-5.650411000	0.072778000	1.371618000
C	-5.959933000	-0.349431000	-0.985885000
C	1.373368000	4.261906000	-2.023458000
C	0.844974000	6.075235000	-0.522648000
C	-6.189006000	-0.697543000	0.343392000
H	-5.824499000	-0.200487000	2.407230000

H	-6.369893000	-0.957223000	-1.785688000
C	1.755569000	5.417561000	-1.345861000
H	2.075798000	3.753715000	-2.676371000
H	1.139189000	6.973980000	0.009187000
H	-6.771062000	-1.582956000	0.577986000
H	2.761160000	5.808125000	-1.461925000
H	4.929882000	1.481946000	3.382982000
H	2.715685000	2.092175000	-0.248397000
H	6.321823000	-1.651233000	-2.517363000
H	4.238127000	-3.322034000	0.844753000
H	-4.447049000	1.802446000	1.862472000
H	-4.991673000	1.047297000	-2.323118000
H	-0.234389000	2.879275000	-2.434952000
H	-1.154563000	6.068261000	0.289909000

P_4

E: -1365.34816032 a.u.

ZPE: 0.006142 a.u.

G: -1365.370773 a.u.

SPE: -1365.46680502 a.u.

Cartesian coordinates:

P	0.449185000	-0.634581000	1.100106000
P	0.449185000	1.270421000	0.000000000
P	0.449185000	-0.634581000	-1.100106000
P	-1.347556000	-0.001259000	0.000000000

AIM analyses: Figure S2 shows the computed (ZORA-BP86-D3/TZ2P) bond paths and critical points (NHC ligands omitted) for **1a**$^+$ and **1b**$^+$.

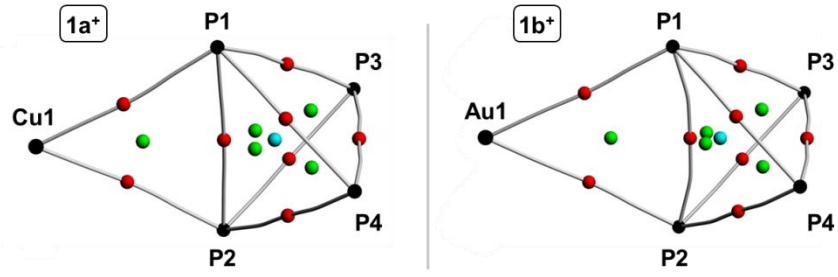


Figure S2. Computed AIM bond paths (NHC ligands omitted); bond critical points (BCP) in red, ring critical points (RCP) in green and cage critical points (CCP) in blue.

ETS-NOCV analyses: Table S1 summarizes the results obtained from the ETS-NOCV analyses of the P_4-M^+ bonds in **1a**$^+$ and **1b**$^+$.

Table S1 ETS-NOCV results using ZORA-BP86-D3/TZ2P (kcal mol^{-1})

	1a$^+$ ([IPrCu(η^2-P_4)]$^+$)	**1b**$^+$ ([IPrAu(η^2-P_4)]$^+$)
ΔE_{total}	–54.8	–56.0
ΔE_{Pauli}	84.8	130.2
ΔE_{elstat}	–69.8	–102.8
ΔE_{orb}	–59.6	–75.0
σ	**–25.9**	**–36.7**
$\pi^{\parallel}$	**–15.1**	**–16.1**
$\pi^{\perp}$	**–5.6**	**–5.3**

3. X-ray Structure Determinations

X-ray crystal structure determination of 1b

$[C_{27}H_{36}AuN_2P_4][C_{16}AlF_{36}O_4] \cdot 0.5CH_2Cl_2$, Fw = 1719.03, colourless plate, 0.64 × 0.26 × 0.09 mm^3, monoclinic, $P2_1/n$ (no. 14), a = 10.7137(3), b = 38.3822(15), c = 14.7478(4) Å, β = 90.909(1) °, V = 6063.8(3) $Å^3$, Z = 4, D_x = 1.883 g/cm^3, μ = 2.74 mm^{-1}. The crystal appeared to be cracked into two fragments. Consequently, two orientation matrices were used for the integration with the Eval15 software[13]. 134937 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. Multiscan absorption correction and scaling was performed with TWINABS[14] (correction range 0.26-0.43). 14091 Reflections were unique (R_{int} = 0.042), of which 12651 were observed [I>2σ(I)]. The structure was solved with Patterson overlay methods using SHELXT.[15] Least-squares refinement was performed with SHELXL-2014[16] against F^2 of all reflections using a HKLF-5 reflection file[17]. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and subsequently refined with a riding model. The aluminate anion was refined with a disorder model. The CH_2Cl_2 solvent molecule was disordered on an inversion center. 1049 Parameters were refined with 4893 restraints (distances, angles and displacement parameters of the disordered groups). R1/wR2 [I > 2σ(I)]: 0.0485 / 0.1210. R1/wR2 [all refl.]: 0.0540 / 0.1230. S = 1.184. Batch scale factors of the second crystal fragment BASF = 0.0532(10). Residual electron density between -1.18 and 1.93 e/$Å^3$. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[18]

X-ray crystal structure determination of 3

$[C_{78}H_{97}Au_2N_4P_4][C_{16}AlF_{36}O_4]$ + disordered solvent, Fw = 2575.54[*], colourless block, 0.33 × 0.27 × 0.21 mm^3, monoclinic, C2/c (no. 15), a = 39.9091(8), b = 25.1072(6), c = 22.5843(8) Å, β = 100.380(1) °, V = 22259.3(8) $Å^3$, Z = 8, D_x = 1.537 g/cm^3 [*], μ = 2.81 mm^{-1}[*]. 195550 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. The Eval15 software[13] was used for the integration of the intensities. Multiscan absorption correction and scaling was performed with SADABS[14] (correction range 0.36-0.43). 25563 Reflections were unique (R_{int} = 0.023), of which 22676 were observed [I>2σ(I)]. The structure was solved with Patterson overlay methods using SHELXT.[15] Least-squares refinement was performed with SHELXL-2014[16] against F^2 of all reflections. The crystal structure contains large voids (1944 $Å^3$ / unit cell), filled with severely disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the Squeeze routine[19] resulting in 351 electrons / unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a

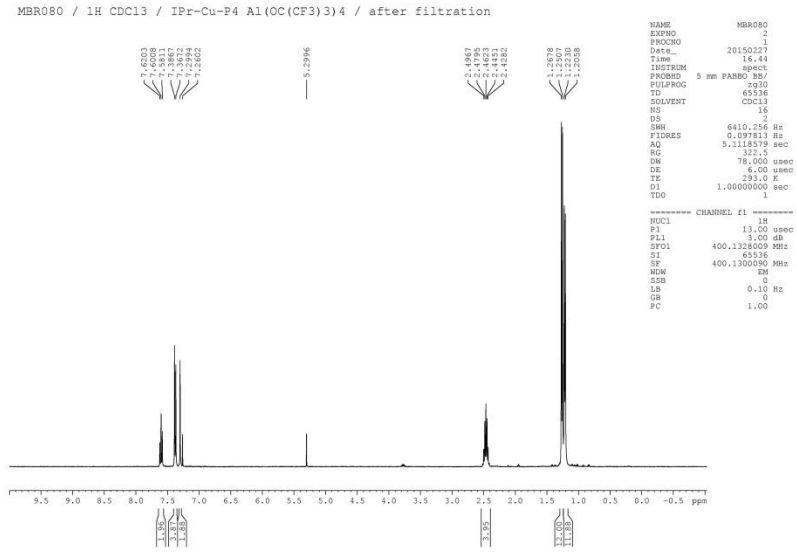
riding model. The aluminate anion was refined with a disorder model. 1622 Parameters were refined with 5625 restraints (distances, angles and displacement parameters in the disordered groups). R1/wR2 [$I > 2\sigma(I)$]: 0.0272 / 0.0690. R1/wR2 [all refl.]: 0.0323 / 0.0719. S = 1.034. Residual electron density between -1.01 and 1.53 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[18]

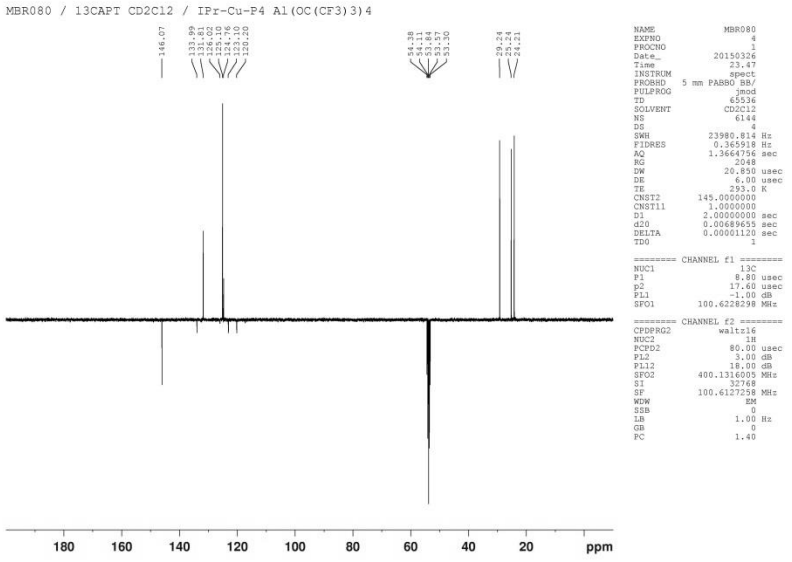
[*] Derived values do not contain the contribution of the disordered solvent molecules.

CCDC 1440355 and 1440356 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

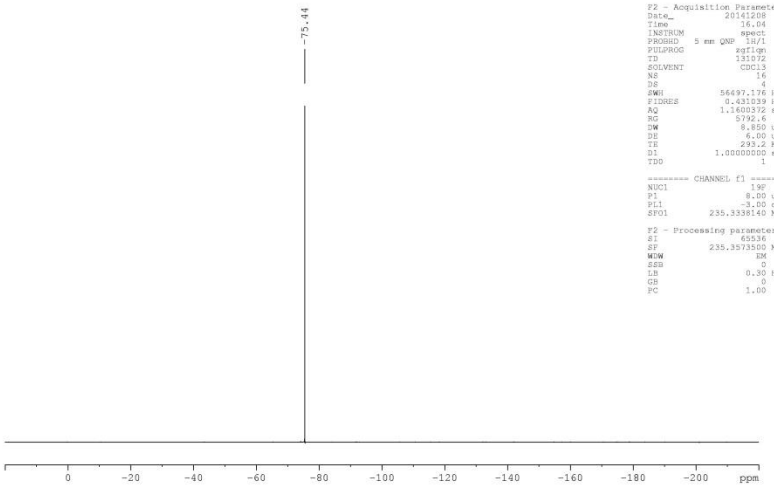
4. NMR Spectra

[IPrCu(η^2–P_4)][Al(OC(CF_3)$_3$)$_4$] (1a)





MBR048 / 19F CDCl3 / IPr-Cu-P4 aluminate / after filtration
F19_NO_processing CDCl3 {D:\NMRDATA} JaapBorger 39

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EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_              20141208
Time                  16.04
INSTRUM               spect
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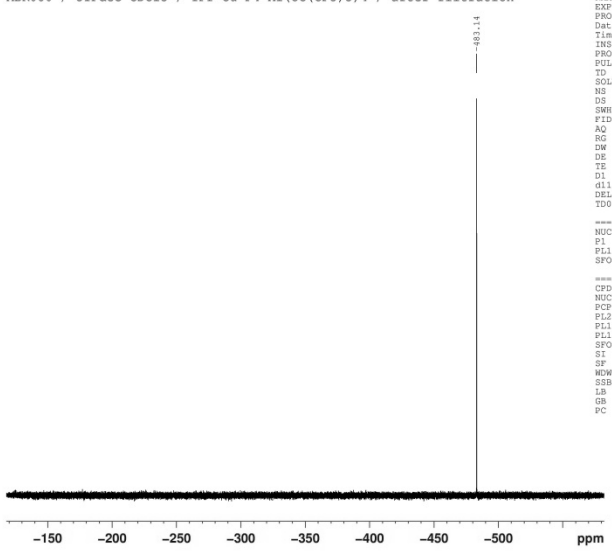
PULPROG             zgflqn
TD                  131072
SOLVENT               CDCl3
NS                       16
DS                        4
SWH               56497.176 Hz
FIDRES                0.431039 Hz
AQ                1.1600372 sec
RG                    5792.6
DW                    8.850 usec
DE                    6.00 usec
TE                   293.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      19F
P1                       8.00 usec
PL1                     -3.00 dB
SFO1           235.3338140 MHz

F2 - Processing parameters
SI                        65536
SF                235.3573500 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                         1.00
```

MBR080 / 31Pdec CDCl3 / IPr-Cu-P4 Al(OC(CF3)3)4 / after filtration

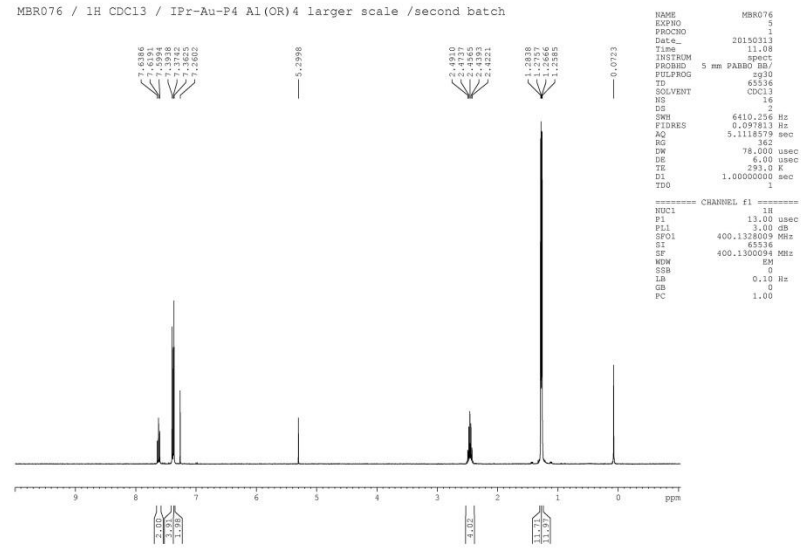



```
NAME                  MBR080
EXPNO                      1
PROCNO                     1
Date_              20150227
Time                  16.39
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       27
DS                        4
SWH               75187.969 Hz
FIDRES                1.147277 Hz
AQ                0.4358644 sec
RG                    9195.2
DW                    6.650 usec
DE                    6.00 usec
TE                   293.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      31P
P1                       6.25 usec
PL1                     -1.00 dB
SFO1           161.9189015 MHz

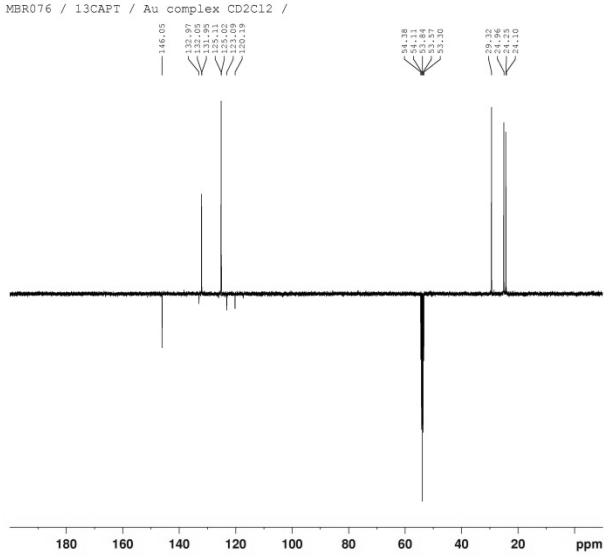
======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                   80.00 usec
PL2                      3.00 dB
PL12                    18.00 dB
PL13                    18.00 dB
SFO2           400.1316005 MHz
SI                        65536
SF                161.9755930 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                         1.40
```

$[IPrAu(\eta^2\text{–}P_4)][Al(OC(CF_3)_3)_4]$ (1b)




```
NAME                MBR076
EXPNO                    5
PROCNO                   1
Date_             20150313
Time                 11.08
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6410.256 Hz
FIDRES            0.097813 Hz
AQ                5.1118579 sec
RG                     362
DW                78.000 usec
DE                 6.00 usec
TE                 293.0 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                 3.00 dB
SFO1          400.1328009 MHz
SI                   65536
SF            400.1300094 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.00
```

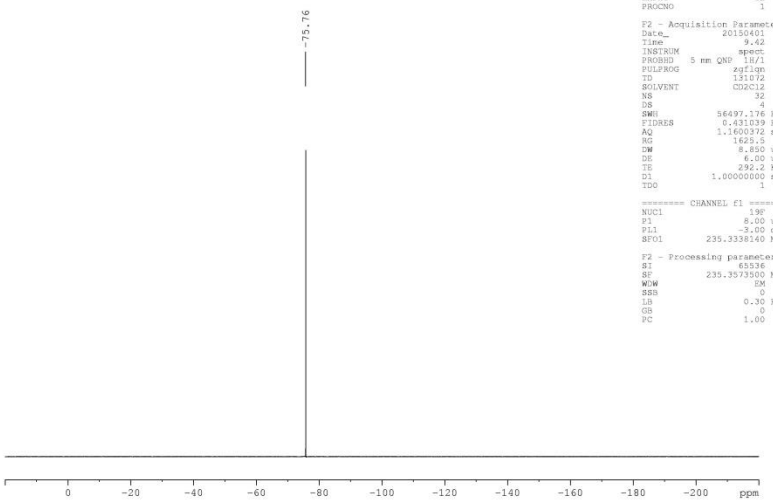



```
NAME                MBR076
EXPNO                    9
PROCNO                   1
Date_             20150331
Time                 23.37
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             jmod
TD                  65536
SOLVENT             CD2Cl2
NS                    6144
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                    16384
DW                20.850 usec
DE                 6.00 usec
TE                 290.9 K
CNST2         145.0000000
CNST11          1.0000000
D1                2.00000000 sec
d20               0.00689655 sec
DELTA             0.00001120 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.80 usec
p2                 17.60 usec
PL1                -1.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               18.00 dB
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127272 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```

MBR076 / 19F / Au complex in CD2Cl2
F19_NO_processing CD2Cl2 {D:\NMRDATA} JaapBorger 15



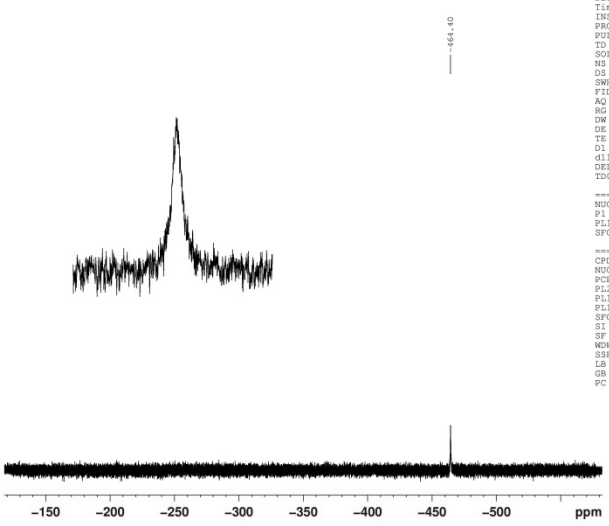

```
Current Data Parameters
NAME                 MBR076
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150401
Time                   9.42
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG             zgflqn
TD                  131072
SOLVENT              CD2Cl2
NS                       32
DS                        4
SWH               56497.176 Hz
FIDRES                0.431039 Hz
AQ                    1.1600372 sec
RG                    1625.5
DW                    8.850 usec
DE                    6.00 usec
TE                    292.2 K
D1                    1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    19F
P1                    8.00 usec
PL1                   -3.00 dB
SFO1             235.3338140 MHz

F2 - Processing parameters
SI                    65536
SF                235.3573500 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

MBR076 / 31Pdec CDCl3 / IPr-Au-P4 Al(OR)4 larger scale / 2nd batch after wash

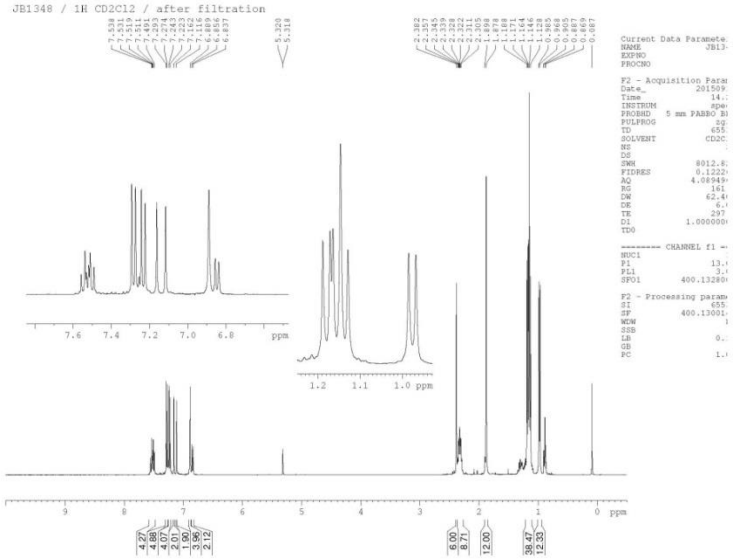


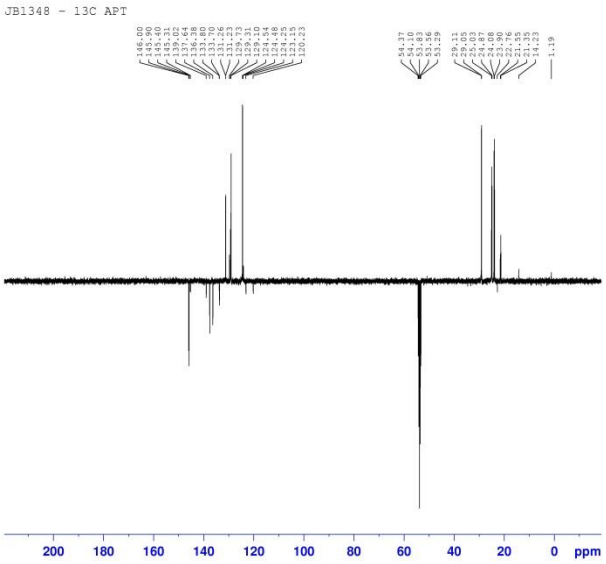

```
NAME                 MBR076
EXPNO                     6
PROCNO                    1
Date_              20150313
Time                  15.22
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       49
DS                        4
SWH               75187.969 Hz
FIDRES                1.147277 Hz
AQ                    0.4358644 sec
RG                    4096
DW                    6.650 usec
DE                    6.00 usec
TE                    293.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    31P
P1                    6.25 usec
PL1                   -1.00 dB
SFO1             161.9189015 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2             400.1316005 MHz
SI                    65536
SF               161.9755930 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

$[DmpP_4{\cdot}(IPrAu)_2][Al(OC(CF_3)_3)_4]$ (3)



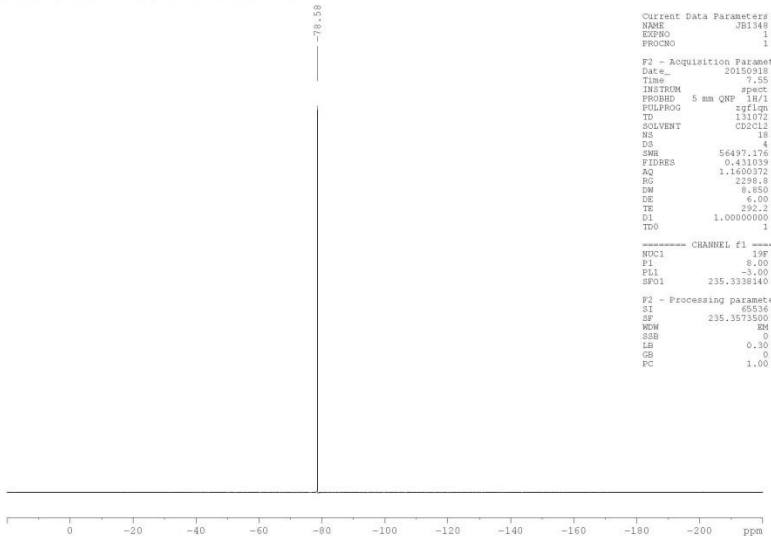



```
NAME                JB1348
EXPNO                    8
PROCNO                   1
Date_             20150917
Time                 21.04
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              jmod
TD                  65536
SOLVENT             CD2Cl2
NS                    3584
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                20.850 usec
DE                 6.00 usec
TE                297.2 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
d20               0.00689655 sec
DELTA             0.00001120 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                    8.80 usec
p2                   17.60 usec
PL1                  -1.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 18.00 dB
SFO2           400.1316005 MHz
SI                    32768
SF             100.6127238 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

JB1348 / 19F CD2Cl2 / after filtration



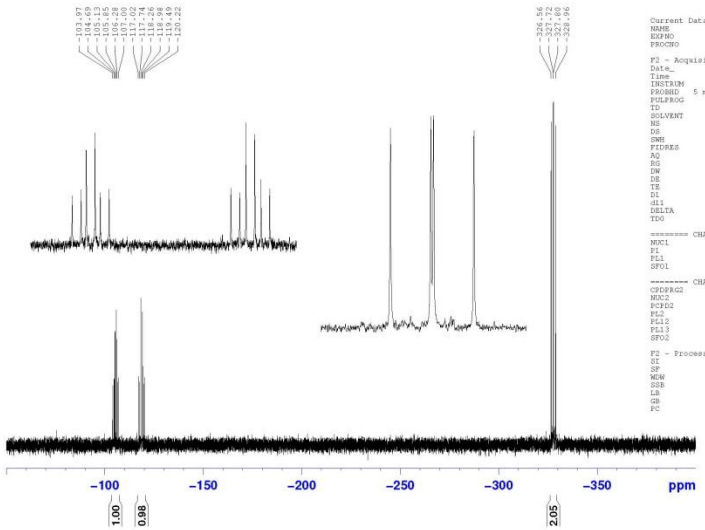

```
Current Data Parameters
NAME                  JB1348
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150918
Time                   7.55
INSTRUM               spect
PROBHD   5 mm QNP  1H/1
PULPROG             zgflqn
TD                  131072
SOLVENT             CD2Cl2
NS                      18
DS                       4
SWH              56497.176 Hz
FIDRES           0.431039 Hz
AQ               1.1600372 sec
RG                  2298.8
DW                  8.850 usec
DE                  6.00 usec
TE                  292.2 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                   19F
P1                  8.00 usec
PL1                -3.00 dB
SFO1          235.3338140 MHz

F2 - Processing parameters
SI                     65536
SF               235.3573500 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                      1.00
```

JB1348 / 31Pdec CD2Cl2 / after filtration




```
Current Data Parameters
NAME                  JB1348
EXPNO                      6
PROCNO                     1

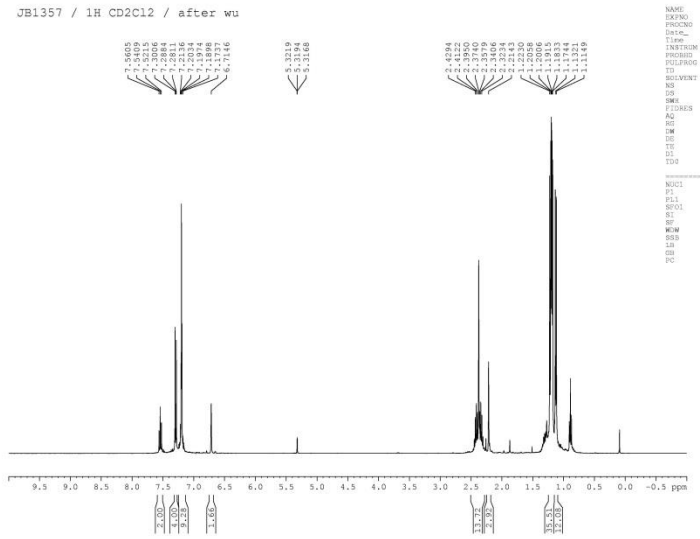
F2 - Acquisition Parameters
Date_              20150917
Time                  14.40
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT             CD2Cl2
NS                      256
DS                        4
SWH              75187.969 Hz
FIDRES           1.147277 Hz
AQ               0.4358644 sec
RG                     6502
DW                 6.650 usec
DE                  6.00 usec
TE                  297.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                   31P
P1                  6.25 usec
PL1                -1.00 dB
SFO1          161.9350991 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2          400.1316005 MHz

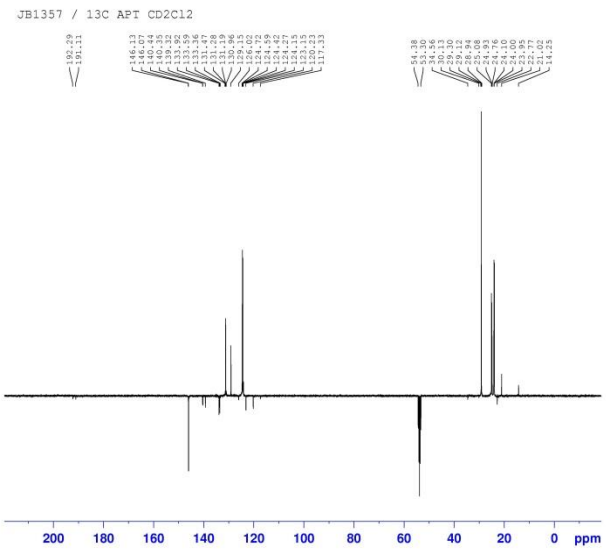
F2 - Processing parameters
SI                     65536
SF               161.9755930 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                      1.40
```

$[MesP_4{\cdot}(IPrAu)_2][Al(OC(CF_3)_3)_4]$ (4)




```
NAME                JB1357
EXPNO                    2
PROCNO                   1
Date_           20151104
Time                15.36
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                  65536
SOLVENT             CD2Cl2
NS                      17
DS                       2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                    71.8
DW                62.400 usec
DE                 6.00 usec
TE                293.0 K
D1             1.00000000 sec
TD0                      1

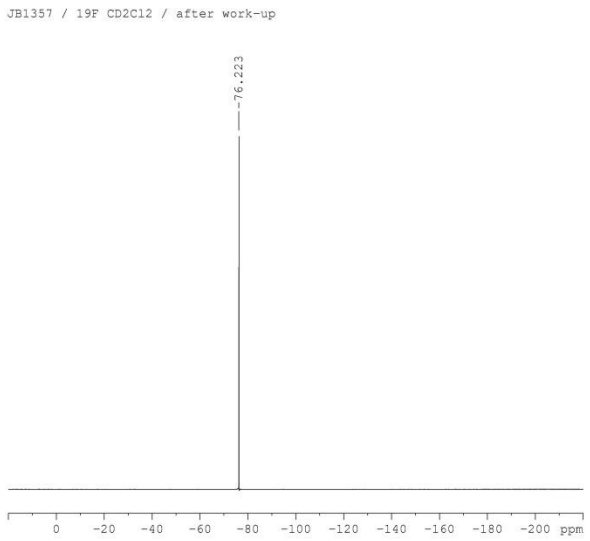
======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                 3.00 dB
SFO1         400.1328009 MHz
SI                   65536
SF           400.1300153 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
```




```
NAME                JB1357
EXPNO                    4
PROCNO                   1
Date_           20151104
Time                22.11
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             jmod
TD                  65536
SOLVENT             CD2Cl2
NS                    4608
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                  2896.3
DW                20.850 usec
DE                 6.00 usec
TE                294.1 K
CNST2          145.0000000
CNST11           1.0000000
D1               2.00000000 sec
d20              0.00689655 sec
DELTA            0.00001120 sec
TD0                      1

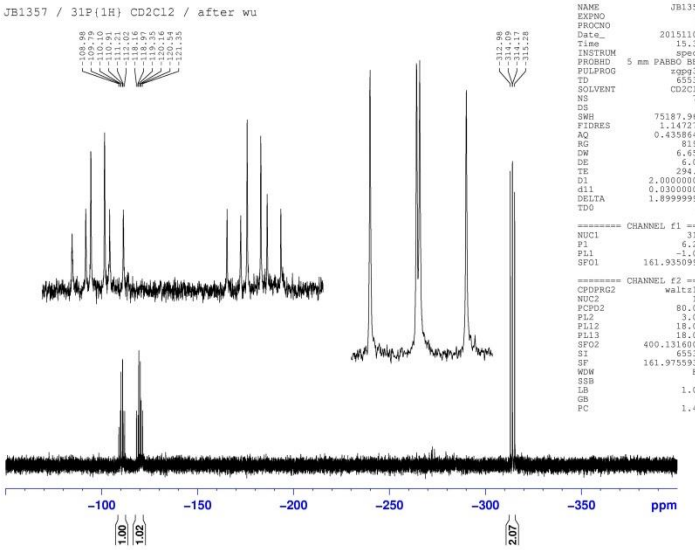
======== CHANNEL f1 ========
NUC1                   13C
P1                  8.80 usec
p2                 17.60 usec
PL1                -1.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               18.00 dB
SFO2          400.1316005 MHz
SI                   32768
SF           100.6127244 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```




```
NAME          JB1357_19F
EXPNO                  1
PROCNO                 1
Date_           20151104
Time               16.03
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG         zgflqn
TD              131072
SOLVENT           CD2Cl2
NS                    18
DS                     4
SWH           56497.176 H
FIDRES         0.431039 H
AQ            1.1600372 s
RG               1149.4
DW                8.850 u
DE                6.00 u
TE               293.2 K
D1           1.00000000 s
TD0                    1

========= CHANNEL f1 ======
NUC1                 19F
P1                  8.00 u
PL1                -3.00 d
SFO1        235.3338140 M
SI                 65536
SF          235.3573500 M
WDW                   EM
SSB                    0
LB                  0.30 H
GB                     0
PC                  1.00
```




```
NAME              JB1357
EXPNO                  1
PROCNO                 1
Date_           20151104
Time               15.31
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD2Cl2
NS                    75
DS                     4
SWH           75187.969 Hz
FIDRES         1.147277 Hz
AQ            0.4358644 sec
RG                  8192
DW                6.650 usec
DE                6.00 usec
TE                294.1 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 31P
P1                  6.25 usec
PL1                -1.00 dB
SFO1        161.9350991 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2        400.1316005 MHz
SI                 65536
SF          161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

5. References

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