Mono- and Diylide-substituted Phosphines (YPhos): Impact of the Ligand Properties on the Catalytic Activity in Gold(I)-catalyzed Hydroaminations

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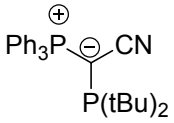
1. Experimental Details

1.1 General methods

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried using an MBraun SPS-800 (THF, toluene, Et_2O, DCM, pentane, hexane) or dried in accordance with standard procedures. H_2O is distilled water. ^{1}H, $^{13}C\{^{1}H\}$, $^{13}C\{^{31}P, ^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were recorded on Avance-400 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (*J*) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, br = broad signal. Signal assignment was supported by DEPT, APT, HSQC and HMBC experiments and by literature studies on similar compounds.[1] Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. IR-Spectra were recorded on a Thermo Nicolet iS5 FT-IR in transmission mode with a Specac "Omni-cell" with KBr plates and a 0.1 mm spacer or with a ATR module at 22 °C. (**Y-K**)[2], (**Y-Na**)[2], dhlorodi(*tert*butyl)phosphine[3], dichloro(*tert*butyl)phosphine[3], dichlorocyclohexylphosphine[3], (**$Y_{CN}PCl_2$**)[4], (**$Y_{CN}PPhCl$**)[4], and (THT)AuCl[5] and were prepared according to published procedures. All other reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification.

1.2 Preparation of the Y_{CN}Phos ligands

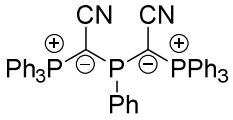
1.2.1 Preparation of $Y_{CN}P^tBu_2$



506 mg (1.37 mmol) sodium yldiide **Y-Na** were dissolved in 15 mL toluene and 0.261 mL (1.37 mmol) of chloro(di-*tert*-butyl)phosphine were added dropwise to the yellow solution. The solution was stirred overnight and filtered to remove the formed NaCl. The solution was concentrated to 8 mL and then overlayered with of 15 mL hexane. Upon standing for 16 h, the product precipitated. The solvent was removed via syringe from the resulting white solid, which was dried *in vacuo* thus giving the product as a colorless solid (281 mg, 631 µmol, 46 %). Single crystals suitable for X-ray diffraction analysis could be obtained by slow diffusion of pentane into a benzene solution.

^{1}H NMR (400.3 MHz, THF-d_8) δ = 7.8 – 7.7 (m, 6H; CH_{PPh3}), 7.6 – 7.6 (m, 3H; CH_{PPh3}), 7.6 – 7.5 (m, 6H; CH_{PPh3}), 1.2 (d, $^{3}J_{HP}$ = 11.6, 18H; C(CH_3)$_3$). $^{13}C\{^{1}H\}$ NMR (100.7 MHz, THF-d_8) δ = 135.1 (dd, $^{2}J_{CP}$ = 8.9, $^{4}J_{CP}$ = 2.5; *C*H$_{PPh3, ortho}$), 132.9 (d, $^{4}J_{CP}$ = 2.9; *C*H$_{PPh3, para}$), 129.1 (d, $^{3}J_{CP}$ = 11.9; *C*H$_{PPh3, meta}$), 128.4 (dd, $^{1}J_{CP}$ = 90.0, $^{3}J_{CP}$ = 3.2; *C*H$_{PPh3, ipso}$), 127.1 (d, $^{2}J_{CP}$ = 12.1; C*C*N), 35.2 (dd, $^{1}J_{CP}$ = 22.2, $^{3}J_{CP}$ = 7.3; PCP*C*(CH$_3$)$_3$), 30.9 (d, $^{2}J_{CP}$ = 15.8 Hz; PCPC(*C*H$_3$)$_3$), 4.5 (dd, $^{1}J_{CP}$ = 130.2, $^{3}J_{CP}$ = 43.3; P*C*P). $^{31}P\{^{1}H\}$ NMR (162.1 MHz, THF-d_8) δ = 29.0 (d, $^{2}J_{PP}$ = 149.6; *P*Ph$_3$), 17.0 (d, $^{2}J_{PP}$ = 149.7; *P*tBu). Anal. Calcd. for $C_{28}H_{33}NP_2$: C, 75.49; H, 7.47; N, 3.14. Found: C, 75.15; C, 7.27; N, 2.89. FT-IR (KBr, ATR, cm^{-1}): ṽ = 3060 (w; $\nu_{as, s}$ (CH$_3$)), 2855 (w), 2126 (m; ν_{as}(CN)), 1587 (w), 1482 (w), 1435 (s), 1100 (s)

1.2.2 Preparation of $(Y_{CN})_2$PPh



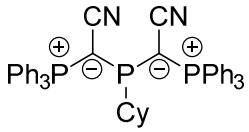
0.513 g (1.51 mmol, 2.05 eq) potassium yldiide **Y-K** were dissolved in 20 mL THF and 0.100 mL (132 mg, 0.737 mmol, 1.00 eq) dichlorophenylphosphine were added dropwise to the yellow solution within a period of 15 min. The resulting solution was stirred overnight upon which a solid formed. The solid was allowed to settle, the supernatant solvent was removed via syringe and the solid was washed 3 times with 5 mL THF. The solid was dissolved in 5 mL DCM, filtered through a filter canula and covered with a layer of 15 mL pentane. Upon standing for 16 h the product precipitated. The

supernatant solvent was removed via syringe from the resulting white solid which was dried in vacuo giving the product as a colorless solid (372 mg, 525 µmol, 71 %).

Alternative route: 1.00 g (2.95 mmol, 1.05 eq) potassium yldiide **Y-K** and 1.24 g (2.79 mmol, 1.00 eq) 2-(chloro(phenyl)phosphanyl)-2-(triphenyl-l5-phosphanylidene)acetonitrile **Y_{CN}PClPh** were dissolved in 20 mL THF. The solution was stirred overnight upon which a solid formed. The solid was allowed to settle, the supernatant solvent was removed via syringe and the solid was washed with 3 times 5 mL THF each. The solid was dissolved in 15 mL DCM, filtered through filter canula and covered with a layer of 30 mL pentane. Upon standing for 16 h the product precipitated. The solvent was removed via syringe from the resulting white solid, which was dried *in vacuo*, thus giving the product as a colorless solid (766 mg, 1.08 mmol, 77 %).

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.65 – 7.48 (m, 20H; C*H*$_{PPh3, PPh}$), 7.44 – 7.35 (m, 12H; C*H*$_{PPh3}$), 7.37 – 7.28 (m, 2H; C*H*$_{PPh}$), 7.23 – 7.15 (m, 1H; C*H*$_{PPh}$). ^{13}C{^{1}H} NMR (100.7 MHz, CD_2Cl_2) δ = 144.6 (td, $^1J_{CP}$ = 11.0, $^3J_{CP}$ = 7.4; *C*$_{PPh, ipso}$), 134.3 (dd, $^2J_{CP}$ = 9.6, $^4J_{CP}$ = 2.4; *C*H$_{PPh3, ortho}$), 132.8 (d, $^4J_{CP}$ = 2.8; *C*H$_{PPh3, para}$), 131.2 (d, $^2J_{CP}$ = 18.3; *C*H$_{PPh, ortho}$), 129.1 (d, $^3J_{CP}$ = 12.3; *C*H$_{PPh3, meta}$), 128.2 (d, $^3J_{CP}$ = 4.9; *C*H$_{PPh, meta}$), 126.9 (dd, $^1J_{CP}$ = 90.8, $^3J_{CP}$ = 3.4; *C*$_{PPh3, ipso}$); 126.7 (s; *C*H$_{PPh, para}$), 125.5 (d, $^2J_{CP}$ = 12.8; C*C*N), 11.2 (ddd, $^1J_{CP}$ = 127.9, $^1J_{CP}$ = 36.2, $^3J_{CP}$ = 7.0; P*C*P). ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2) δ = 26.7 (d, $^2J_{PP}$ = 160.0; *P*Ph_3), -26.4 (dd, $^2J_{PP}$ = 160.2; *P*Ph). Anal. Calcd. for $C_{47}H_{37}Cl_2N_2P_3$: C, 71.13; H, 4.70; N, 3.53. Found: C, 71.07; H, 4.47; N, 3.71. FT-IR (KBr, ATR, cm^{-1}): ṽ = 3054 (w; ν_s (CH)), 2134 (s; ν_{as}(CN)), 1587 (w), 1481 (w; δ_s (CH_2)), 1435 (s), 1267 (s), 1099 (s).

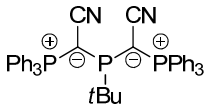
1.2.3 Preparation of $(Y_{CN})_2$PCy



1.36 g (4.00 mmol, 2.05 eq) potassium yldiide **Y-K** were dissolved in 20 mL THF and 0.300 mL (361 mg, 1.95 mmol, 1.00 eq) dichlorocyclohexylphosphine were added dropwise to the yellow solution within 8 min. The solution was stirred overnight upon which a solid formed. The solid was allowed to settle, the supernatant solvent was removed via syringe. The solid was dissolved in 115 mL DCM, filtered through filter canula and covered with a layer of 100 mL pentane Upon standing for 16 h the product precipitated. The solvent was removed via syringe from the solid, which was dried *in vacuo* thus giving the product as a colorless solid (1.02 g, 1.43 mmol, 73 %).

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.61 – 7.51 (m, 6H), 7.51 – 7.41 (m, 11H), 7.39 – 7.26 (m, 12H), 2.47 – 2.28 (m, 1H), 2.04 – 1.82 (m, 2H), 1.67 – 1.42 (m, 3H), 1.39 – 1.23 (m, 2H), 1.09 – 0.94 (m, 1H), 0.78 – 0.64 (m, 2H). ^{13}C{^{1}H} NMR (100.7 MHz, CD_2Cl_2) δ = 134.4 (dd, $^2J_{CP}$ = 9.6, 2.5; *C*H$_{PPh3, ortho}$), 132.5 (d, $^4J_{CP}$ = 2.7; *C*H$_{PPh3, para}$), 128.9 (d, $^3J_{CP}$ = 12.3; *C*H$_{PPh3, meta}$), 127.4 (dd, $^1J_{CP}$ = 90.4, $^3J_{CP}$ = 2.5; *C*$_{PPh3, ipso}$), 125.7 (d, $^2J_{CP}$ = 13.0; C*C*N), 37.5 (td, $^1J_{CP}$ = 8.9, $^3J_{CP}$ = 2.2; *C*H$_{, Cy-1}$), 30.4 (d, $^2J_{CP}$ = 18.3; *C*H$_{2, Cy-2}$), 27.2 (d, $^3J_{CP}$ = 7.7; *C*H$_{2, Cy-3}$), 27.1 (s; *C*H$_{2, Cy-4}$), 9.1 (ddd, $^1J_{CP}$ = 127.6, $^1J_{CP}$ = 43.1, $^3J_{CP}$ = 5.9). ^{31}P{^{1}H} NMR (162.2 MHz, CD_2Cl_2) δ = 26.0 (d, $^2J_{PP}$ =140.8; *P*Ph_3), -31.2 (t, $^2J_{PP}$ =140.5; *P*Cy). Anal. Calcd. for $C_{47.5}H_{44}Cl_3N_2P_3$: C, 67.75; H, 5.42; N, 3.50. Found: C, 67.84; H, 5.250; N, 3.36. FT-IR (KBr, ATR, cm^{-1}): ṽ = 3054 (w; ν_s (CH)), 2921 (m; ν_s (CH_2)), 2847 (m; ν_s (CH_2)), 2131 (s; ν_{as}(CN)), 1586 (w), 1481 (w; δ_s (CH_2)), 1435 (s), 1263 (m), 1098 (s).

1.2.4 Preparation of $(Y_{CN})_2P^tBu$

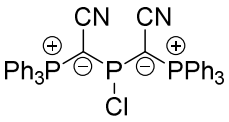


500 mg (1.47 mmol) potassium yldiide **Y-K** were dissolved in 5 mL dry THF and a solution of 114 mg (719 µmol) dichloro-*tert*-butylphosphine in 25 mL dry THF was added dropwise. The solution was stirred overnight. The solution was transferred to a centrifuge flask and was centrifuged at 2000 rpm for 20 min. The supernatant solvent was removed via syringe from the settled solid and the solid was washed with 30 mL THF and again centrifuged. The solid was extracted 3 time with 30 mL DCM and filtered through filter canula. The combined solutions were covered with a layer of 30 mL pentane. Upon standing for 16 h the product

precipitated. The solvent was removed *in vacuo* thus giving the product as a white solid. (320 mg, 464 µmol, 64 %)

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.60 – 7.53 (m, 6H; C*H*$_{PPh3}$), 7.52 – 7.45 (m, 12H; C*H*$_{PPh3}$), 7.41 – 7.34 (m, 12H; C*H*$_{PPh3}$) 0.93 (d, $^{3}J_{HP}$ = 13.9 Hz, 9H; C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (100.7 MHz, CD_2Cl_2) δ = 134.6 (dd, $^{2}J_{CP}$ = 9.3, $^{4}J_{CP}$ = 2.5; *C*H$_{PPh3, ortho}$), 132.6 (d, $^{4}J_{CP}$ = 2.7; *C*H$_{PPh3, para}$), 128.9 (d, $^{3}J_{CP}$ = 12.2; *C*H$_{PPh3, meta}$), 127.5 (dd, $^{1}J_{CP}$ = 90.3, $^{3}J_{CP}$ = 3.5; *C*H$_{PPh3, ipso}$), 127.1 (d, $^{2}J_{CP}$ = 12.8; C*C*N), 36.7 (dd, $^{1}J_{CP}$ = 17.6, $^{3}J_{CP}$ = 9.8; PCP*C*(CH$_3$)$_3$), 28.5 (d, $^{2}J_{CP}$ = 16.7 Hz; PCPC(*C*H$_3$)$_3$), 7.7 (ddd, $^{1}J_{CP}$ = 125.3, $^{1}J_{CP}$ = 41.7, $^{3}J_{CP}$ = 8.3; P*C*P). ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2) δ = 27.9 (d, $^{2}J_{PP}$ = 161.2; *P*Ph$_3$), -24.4 (t, $^{2}J_{PP}$ = 161.2; *P*tBu). Anal. Calcd. for $C_{28}H_{33}AuClNP_2$: C, 49.61; H, 4.91; N, 2.07. Found: C, 49.27; H, 4.73; N, 2.07. FT-IR (KBr, ATR, cm^{-1}): ṽ = 3048 (w; $\nu_{as, s}$ (CH$_3$)), 2851 (w), 2128 (s; ν_{as}(CN)), 1587 (w), 1481 (w), 1436 (s), 1103 (s)

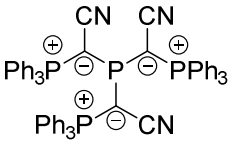
1.2.5 Preparation of $(Y_{CN})_2PCl$



203 mg (597 µmol) potassium yldiide **Y-K** and 240 mg (597 µmol) 2-(dichlorophosphanyl)-2-(triphenyl-l5-phosphanylidene)acetonitrile $\mathbf{Y_{CN}PCl_2}$ were dissolved in 25 mL THF. The solution was stirred overnight, upon which a solid formed. The supernatant solvent was then removed via syringe, the obtained solid dissolved in 15 mL DCM and was filtered through s filter canula. The solution was overlayered with of 25 mL pentane. Upon standing for 16 h the product with Y-H_2Cl precipitated.

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 8.03 – 7.20 (m, 30H; C*H*$_{PPh3}$). ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2): δ = 112.4 (t, $^{2}J_{PP}$ = 167.9 Hz; *P*Cl), 24.8 (d, $^{2}J_{PP}$ = 168.2 Hz; *P*Ph$_3$)

1.2.6 Preparation of $(Y_{CN})_3P$

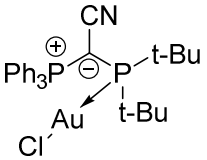


230 mg (345 µmol) of $(Y_{CN})_2PCl$ (with impurities of phosphonium salt) and 117 mg (345 µmol) potassium yldiide **Y-K** were dissolved in 10 mL THF. The solution was stirred overnight, upon which a solid formed. The supernatant solvent was then removed via syringe, the obtained solid dissolved in 4 mL DCM and was filtered through a filter canula. The solution was covered with a layer of 15 mL pentane. Upon standing for 16 h the product with Y-H_2Cl precipitated. Single yellow crystals suitable for x-ray diffraction could be obtained by slow diffusion of pentane into a THF solution.

^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2): = 23.0 (d, $^{2}J_{PP}$ = 154.5 Hz; *P*Ph$_3$), -33.3 – -40.8 (br, *P*(CP)$_3$)

1.3 Preparation of the metal complexes

1.3.1 Preparation of $Y_{CN}P^tBu_2$·AuCl

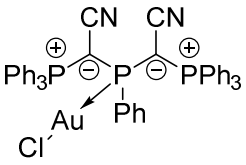


(469 mg, 1.05 mmol) of $\mathbf{Y_{CN}P^tBu_2}$ and (THT)AuCl (340 mg, 1.06 mmol) were dissolved in 2 mL dry THF and stirred overnight giving a suspension of the product complex. The supernatant solvent was removed via syringe and the solid was dissolved in 8 mL DCM and covered with a layer of 16 mL pentane. Upon standing for 16 h the product precipitated. The supernatant solvent was removed with a syringe from the solid which was dried in vacuo, thus giving the product as a colorless solid (585 mg, 863 mmol, 82 %).

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.86 – 7.77 (m, 6H; C*H*$_{PPh3}$), 7.76 – 7.67 (m, 3H; C*H*$_{PPh3, para}$), 7.63 – 7.52 (m, 6H; C*H*$_{PPh3}$), 1.46 (d, $^{3}J_{HP}$ = 16.0 Hz, 18H; C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (100.7 MHz, CD_2Cl_2) δ =

134.7 (d, $^2J_{CP}$ = 9.4; *C*H$_{PPh3, ortho}$), 133.9 (d, $^4J_{CP}$ = 3.0; *C*H$_{PPh3, para}$), 129.8 (d, $^3J_{CP}$ = 12.5; *C*H$_{PPh3, meta}$), 126.3 (d, $^2J_{CP}$ = 6.9; C*C*N), 124.8 (d, $^1J_{CP}$ = 92.4; *C*$_{PPh3, ipso}$), 40.7 (dd, $^1J_{CP}$ = 30.5, $^3J_{CP}$ = 3.0; PCP*C*(CH$_3$)$_3$), 30.9 (d, $^3J_{CP}$ = 6.2; PCPC(*C*H$_3$)$_3$), 6.8 (dd, $^1J_{CP}$ = 125.1, $^3J_{CP}$ = 55.7; P*C*P). ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2) δ = 56.1 (d, $^2J_{PP}$ = 45.5; *P*^{t}Bu), 29.4 (d, $^2J_{PP}$ = 45.9; *P*Ph$_3$). Anal. Calcd. for $C_{28}H_{33}AuClNP_2$: C, 49.61; H, 4.91; N, 2.07. Found: C, 49.27; H, 4.72; N, 2.07. FT-IR (KBr, ATR, cm^{-1}): ṽ = 2914 (m), 2846 (m), 2146 (m; ν_{as}(CN)), 1481 (w), 1434 (s), 1099 (s)

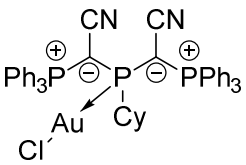
1.3.2 Preparation of $(Y_{CN})_2$PPh·AuCl



(126 mg, 178 µmol) of **$(Y_{CN})_2$PPh** and (THT)AuCl (57.0 mg, 178 µmol) were dissolved in 2 mL dry THF and stirred overnight upon which a solid formed. The solid was allowed to settle, the supernatant solvent was removed via syringe and the solid was dissolved in 7.5 mL DCM and covered with a layer of 20 mL pentane. Upon standing for 16 h the product precipitated. The supernatant solvent was removed via syringe from the solid, which was dried in vacuo thus giving the product as a colorless solid (151 mg, 160 µmol, 90 %).

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.81 – 7.71 (m, 2H; C*H*$_{PPh}$), 7.71 – 7.60 (m, 18H; C*H*$_{PPh3}$), 7.54 – 7.43 (m, 12H; C*H*$_{PPh3}$), 7.39 – 7.32 (m, 1H; C*H*$_{PPh}$), 7.32 – 7.26 (m, 2H; C*H*$_{PPh}$). ^{13}C NMR (100.7 MHz, CD_2Cl_2) δ = 138.4 (d, $^1J_{CP}$ = 66.5; *C*$_{PPh, ipso}$), 134.7 (d, $^2J_{CP}$ = 10.1; *C*H$_{PPh3, ortho}$), 133.6 (d, *J*=2.8; *C*H$_{PPh3, para}$), 133.1 (d, $^2J_{CP}$ = 15.8; *C*H$_{PPh, ortho}$), 131.0 (d, $^4J_{CP}$ = 2.7; *C*H$_{PPh, para}$), 129.5 (d, $^3J_{CP}$ = 12.8; *C*H$_{PPh3, meta}$), 128.6 (d, $^3J_{CP}$ = 12.8; *C*H$_{PPh, meta}$), 124.3 (dd, $^1J_{CP}$ = 92.4, 1.5; *C*$_{PPh3, ipso}$), 124.0 (d, $^2J_{CP}$ = 8.7; C*C*N), 11.8 (ddd, $^1J_{CP}$ = 120.9, $^1J_{CP}$ = 74.0, $^3J_{CP}$ = 7.5; P*C*P). ^{31}P NMR (162.1 MHz, CD_2Cl_2) δ = 24.4 (d, $^2J_{PP}$ = 62.5; *P*Ph$_3$), 16.5 (dd, $^2J_{PP}$ = 62.6; *P*Ph). Anal. Calcd. for $C_{47}H_{37}AuCl_3N_2P_3$: C, 55.02; H, 3.63; N, 2.73. Found: C, 55.34; H, 3.56; N, 3.11. FT-IR (KBr, ATR, cm^{-1}): ṽ =3056 (w), 2150 (m; ν_{as}(CN)), 2136 (m; ν_{as}(CN)), 1587 (w), 1481 (w), 1435 (s), 1171 (s), 1101 (s)

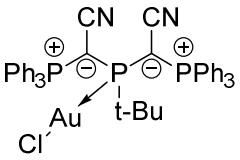
1.3.3 Preparation of $(Y_{CN})_2$PCy·AuCl



(126 mg, 178 µmol) of **$(Y_{CN})_2$PCy** and (THT)AuCl (57.0 mg, 178 µmol) were dissolved in 2 mL dry THF and stirred upon which a solid formed. The solid was allowed to settle, the supernatant solvent was removed via syringe and the solid was dissolved in 7.5 mL DCM and overlayered with of 20 mL pentane. Upon standing for 16 h the product precipitated. The supernatant solvent was removed with a syringe from the solid, which was dried in vacuo thus giving the product as a colorless solid (331 mg, 349 µmol, 83 %).

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.80 – 7.69 (m, 12H; C*H*$_{PPh3}$), 7.69 – 7.62 (m, 6H; C*H*$_{PPh3}$), 7.54 – 7.43 (m, 12H; C*H*$_{PPh3}$), 2.31 – 2.15 (m, 1H; C*H*$_{Cy}$), 2.15 – 2.00 (m, 2H; C*H*$_{2, Cy}$), 1.81 – 1.68 (m, 2H; C*H*$_{2, Cy}$), 1.68 – 1.58 (m, 1H; C*H*$_{2, Cy}$), 1.37 – 1.05 (m, 5H; C*H*$_{2, Cy}$). ^{13}C{^{1}H} NMR (100.7 MHz, CD_2Cl_2) δ = 134.2 (d, $^2J_{CP}$ = 9.9; *C*H$_{PPh3, ortho}$), 133.2 (d, $^4J_{CP}$ = 3.1; *C*H$_{PPh3, para}$), 129.2 (d, $^3J_{CP}$ = 12.6; *C*H$_{PPh3, meta}$), 124.7 (dd, $^1J_{CP}$ = 92.2, $^1J_{CP}$ = 1.0; *C*$_{PPh3, ipso}$), 124.2 (d, $^2J_{CP}$ = 8.1; C*C*N), 41.2 (d, $^1J_{CP}$ = 48.5, $^2J_{CP}$ = 3.88; *C*H$_{Cy-1}$), 30.2 (d, $^2J_{CP}$ = 3.8; *C*H$_{Cy-2}$), 26.6 (d, $^3J_{CP}$ = 16.0; *C*H$_{Cy-3}$), 25.9 (d, $^4J_{CP}$ = 1.6; *C*H$_{Cy-4}$), 11.6 (ddd, $^1J_{CP}$ = 121.9, $^1J_{CP}$ = 62.1, $^3J_{CP}$ = 3.8; P*C*P). ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2) δ = 24.4 (d, $^2J_{PP}$ = 51.3; *P*Ph$_3$), 18.5 (t, $^2J_{PP}$ = 50.9; *P*Cy). Anal. Calcd. for $C_{46}H_{41}AuClN_2P_3$: C, 58.33; H, 4.36; N, 2.96. Found: C, 58.01; H, 4.312; N, 2.91. FT-IR (KBr, ATR, cm^{-1}): ṽ = 3054 (w), 2918 (m), 2846 (m), 2140 (m; ν_{as}(CN)), 1586 (w), 1481 (w), 1434 (m), 1097 (s)

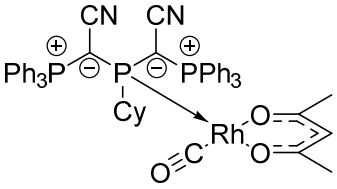
1.3.4 Preparation of $(Y_{CN})_2P^tBu{\cdot}AuCl$



(83.0 mg, 113 µmol) of **$(Y_{CN})_2P^tBu$** and (THT)AuCl (36.2 mg, 113 µmol) were dissolved in 2 mL dry THF and stirred overnight upon which a solid formed. The solid was allowed to settle, the supernatant solvent was removed via syringe and the solid was dissolved in 5 mL DCM and the resulting solution covered with a layer of 15 mL pentane. Upon standing for 16 h the product precipitated. The supernatant solvent was removed via syringe from the resulting solid, which was dried in vacuo thus giving the product as a colorless solid (34.0 mg, 36.9 µmol, 33 %).

^{1}H NMR (400.3 MHz, CD_2Cl_2) δ = 7.83 – 7.73 (m, 12H; C$H_{PPh3,\ ortho}$), 7.65 (m, 6H; C$H_{PPh3,\ para}$), 7.49 (m, 12H; C$H_{PPh3,\ meta}$), 1.33 – 1.24 (m, 9H; C(CH_3)$_3$). ^{13}C{^{31}P, ^{1}H} NMR (100.7 MHz, CD_2Cl_2) δ = 134.7 (*C*H$_{PPh3,\ ortho}$), 133.6 (*C*H$_{PPh3,\ para}$), 129.9 (*C*H$_{PPh3,\ meta}$), 125.6 (*C*H$_{PPh3,\ ipso}$), 125.2 (C*C*N), 42.1 (PCP*C*(CH$_3$)$_3$), 28.6 (PCPC(*C*H$_3$)$_3$), 11.3 (P*C*P). ^{31}P{^{1}H} NMR (162.1 MHz, CD_2Cl_2) δ = 26.58, 26.41, 26.15, 26.07, 25.98, 25.95, 25.71, 25.47 (m) spectra of higher order (AB_2 spin pattern). Calcd. Parameters: δ = 26.2, 25.8; $^2J_{PP}$ = 55.1. Anal. Calcd. for $C_{44}H_{39}AuClN_2P_3$: C, 57.37; H, 4.27; N, 3.04. Found: C, 57.28; H, 4.24; N, 3.11.FT-IR (KBr, ATR, cm^{-1}): ṽ = 3054 (w), 2961 (m), 2854 (m), 2147 (m; ν_{as}(CN)), 2134 (m; ν_{as}(CN)), 1480 (w), 1435 (m), 1259 (m), 1095 (s)

1.3.5 Preparation of $(Y_{CN})_2PCy{\cdot}Rh(acac)CO$



13.9 mg (194 µmol) of **$(Y_{CN})_2PCy$** and (acetylacetonato)dicarbonyl rhodium(I) (5.00 mg, 194 µmol) were dissolved in 1 mL dry DCM. After the gas evaporation stopped, the solvent was removed in vacuo. The solid was dissolved in 1 mL $CDCl_3$. Orange crystals could be obtained by slow evaporation of pentane. The supernatant solvent was removed with a syringe from the resulting orange solid, which was dried in vacuo thus giving the product as a orange solid (6.10 mg, 6.35 µmol, 33 %).

^{1}H NMR (400.3 MHz, $CDCl_3$) δ = 7.94 – 7.83 (m, 12H; C$H_{PPh3,\ ortho}$), 7.56 – 7.47 (m, 6H; C$H_{PPh3,\ para}$), 7.47 – 7.37 (m, 12H; C$H_{PPh3,\ meta}$), 5.10 (s, 1H; COC*H*CO), 2.01 – 1.91 (m, 2H; C$H_{2,\ PCy}$), 1.80 (s, 3H; COCH_3), 1.67 – 1.46 (m, 6H; C$H_{2,\ PCy}$), 1.33 (s, 4H; COCH_3, C$H_{,\ PCy}$), 1.11 (q, *J*=13.5, 12.9, 1H; C$H_{2,\ PCy}$), 0.95 – 0.76 (m, 2H; C$H_{2,\ PCy}$). ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$) δ = 189.8 (br; Rh*C*O), 185.8 (s; CC*C*O), 183.7(s; CC*C*O), 134.8 (d, $^2J_{CP}$ = 9.8; *C*H$_{PPh3,\ ortho}$), 132.4 (d, $^4J_{CP}$ = 2.7; *C*H$_{PPh3,\ para}$), 128.6 (d, $^3J_{CP}$ = 12.8; *C*H$_{PPh3,\ meta}$), 126.4 (d, $^2J_{CP}$ = 7.8; C*C*N), 126.3 (d, $^1J_{CP}$ = 92.0; *C*$_{PPh3,\ ipso}$), 100.9 (s; COCHCO), 44.4 (d, $^1J_{CP}$ = 40.5; *C*H$_{,\ PCy,\ C\text{-}1}$), 28.8 (s; *C*H$_{2,\ PCy,\ C\text{-}2,2'}$), 27.7 (d, $^3J_{RhC}$ = 5.7; CO*C*H$_3$), 27.2 (s; *C*H$_{2,\ PCy,\ C\text{-}3}$), 27.1 (s; *C*H$_{2,\ PCy,\ C\text{-}3'}$), 26.4 (s; *C*H$_{2,\ PCy,\ C\text{-}4}$), 25.9 (s; CO*C*H$_3$), 12.6 – 10.0 (m; P*C*P). ^{31}P{^{1}H} NMR (162.2 MHz, $CDCl_3$) δ = 45.5, 25.1 (d, $^2J_{PP}$ = 56.9; *P*Ph$_3$).

1.4 Procedures for the gold-catalyzed reactions

1.4.1 General procedure for the gold-catalysed hydroamination

A 2 mL glass vial with a rubber cap and a stir bar was charged in a glovebox with the indicated amount of LAuCl and $NaBAr^F$. The amine (5.05 mmol) and the alkyne (5.0 mmol) were added outside the glovebox via syringe or directly as a solid. The vial was heated in a metal block to the indicated temperature (e.g. RT or 50 °C) while stirring. Small aliquots were removed by syringe and added directly to an NMR tube to monitor reaction progress. In order to prevent ketone formation molecular sieve was added to the NMR tube. Yields were calculated by integration of the peak for the alkyne starting material with respect to the peak for the imine product in the ^{1}H NMR spectrum.

The results of the catalyst comparison are presented in Figure 5 and Table 3 in the manuscript. For comparison we also tested CyJohnPhos in the catalysis. The results are given in the following Table:

Table S1. Results of the hydroamination of phenylacetylene with aniline with CyJohnPhos·AuCl as catalyst at 50 °C; reaction conditions as mentioned above.

Time [h]	Conversion [%]
1	86
3	98
5	99
24	100

1.4.2 Synthesis of Phenyl-(1-phenylethylidene)amine

$Y_{CN}P^tBu_2$·AuCl (14 mg, 20 µmol), $NaBAr^F_4$ (18 mg, 20 µmol), Aniline (1.8 mL, 1.9 g, 20 mmol) and Phenylacetylene (2.2 mL, 2.0 g, 20 mmol) were added to a flask. The solution was heated to 50 °C and stirred for 5 h. An NMR of the reaction mixture indicated complete conversion. The contents of the flask were directly distilled through a 10 cm vigreux column at 0.1 mbar. After a small forerun at ~40° C the product was collected at 144-146 °C as a light yellow liquid that solidified upon standing. (3.3 g, 17 mmol, 85 %)

^{1}H NMR (400.3 MHz, $CDCl_3$): δ = 8.02 – 7.95 (m, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.31 (m, 2H), 7.13 – 7.06 (m, 1H), 6.84 – 6.78 (m, 2H), 2.24 (s, 3H).

1.4.3 Synthesis of 1-Phenyl-*N*-(o-tolyl)ethan-1-imine

$Y_{CN}P^tBu_2$·AuCl (14 mg, 20 µmol), $NaBAr^F_4$ (18 mg, 20 µmol), *o*-Toluidine (2.1 mL, 2.1 g, 20 mmol) and Phenylacetylene (2.2 mL, 2.0 g, 20 mmol) were added to a flask. The solution was heated to 50 °C and stirred for 5 h. An NMR of the reaction mixture indicated complete conversion. The contents of the flask were directly distilled through Kugelrohr distillation at 0.1 mbar. After a small forerun at 90° C the product was collected at 110 °C as a light yellow liquid that solidified upon standing. (3.5 g, 17 mmol, 84 %)

^{1}H NMR (400.3 MHz, $CDCl_3$): δ = 8.07 – 7.98 (m, 2H), 7.52 – 7.43 (m, 3H), 7.25 – 7.14 (m, 2H), 7.05 – 6.97 (m, 1H), 6.71 – 6.61 (m, 1H), 2.18 (s, 3H), 2.11 (s, 3H).

1.4.4 Synthesis of 1-(4-Methoxyphenyl)-*N*-phenylethan-1-imine

$Y_{CN}P^tBu_2$·AuCl (14 mg, 20 µmol), $NaBAr^F_4$ (18 mg, 20 µmol), 4-Methoxyaniline (2.6 g, 20 mmol) and Phenylacetylene (2.2 mL, 2.0 g, 20 mmol) were added to a flask. The solution was heated to 50 °C and stirred for 5 h. An NMR of the reaction mixture indicated complete conversion. The contents of the flask were directly distilled through Kugelrohr distillation at 0.1 mbar. After a small forerun at 90° C the product was collected at 150 °C as a light yellow liquid that solidified upon standing. (3.8 g, 17 mmol, 83 %)

^{1}H NMR (400.3 MHz, $CDCl_3$): δ = 8.01 – 7.93 (m, 2H), 7.49 – 7.40 (m, 3H), 6.94 – 6.87 (m, 2H), 6.80 – 6.74 (m, 2H), 3.82 (s, 3H), 2.26 (s, 3H).

1.4.5 Synthesis of a mixture of *E*- and *Z*-*N*-phenylhexan-2-imine

$(Y_{CN})_2PCy$·AuCl (38 mg, 40 µmol), $NaBAr^F_4$ (36 mg, 40 µmol), Aniline (1.8 mL, 1.9 g, 20 mmol) and 1-Hexyne (2.3 mL, 1.6 g, 20 mmol) were added to a flask. The solution was heated to 80 °C and stirred for 24 h. The contents of the flask were directly distilled through Kugelrohr distillation at $1 \cdot 10^{-3}$ mbar. After a small forerun at 40 °C the product was collected at 120 °C. (2.6 g, 15 mmol, 77 %)

Z-*N*-phenylhexan-2-imine

^{1}H NMR (400.3 MHz, $CDCl_3$): δ = 7.32 – 7.23 (m, 2H), 7.07 – 6.98 (m, 1H), 6.72 – 6.65 (m, 2H), 2.46 – 2.37 (m, 2H), 1.77 (s, 3H), 1.71 – 1.16 (m, 4H), 0.97 (t, *J*=7.4, 3H).

E-*N*-phenylhexan-2-imine

^{1}H NMR (400.3 MHz, $CDCl_3$): δ = 7.32 – 7.23 (m, 2H), 7.07 – 6.98 (m, 1H), 6.72 – 6.65 (m, 2H), 2.15 (s, 3H), 2.13 (t, *J*=7.9, 2H), 1.71 – 1.16 (m, 4H), 0.81 (t, *J*=7.4, 3H).

1.4.6 Synthesis of *N*,1,2-triphenylethan-1-imine

$(Y_{CN})_2$PCy· AuCl (38 mg, 40 µmol), $NaBAr^F_4$ (36 mg, 40 µmol), Aniline (1.8 mL, 1.9 g, 20 mmol) and Diphenylacetylen (3.6 g, 20 mmol) were added to a flask. The solution was heated to 80 °C and stirred for 48 h. The contents of the flask were directly distilled through Kugelrohr distillation at $1 \cdot 10^{-3}$ mbar. After a small forerun at 40 °C the product was collected at 130 °C. (3.9 g, 14 mmol, 72 %)

^{1}H NMR (400.3 MHz, $CDCl_3$) δ = 8.77 – 6.57 (m, 15H), 4.17 (s, 1H) amine peak not observed.

1.4.7 Synthesis of 1-(4-fluorophenyl)-*N*-phenylethan-1-imine

$(Y_{CN})_2$PCy· AuCl (19 mg, 20 µmol), $NaBAr^F_4$ (18 mg, 20 µmol), Aniline (1.8 mL, 1.9 g, 20 mmol) and 4-Fluorophenylacetylene (2.6 mL, 2.4 g, 20 mmol) were added to a flask. The solution was heated to 50 °C and stirred for 24 h. The contents of the flask were directly distilled through Kugelrohr distillation at $1 \cdot 10^{-3}$ mbar. After a small forerun at 40 °C the product was collected at 120 °C. (3.9 g, 14 mmol, 72 %)

^{1}H NMR (400.3 MHz, $CDCl_3$) δ = 8.18 – 7.81 (m, 2H), 7.43 – 7.32 (m, 2H), 7.19 – 7.01 (m, 3H), 6.85 – 6.65 (m, 2H), 2.22 (s, 3H).

1.4.8 Synthesis of a mixture of *N*,1-diphenylpropan-1-imine and *N*,1-diphenylpropan-2-imine

$(Y_{CN})_2$PCy· AuCl (38 mg, 40 µmol), $NaBAr^F_4$ (36 mg, 40 µmol), Aniline (1.8 mL, 1.9 g, 20 mmol) and 1-Phenyl-1-propyne (2.5 mL, 2.3 g, 20 mmol) were added to a flask. The solution was heated to 80 °C and stirred for 48 h. The contents of the flask were directly distilled through Kugelrohr distillation at $1 \cdot 10^{-3}$ mbar. After a small forerun at 40 °C the product was collected at 110 °C. (3.9 g, 14 mmol, 72 %)

N,1-diphenylpropan-1-imine:

^{1}H NMR (400.3 MHz, $CDCl_3$) δ = 7.43 – 7.35 (m, 2H), 7.31 – 7.16 (m, 4H), 3.65 (s, 2H), 6.77 – 6.69 (m, 2H), 6.69 – 6.61 (m, 2H), 1.63 (s, 3H).

N,1-diphenylpropan-2-imine:

^{1}H NMR (400.3 MHz, $CDCl_3$) δ = δ 7.86 – 7.83 (m, 2H), 7.31 – 7.16 (m, 4H), 7.06 – 6.94 (m, 4H), 2.58 (q, $^3J_{HH}$ = 7.6, 2H), 1.00 (t, $^3J_{HH}$ = 7.6, 3H).

1.4.9 Correlation of the TEP and the buried volume with the reaction rate

Table S2. Data for the correlation of the buried volume with the obtained yield.

ligand	$\%V_{bur}$	Conversion after 3h, @ 50°C	Conversion after 24h @rt
$(Y_{CN})PPh_2$	44,3	55	53
$(Y_{CN})PCy_2$	45,4	93	82
$(Y_{CN})PtBu_2$	50,8	97	98
$(Y_{CN})_2PPh$	57,2	64	53
$(Y_{CN})_2PCy$	55,2	97	84
$(Y_{CN})_2P$*t*Bu	62,7	84	63

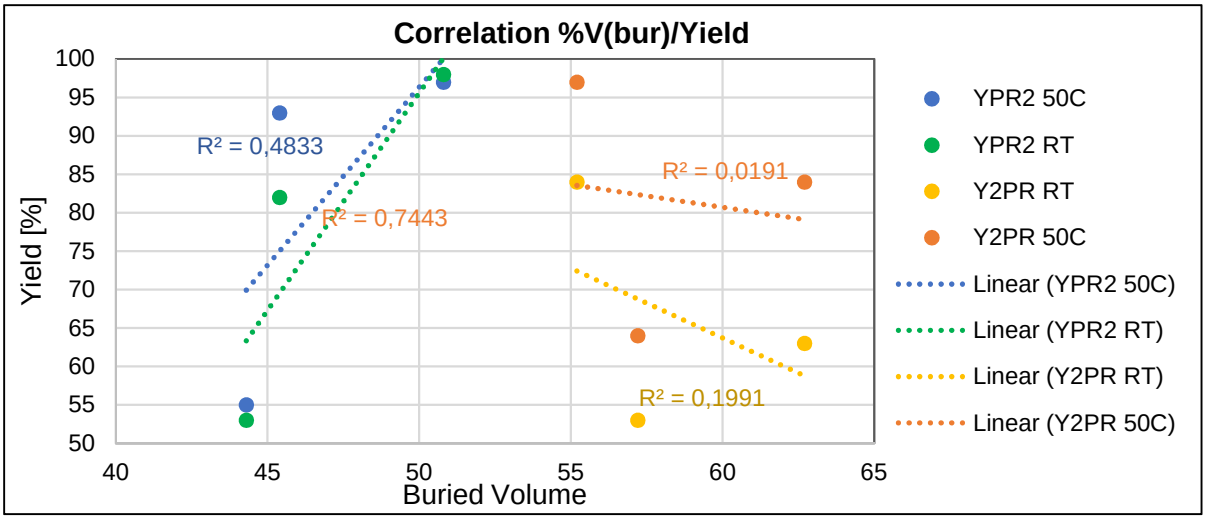


Figure S1. Correlation between the yield and the buried volume of the mono- and diylidephosphine; No linear correlation.

Table S 3. Data for the Correlation of the buried volume with the observed/actual reaction rate and the difference between the expected and actual reaction rate. The expected reaction rate was calculated based on the formula for the correlation between the TEP and the reaction rate for the monoylidephosphines (Figure 6).

ligand	$\%V_{bur}$	expected rate, r_e [M/h]	actual rate, r_a [M/h]	$r_e - r_a$ [M/h]	expected rate, r_e [M/h]	actual rate, r_a [M/h]	$r_e - r_a$ [M/h]
$(Y_{CN})PPh_2$	44,3	2,29	2,33	-0,04	0,39	0,39	0,01
$(Y_{CN})PCy_2$	45,4	5,46	4,76	0,70	1,15	0,92	0,23
$(Y_{CN})PtBu_2$	50,8	6,31	6,70	-0,39	1,36	1,46	-0,10
$(Y_{CN})_2PPh$	57,2	4,35	2,43	1,93	0,89	0,39	0,50
$(Y_{CN})_2PCy$	55,2	6,13	6,21	-0,08	1,31	0,63	0,68
$(Y_{CN})_2P$*t*Bu	62,7	6,56	3,59	2,97	1,42	0,32	1,10

Figure S2. Correlation of the buried volume with the observed/actual reaction rate r_a and the difference between the expected and actual reaction rate (r_e-r_a).

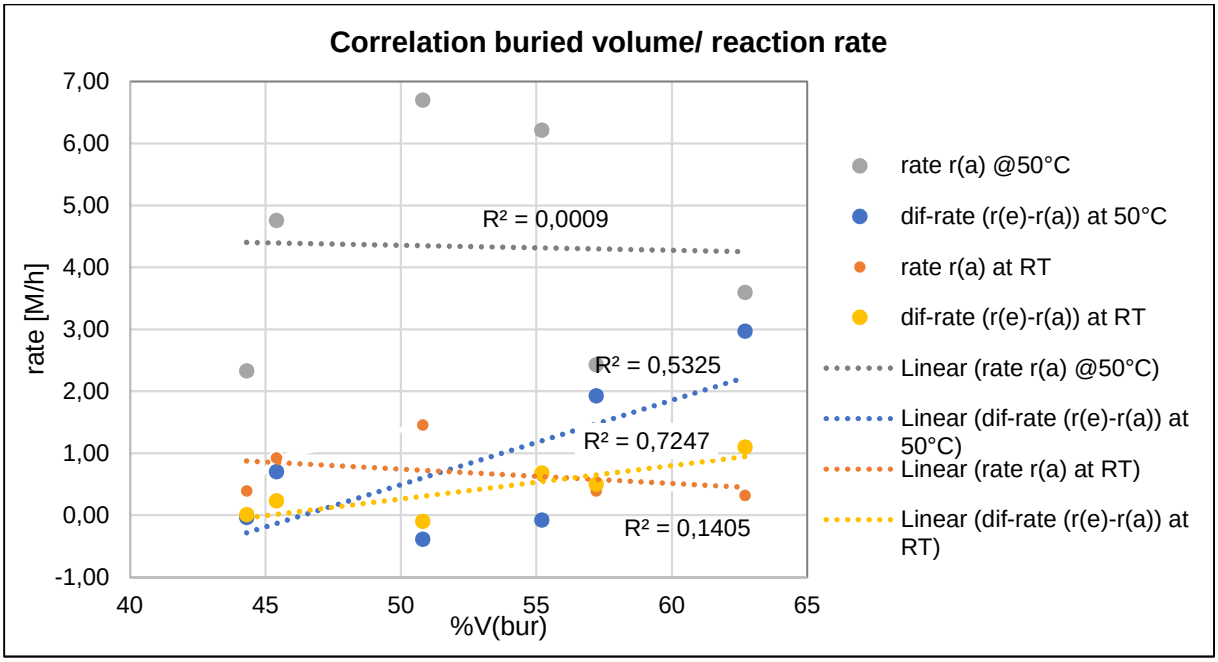


Table S4. Data for the correlation between the Tolman electronic parameter and the reaction rate.

ligands	TEP	Rate between 0-30 min [M/h]	Rate between 0-1 h [M/h]	Rate between 0-1 h [M/h]	Rate between 0-3 h [M/h]
$(Y_{CN})PPh_2$	2066,7	2,33	1,55	0,27	0,39
$(Y_{CN})PCy_2$	2057,8	4,76	3,40	0,53	0,92
$(Y_{CN})PtBu_2$	2055,4	6,70	3,93	0,78	1,46
$(Y_{CN})_2PPh$	2060,9	2,43	1,84	0,28	0,39
$(Y_{CN})_2PCy$	2055,9	6,21	3,59	0,49	0,63
$(Y_{CN})_2PtBu$	2054,7	3,59	2,52	0,26	0,32

Reaction rates were measured within the first 30 and 60 min of the reactions at 50°C and between the first and the first three hours of the reactions at RT. Since a true linear progression is only the case of the shorter reaction times (c.f. Figure 5), the correlation with these rates are discussed in the manuscript, albeit the fit for the longer reaction times is slightly better (Figure S2).

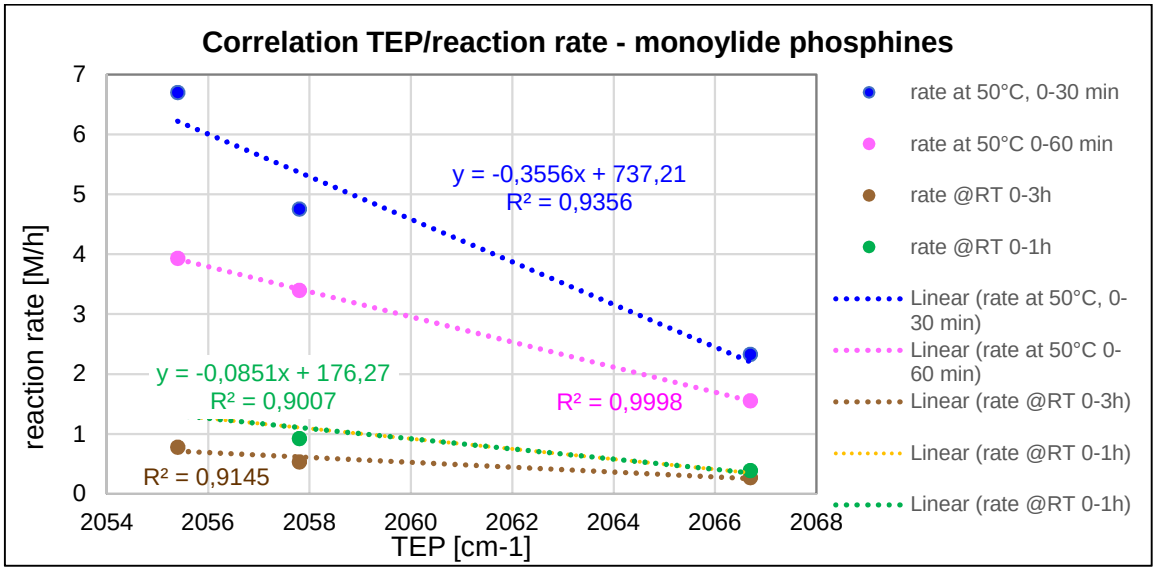


Figure S3. Correlation between the TEP and the reaction rates obtained with the monoylide phosphine-based catalysts

1.5 Procedures for the measurement of the IR-Spectra

Procedure for $\tilde{\nu}(CO)_{Rh}$ determination:[6] 5 mg (19.4 µmol) $Rh(acac)(CO)_2$ were dissolved in 1 mL of DCM in a glovebox. 19.4 µmol of the phosphine were added to the solution and the solution was stirred for 15 min until gas evolution ceased. The solution was added into the IR cell using a syringe. The cell was closed, taken outside the glovebox and an IR spectrum was recorded. Independent of the phosphine used the IR spectrum always shows two strong bands at 2083.4 cm^{-1} and 2011.8 cm^{-1} (acac vibrations) which are almost identical to the IR peaks observed in $Rh(acac)(CO)_2$[7] and an additional strong band between 1975–1940 cm^{-1} corresponding to the carbonyl stretching frequency.

Table S5. Survey of phosphorus ligands with known TEP and $\tilde{\nu}(CO)_{Rh}$.

Ligand	solvent	$\tilde{\nu}(CO)_{Rh}$ [cm^{-1}]	cald TEP [cm^{-1}]
PPh_3[6]	CH_2Cl_2	1978.0	2069.1
$Y_{CN}PPh_2$[3a]	CH_2Cl_2	1973.8	2066.7

$(Y_{CN})_2PPh$	CH_2Cl_2	1963.6	2060.9
PCy_3[6]	CH_2Cl_2	1958.7	2058.1
$Y_{CN}PCy_2$[3a]	CH_2Cl_2	1958.3	2057.8
$(Y_{CN})_2PCy$	CH_2Cl_2	1955.0	2055.9
$P(^tBu)_3$[6]			2056.1
$Y_{CN}P(^tBu)_2$	CH_2Cl_2	1954.1	2055.4

2. NMR spectra

2.1 NMR spectra of $(Y_{CN})_2PCl$ and $(Y_{CN})_3P$

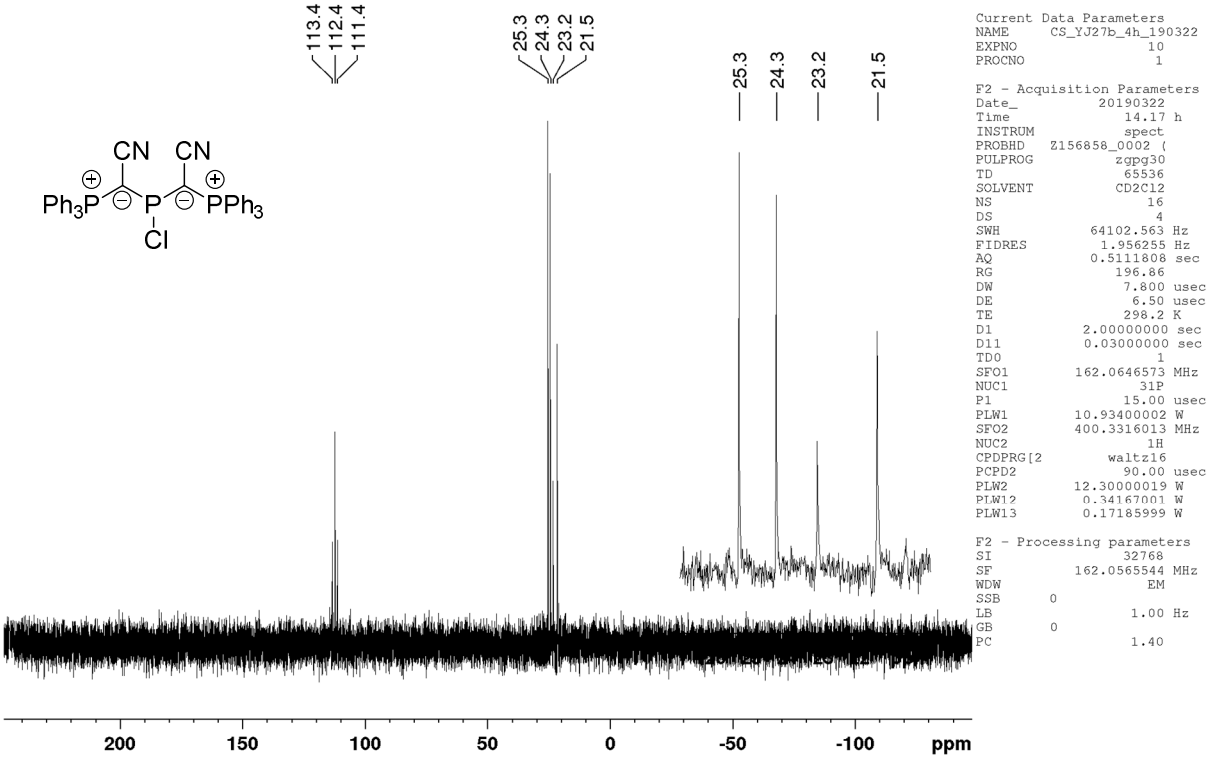


Figure S4. $^{31}P\{^1H\}$ NMR spectrum of **$(Y_{CN})_2PCl$.**

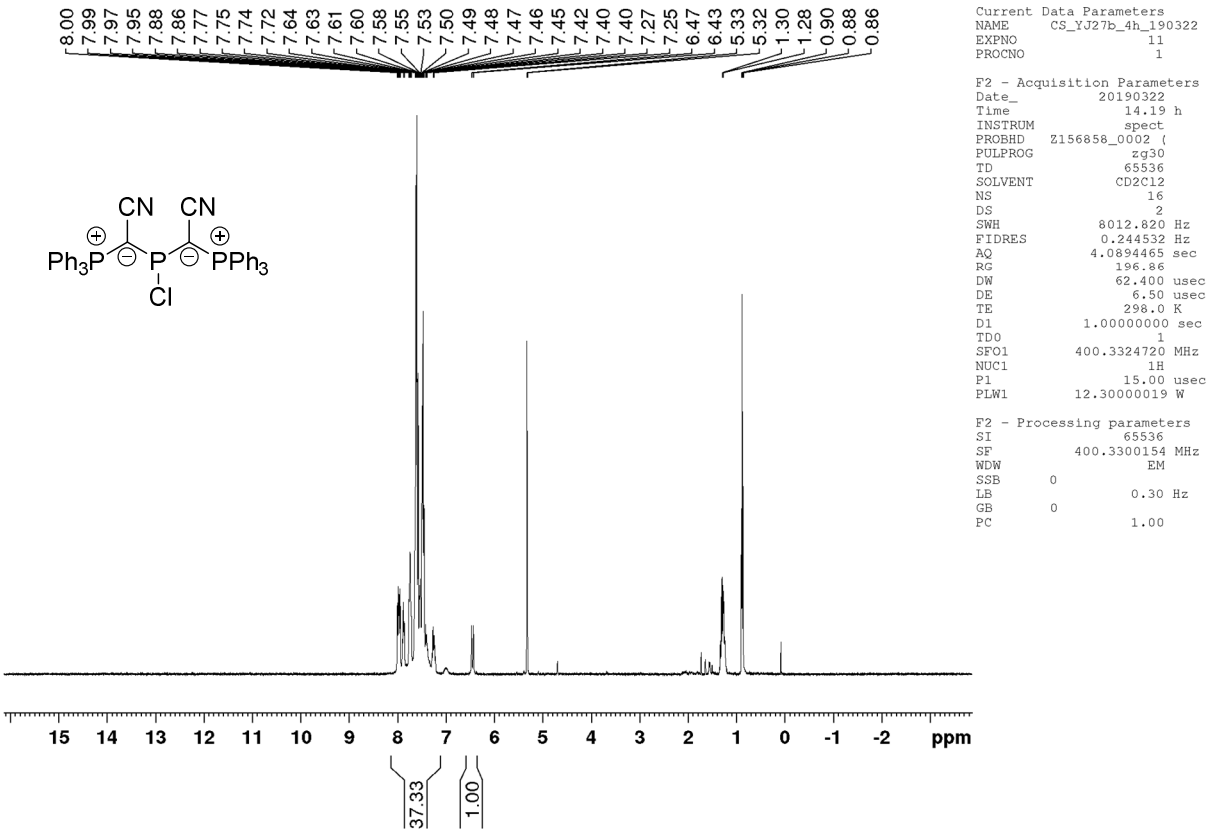


Figure S5. ^1H NMR spectrum of **$(Y_{CN})_2PCl$.**

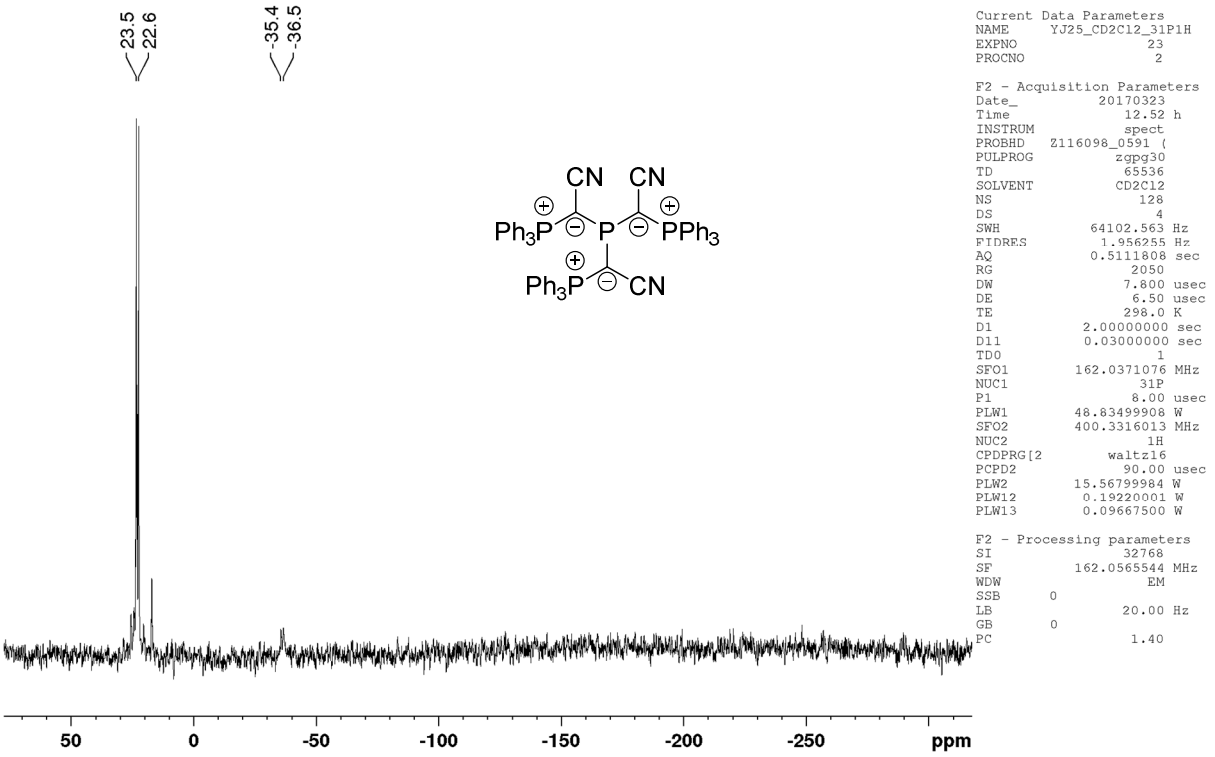


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **$(Y_{CN})_3P$.**

2.2 NMR spectra of the isolated compounds

2.2.1 $Y_{CN}P^tBu_2$

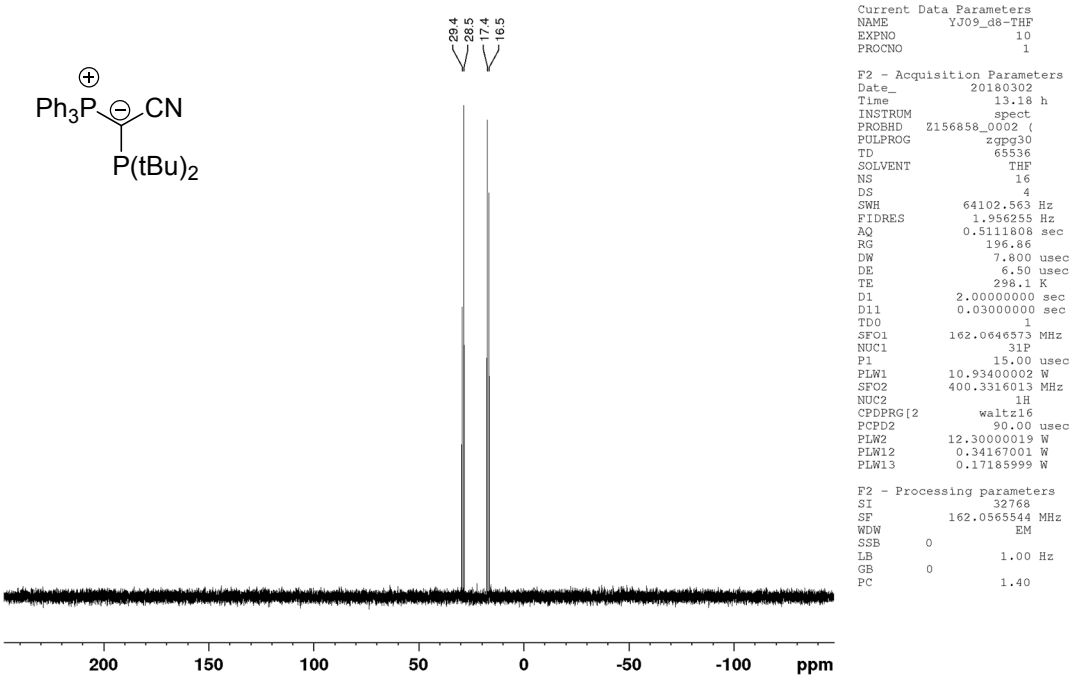


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **$Y_{CN}P^tBu_2$.**

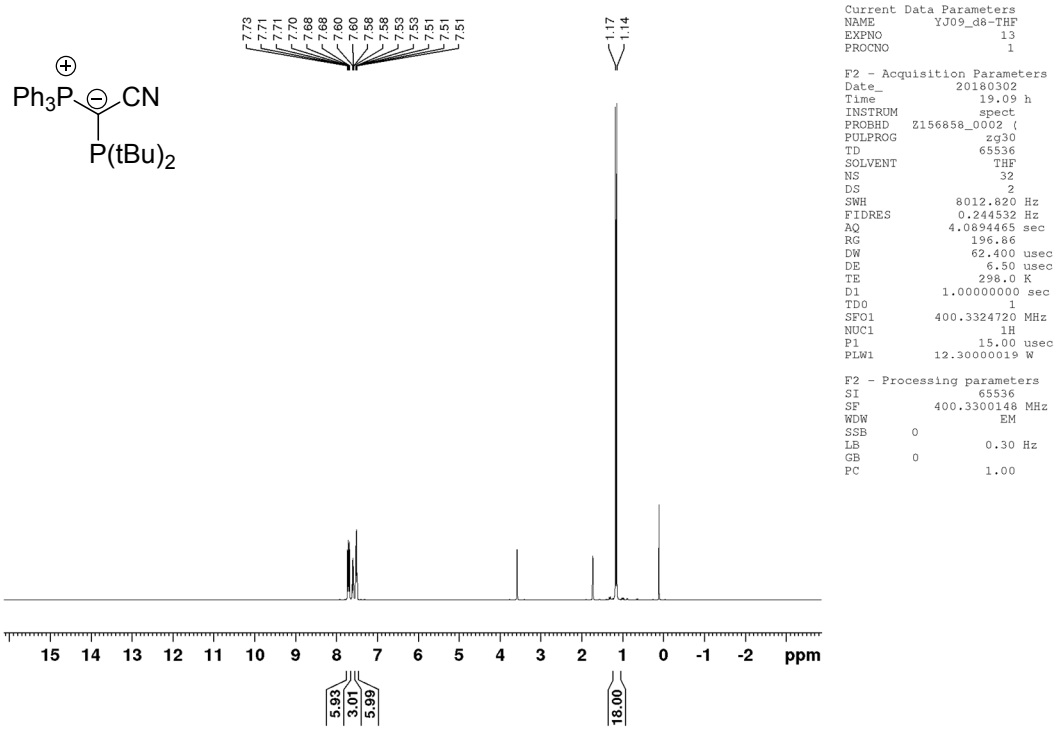


Figure S8. ^{1}H NMR spectrum of $\mathbf{Y_{CN}P^{t}Bu_2}$ (signal at 0 ppm corresponds to silicon grease).

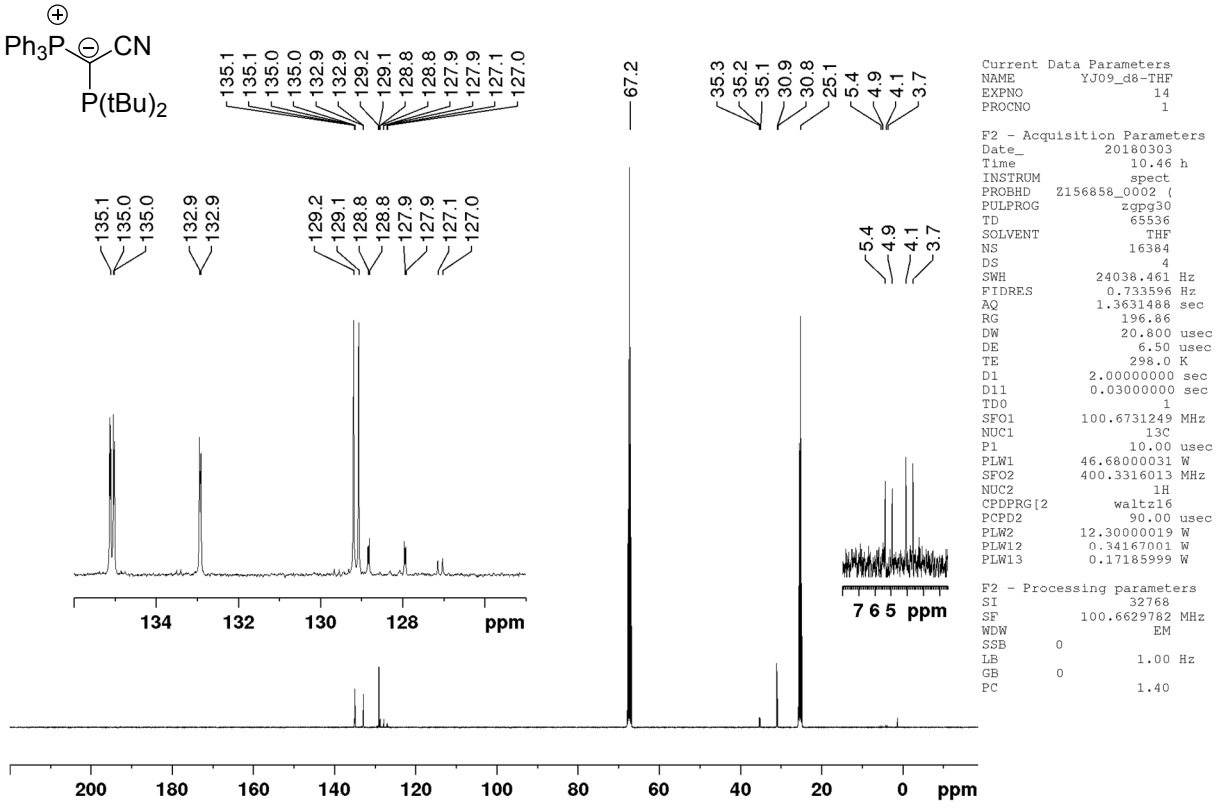
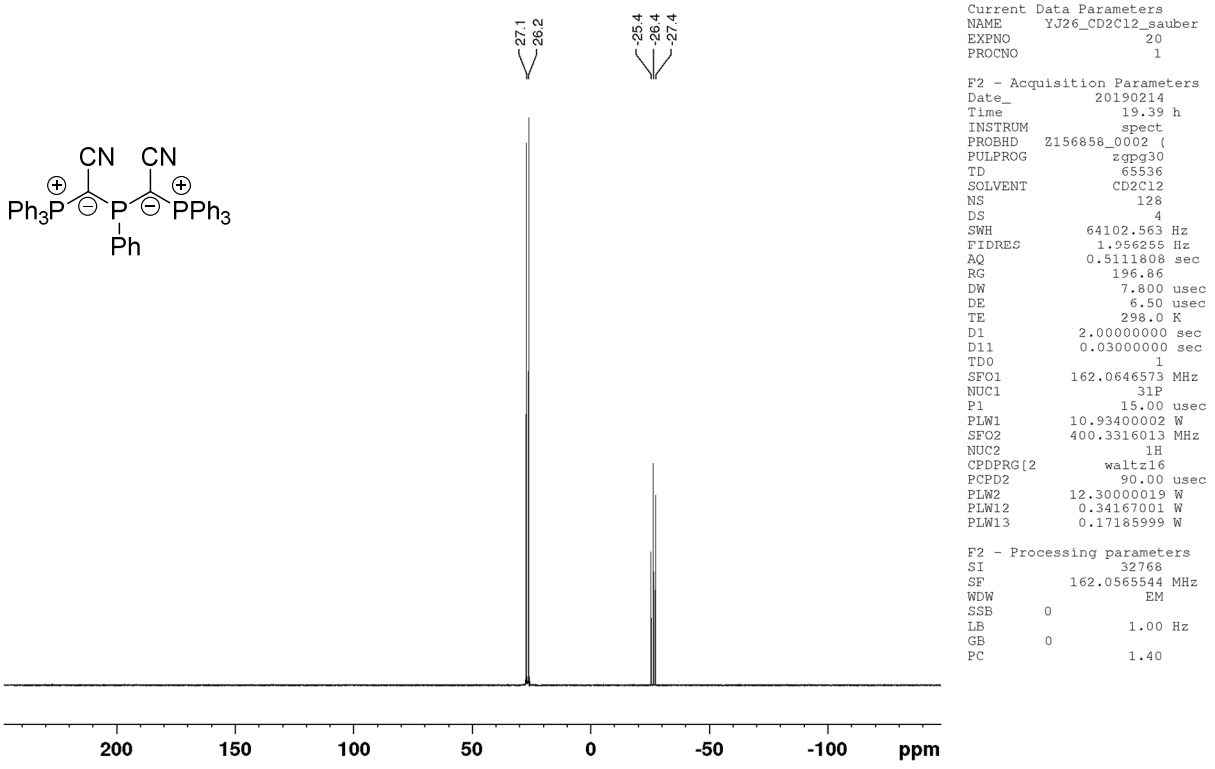


Figure S9. ^{13}C{^{1}H} NMR spectrum of $\mathbf{Y_{CN}P^{t}Bu_2}$ (signal at 0 ppm corresponds to silicon grease).

2.2.2 $(Y_{CN})_2PPh$

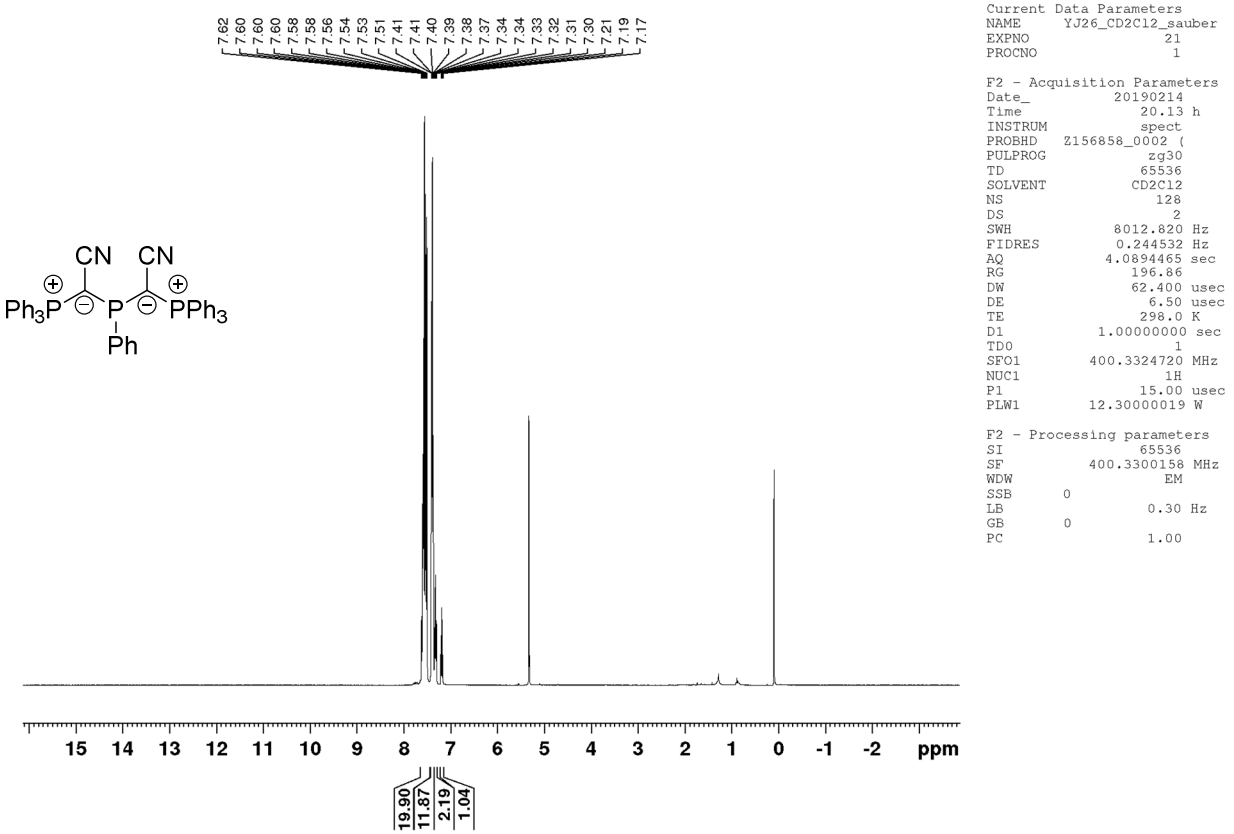



```
Current Data Parameters
NAME      YJ26_CD2Cl2_sauber
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_           20190214
Time              19.39 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG           zgpg30
TD                65536
SOLVENT           CD2Cl2
NS                  128
DS                    4
SWH           64102.563 Hz
FIDRES         1.956255 Hz
AQ            0.5111808 sec
RG               196.86
DW                7.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        162.0646573 MHz
NUC1                31P
P1                15.00 usec
PLW1        10.93400002 W
SFO2        400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        12.30000019 W
PLW12        0.34167001 W
PLW13        0.17185999 W

F2 - Processing parameters
SI                32768
SF          162.0565544 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S10. $^{31}P\{^1H\}$ NMR spectrum of **$(Y_{CN})_2PPh$.**

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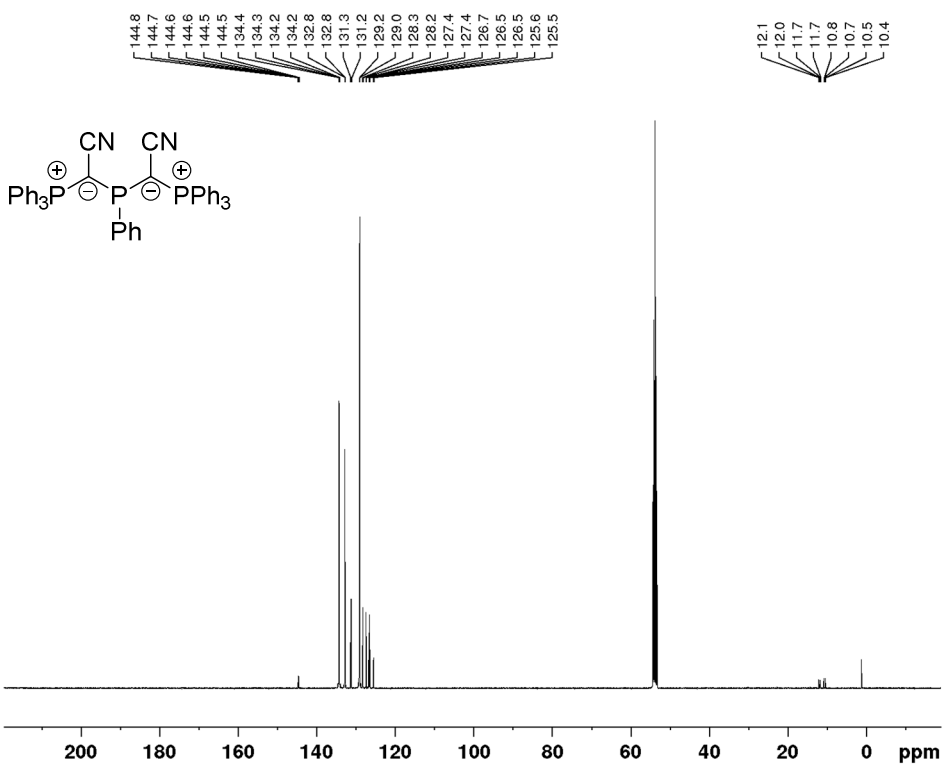
Current Data Parameters
NAME      YJ26_CD2Cl2_sauber
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
Date_           20190214
Time              20.13 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG             zg30
TD                65536
SOLVENT           CD2Cl2
NS                  128
DS                    2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ            4.0894465 sec
RG               196.86
DW                62.400 usec
DE                6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1
SFO1        400.3324720 MHz
NUC1                1H
P1                15.00 usec
PLW1        12.30000019 W

F2 - Processing parameters
SI                65536
SF          400.3300158 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Figure S11. ^1H NMR spectra of **$(Y_{CN})_2PPh$** (signal at 0 ppm corresponds to silicon grease).



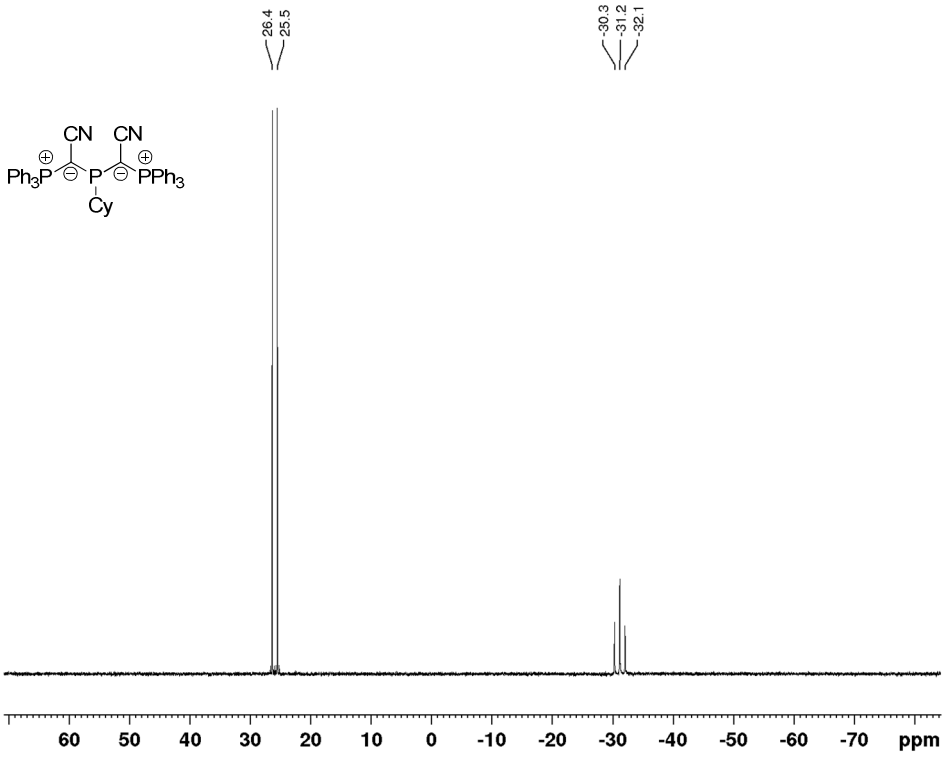

```
Current Data Parameters
NAME      YJ26_CD2Cl2_sauber
EXPNO                   22
PROCNO                   1

F2 - Acquisition Parameters
Date_           20190217
Time              17.15 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG           zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                 16384
DS                     4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               196.86
DW               20.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        100.6731249 MHz
NUC1                13C
P1                10.00 usec
PLW1        46.68000031 W
SFO2        400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        12.30000019 W
PLW12        0.34167001 W
PLW13        0.17185999 W

F2 - Processing parameters
SI                 32768
SF          100.6630195 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S12. $^{13}C\{^{1}H\}$ NMR spectra of **$(Y_{CN})_2$PPh** (signal at 0 ppm corresponds to silicon grease).

2.2.3 $(Y_{CN})_2$PCy




```
Current Data Parameters
NAME      CS_YJ28x_5_190318
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_           20190318
Time              18.09 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG           zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                   128
DS                     4
SWH           64102.563 Hz
FIDRES         1.956255 Hz
AQ            0.5111808 sec
RG               196.86
DW                7.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        162.0646573 MHz
NUC1                31P
P1                15.00 usec
PLW1        10.93400002 W
SFO2        400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        12.30000019 W
PLW12        0.34167001 W
PLW13        0.17185999 W

F2 - Processing parameters
SI                 32768
SF          162.0565544 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **$(Y_{CN})_2$PCy** in DCM.

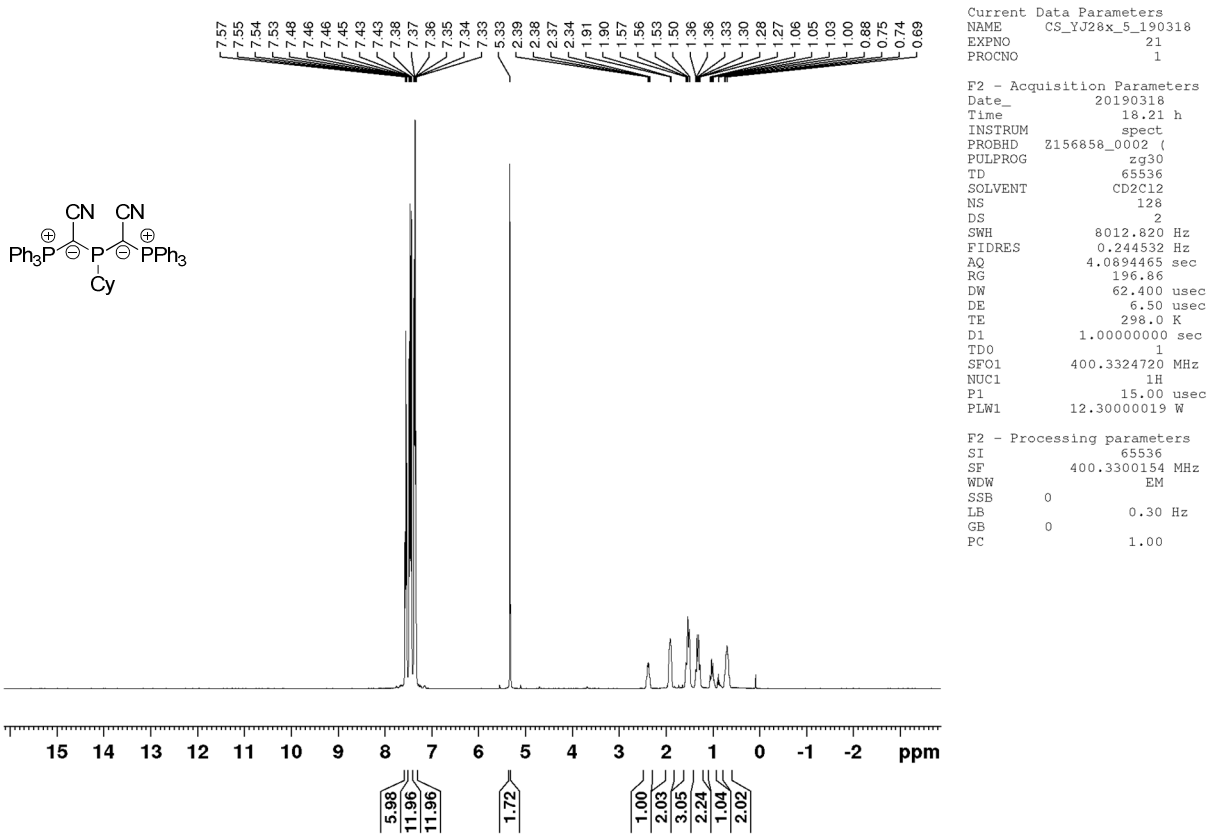


Figure S14. ^{1}H NMR spectrum of **$(Y_{CN})_2$PCy** in DCM (signal at 0 ppm corresponds to silicon grease).

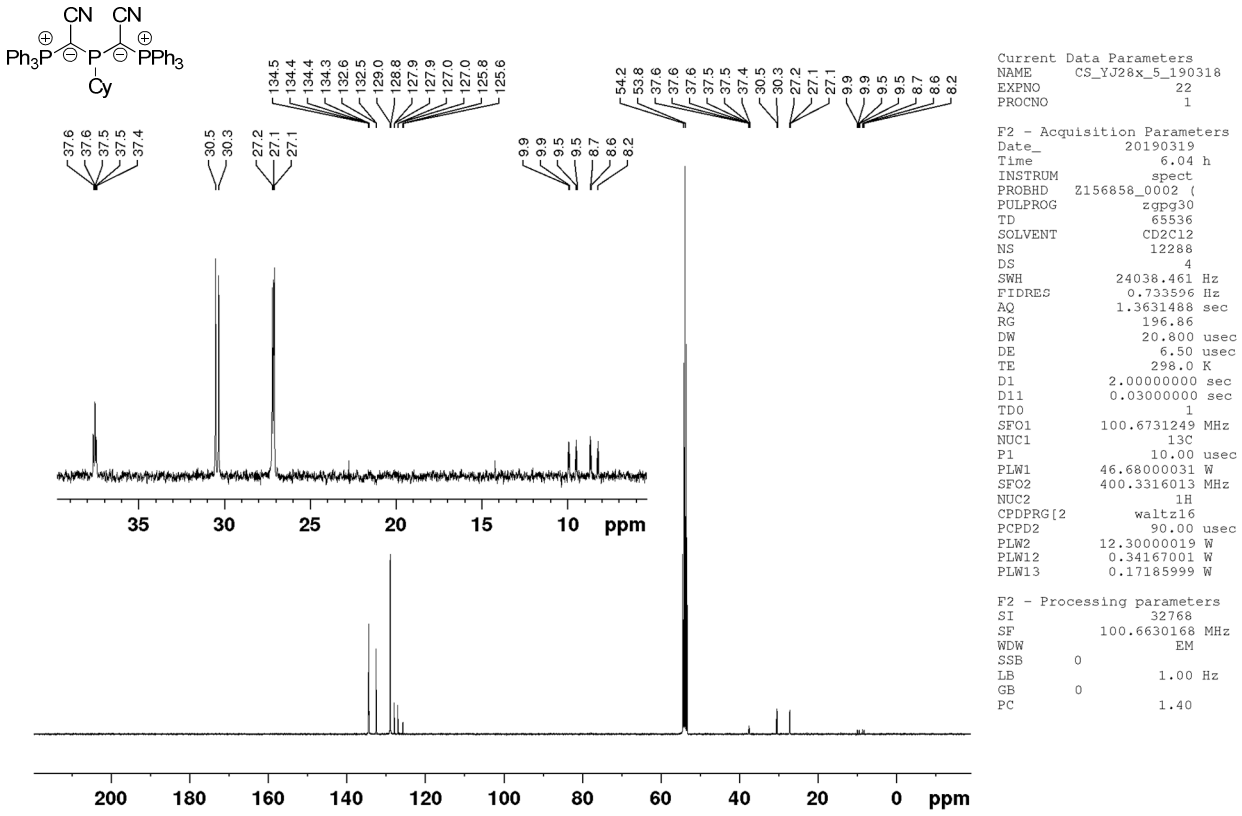
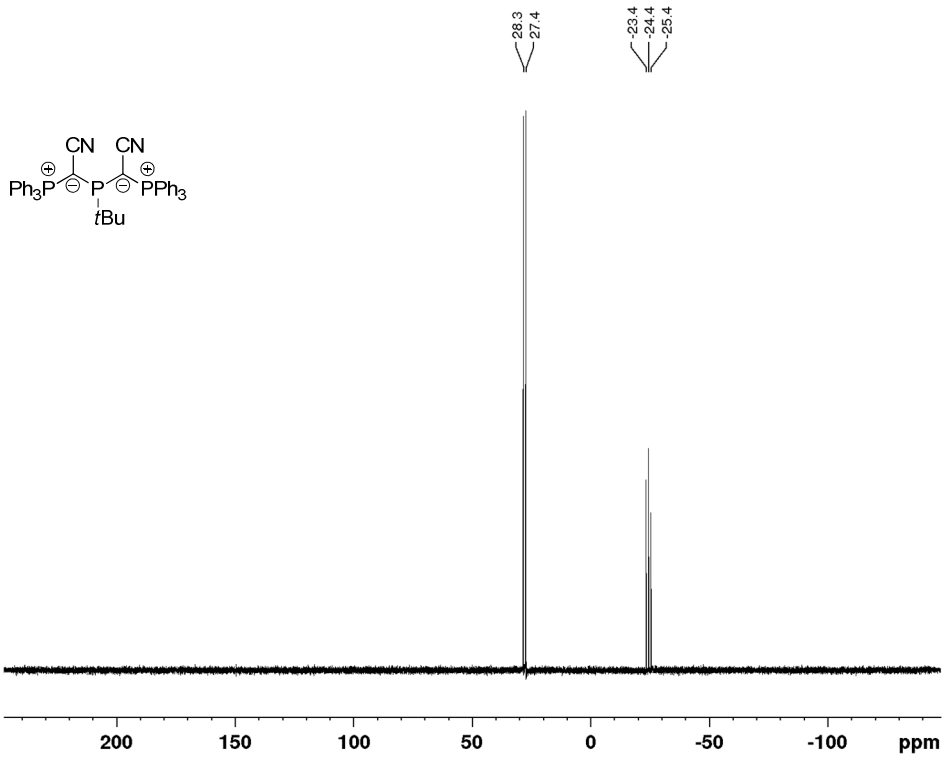


Figure S15. ^{13}C{^{1}H} NMR spectrum of **$(Y_{CN})_2$PCy** in DCM.

2.2.4 $(Y_{CN})_2P^tBu$

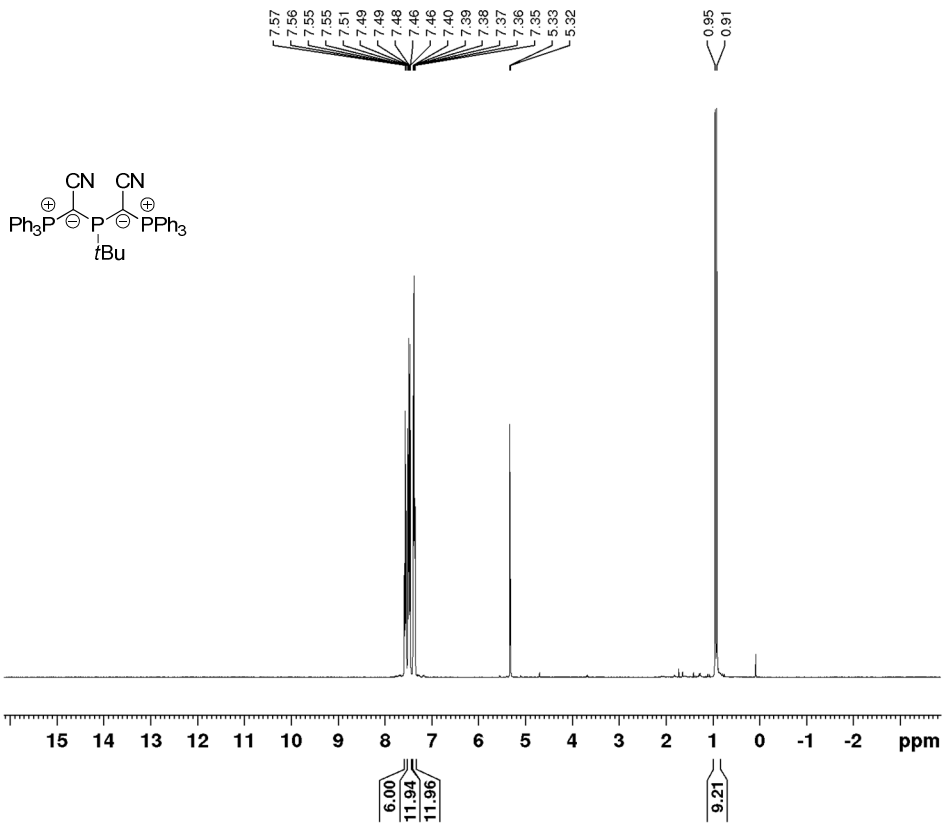



```
Current Data Parameters
NAME      CS_YJ24b_2f_190116
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190118
Time              18.39 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG           zgpg30
TD                65536
SOLVENT           CD2Cl2
NS                  128
DS                    4
SWH           64102.563 Hz
FIDRES         1.956255 Hz
AQ            0.5111808 sec
RG               196.86
DW                7.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        162.0646573 MHz
NUC1                31P
P1                15.00 usec
PLW1        10.93400002 W
SFO2        400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        12.30000019 W
PLW12        0.34167001 W
PLW13        0.17185999 W

F2 - Processing parameters
SI                32768
SF          162.0565544 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

FigureS 16. $^{31}P\{^1H\}$ NMR spectrum of **$(Y_{CN})_2P^tBu$.**

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Current Data Parameters
NAME      CS_YJ24b_2f_190116
EXPNO                 14
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190118
Time              18.51 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG             zg30
TD                65536
SOLVENT           CD2Cl2
NS                  128
DS                    2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ            4.0894465 sec
RG               196.86
DW                62.400 usec
DE                6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1
SFO1        400.3324720 MHz
NUC1                1H
P1                15.00 usec
PLW1        12.30000019 W

F2 - Processing parameters
SI                65536
SF          400.3300155 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Figure S17. ^1H NMR spectrum of **$(Y_{CN})_2P^tBu$** (signal at 0 ppm corresponds to silicon grease).

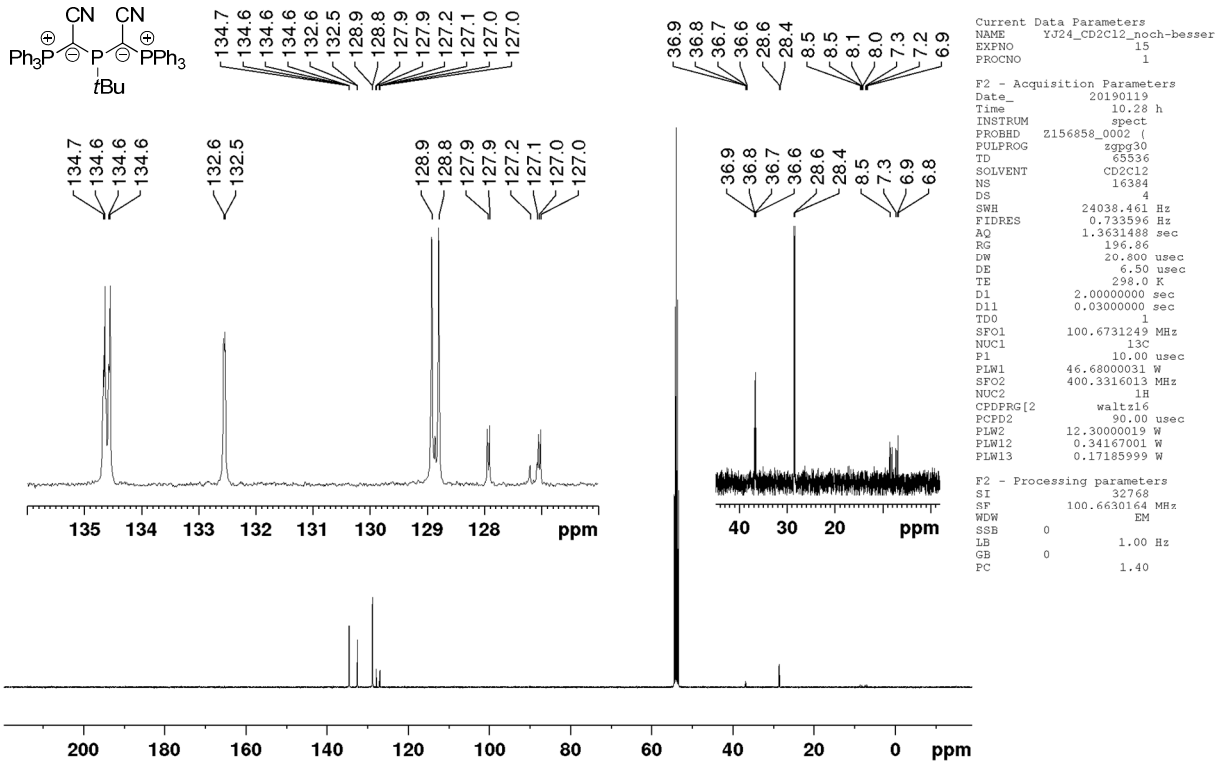


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **$(Y_{CN})_2P^tBu$**.

2.2.5 $Y_{CN}P^tBu_2{\cdot}AuCl$

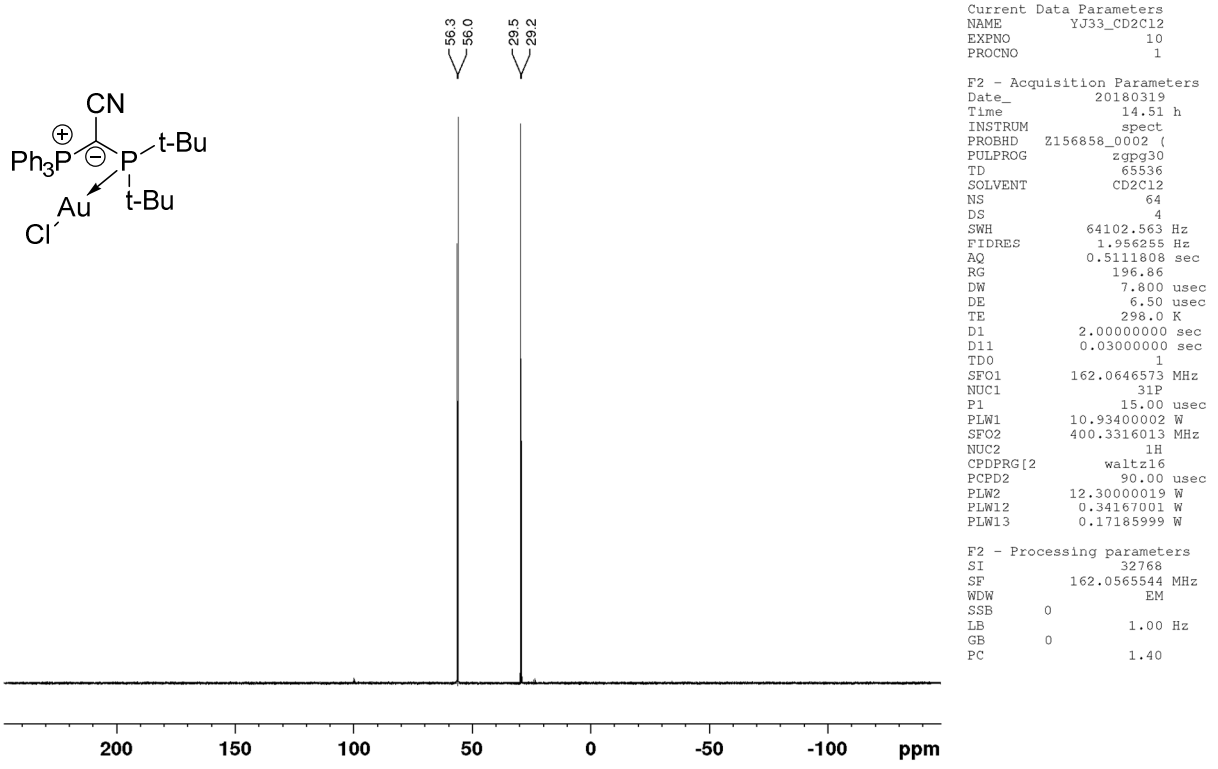
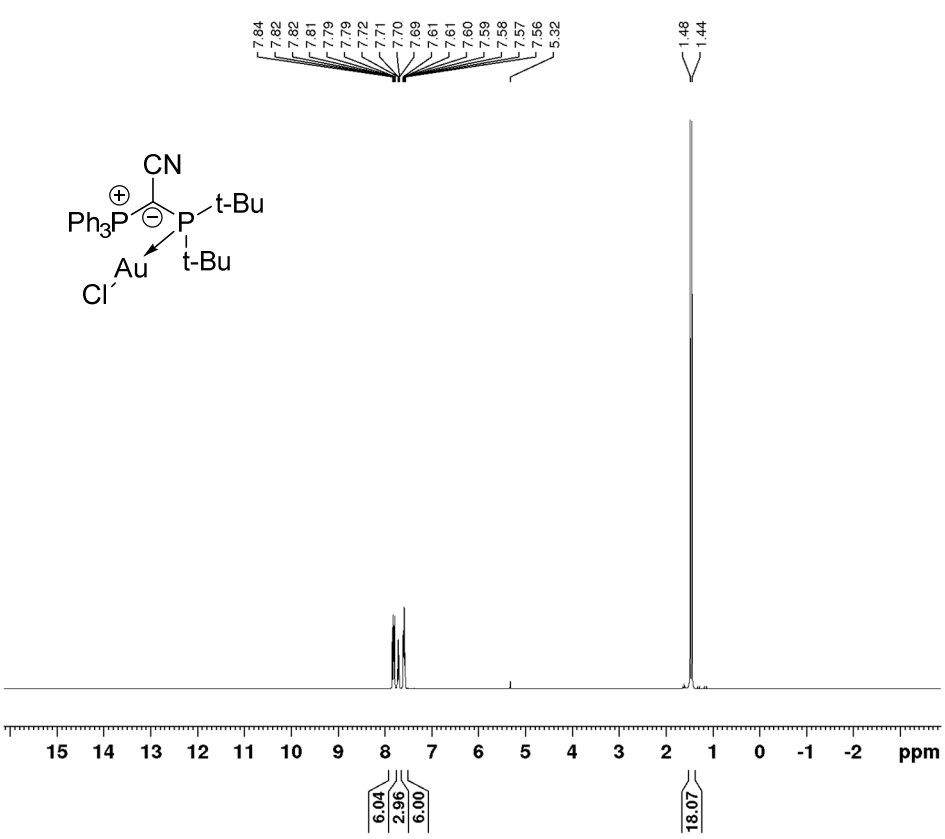


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **$Y_{CN}P^tBu_2{\cdot}AuCl$**.

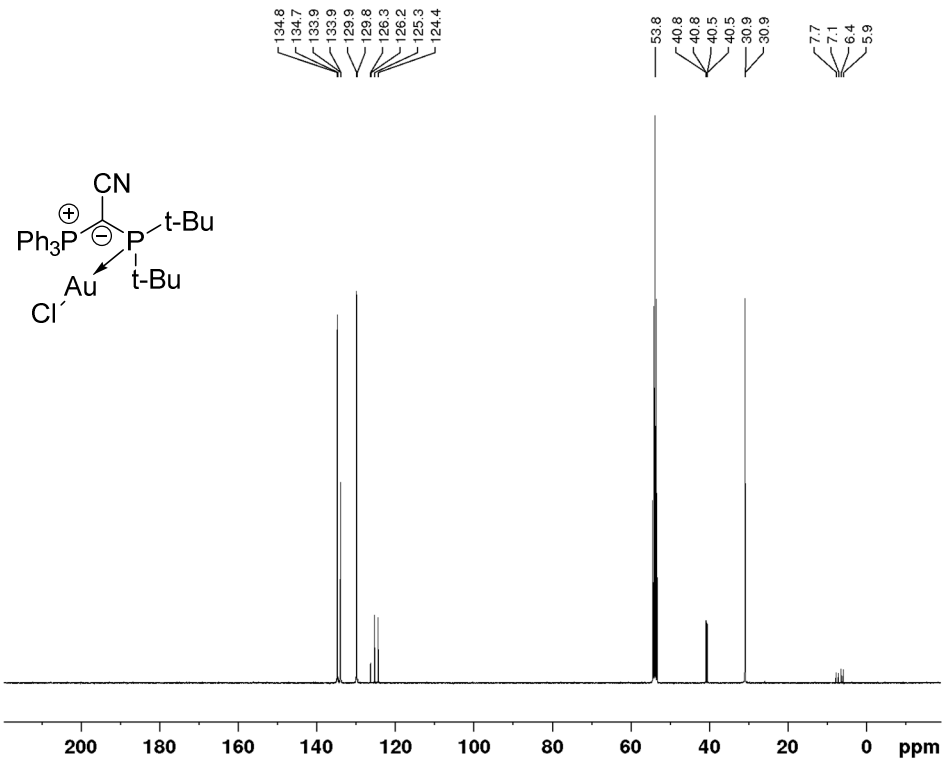



```
Current Data Parameters
NAME         YJ33_CD2Cl2
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180319
Time               18.05 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG             zg30
TD                 65536
SOLVENT           CD2Cl2
NS                    64
DS                     2
SWH             8012.820 Hz
FIDRES             0.244532 Hz
AQ              4.0894465 sec
RG                177.28
DW                62.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          400.3324720 MHz
NUC1                  1H
P1                15.00 usec
PLW1          12.30000019 W

F2 - Processing parameters
SI                 65536
SF            400.3300155 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Figure S20. ^{1}H NMR spectrum of **$Y_{CN}P^{t}Bu_2$·AuCl**.



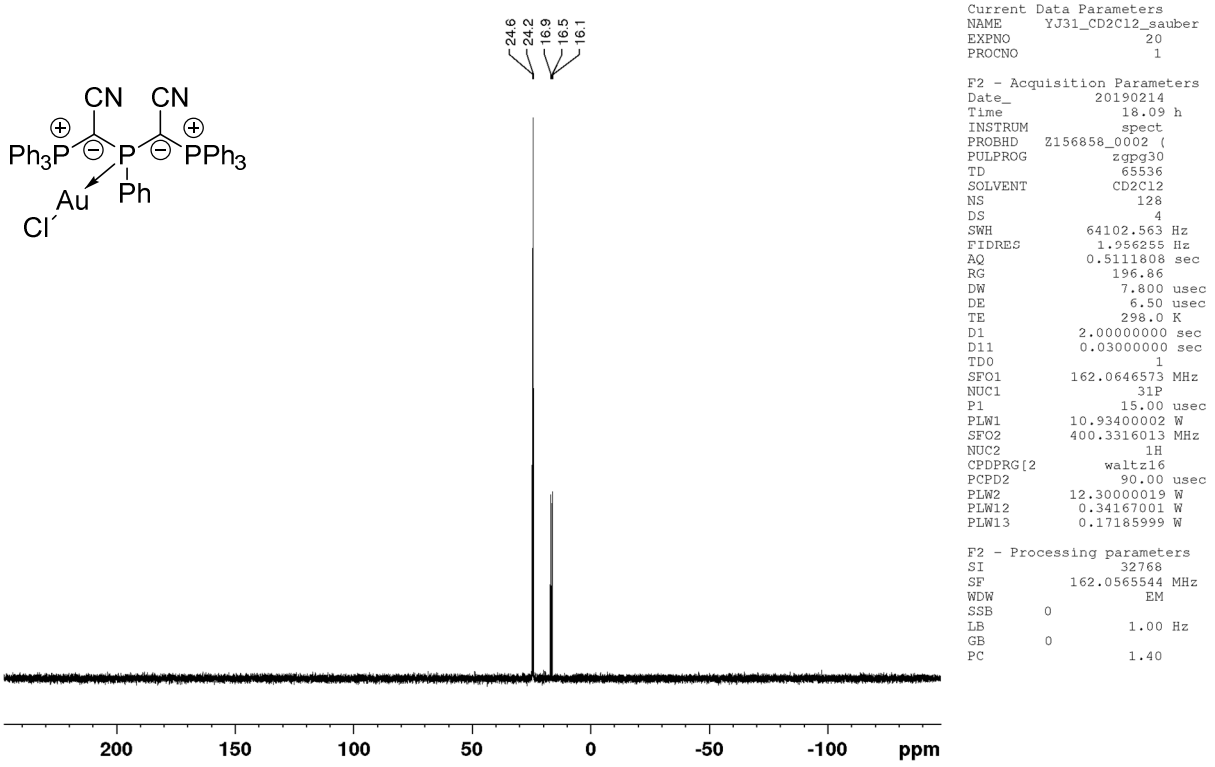

```
Current Data Parameters
NAME         YJ33_CD2Cl2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180320
Time               8.44 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG          zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                 15360
DS                     4
SWH            24038.461 Hz
FIDRES             0.733596 Hz
AQ              1.3631488 sec
RG                196.86
DW                20.800 usec
DE                 6.50 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6731249 MHz
NUC1                  13C
P1                10.00 usec
PLW1          46.68000031 W
SFO2          400.3316013 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          12.30000019 W
PLW12          0.34167001 W
PLW13          0.17185999 W

F2 - Processing parameters
SI                 32768
SF            100.6630183 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S21. ^{13}C{^{1}H} NMR spectrum of **$Y_{CN}P^{t}Bu_2$·AuCl**.

2.2.6 $(Y_{CN})_2$PPh·AuCl

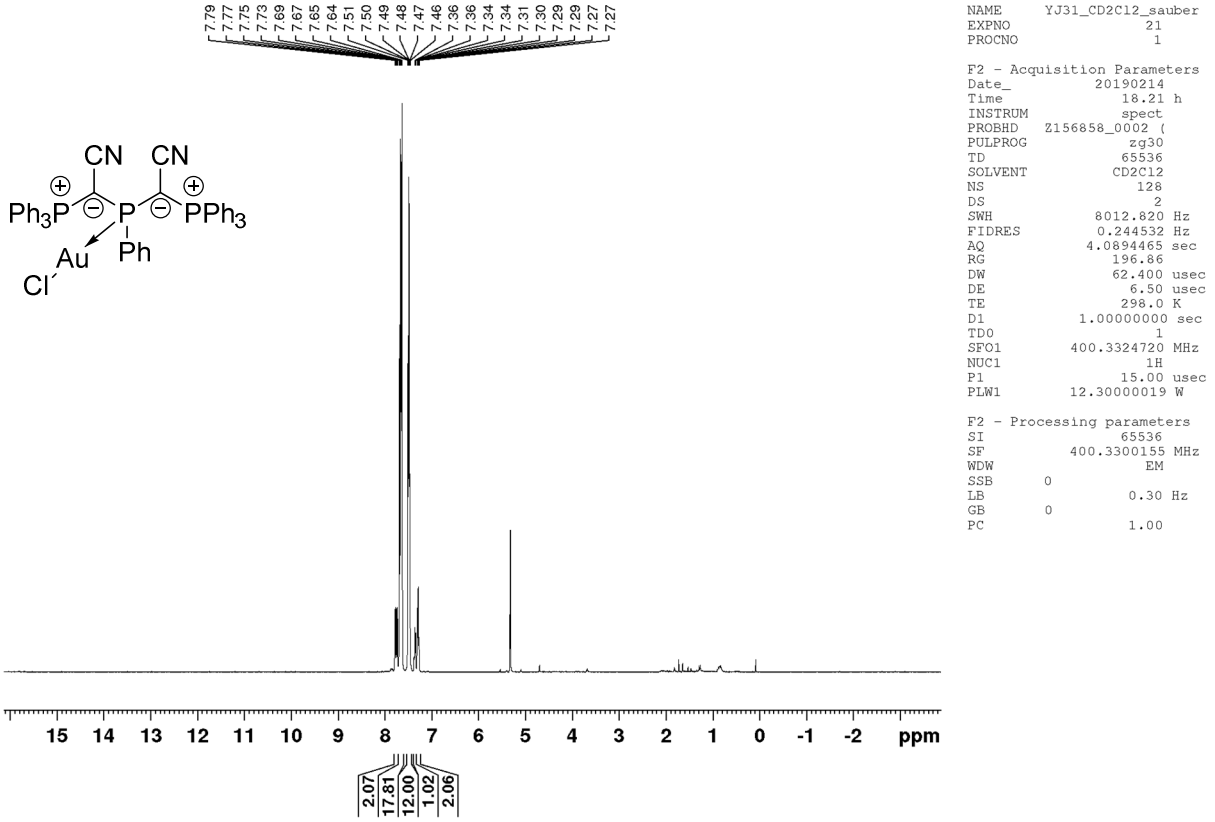



```
Current Data Parameters
NAME      YJ31_CD2Cl2_sauber
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_           20190214
Time              18.09 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG           zgpg30
TD                65536
SOLVENT           CD2Cl2
NS                  128
DS                    4
SWH           64102.563 Hz
FIDRES         1.956255 Hz
AQ            0.5111808 sec
RG               196.86
DW                7.800 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        162.0646573 MHz
NUC1                31P
P1                15.00 usec
PLW1        10.93400002 W
SFO2        400.3316013 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        12.30000019 W
PLW12        0.34167001 W
PLW13        0.17185999 W

F2 - Processing parameters
SI                32768
SF          162.0565544 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S22. $^{31}P\{^1H\}$ NMR spectrum of **$(Y_{CN})_2$PPh·AuCl**.




```
Current Data Parameters
NAME      YJ31_CD2Cl2_sauber
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
Date_           20190214
Time              18.21 h
INSTRUM             spect
PROBHD    Z156858_0002 (
PULPROG             zg30
TD                65536
SOLVENT           CD2Cl2
NS                  128
DS                    2
SWH            8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG               196.86
DW                62.400 usec
DE                6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1
SFO1        400.3324720 MHz
NUC1                1H
P1                15.00 usec
PLW1        12.30000019 W

F2 - Processing parameters
SI                65536
SF          400.3300155 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Figure S23. ^1H NMR spectrum of **$(Y_{CN})_2$PPh·AuCl** (signal at 0 ppm corresponds to silicon grease; signals between 0.5-2 ppm to traces of solvents).

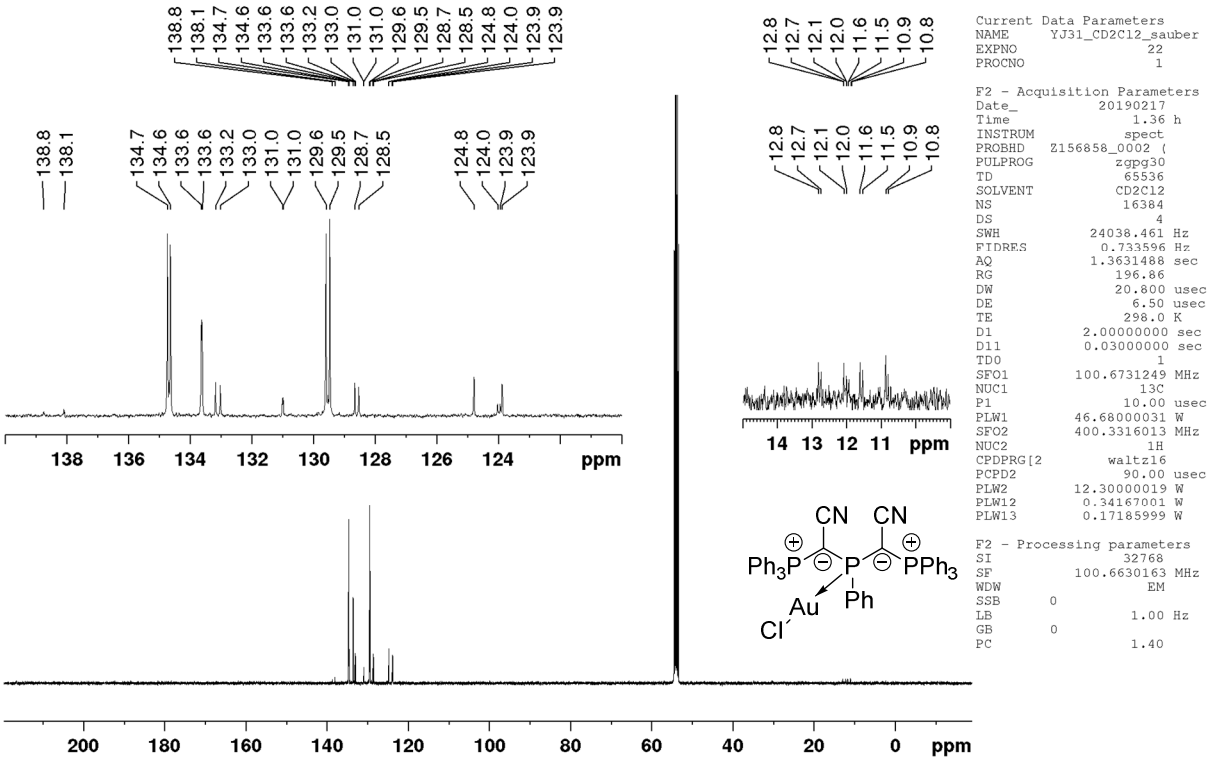


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **$(Y_{CN})_2$PPh·AuCl**.

2.2.7 $(Y_{CN})_2$PCy·AuCl

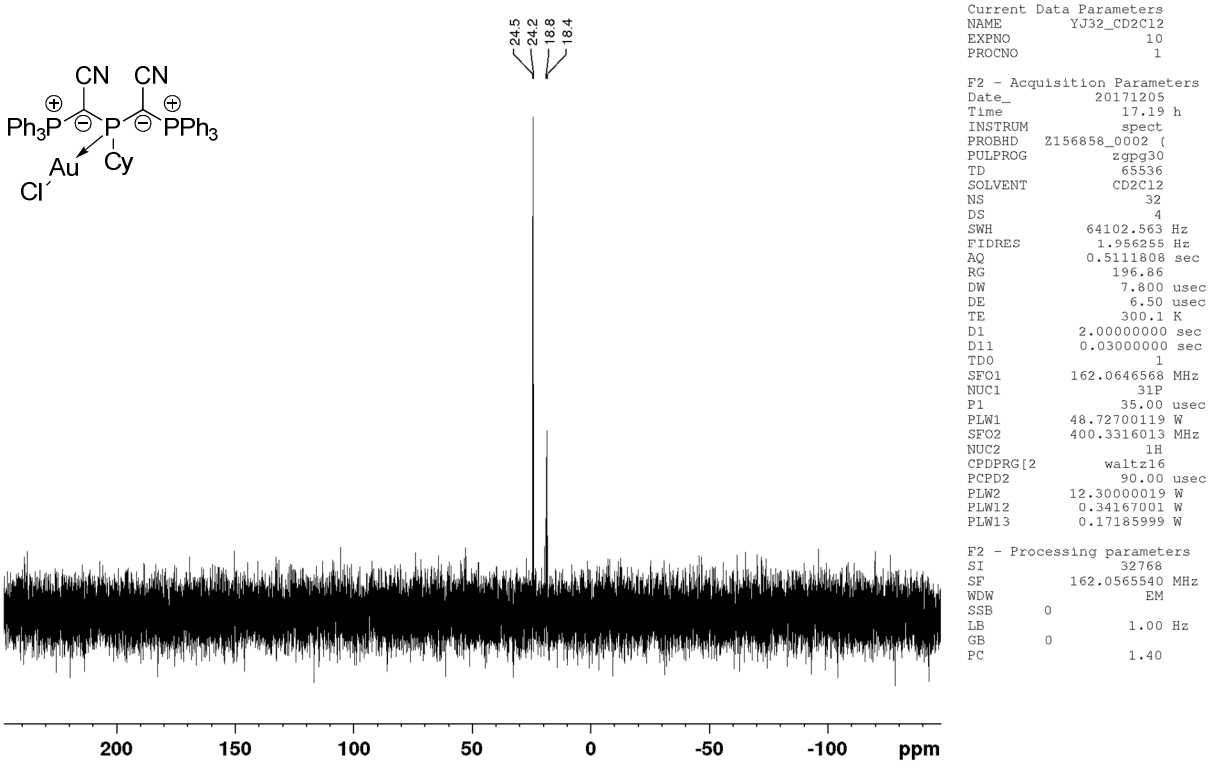


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **$(Y_{CN})_2$PCy·AuCl.**

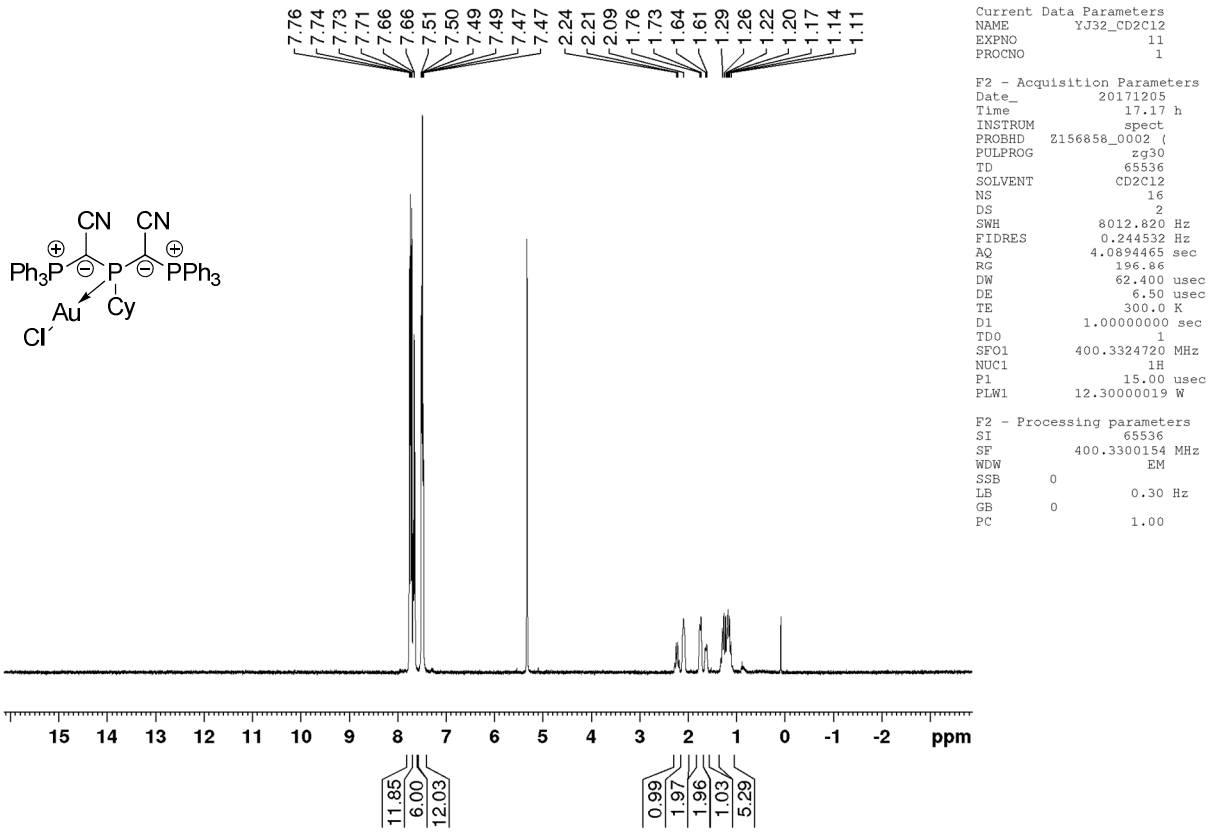


Figure S26. ^{1}H NMR spectrum of **$(Y_{CN})_2$PCy·AuCl** (signal at 0 ppm corresponds to silicon grease).

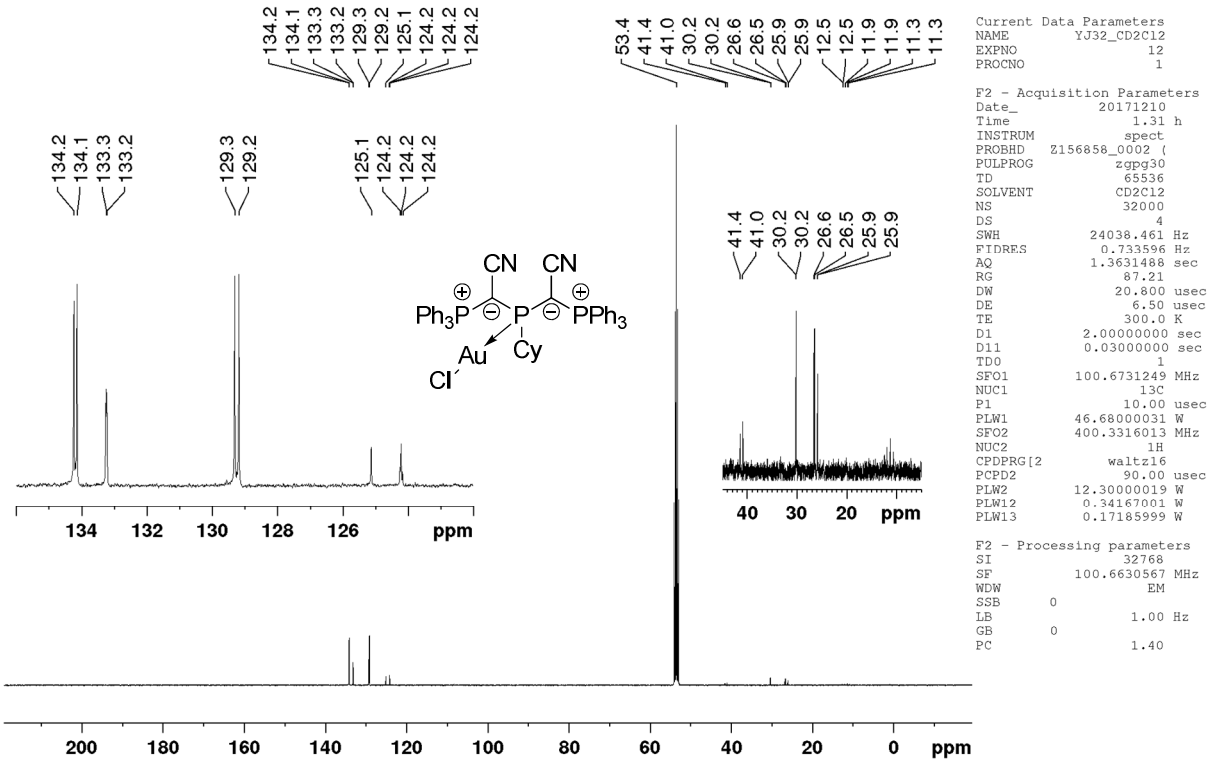


Figure S27. ^{13}C{^{1}H} NMR spectrum of **$(Y_{CN})_2$PCy·AuCl.**

2.2.8 $(Y_{CN})_2P^tBu{\cdot}AuCl$

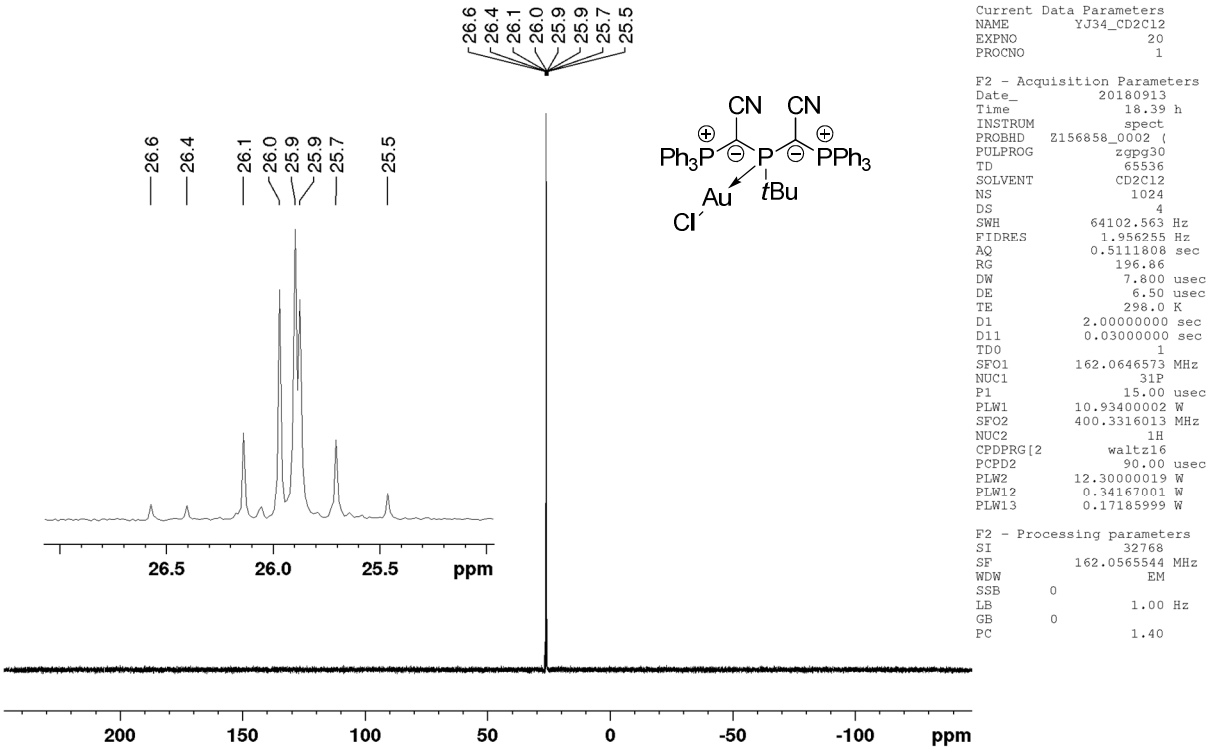


Figure S28. $^{31}P\{^1H\}$ NMR spectrum of **$(Y_{CN})_2P^tBu{\cdot}AuCl$**.

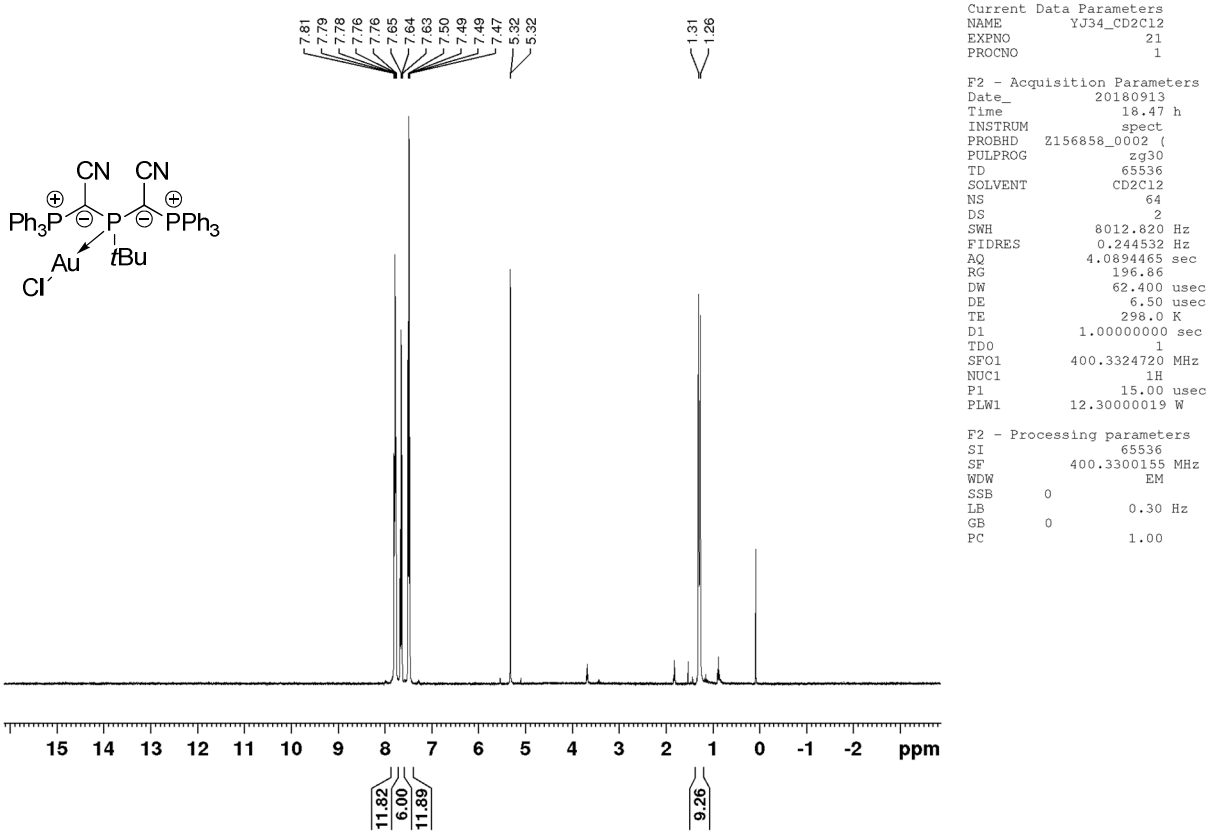


Figure S29. ^1H NMR spectrum of **$(Y_{CN})_2P^tBu{\cdot}AuCl$** (small signals between 0 and 2 ppm belong to silicon grease and pentane).

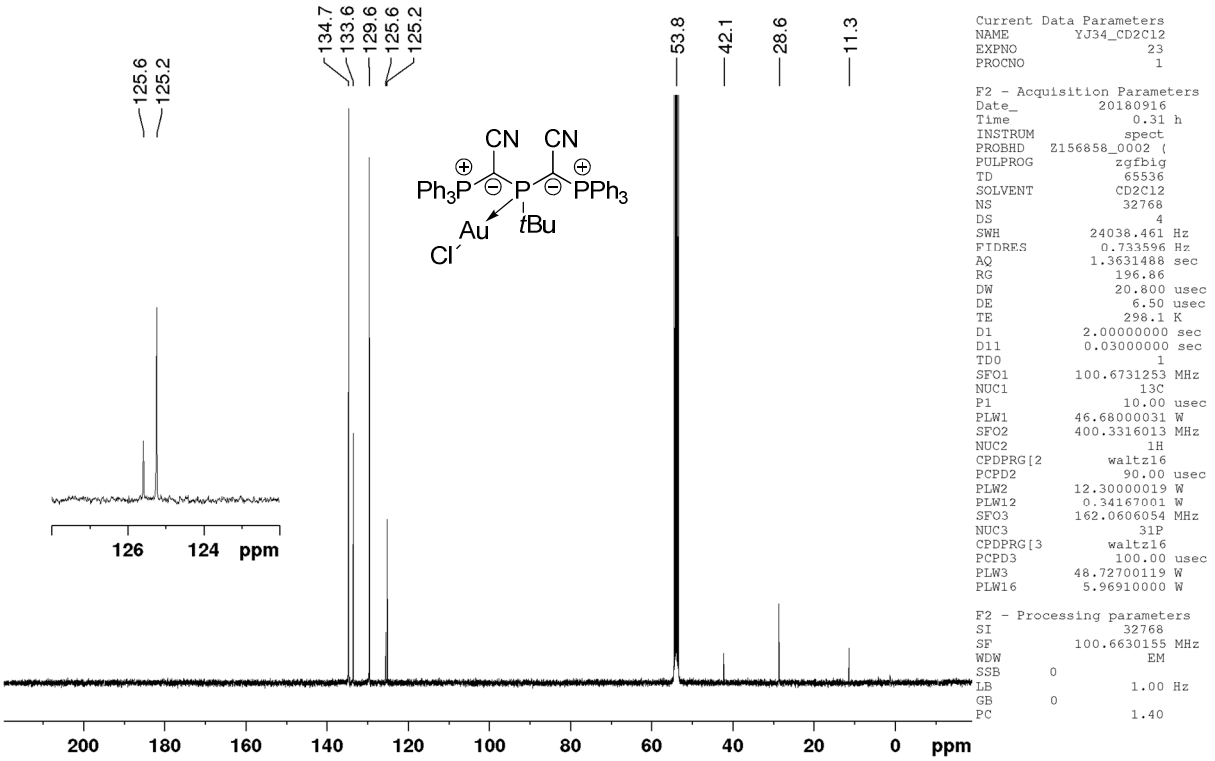


Figure S30. $^{13}C\{^{31}P, ^{1}H\}$ NMR spectrum of **$(Y_{CN})_2P^tBu{\cdot}AuCl$**.

2.2.9 $(Y_{CN})_2PCy{\cdot}Rh(acac)CO$

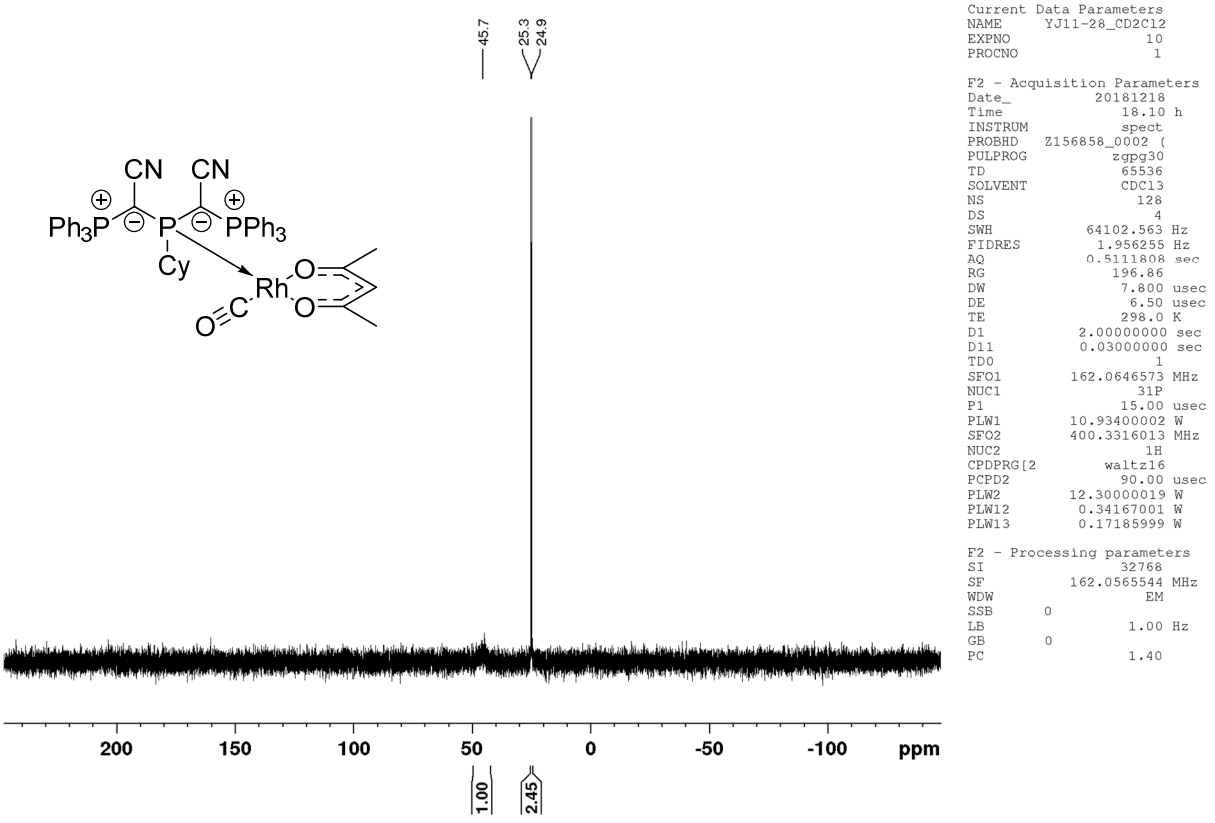


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of **$(Y_{CN})_2PCy{\cdot}Rh(acac)CO$**.

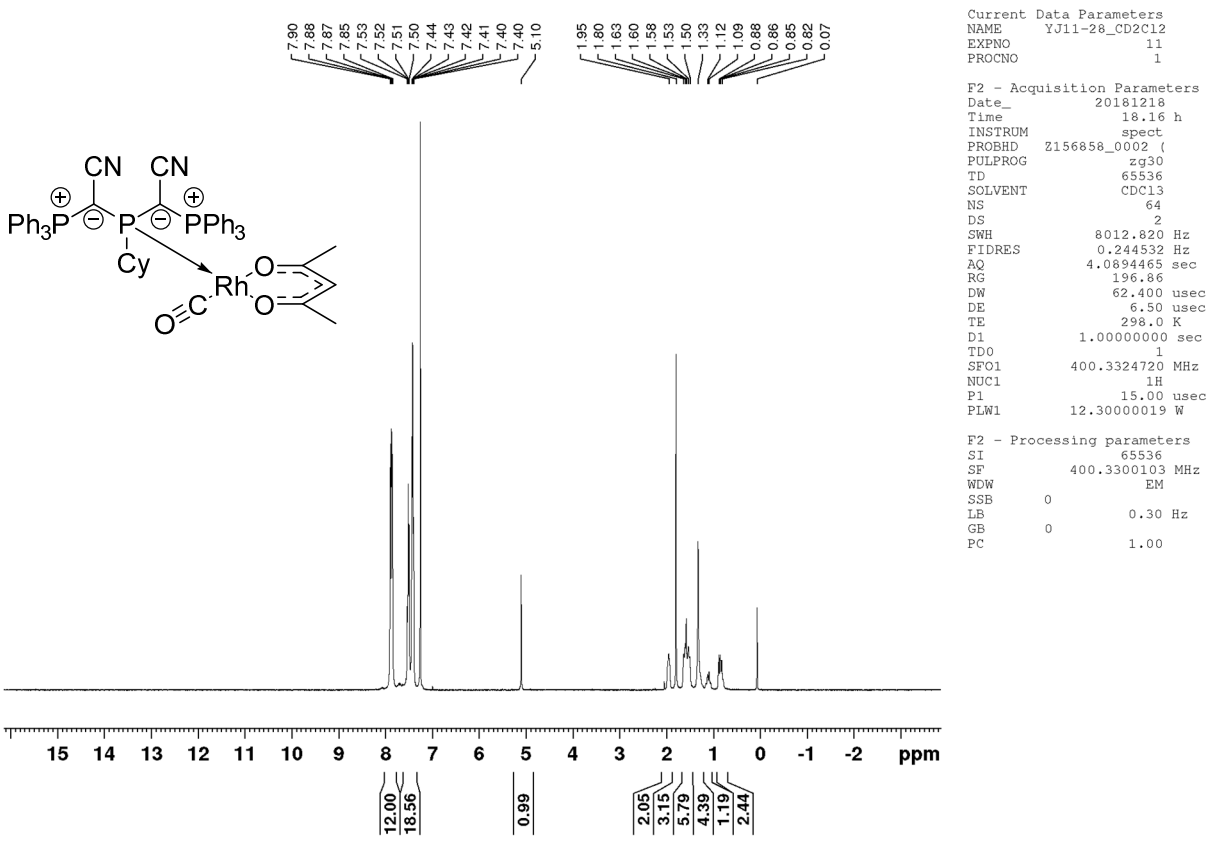


Figure S32. ^{1}H NMR spectrum of **$(Y_{CN})_2$PCy·Rh(acac)CO** (signal at 0 ppm corresponds to silicon grease).

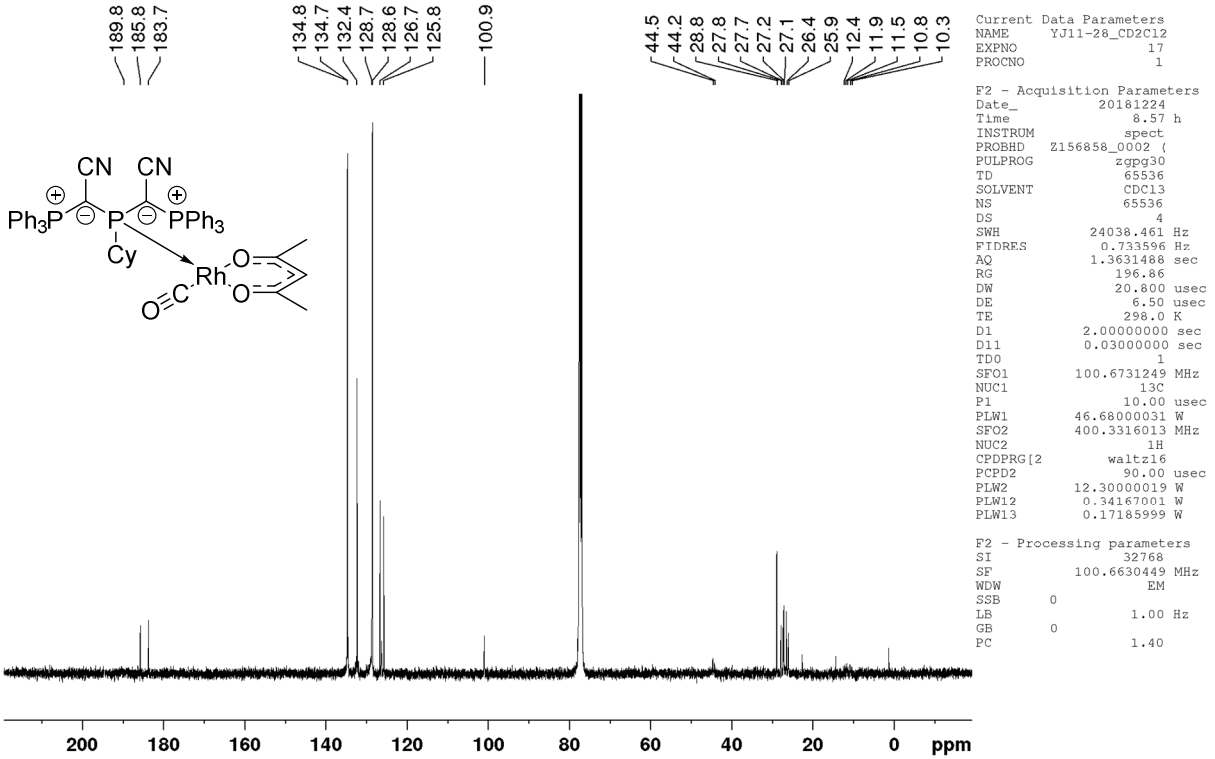


Figure S33. ^{13}C{^{1}H} NMR spectrum of **$(Y_{CN})_2$PCy·Rh(acac)CO**.

2.3 NMR spectra of the isolated compounds of the catalysis

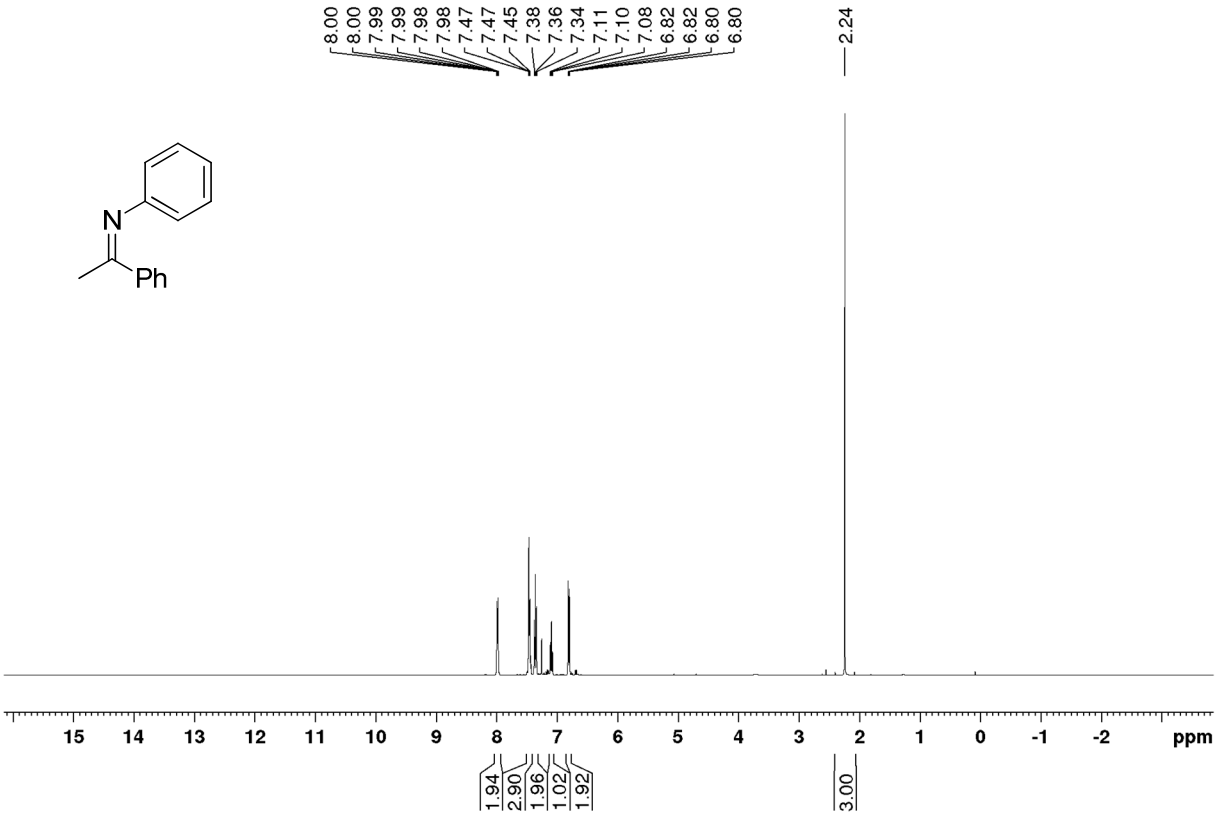


Figure S34. ^{1}H NMR spectrum of Phenyl-(1-phenylethylidene)amine.

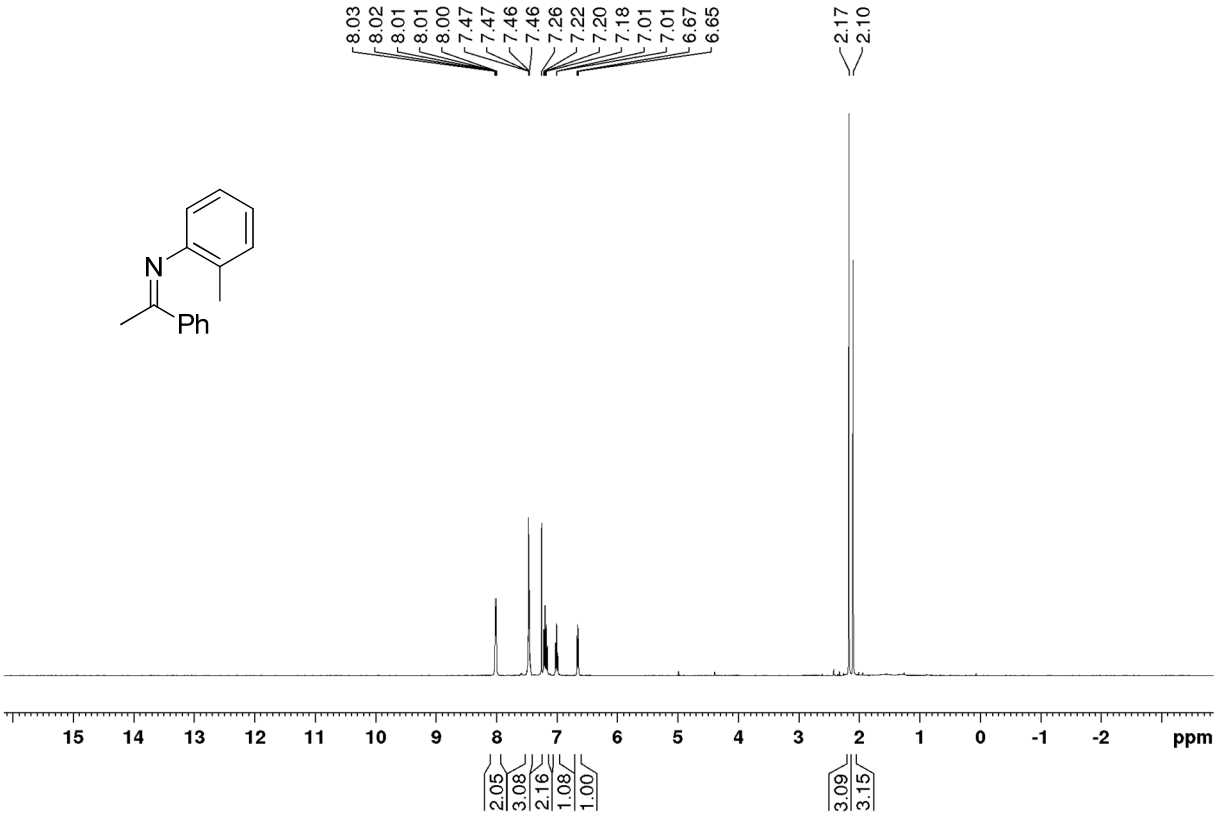


Figure S35. ^{1}H NMR spectrum of 1-Phenyl-*N*-(o-tolyl)ethan-1-imine.

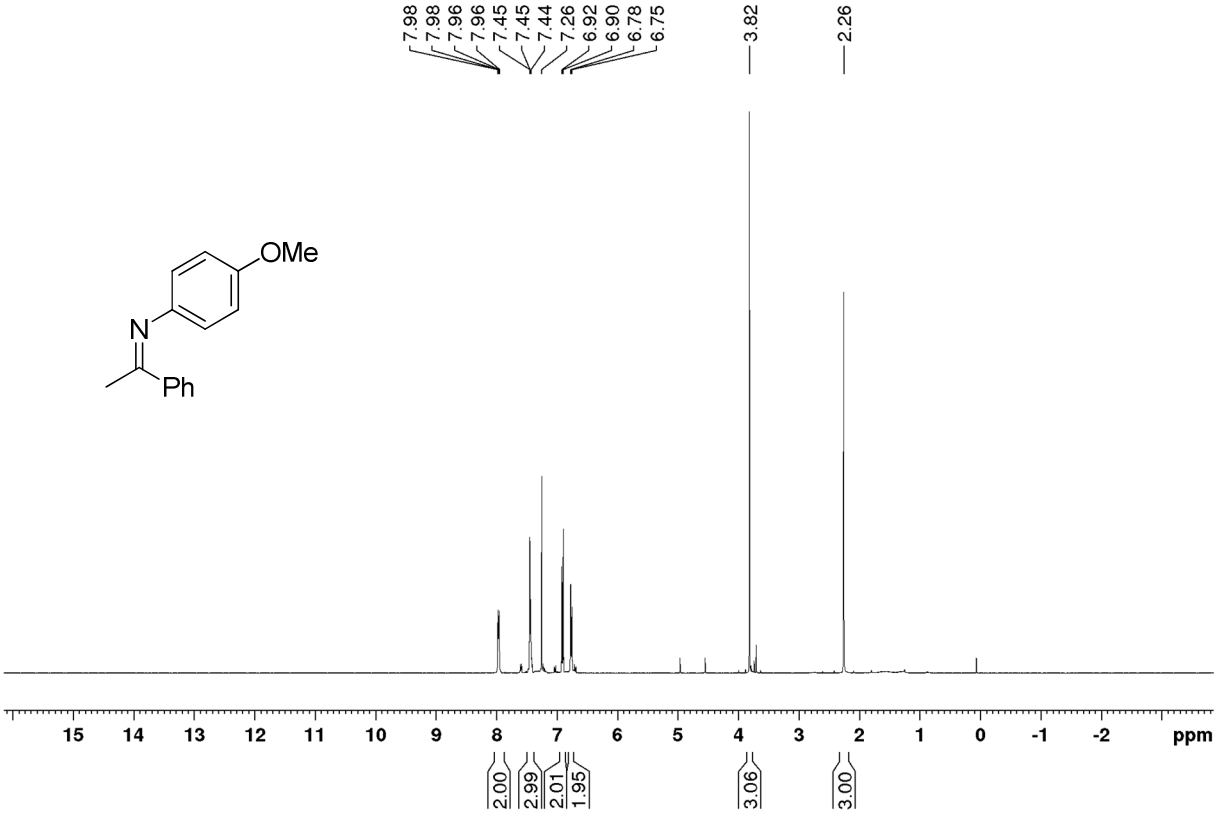


Figure S36. [1]H NMR spectrum of 1-(4-Methoxyphenyl)-*N*-phenylethan-1-imine (signal at 0 ppm corresponds to silicon grease).

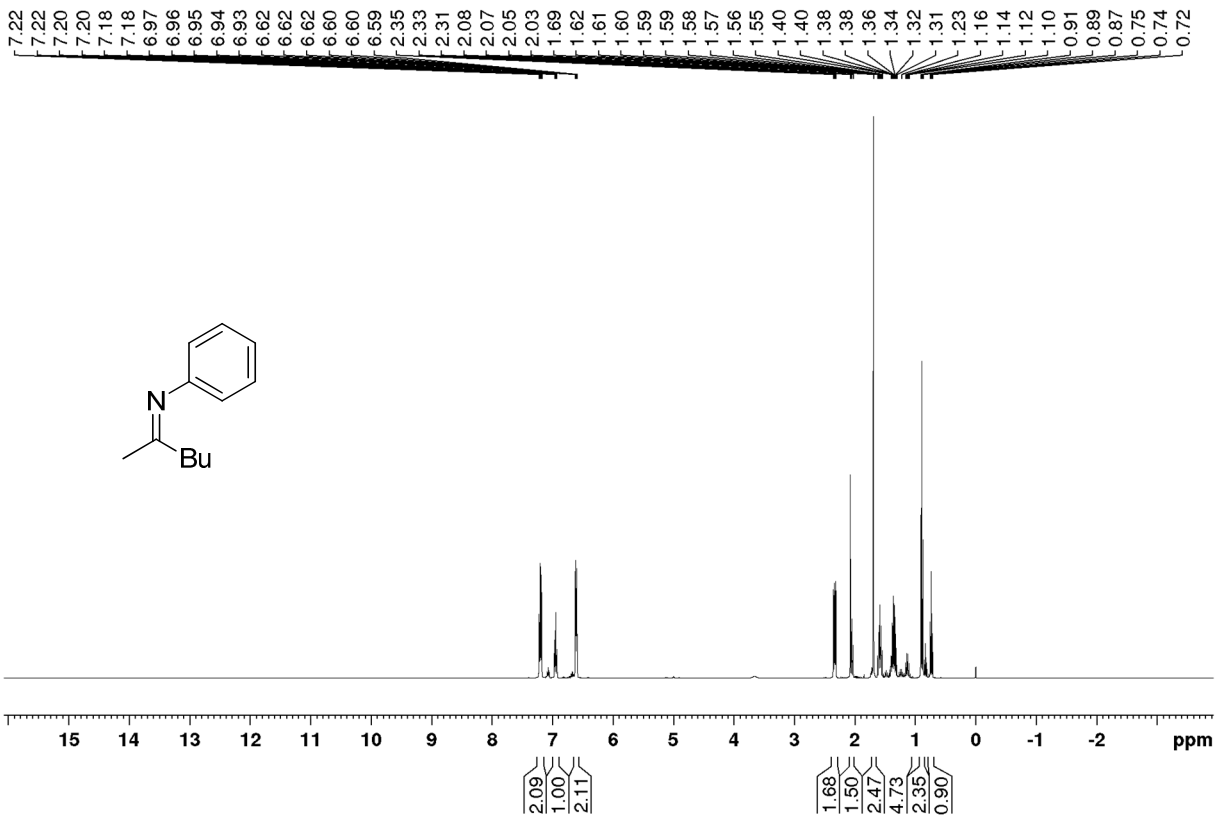


Figure S37. [1]H NMR spectrum of the mixture *E*- and *Z*-*N*-phenylhexan-2-imine.

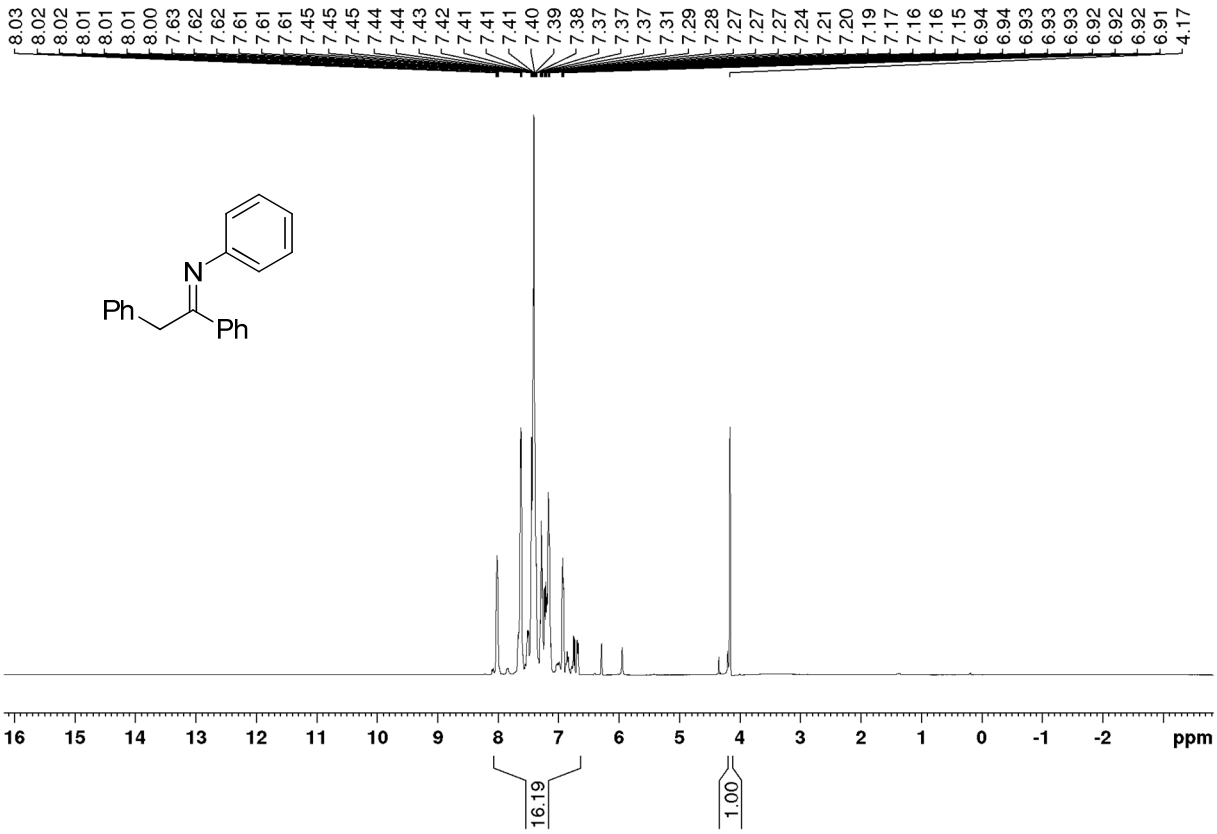


Figure S38. ^{1}H NMR spectrum of *N*,1,2-triphenylethan-1-imine.

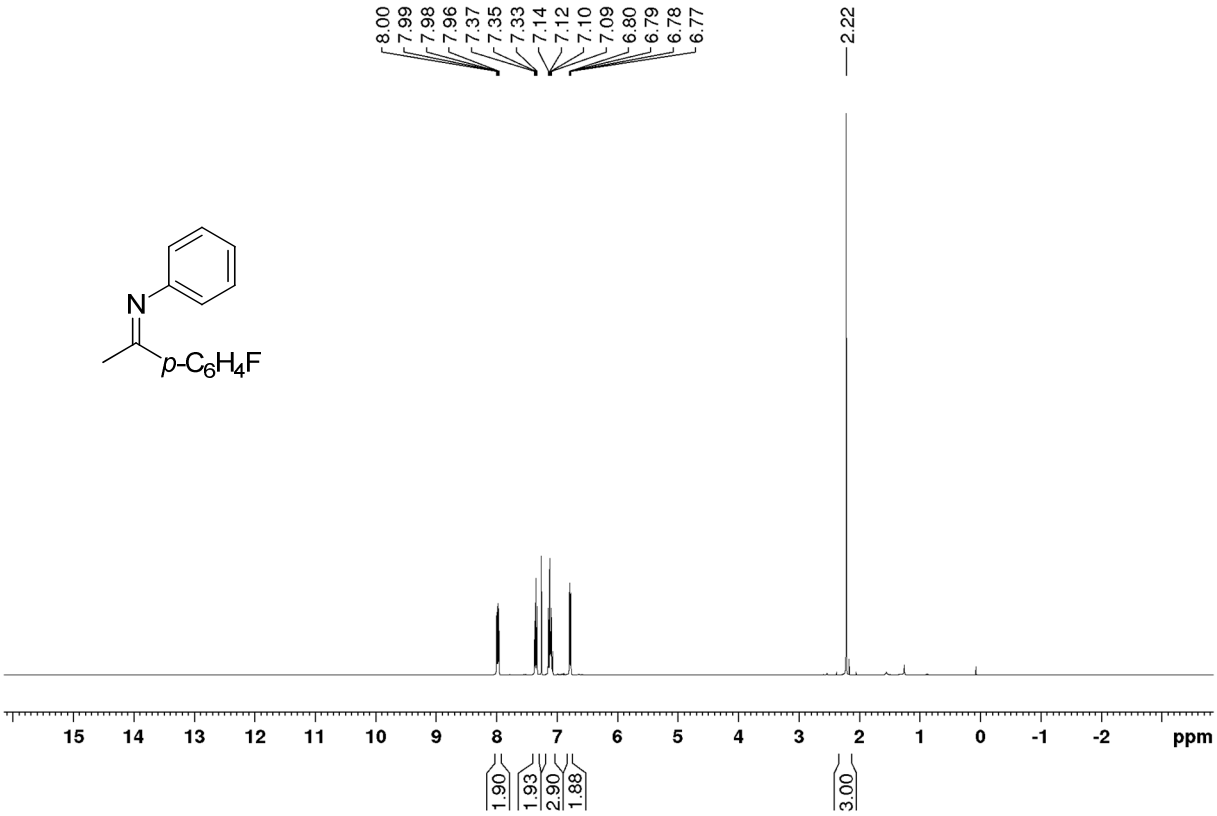


Figure S39. ^{1}H NMR spectrum of 1-(4-fluorophenyl)-*N*-phenylethan-1-imine.

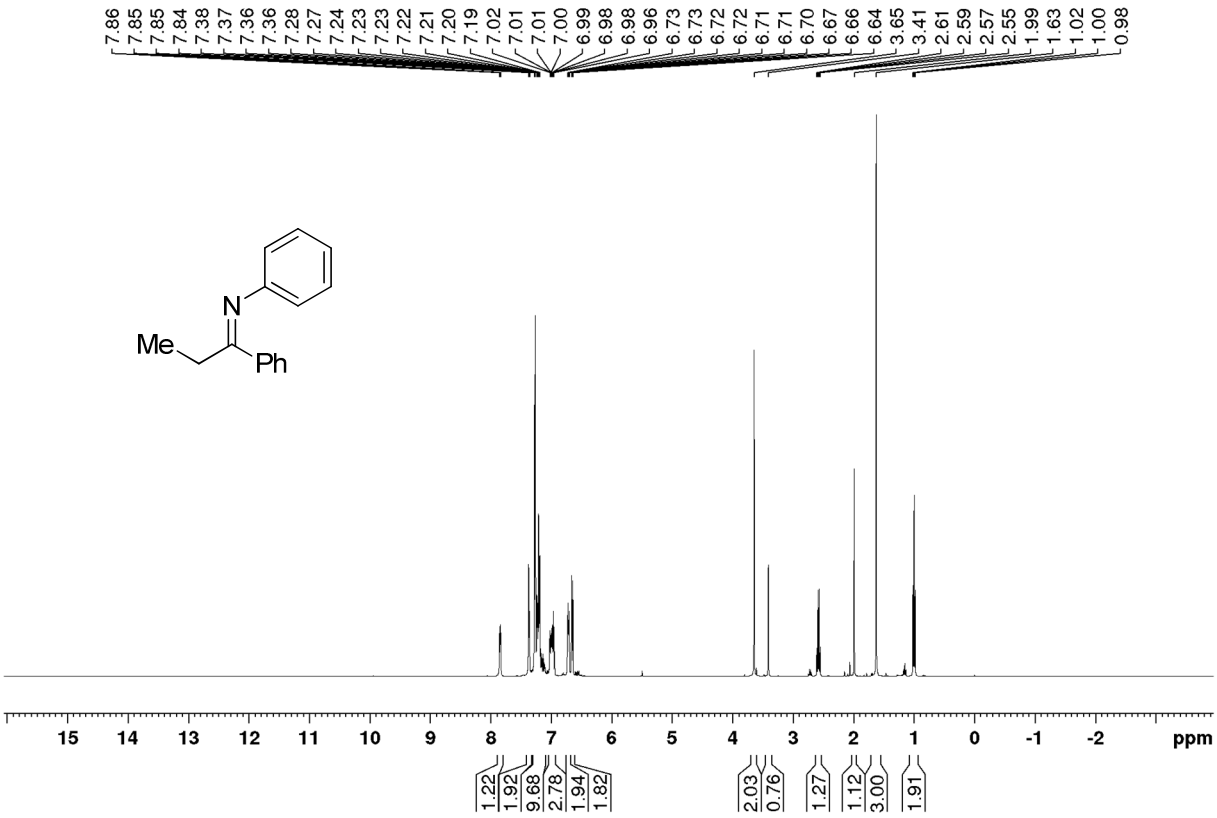


Figure S40. ^{1}H NMR spectrum of the mixture *N*,1-diphenylpropan-1-imine and *N*,1-diphenylpropan-2-imine.

3. Crystal Structure Determination

3.1 General information

Data collection of all compounds was conducted either with an Oxford Synergy (**$(Y_{CN})_2$PCl**, **$(Y_{CN})_2$PCy·Rh(CO)(acac)**) or Oxford SuperNova (**$Y_{CN}P^tBu_2$**, **$(Y_{CN})_2$PPh**, **$(Y_{CN})_2$PCy**, **$(Y_{CN})_2P^tBu$, $(Y_{CN})_3$P, $Y_{CN}P^tBu_2$·AuCl, $(Y_{CN})_2$PPh·AuCl, $(Y_{CN})_2$PCy·AuCl, $(Y_{CN})_2P^tBu$·AuCl).** The structures were solved using direct methods, refined with the Shelx software package[8] and expanded using Fourier techniques. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were affected at 100 K. Crystallographic data (including structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1943517-1943526. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

Details on the structure solutions

The structure of **$(Y_{CN})_2$PCy** contained a CH_2Cl_2 solvent molecules disordered over two sites. The occupancy of the two sites was 0.81:0.19.

The structure of **$(Y_{CN})_3$P** contained a highly disordered solvent molecule that was treated by using the PLATON/SQUEZZE routine.[8]

The structure of **$(Y_{CN})_2$PPh·AuCl** contained a CH_2Cl_2 solvent molecules disordered over two sites. This was modelled using the SADI instruction. The occupancy of the two sites was 0.66:0.34.

The structure of **$(Y_{CN})_2$PCy·Rh(CO)(acac)** contained a $CHCl_3$ solvent molecules disordered over two sites. This was modelled using the RIGU instruction. The occupancy of the two sites was 0.86:0.14.

Table S6. Data collection and structure refinement details for the compounds **$Y_{CN}P^tBu_2$, $(Y_{CN})_2$PPh** and **$(Y_{CN})_2$PCy**.

Compound	**$Y_{CN}P^tBu_2$**	**$(Y_{CN})_2$PPh**	**$(Y_{CN})_2$PCy**
CCDC No.	1943525	1943520	1943518
Formula	$C_{62}H_{72}N_2P_4$	$C_{47}H_{37}Cl_2N_2P_3$	$C_{97}H_{92}Cl_{10}N_4P_6$
Formula weight [g·mol^{-1}]	969.09	793.59	1854.06
Temperature [K]	100(2)	100(2)	100(2)
Wave length [Å]	1.54184	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1$	*P*-1
a [Å]	10.1896(2)	10.3342(2)	10.2673(11)
b [Å]	17.4204(4)	22.3144(11)	12.110(2)
c [Å]	17.4304(4)	17.0157(3)	19.820(2)
α [°]	67.712(2)	90	103.947(12)
β [°]	73.191(2)	92.007(2)	99.881(9)
γ [°]	73.1212(19)	90	100.687(11)
Volume [Å^3]	2682.91(11)	3921.4(2)	2289.0(5)
Z	2	4	1
Calc. density [Mg·m^{-3}]	1.200	1.344	1.345

μ [mm^{-1}]	1.602	2.929	4.157
F(000)	1036	1648	962
Crystal dimensions [mm]	0.354 x 0.084 x 0.047	0.237 x 0.169 x 0.060	0.143 x 0.103 x 0.031
Theta range [°]	4.555 to 72.125	3.268 to 70.999	3.872 to 69.976
Index ranges	–12 ≤ h ≤ 12	–11 ≤ h ≤ 12	–12 ≤ h ≤ 9
	–21 ≤ k ≤ 21	–27 ≤ k ≤ 27	–13 ≤ k ≤ 14
	–21 ≤ l ≤ 21	–15 ≤ l ≤ 20	–23 ≤ l ≤ 24
Reflections collected	50208	33692	15578
Independent reflections	10570 [R_{int} = 0.0606]	15150 [R_{int} = 0.0270]	8610 [R_{int} = 0.0267]
Data/Restraints/Parameter	10570 / 0 / 627	15150 / 1 / 974	8610 / 0 / 560
Goodness-of-fit on F^2	1.048	1.024	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0393 wR2 = 0.1022	R1 = 0.0309 wR2 = 0.0796	R1 = 0.0366 wR2 = 0.0913
R indices (all data)	R1 = 0.0411 wR2 = 0.1038	R1 = 0.0325 wR2 = 0.0806	R1 = 0.0452 wR2 = 0.0966
Largest diff. peak and hole [e·Å^{-3}]	0.685 and -0.310	0.560 and -0.466	0.717 and -0.586

Table S7. Data collection and structure refinement details for the compounds **$(Y_{CN})_3P$**, **$(Y_{CN})_2P^tBu{\cdot}AuCl$** and **$(Y_{CN})_2PCy{\cdot}Rh(CO)(acac)$**.

Compound	**$(Y_{CN})_2P^tBu$**	**$(Y_{CN})_3P$**	**$(Y_{CN})_2PCy{\cdot}Rh(CO)(acac)$**
CCDC No.	1943522	1943523	1943526
Formula	$C_{45}H_{41}Cl_2N_2P_3$	$C_{252}H_{204}N_{12}O_3P_{16}$	$C_{55}H_{51}Cl_9N_2O_3P_3Rh$
Formula weight [g·mol^{-1}]	773.61	3943.78	1302.84
Temperature [K]	100(2)	100(2)	100(2)
Wave length [Å]	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/n$	P-3	$P2_1/c$
a [Å]	9.8538(3)	35.1836(7)	11.00739(5)
b [Å]	22.9455(7)	35.1836(7)	22.02102(12)
c [Å]	17.3019(6)	9.7068(2)	24.05162(13)
α [°]	90	90	90
β [°]	93.031(3)	90	102.9893(5)
γ [°]	90	120	90
Volume [Å^3]	3906.5(2)	10406.1(5)	5680.79(5)
Z	4	2	4
Calc. density [Mg·m^{-3}]	1.315	1.259	1.5233
μ [mm^{-1}]	2.922	1.689	7.487
F(000)	1616	4128	2648
Crystal dimensions [mm]	0.385 x 0.068 x 0.037	0.368 x 0.092 x 0.041	0.288 x 0.142 x 0.077
Theta range [°]	3.853 to 74.992	3.838 to 69.968	2.753 to 74.997
Index ranges	–12 ≤ h ≤ 11	–34 ≤ h ≤ 42	-12 ≤ h ≤ 13
	–28 ≤ k ≤ 28	–38 ≤ k ≤ 30	–25 ≤ k ≤ 27

	–18 ≤ l ≤ 21	–11 ≤ l ≤ 9	–29 ≤ l ≤ 30
Reflections collected	18240	24302	51112
Independent reflections	7986 [R_{int} = 0.0495]	13078 [R_{int} = 0.0402]	11595 [R_{int} = 0.0271]
Data/Restraints/Parameter	7986 / 0 / 472	13078 / 242 / 944	11595 / 0 / 692
Goodness-of-fit on F^2	1.014	1.007	1.042
Final R indices [I>2sigma(I)]	$R1$ = 0.0434 w$R2$ = 0.1004	$R1$ = 0.0428 w$R2$ = 0.1037	$R1$ = 0.0295 w$R2$ = 0.0766
R indices (all data)	$R1$ = 0.0644 w$R2$ = 0.1130	$R1$ = 0.0507 w$R2$ = 0.1076	$R1$ = 0.0305 w$R2$ = 0.0772
Largest diff. peak and hole [e·Å^{-3}]	0.474 and -0.419	0.402 and -0.306	0.858 and -0.789

Table S 8. Data collection and structure refinement details for the compounds **$Y_{CN}P^tBu_2$·AuCl**, **$(Y_{CN})_2$PPh·AuCl** and **$(Y_{CN})_2$PCy·AuCl**.

Compound	**$Y_{CN}P^tBu_2$·AuCl**	**$(Y_{CN})_2$PPh·AuCl**	**$(Y_{CN})_2$PCy·AuCl**
CCDC No.	1943524	1943519	1943517
Formula	$C_{28}H_{33}AuClNP_2$	$C_{47}H_{37}AuCl_3N_2P_3$	$C_{46}H_{41}AuCl_1N_2P_3$
Formula weight [g·mol^{-1}]	677.91	1026.01	947.13
Temperature [K]	100(2)	100(2)	100(2)
Wave length [Å]	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	*P*-1	$P2_1/n$
a [Å]	11.78322(18)	12.5994(8)	17.5516(7)
b [Å]	9.40736(13)	13.2954(8)	12.9246(2)
c [Å]	24.6670(4)	13.5256(8)	17.7238(7)
α [°]	90	70.090(5)	90
β [°]	102.4825(16)	93.8160(10)	93.431(4)
γ [°]	90	78.391(5)	90
Volume [Å^3]	2669.68(7)	2085.9(2)	4013.4(2)
Z	4	2	4
Calc. density [Mg·m^{-3}]	1.687	1.634	1.567
μ [mm^{-1}]	12.528	9.766	8.899
F(000)	1336	1016	1888
Crystal dimensions [mm]	0.211 x 0.150 x 0.072	0.332 x 0.255 x 0.215	0.277 x 0.084 x 0.031
Theta range [°]	3.671 to 74.957	3.477 bis 74.558	3.442 to 71.999
Index ranges	-14 ≤ h ≤ 12	–15 ≤ h ≤ 15	–21 ≤ h ≤ 20
	-11 ≤ k ≤ 11	–16 ≤ k ≤ 15	–13 ≤ k ≤ 15
	-30 ≤ l ≤ 30	–16 ≤ l ≤ 16	–21 ≤ l ≤ 21
Reflections collected	21894	15135	16094
Independent reflections	5471 [R_{int} = 0.0309]	8272 [R_{int} = 0.0203]	7808 [R_{int} = 0.0287]
Data/Restraints/Parameter	5471 / 0 / 304	8272 / 7 / 533	7808 / 0 / 478
Goodness-of-fit on F^2	1.061	1.110	1.034

Final R indices [I>2sigma(I)]	*R*1 = 0.0216, w*R*2 = 0.0551	*R*1 = 0.0231 w*R*2 = 0.0585	*R*1 = 0.0294 w*R*2 = 0.0740
R indices (all data)	*R*1 = 0.0234, w*R*2 = 0.0564	*R*1 = 0.0255 w*R*2 = 0.0593	*R*1 = 0.0347 w*R*2 = 0.0784
Largest diff. peak and hole [e·Å^{-3}]	0.851 and -1.017	0.774 and –1.501	1.368 and –1.007

Table S9. Data collection and structure refinement details for **$(Y_{CN})_2P^tBu{\cdot}AuCl$**.

Compound	**$(Y_{CN})_2P^tBu{\cdot}AuCl$**
CCDC No.	1943521
Formula	$C_{44}H_{39}AuClN_2P_3$
Formula weight [g·mol^{-1}]	921.10
Temperature [K]	100(2)
Wave length [Å]	1.54184
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	10.8276(2)
b [Å]	33.9018(4)
c [Å]	11.4594(2)
α [°]	90
β [°]	113.030(2)
γ [°]	90
Volume [Å^3]	3871.21(12)
Z	4
Calc. density [Mg·m^{-3}]	1.580
μ [mm^{-1}]	9.207
F(000)	1832
Crystal dimensions [mm]	0.488 x 0.094 x 0.044
Theta range [°]	4.391 to 74.977
Index ranges	-13 ≤ h ≤ 13
	-41 ≤ k ≤ 42
	-14 ≤ l ≤ 14
Reflections collected	31090
Independent reflections	7947 [R_{int} = 0.0291]
Data/Restraints/Parameter	7947 / 0 / 463
Goodness-of-fit on F^2	1.119
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0619
R indices (all data)	R1 = 0.0299, wR2 = 0.0627
Largest diff. peak and hole [e·Å^{-3}]	0.789 and -1.209

3.2 Crystal structures of Y_{CN}Phos ligands

3.2.1 Crystal Structure Determination of $Y_{CN}P^tBu_2$

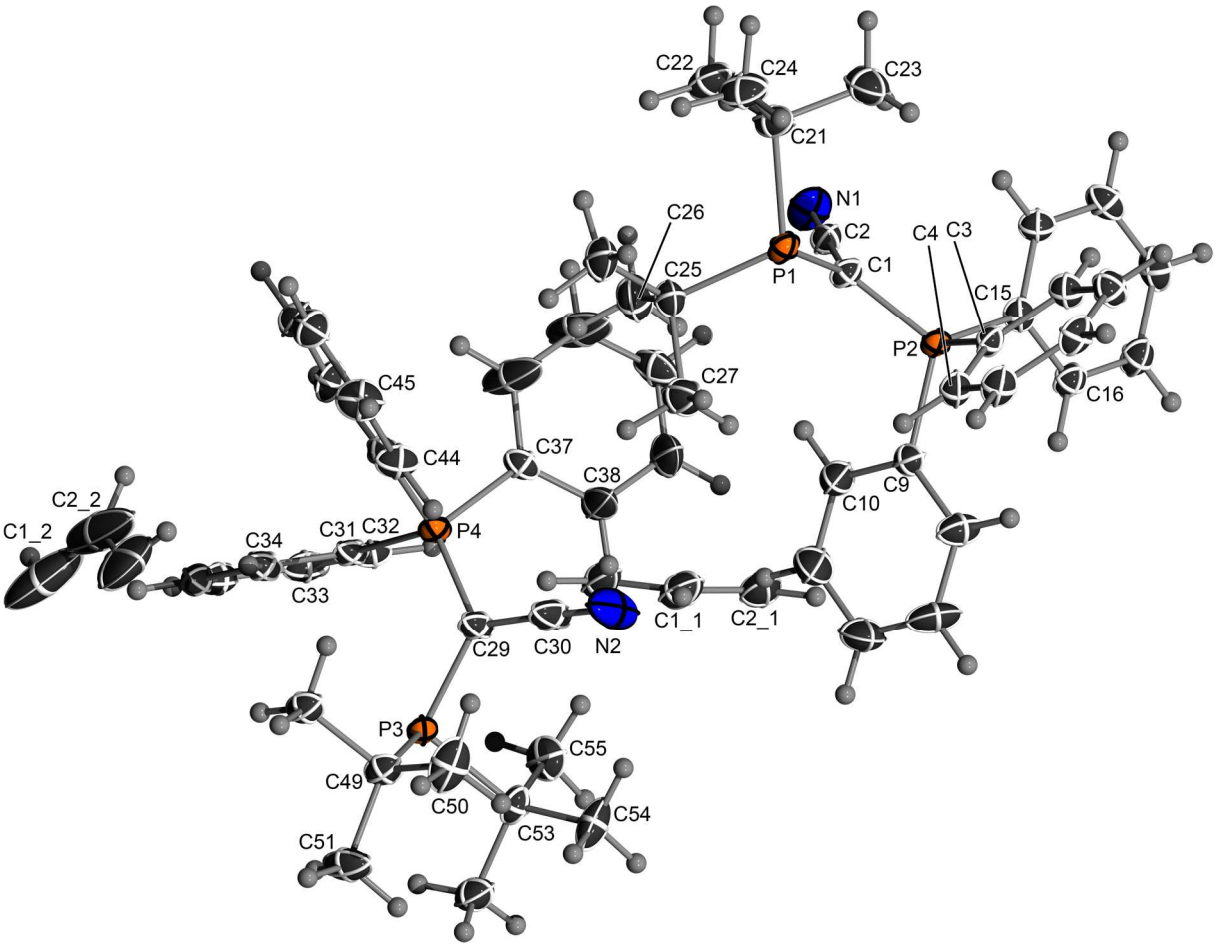


Figure S41 ORTEP Plot of $Y_{CN}P^tBu_2$. Ellipsoids are drawn at the 50% probability level.

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $Y_{CN}P^tBu_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	4571(1)	1942(1)	2620(1)	21(1)
P(2)	2018(1)	3280(1)	2079(1)	18(1)
P(3)	501(1)	2527(1)	8114(1)	18(1)
P(4)	3152(1)	2819(1)	6767(1)	19(1)
N(1)	4698(2)	4297(1)	2081(1)	35(1)
N(2)	842(3)	2076(2)	6045(2)	60(1)
C(1)	3663(2)	3043(1)	2280(1)	20(1)
C(2)	4210(2)	3733(1)	2178(1)	24(1)
C(3)	1730(2)	2501(1)	1723(1)	20(1)
C(4)	1391(2)	1737(1)	2297(1)	25(1)
C(5)	1169(2)	1156(1)	2006(2)	28(1)
C(6)	1289(2)	1330(1)	1143(2)	29(1)
C(7)	1629(2)	2084(1)	574(1)	28(1)
C(8)	1855(2)	2668(1)	859(1)	25(1)
C(9)	607(2)	3358(1)	2982(1)	22(1)

C(10)	855(3)	3602(2)	3588(2)	36(1)
C(11)	-177(3)	3676(2)	4287(2)	50(1)
C(12)	-1467(3)	3501(2)	4385(2)	47(1)
C(13)	-1727(3)	3273(2)	3783(2)	46(1)
C(14)	-700(2)	3204(2)	3070(2)	34(1)
C(15)	1710(2)	4299(1)	1263(1)	20(1)
C(16)	391(2)	4834(1)	1289(1)	24(1)
C(17)	154(2)	5581(1)	635(2)	29(1)
C(18)	1221(3)	5804(1)	-53(1)	30(1)
C(19)	2543(2)	5282(1)	-86(1)	28(1)
C(20)	2795(2)	4533(1)	575(1)	24(1)
C(21)	6371(2)	1956(2)	1908(2)	32(1)
C(22)	7352(3)	2378(2)	2085(2)	40(1)
C(23)	6142(3)	2434(2)	1007(2)	43(1)
C(24)	7107(3)	1033(2)	1974(2)	40(1)
C(25)	4707(2)	1721(2)	3750(1)	31(1)
C(26)	4917(3)	2444(2)	3949(2)	45(1)
C(27)	3278(3)	1499(2)	4277(2)	41(1)
C(28)	5829(3)	930(2)	4027(2)	40(1)
C(29)	1556(2)	2531(1)	7082(1)	25(1)
C(30)	1185(3)	2280(2)	6509(2)	38(1)
C(31)	3401(2)	3267(1)	7478(1)	21(1)
C(32)	3144(2)	4145(1)	7294(1)	24(1)
C(33)	3429(2)	4478(2)	7822(2)	29(1)
C(34)	3945(2)	3940(2)	8537(2)	30(1)
C(35)	4167(2)	3068(2)	8737(1)	28(1)
C(36)	3907(2)	2729(1)	8204(1)	25(1)
C(37)	3336(2)	3607(1)	5717(1)	23(1)
C(38)	2191(3)	4070(3)	5391(2)	71(1)
C(39)	2304(3)	4687(3)	4592(2)	72(1)
C(40)	3557(3)	4832(2)	4120(2)	37(1)
C(41)	4691(4)	4377(3)	4446(3)	90(2)
C(42)	4596(3)	3755(2)	5231(2)	81(2)
C(43)	4673(2)	1969(1)	6698(1)	23(1)
C(44)	4506(2)	1206(2)	6691(2)	30(1)
C(45)	5673(3)	563(2)	6607(2)	36(1)
C(46)	7003(3)	688(2)	6503(2)	33(1)
C(47)	7176(2)	1441(2)	6519(2)	32(1)
C(48)	6009(2)	2077(1)	6628(2)	29(1)
C(49)	349(2)	1382(1)	8682(1)	25(1)
C(50)	-26(3)	916(2)	8215(2)	42(1)
C(51)	-690(3)	1327(2)	9526(2)	40(1)
C(52)	1811(2)	933(1)	8874(1)	28(1)
C(53)	-1258(2)	3209(1)	7893(1)	25(1)
C(54)	-2072(3)	2929(2)	7468(2)	40(1)
C(55)	-934(3)	4083(1)	7339(2)	36(1)
C(56)	-2206(2)	3317(2)	8722(2)	34(1)
C11	633(3)	9316(2)	5590(2)	44(1)
C21	-66(3)	9177(2)	5094(2)	42(1)
C31	-700(3)	9873(2)	4503(2)	43(1)

C12	5521(4)	658(3)	9922(5)	101(2)
C22	5779(4)	404(4)	9242(4)	101(2)
C32	5235(4)	-254(4)	9303(4)	95(2)

Table S11. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$Y_{CN}P^tBu_2$**. The anisotropic displacement factor exponent takes the form: $–2\pi^2$ [$h^2a^{\cdot 2}U^{11}$ + ... + 2 h k a·b·U^{12}].

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
P(1)	18(1)	19(1)	25(1)	-4(1)	-6(1)	-6(1)
P(2)	16(1)	16(1)	19(1)	-3(1)	-4(1)	-6(1)
P(3)	18(1)	19(1)	19(1)	-3(1)	-4(1)	-7(1)
P(4)	20(1)	21(1)	18(1)	-5(1)	-1(1)	-11(1)
N(1)	36(1)	29(1)	45(1)	-10(1)	-10(1)	-16(1)
N(2)	53(2)	110(2)	44(1)	-48(2)	8(1)	-47(2)
C(1)	18(1)	18(1)	24(1)	-5(1)	-4(1)	-6(1)
C(2)	20(1)	26(1)	25(1)	-7(1)	-7(1)	-6(1)
C(3)	16(1)	21(1)	24(1)	-4(1)	-6(1)	-6(1)
C(4)	27(1)	24(1)	25(1)	-2(1)	-9(1)	-10(1)
C(5)	31(1)	22(1)	32(1)	0(1)	-11(1)	-14(1)
C(6)	29(1)	27(1)	37(1)	-11(1)	-11(1)	-10(1)
C(7)	32(1)	30(1)	25(1)	-9(1)	-6(1)	-11(1)
C(8)	28(1)	21(1)	25(1)	-4(1)	-5(1)	-9(1)
C(9)	20(1)	19(1)	23(1)	-2(1)	-4(1)	-3(1)
C(10)	25(1)	52(2)	33(1)	-20(1)	-8(1)	-1(1)
C(11)	38(2)	77(2)	35(1)	-29(1)	-7(1)	2(1)
C(12)	34(1)	59(2)	33(1)	-15(1)	5(1)	-1(1)
C(13)	25(1)	55(2)	56(2)	-23(1)	9(1)	-16(1)
C(14)	24(1)	40(1)	42(1)	-18(1)	0(1)	-12(1)
C(15)	24(1)	17(1)	22(1)	-4(1)	-6(1)	-7(1)
C(16)	22(1)	23(1)	27(1)	-6(1)	-6(1)	-6(1)
C(17)	27(1)	26(1)	33(1)	-5(1)	-11(1)	-3(1)
C(18)	41(1)	21(1)	28(1)	0(1)	-12(1)	-9(1)
C(19)	36(1)	23(1)	23(1)	-4(1)	-2(1)	-14(1)
C(20)	24(1)	22(1)	25(1)	-7(1)	-4(1)	-7(1)
C(21)	25(1)	28(1)	30(1)	-1(1)	1(1)	-2(1)
C(22)	24(1)	38(1)	50(2)	-5(1)	-3(1)	-10(1)
C(23)	40(1)	44(1)	32(1)	-11(1)	1(1)	1(1)
C(24)	28(1)	34(1)	48(1)	-14(1)	-1(1)	1(1)
C(25)	30(1)	35(1)	24(1)	-2(1)	-10(1)	-6(1)
C(26)	51(2)	52(2)	36(1)	-13(1)	-18(1)	-11(1)
C(27)	34(1)	43(1)	34(1)	-1(1)	-2(1)	-7(1)
C(28)	35(1)	43(1)	34(1)	1(1)	-16(1)	-4(1)
C(29)	23(1)	33(1)	22(1)	-10(1)	1(1)	-15(1)
C(30)	29(1)	61(2)	33(1)	-23(1)	5(1)	-26(1)
C(31)	18(1)	26(1)	22(1)	-7(1)	1(1)	-13(1)
C(32)	18(1)	26(1)	28(1)	-9(1)	0(1)	-10(1)
C(33)	24(1)	30(1)	37(1)	-17(1)	2(1)	-12(1)
C(34)	24(1)	42(1)	35(1)	-24(1)	2(1)	-14(1)
C(35)	23(1)	42(1)	24(1)	-12(1)	-2(1)	-14(1)
C(36)	26(1)	26(1)	24(1)	-7(1)	-1(1)	-13(1)

C(37)	27(1)	21(1)	21(1)	-6(1)	-2(1)	-9(1)
C(38)	28(1)	116(3)	28(1)	24(2)	-6(1)	-19(2)
C(39)	39(2)	113(3)	30(1)	22(2)	-15(1)	-16(2)
C(40)	45(1)	29(1)	26(1)	1(1)	0(1)	-10(1)
C(41)	35(2)	80(3)	71(2)	47(2)	7(2)	-7(2)
C(42)	25(1)	69(2)	76(2)	45(2)	-2(1)	-4(1)
C(43)	25(1)	23(1)	20(1)	-5(1)	-4(1)	-8(1)
C(44)	30(1)	28(1)	34(1)	-12(1)	0(1)	-13(1)
C(45)	39(1)	27(1)	41(1)	-14(1)	-1(1)	-10(1)
C(46)	34(1)	27(1)	32(1)	-8(1)	-6(1)	1(1)
C(47)	24(1)	37(1)	37(1)	-11(1)	-11(1)	-4(1)
C(48)	28(1)	27(1)	34(1)	-9(1)	-12(1)	-7(1)
C(49)	22(1)	18(1)	30(1)	-2(1)	-4(1)	-7(1)
C(50)	47(2)	23(1)	63(2)	-8(1)	-28(1)	-10(1)
C(51)	32(1)	30(1)	37(1)	5(1)	4(1)	-6(1)
C(52)	24(1)	24(1)	31(1)	-2(1)	-4(1)	-6(1)
C(53)	24(1)	21(1)	31(1)	-6(1)	-11(1)	-5(1)
C(54)	36(1)	36(1)	58(2)	-19(1)	-29(1)	2(1)
C(55)	40(1)	22(1)	37(1)	-1(1)	-10(1)	-4(1)
C(56)	22(1)	36(1)	40(1)	-10(1)	-4(1)	-3(1)
C11	25(1)	48(2)	40(1)	8(1)	-8(1)	-9(1)
C21	25(1)	42(1)	49(2)	-3(1)	-5(1)	-10(1)
C31	26(1)	57(2)	41(1)	-5(1)	-6(1)	-15(1)
C12	32(2)	55(2)	186(6)	-5(3)	-30(3)	-5(2)
C22	31(2)	82(3)	116(4)	36(3)	-7(2)	-2(2)
C32	34(2)	117(4)	108(4)	-20(3)	-28(2)	11(2)

3.2.2 Crystal Structure Determination of $(Y_{CN})_2PPh$

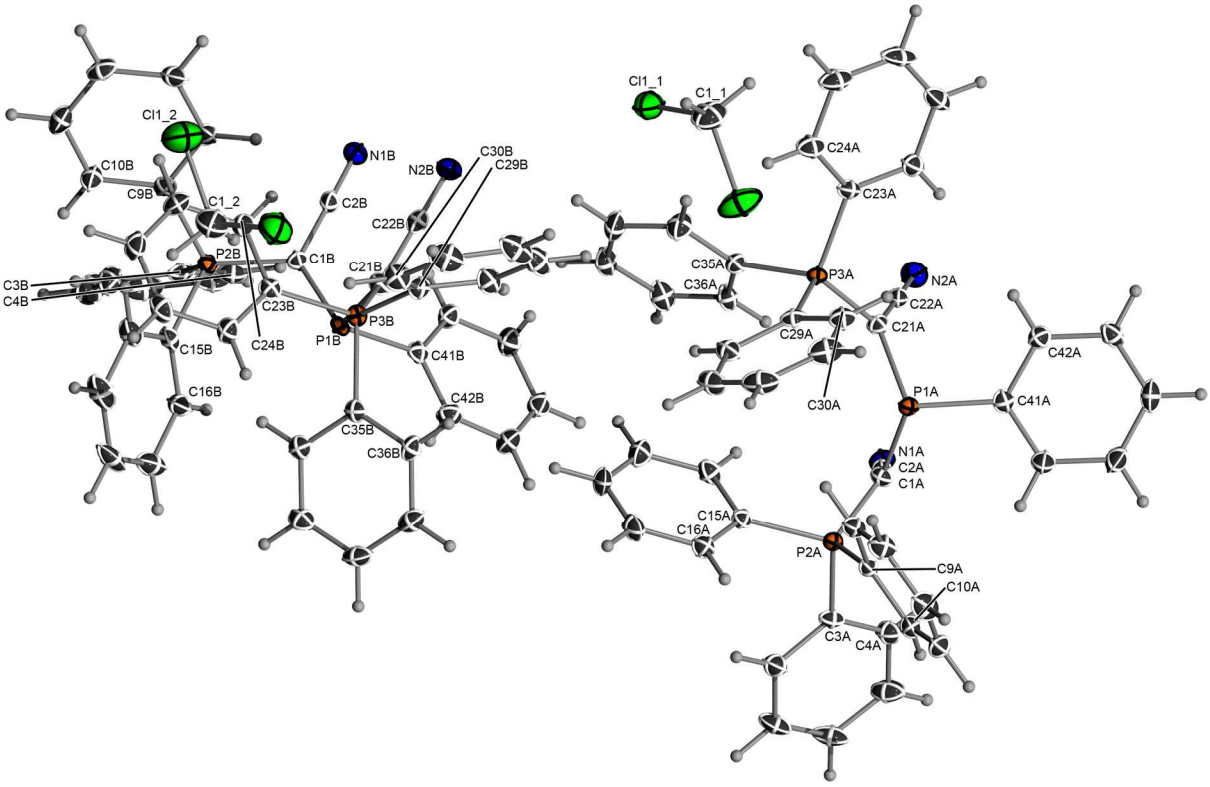


Figure S42 ORTEP Plot of **$(Y_{CN})_2PPh$**. Ellipsoids are drawn at the 50% probability level.

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2PPh$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1A)	481(1)	4023(1)	6740(1)	12(1)
P(2A)	2065(1)	5082(1)	7238(1)	11(1)
P(3A)	811(1)	3589(1)	5063(1)	11(1)
N(1A)	-1185(2)	5542(1)	6408(1)	18(1)
N(2A)	-2388(2)	4266(1)	5244(2)	22(1)
C(1A)	561(3)	4819(1)	6940(2)	14(1)
C(2A)	-387(3)	5221(1)	6648(2)	14(1)
C(3A)	1923(3)	5813(1)	7681(2)	15(1)
C(4A)	796(3)	5960(1)	8068(2)	20(1)
C(5A)	669(3)	6524(2)	8399(2)	27(1)
C(6A)	1662(3)	6937(1)	8355(2)	27(1)
C(7A)	2802(3)	6788(1)	7997(2)	25(1)
C(8A)	2936(3)	6228(1)	7658(2)	21(1)
C(9A)	2841(3)	4592(1)	7955(2)	14(1)
C(10A)	2801(3)	4728(1)	8754(2)	17(1)
C(11A)	3378(3)	4345(2)	9308(2)	22(1)
C(12A)	4005(3)	3830(1)	9064(2)	25(1)
C(13A)	4054(3)	3697(1)	8266(2)	22(1)
C(14A)	3471(3)	4071(1)	7712(2)	17(1)
C(15A)	3196(3)	5163(1)	6450(2)	14(1)
C(16A)	4534(3)	5095(1)	6575(2)	18(1)

C(17A)	5357(3)	5162(1)	5952(2)	23(1)
C(18A)	4847(3)	5302(2)	5214(2)	27(1)
C(19A)	3525(3)	5374(2)	5087(2)	26(1)
C(20A)	2694(3)	5302(1)	5705(2)	20(1)
C(21A)	-139(3)	3917(1)	5753(2)	14(1)
C(22A)	-1374(3)	4113(1)	5480(2)	16(1)
C(23A)	131(3)	2897(1)	4663(2)	15(1)
C(24A)	862(3)	2524(1)	4185(2)	22(1)
C(25A)	320(4)	2000(2)	3874(2)	27(1)
C(26A)	-930(4)	1840(1)	4051(2)	28(1)
C(27A)	-1645(3)	2199(2)	4531(2)	25(1)
C(28A)	-1130(3)	2729(1)	4838(2)	19(1)
C(29A)	2379(3)	3394(1)	5488(2)	15(1)
C(30A)	2454(3)	2911(1)	6004(2)	19(1)
C(31A)	3646(3)	2746(1)	6345(2)	26(1)
C(32A)	4756(3)	3059(2)	6160(2)	28(1)
C(33A)	4684(3)	3543(2)	5654(2)	25(1)
C(34A)	3490(3)	3716(1)	5314(2)	19(1)
C(35A)	1109(3)	4078(1)	4239(2)	15(1)
C(36A)	662(3)	4667(1)	4259(2)	17(1)
C(37A)	1017(3)	5071(1)	3681(2)	22(1)
C(38A)	1827(3)	4893(2)	3094(2)	23(1)
C(39A)	2235(3)	4305(2)	3056(2)	25(1)
C(40A)	1873(3)	3897(1)	3622(2)	23(1)
C(41A)	-855(3)	3764(1)	7337(2)	15(1)
C(42A)	-1592(3)	3262(1)	7108(2)	19(1)
C(43A)	-2473(3)	3008(1)	7608(2)	20(1)
C(44A)	-2622(3)	3245(1)	8352(2)	23(1)
C(45A)	-1888(4)	3735(2)	8592(2)	28(1)
C(46A)	-1007(3)	3991(1)	8088(2)	24(1)
P(1B)	5383(1)	6127(1)	1704(1)	11(1)
P(2B)	5793(1)	6608(1)	68(1)	12(1)
P(3B)	7017(1)	5082(1)	2214(1)	12(1)
N(1B)	2671(2)	5856(1)	78(2)	21(1)
N(2B)	3741(2)	4605(1)	1389(2)	18(1)
C(1B)	4809(3)	6243(1)	710(2)	14(1)
C(2B)	3636(3)	6023(1)	369(2)	15(1)
C(3B)	5049(3)	7289(1)	-327(2)	17(1)
C(4B)	3803(3)	7438(1)	-119(2)	20(1)
C(5B)	3232(3)	7967(2)	-403(2)	26(1)
C(6B)	3912(4)	8338(2)	-896(2)	31(1)
C(7B)	5159(4)	8194(2)	-1098(2)	33(1)
C(8B)	5733(4)	7673(1)	-815(2)	25(1)
C(9B)	6203(3)	6134(1)	-757(2)	15(1)
C(10B)	7013(3)	6338(1)	-1343(2)	20(1)
C(11B)	7367(3)	5952(2)	-1940(2)	22(1)
C(12B)	6935(3)	5364(2)	-1955(2)	22(1)
C(13B)	6117(3)	5164(1)	-1386(2)	22(1)
C(14B)	5751(3)	5547(1)	-784(2)	17(1)
C(15B)	7296(3)	6847(1)	542(2)	16(1)

C(16B)	7262(3)	7337(1)	1056(2)	22(1)
C(17B)	8397(4)	7545(2)	1421(2)	29(1)
C(18B)	9570(3)	7272(2)	1267(2)	30(1)
C(19B)	9608(3)	6786(2)	766(2)	28(1)
C(20B)	8474(3)	6568(1)	402(2)	21(1)
C(21B)	5526(3)	5329(1)	1876(2)	14(1)
C(22B)	4572(3)	4926(1)	1613(2)	14(1)
C(23B)	8215(3)	5058(1)	1464(2)	15(1)
C(24B)	7789(3)	4964(1)	682(2)	18(1)
C(25B)	8683(3)	4954(1)	89(2)	22(1)
C(26B)	9988(3)	5043(1)	263(2)	24(1)
C(27B)	10416(3)	5135(1)	1038(2)	22(1)
C(28B)	9537(3)	5142(1)	1635(2)	18(1)
C(29B)	6898(3)	4341(1)	2629(2)	16(1)
C(30B)	7922(3)	3939(1)	2601(2)	21(1)
C(31B)	7809(3)	3375(2)	2946(2)	29(1)
C(32B)	6693(4)	3216(2)	3311(2)	30(1)
C(33B)	5679(3)	3624(2)	3356(2)	26(1)
C(34B)	5780(3)	4187(1)	3017(2)	19(1)
C(35B)	7689(3)	5564(1)	2978(2)	14(1)
C(36B)	7652(3)	5391(1)	3767(2)	17(1)
C(37B)	8111(3)	5778(2)	4356(2)	21(1)
C(38B)	8609(3)	6331(1)	4157(2)	23(1)
C(39B)	8666(3)	6500(1)	3373(2)	20(1)
C(40B)	8210(3)	6120(1)	2781(2)	16(1)
C(41B)	4012(3)	6309(1)	2322(2)	14(1)
C(42B)	4336(3)	6396(1)	3121(2)	20(1)
C(43B)	3393(3)	6537(1)	3653(2)	22(1)
C(44B)	2107(3)	6588(1)	3403(2)	20(1)
C(45B)	1773(3)	6495(1)	2616(2)	21(1)
C(46B)	2711(3)	6365(1)	2079(2)	18(1)
C11	3989(4)	1652(2)	3739(2)	36(1)
Cl11	3790(1)	2215(1)	3011(1)	39(1)
Cl21	4259(1)	1976(1)	4674(1)	43(1)
C12	11085(4)	3610(2)	1172(2)	39(1)
Cl12	10728(1)	3332(1)	226(1)	54(1)
Cl22	11200(1)	3022(1)	1868(1)	43(1)

Table S13. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_2PPh$**. The anisotropic displacement factor exponent takes the form: $–2\pi^2$ [$h^2a^{\cdot 2}U^{11}$ + ... + 2 h k a·b·U^{12}].

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
P(1A)	12(1)	11(1)	13(1)	-2(1)	0(1)	-1(1)
P(2A)	12(1)	11(1)	12(1)	-1(1)	0(1)	-1(1)
P(3A)	12(1)	10(1)	12(1)	-1(1)	1(1)	0(1)
N(1A)	20(1)	18(1)	17(1)	0(1)	-1(1)	1(1)
N(2A)	16(1)	26(1)	23(1)	-2(1)	-1(1)	3(1)
C(1A)	14(1)	12(1)	16(1)	-2(1)	-1(1)	0(1)

C(2A)	16(1)	13(1)	13(1)	-3(1)	4(1)	-4(1)
C(3A)	18(1)	12(1)	15(1)	-1(1)	-3(1)	0(1)
C(4A)	19(1)	20(1)	22(1)	-4(1)	1(1)	0(1)
C(5A)	23(1)	26(2)	32(2)	-12(1)	-2(1)	4(1)
C(6A)	30(2)	16(1)	35(2)	-10(1)	-8(1)	3(1)
C(7A)	28(2)	15(1)	33(2)	-4(1)	-5(1)	-7(1)
C(8A)	20(1)	19(1)	23(1)	-3(1)	-1(1)	-3(1)
C(9A)	14(1)	13(1)	15(1)	1(1)	-1(1)	-3(1)
C(10A)	17(1)	19(1)	16(1)	-1(1)	2(1)	-5(1)
C(11A)	28(2)	25(1)	15(1)	2(1)	-2(1)	-8(1)
C(12A)	28(2)	21(1)	24(1)	9(1)	-7(1)	-2(1)
C(13A)	24(1)	17(1)	24(1)	1(1)	-3(1)	1(1)
C(14A)	18(1)	15(1)	18(1)	-1(1)	-1(1)	-2(1)
C(15A)	16(1)	12(1)	16(1)	-1(1)	3(1)	-2(1)
C(16A)	17(1)	19(1)	18(1)	-1(1)	0(1)	-1(1)
C(17A)	16(1)	26(2)	29(2)	-5(1)	7(1)	-4(1)
C(18A)	26(2)	33(2)	23(2)	-3(1)	13(1)	-10(1)
C(19A)	28(2)	32(2)	18(1)	4(1)	3(1)	-6(1)
C(20A)	18(1)	19(1)	22(2)	3(1)	-1(1)	-1(1)
C(21A)	13(1)	13(1)	15(1)	-2(1)	1(1)	0(1)
C(22A)	19(1)	15(1)	14(1)	-3(1)	3(1)	-4(1)
C(23A)	18(1)	12(1)	14(1)	-1(1)	-3(1)	-1(1)
C(24A)	26(2)	16(1)	22(2)	-2(1)	-1(1)	2(1)
C(25A)	39(2)	17(1)	24(2)	-6(1)	-3(1)	2(1)
C(26A)	45(2)	12(1)	25(2)	-2(1)	-11(1)	-5(1)
C(27A)	27(2)	22(2)	26(2)	6(1)	-7(1)	-11(1)
C(28A)	22(1)	18(1)	18(1)	0(1)	-1(1)	-4(1)
C(29A)	15(1)	14(1)	15(1)	-4(1)	-2(1)	4(1)
C(30A)	21(1)	15(1)	20(1)	-2(1)	-1(1)	3(1)
C(31A)	31(2)	21(1)	25(2)	-1(1)	-9(1)	11(1)
C(32A)	22(1)	32(2)	31(2)	-11(1)	-10(1)	10(1)
C(33A)	16(1)	28(2)	31(2)	-11(1)	1(1)	0(1)
C(34A)	16(1)	18(1)	23(1)	-4(1)	1(1)	0(1)
C(35A)	16(1)	16(1)	13(1)	1(1)	0(1)	-2(1)
C(36A)	14(1)	18(1)	19(1)	4(1)	0(1)	0(1)
C(37A)	18(1)	20(1)	27(2)	8(1)	-1(1)	2(1)
C(38A)	19(1)	29(2)	19(1)	12(1)	-4(1)	-4(1)
C(39A)	23(2)	34(2)	18(1)	5(1)	5(1)	0(1)
C(40A)	27(2)	19(1)	24(2)	0(1)	6(1)	3(1)
C(41A)	14(1)	15(1)	15(1)	2(1)	0(1)	1(1)
C(42A)	22(1)	19(1)	15(1)	-1(1)	0(1)	-2(1)
C(43A)	17(1)	21(1)	21(1)	4(1)	-4(1)	-4(1)
C(44A)	21(1)	25(1)	23(1)	8(1)	7(1)	1(1)
C(45A)	40(2)	25(2)	20(1)	-4(1)	13(1)	-4(1)
C(46A)	31(2)	20(1)	22(1)	-5(1)	8(1)	-7(1)
P(1B)	11(1)	11(1)	12(1)	1(1)	0(1)	0(1)
P(2B)	12(1)	10(1)	12(1)	1(1)	0(1)	-1(1)
P(3B)	11(1)	11(1)	12(1)	1(1)	0(1)	1(1)
N(1B)	18(1)	27(1)	18(1)	-1(1)	0(1)	-4(1)
N(2B)	19(1)	16(1)	20(1)	0(1)	-2(1)	-2(1)

C(1B)	13(1)	16(1)	12(1)	1(1)	0(1)	-1(1)
C(2B)	16(1)	16(1)	12(1)	2(1)	2(1)	-1(1)
C(3B)	26(1)	11(1)	13(1)	-1(1)	-4(1)	0(1)
C(4B)	23(1)	16(1)	22(1)	-3(1)	-4(1)	2(1)
C(5B)	29(2)	20(1)	29(2)	-6(1)	-9(1)	6(1)
C(6B)	50(2)	17(1)	24(2)	1(1)	-14(1)	9(1)
C(7B)	61(2)	16(2)	23(2)	5(1)	4(2)	1(2)
C(8B)	37(2)	17(1)	23(2)	2(1)	7(1)	1(1)
C(9B)	13(1)	17(1)	14(1)	0(1)	0(1)	1(1)
C(10B)	23(1)	19(1)	18(1)	1(1)	6(1)	0(1)
C(11B)	23(1)	27(2)	16(1)	2(1)	5(1)	4(1)
C(12B)	16(1)	29(2)	19(1)	-9(1)	-1(1)	7(1)
C(13B)	18(1)	22(1)	26(2)	-10(1)	-1(1)	-3(1)
C(14B)	15(1)	19(1)	19(1)	-4(1)	2(1)	-2(1)
C(15B)	14(1)	16(1)	18(1)	5(1)	-1(1)	-3(1)
C(16B)	24(2)	20(1)	22(1)	-2(1)	-2(1)	-6(1)
C(17B)	35(2)	24(2)	26(2)	1(1)	-10(1)	-8(1)
C(18B)	26(2)	31(2)	34(2)	10(1)	-14(1)	-15(1)
C(19B)	16(1)	32(2)	38(2)	14(1)	-6(1)	-2(1)
C(20B)	18(1)	21(1)	24(2)	5(1)	1(1)	-2(1)
C(21B)	12(1)	12(1)	16(1)	0(1)	0(1)	2(1)
C(22B)	15(1)	14(1)	12(1)	1(1)	2(1)	4(1)
C(23B)	15(1)	13(1)	16(1)	0(1)	0(1)	1(1)
C(24B)	17(1)	19(1)	18(1)	-2(1)	0(1)	0(1)
C(25B)	26(2)	25(2)	16(1)	-5(1)	2(1)	-1(1)
C(26B)	22(1)	26(1)	24(2)	-2(1)	10(1)	-1(1)
C(27B)	13(1)	23(1)	28(2)	-1(1)	3(1)	1(1)
C(28B)	16(1)	21(1)	18(1)	1(1)	1(1)	2(1)
C(29B)	19(1)	13(1)	15(1)	2(1)	-2(1)	0(1)
C(30B)	21(2)	18(1)	26(2)	1(1)	0(1)	4(1)
C(31B)	30(2)	18(2)	38(2)	3(1)	-7(1)	7(1)
C(32B)	34(2)	18(1)	37(2)	10(1)	-10(1)	-3(1)
C(33B)	26(2)	23(2)	29(2)	9(1)	-3(1)	-4(1)
C(34B)	19(1)	17(1)	21(1)	4(1)	-1(1)	1(1)
C(35B)	10(1)	16(1)	17(1)	-2(1)	0(1)	2(1)
C(36B)	15(1)	20(1)	15(1)	1(1)	1(1)	3(1)
C(37B)	20(1)	28(2)	16(1)	-4(1)	0(1)	5(1)
C(38B)	20(1)	26(1)	21(1)	-11(1)	-2(1)	2(1)
C(39B)	18(1)	17(1)	26(2)	-4(1)	2(1)	1(1)
C(40B)	13(1)	18(1)	17(1)	-1(1)	0(1)	2(1)
C(41B)	16(1)	11(1)	17(1)	1(1)	2(1)	0(1)
C(42B)	18(1)	24(1)	18(1)	-1(1)	-2(1)	1(1)
C(43B)	26(1)	26(1)	15(1)	-2(1)	2(1)	-1(1)
C(44B)	21(1)	22(1)	19(1)	-1(1)	5(1)	0(1)
C(45B)	17(1)	24(1)	22(1)	1(1)	2(1)	3(1)
C(46B)	18(1)	21(1)	15(1)	0(1)	0(1)	1(1)
C11	48(2)	26(2)	34(2)	-7(1)	4(2)	4(2)
Cl11	56(1)	31(1)	28(1)	-4(1)	4(1)	-10(1)
Cl21	44(1)	54(1)	32(1)	-10(1)	-10(1)	18(1)
C12	47(2)	32(2)	39(2)	-5(2)	4(2)	-7(2)

Cl12	60(1)	61(1)	42(1)	-16(1)	-2(1)	-8(1)
Cl22	50(1)	30(1)	48(1)	-2(1)	10(1)	-6(1)

3.2.3 Crystal Structure Determination of $(Y_{CN})_2PCy$

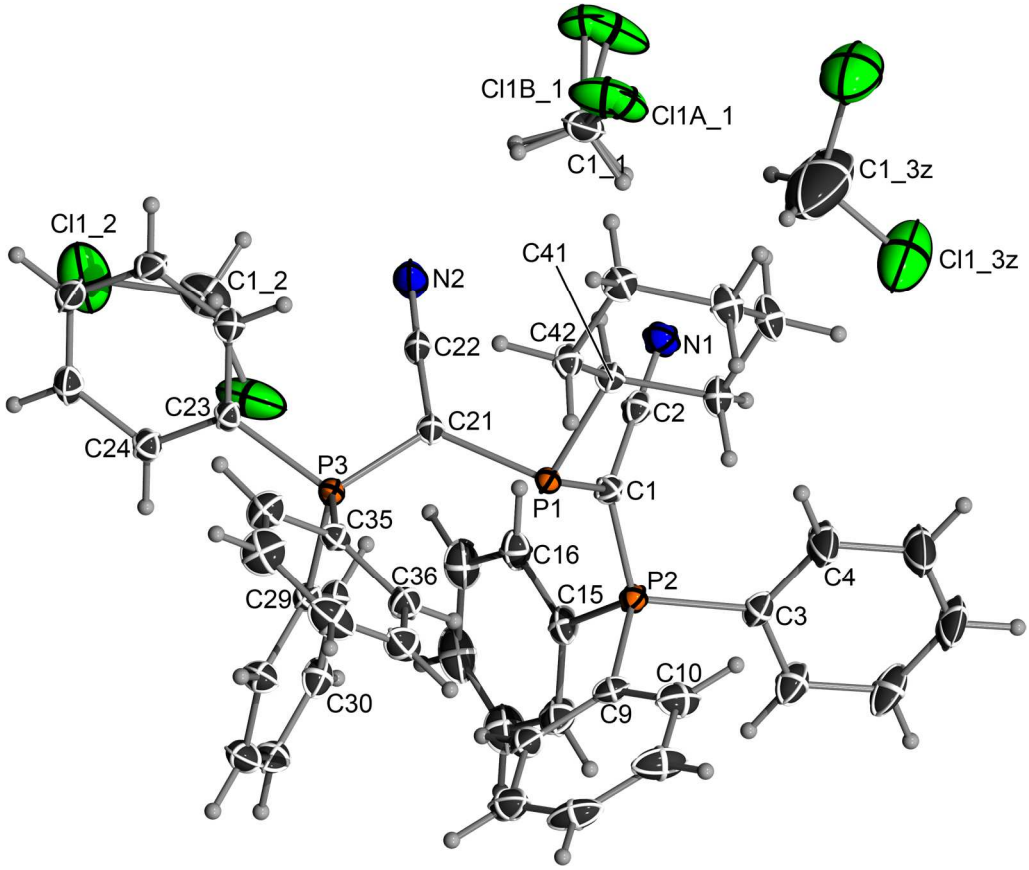


Figure S43 ORTEP Plot of **$(Y_{CN})_2PCy$**. Ellipsoids are drawn at the 50% probability level.

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2PCy$.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	6036(1)	6292(1)	2519(1)	13(1)
P(2)	6927(1)	7877(1)	4054(1)	15(1)
P(3)	5801(1)	7608(1)	1392(1)	13(1)
N(1)	3359(2)	6154(2)	3643(1)	24(1)
N(2)	2471(2)	6641(2)	1819(1)	37(1)
C(1)	5687(2)	6863(2)	3383(1)	16(1)
C(2)	4411(2)	6494(2)	3529(1)	18(1)
C(3)	7152(2)	7444(2)	4878(1)	21(1)
C(4)	6603(3)	6296(2)	4851(1)	43(1)
C(5)	6779(3)	5925(3)	5467(1)	54(1)
C(6)	7501(3)	6705(2)	6111(1)	42(1)
C(7)	8066(3)	7839(2)	6140(1)	36(1)

C(8)	7900(2)	8218(2)	5529(1)	28(1)
C(9)	8532(2)	7992(2)	3793(1)	18(1)
C(10)	9194(2)	7090(2)	3821(1)	29(1)
C(11)	10366(2)	7080(2)	3560(1)	34(1)
C(12)	10873(2)	7953(2)	3268(1)	33(1)
C(13)	10220(2)	8853(2)	3247(1)	29(1)
C(14)	9049(2)	8880(2)	3512(1)	22(1)
C(15)	6577(2)	9322(2)	4275(1)	19(1)
C(16)	5255(2)	9403(2)	4013(1)	22(1)
C(17)	4901(2)	10477(2)	4173(1)	30(1)
C(18)	5862(3)	11475(2)	4597(1)	34(1)
C(19)	7169(3)	11401(2)	4855(1)	35(1)
C(20)	7542(2)	10336(2)	4699(1)	27(1)
C(21)	5006(2)	6815(2)	1879(1)	16(1)
C(22)	3621(2)	6730(2)	1836(1)	21(1)
C(23)	4523(2)	7787(2)	698(1)	16(1)
C(24)	4480(2)	8891(2)	612(1)	18(1)
C(25)	3478(2)	9001(2)	79(1)	23(1)
C(26)	2530(2)	8016(2)	-370(1)	24(1)
C(27)	2574(2)	6916(2)	-286(1)	23(1)
C(28)	3565(2)	6796(2)	247(1)	20(1)
C(29)	6772(2)	9073(2)	1906(1)	16(1)
C(30)	6340(2)	9640(2)	2493(1)	18(1)
C(31)	7056(2)	10765(2)	2901(1)	22(1)
C(32)	8196(2)	11316(2)	2720(1)	26(1)
C(33)	8627(2)	10756(2)	2131(1)	27(1)
C(34)	7917(2)	9636(2)	1720(1)	21(1)
C(35)	7032(2)	6970(2)	978(1)	16(1)
C(36)	8194(2)	6824(2)	1401(1)	23(1)
C(37)	9193(2)	6437(2)	1085(1)	28(1)
C(38)	9047(2)	6196(2)	351(1)	30(1)
C(39)	7891(2)	6318(2)	-71(1)	33(1)
C(40)	6886(2)	6705(2)	243(1)	24(1)
C(41)	5111(2)	4728(2)	2276(1)	16(1)
C(42)	5332(2)	4103(2)	1548(1)	18(1)
C(43)	4714(2)	2782(2)	1328(1)	22(1)
C(44)	5263(2)	2231(2)	1899(1)	25(1)
C(45)	4990(2)	2826(2)	2616(1)	24(1)
C(46)	5622(2)	4146(2)	2845(1)	20(1)
Cl1A1	1219(5)	3125(4)	1837(2)	34(1)
Cl2A1	-898(3)	4255(3)	2285(1)	35(1)
Cl1B1	1100(30)	3220(20)	1739(19)	60(5)
Cl2B1	-760(30)	4178(15)	2450(30)	65(5)
C11	822(2)	4458(2)	2250(1)	34(1)
Cl12	914(1)	9893(1)	915(1)	63(1)
Cl22	2697(1)	9976(1)	2254(1)	59(1)
C12	1540(3)	9074(2)	1466(2)	43(1)
Cl13	1518(3)	5908(2)	5761(1)	80(1)
Cl23	-546(3)	4252(2)	4563(1)	79(1)
C13	618(14)	5579(10)	4917(7)	132(6)

Table S15. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_2$PCy**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{\cdot 2}U^{11} + ... + 2\ h\ k\ a{\cdot}b{\cdot}U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	13(1)	15(1)	12(1)	5(1)	2(1)	3(1)
P(2)	16(1)	16(1)	12(1)	3(1)	1(1)	3(1)
P(3)	13(1)	14(1)	12(1)	4(1)	2(1)	3(1)
N(1)	21(1)	27(1)	25(1)	8(1)	7(1)	4(1)
N(2)	19(1)	55(1)	51(1)	38(1)	11(1)	11(1)
C(1)	15(1)	16(1)	14(1)	4(1)	2(1)	2(1)
C(2)	21(1)	18(1)	14(1)	3(1)	2(1)	5(1)
C(3)	21(1)	26(1)	16(1)	7(1)	2(1)	7(1)
C(4)	61(2)	34(1)	23(1)	14(1)	-9(1)	-6(1)
C(5)	76(2)	42(1)	32(1)	22(1)	-9(1)	-8(1)
C(6)	56(2)	52(2)	21(1)	20(1)	2(1)	15(1)
C(7)	48(1)	41(1)	16(1)	3(1)	-2(1)	18(1)
C(8)	36(1)	27(1)	20(1)	4(1)	-1(1)	10(1)
C(9)	14(1)	20(1)	17(1)	1(1)	-1(1)	1(1)
C(10)	23(1)	21(1)	40(1)	4(1)	3(1)	6(1)
C(11)	20(1)	28(1)	48(1)	-3(1)	3(1)	8(1)
C(12)	17(1)	45(1)	28(1)	-4(1)	4(1)	5(1)
C(13)	19(1)	40(1)	24(1)	9(1)	4(1)	1(1)
C(14)	18(1)	26(1)	20(1)	6(1)	1(1)	4(1)
C(15)	26(1)	19(1)	13(1)	4(1)	7(1)	7(1)
C(16)	25(1)	24(1)	20(1)	9(1)	9(1)	9(1)
C(17)	38(1)	33(1)	30(1)	14(1)	17(1)	20(1)
C(18)	59(2)	25(1)	26(1)	8(1)	20(1)	21(1)
C(19)	57(2)	19(1)	21(1)	-1(1)	5(1)	7(1)
C(20)	35(1)	23(1)	19(1)	3(1)	0(1)	4(1)
C(21)	15(1)	17(1)	15(1)	7(1)	3(1)	4(1)
C(22)	20(1)	23(1)	22(1)	14(1)	3(1)	5(1)
C(23)	14(1)	20(1)	14(1)	7(1)	5(1)	5(1)
C(24)	18(1)	21(1)	17(1)	6(1)	5(1)	5(1)
C(25)	25(1)	26(1)	25(1)	14(1)	7(1)	11(1)
C(26)	19(1)	37(1)	19(1)	13(1)	2(1)	8(1)
C(27)	19(1)	29(1)	17(1)	6(1)	1(1)	2(1)
C(28)	20(1)	22(1)	18(1)	7(1)	4(1)	4(1)
C(29)	14(1)	16(1)	16(1)	5(1)	0(1)	3(1)
C(30)	20(1)	19(1)	18(1)	7(1)	4(1)	6(1)
C(31)	31(1)	18(1)	18(1)	4(1)	2(1)	10(1)
C(32)	29(1)	15(1)	26(1)	3(1)	-3(1)	2(1)
C(33)	23(1)	21(1)	34(1)	9(1)	5(1)	-1(1)
C(34)	20(1)	21(1)	23(1)	5(1)	7(1)	2(1)
C(35)	16(1)	14(1)	20(1)	5(1)	6(1)	3(1)
C(36)	19(1)	28(1)	27(1)	13(1)	6(1)	7(1)
C(37)	19(1)	27(1)	44(1)	17(1)	10(1)	9(1)
C(38)	28(1)	22(1)	44(1)	8(1)	20(1)	10(1)
C(39)	36(1)	37(1)	26(1)	3(1)	14(1)	13(1)
C(40)	25(1)	28(1)	21(1)	4(1)	6(1)	9(1)

C(41)	16(1)	15(1)	15(1)	4(1)	4(1)	4(1)
C(42)	22(1)	18(1)	16(1)	5(1)	4(1)	5(1)
C(43)	25(1)	18(1)	20(1)	2(1)	6(1)	6(1)
C(44)	36(1)	18(1)	26(1)	7(1)	12(1)	11(1)
C(45)	36(1)	20(1)	24(1)	10(1)	14(1)	11(1)
C(46)	27(1)	20(1)	18(1)	8(1)	7(1)	10(1)
Cl1A1	26(1)	32(1)	45(1)	11(1)	14(1)	4(1)
Cl2A1	22(1)	39(1)	38(1)	4(1)	6(1)	3(1)
Cl1B1	34(5)	63(8)	74(9)	1(5)	27(6)	-2(4)
Cl2B1	42(6)	30(3)	121(13)	6(7)	45(7)	2(3)
C11	22(1)	26(1)	52(1)	15(1)	2(1)	-1(1)
Cl12	71(1)	76(1)	78(1)	40(1)	49(1)	46(1)
Cl22	48(1)	52(1)	60(1)	-4(1)	24(1)	-16(1)
C12	43(1)	34(1)	50(2)	7(1)	19(1)	3(1)
Cl13	127(2)	46(1)	53(1)	3(1)	-13(1)	30(1)
Cl23	96(2)	58(1)	63(1)	3(1)	-9(1)	9(1)
C13	153(12)	86(7)	105(9)	14(7)	-64(9)	2(7)

3.2.4 Crystal Structure Determination of $(Y_{CN})_2P^tBu$

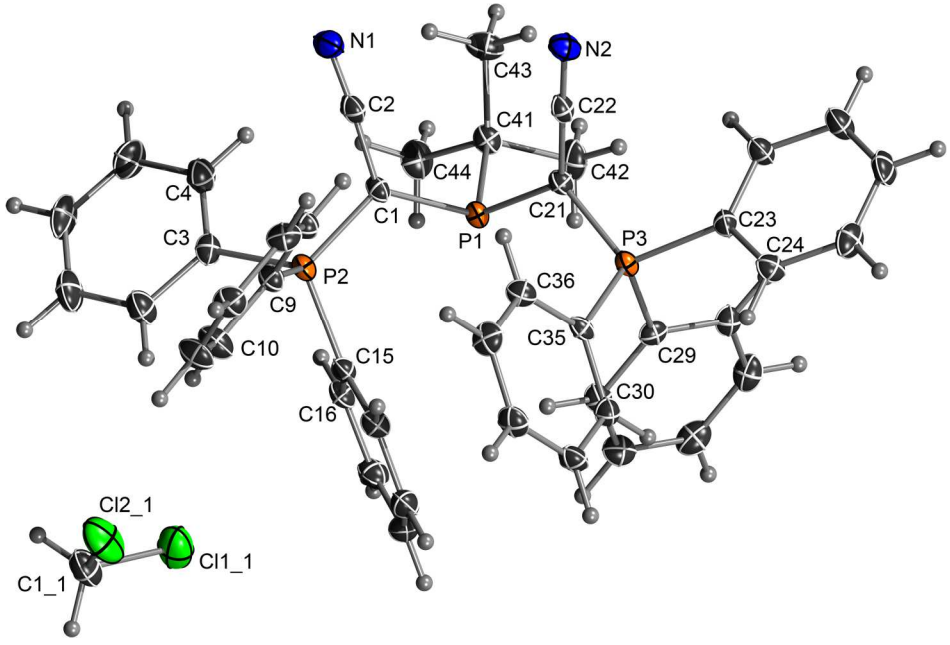


Figure S44 ORTEP Plot of **$(Y_{CN})_2P^tBu$**. Ellipsoids are drawn at the 50% probability level.

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2P^tBu$.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	2660(1)	3492(1)	4202(1)	14(1)
P(2)	2964(1)	4079(1)	2639(1)	14(1)
P(3)	4406(1)	2468(1)	4587(1)	14(1)
N(1)	-155(2)	3253(1)	2530(1)	26(1)
N(2)	1096(2)	1951(1)	3773(1)	22(1)
C(1)	2046(2)	3632(1)	3216(1)	16(1)
C(2)	831(2)	3416(1)	2855(1)	19(1)
C(3)	2059(2)	4750(1)	2374(1)	19(1)

C(4)	740(3)	4821(1)	2602(2)	26(1)
C(5)	17(3)	5328(1)	2413(2)	32(1)
C(6)	600(3)	5761(1)	1986(2)	31(1)
C(7)	1917(3)	5694(1)	1752(2)	34(1)
C(8)	2648(3)	5193(1)	1949(2)	29(1)
C(9)	3391(2)	3732(1)	1736(1)	18(1)
C(10)	4231(3)	4019(1)	1229(2)	27(1)
C(11)	4638(3)	3737(1)	572(2)	27(1)
C(12)	4207(2)	3173(1)	409(1)	24(1)
C(13)	3374(2)	2889(1)	909(1)	23(1)
C(14)	2968(2)	3166(1)	1576(1)	19(1)
C(15)	4575(2)	4288(1)	3107(1)	17(1)
C(16)	4629(2)	4753(1)	3632(1)	19(1)
C(17)	5868(3)	4913(1)	3992(1)	24(1)
C(18)	7049(3)	4616(1)	3820(2)	26(1)
C(19)	7000(3)	4157(1)	3298(2)	25(1)
C(20)	5760(2)	3988(1)	2946(1)	20(1)
C(21)	2791(2)	2708(1)	4325(1)	16(1)
C(22)	1860(2)	2297(1)	4020(1)	16(1)
C(23)	4371(2)	1742(1)	4993(1)	18(1)
C(24)	5463(2)	1361(1)	4922(1)	20(1)
C(25)	5475(3)	823(1)	5287(2)	26(1)
C(26)	4402(3)	661(1)	5726(2)	27(1)
C(27)	3316(3)	1038(1)	5807(2)	27(1)
C(28)	3294(3)	1576(1)	5437(1)	22(1)
C(29)	5248(2)	2927(1)	5315(1)	16(1)
C(30)	5917(2)	3435(1)	5102(1)	19(1)
C(31)	6550(3)	3786(1)	5668(2)	23(1)
C(32)	6510(3)	3633(1)	6446(2)	26(1)
C(33)	5841(3)	3132(1)	6658(1)	25(1)
C(34)	5214(2)	2774(1)	6097(1)	20(1)
C(35)	5509(2)	2437(1)	3782(1)	16(1)
C(36)	4907(2)	2367(1)	3042(1)	20(1)
C(37)	5717(3)	2313(1)	2408(1)	24(1)
C(38)	7119(3)	2337(1)	2512(1)	24(1)
C(39)	7735(2)	2412(1)	3250(1)	22(1)
C(40)	6930(2)	2462(1)	3883(1)	19(1)
C(41)	1231(2)	3696(1)	4830(1)	18(1)
C(42)	1746(3)	3566(1)	5667(1)	28(1)
C(43)	-106(3)	3375(1)	4657(2)	26(1)
C(44)	1002(3)	4352(1)	4750(2)	27(1)
Cl11	6261(1)	5808(1)	2462(1)	45(1)
Cl21	6478(1)	5316(1)	926(1)	45(1)
C11	6421(3)	5963(1)	1478(2)	33(1)

Table S17. Anisotropic displacement parameters (Å^2 x 10^3) for **$(Y_{CN})_2P^tBu$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{\cdot 2}U^{11}$ + ... + 2 h k a·b·U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	17(1)	12(1)	13(1)	1(1)	3(1)	0(1)

P(2)	18(1)	12(1)	14(1)	1(1)	3(1)	-1(1)
P(3)	16(1)	12(1)	14(1)	1(1)	3(1)	1(1)
N(1)	25(1)	33(1)	21(1)	2(1)	1(1)	-9(1)
N(2)	22(1)	17(1)	26(1)	-2(1)	2(1)	-2(1)
C(1)	19(1)	16(1)	12(1)	1(1)	3(1)	-2(1)
C(2)	21(1)	21(1)	16(1)	3(1)	6(1)	-1(1)
C(3)	24(1)	14(1)	17(1)	-1(1)	-2(1)	1(1)
C(4)	28(1)	23(1)	28(1)	3(1)	4(1)	5(1)
C(5)	31(1)	29(1)	36(1)	-1(1)	0(1)	12(1)
C(6)	45(2)	14(1)	32(1)	-1(1)	-10(1)	8(1)
C(7)	47(2)	19(1)	34(1)	8(1)	-1(1)	1(1)
C(8)	34(1)	22(1)	32(1)	6(1)	5(1)	-1(1)
C(9)	20(1)	20(1)	14(1)	0(1)	4(1)	0(1)
C(10)	32(1)	22(1)	26(1)	-2(1)	10(1)	-6(1)
C(11)	29(1)	32(1)	22(1)	0(1)	12(1)	-4(1)
C(12)	22(1)	31(1)	18(1)	-5(1)	6(1)	3(1)
C(13)	22(1)	24(1)	23(1)	-6(1)	2(1)	-1(1)
C(14)	20(1)	21(1)	18(1)	0(1)	2(1)	-1(1)
C(15)	18(1)	16(1)	18(1)	3(1)	2(1)	-3(1)
C(16)	23(1)	15(1)	21(1)	0(1)	3(1)	-2(1)
C(17)	28(1)	22(1)	24(1)	-1(1)	1(1)	-6(1)
C(18)	22(1)	29(1)	27(1)	5(1)	-3(1)	-6(1)
C(19)	22(1)	24(1)	29(1)	6(1)	4(1)	0(1)
C(20)	21(1)	18(1)	22(1)	1(1)	4(1)	-2(1)
C(21)	17(1)	14(1)	16(1)	0(1)	2(1)	0(1)
C(22)	18(1)	14(1)	18(1)	2(1)	5(1)	4(1)
C(23)	21(1)	16(1)	17(1)	3(1)	1(1)	0(1)
C(24)	21(1)	16(1)	24(1)	-1(1)	4(1)	0(1)
C(25)	30(1)	17(1)	30(1)	0(1)	-2(1)	6(1)
C(26)	36(1)	15(1)	29(1)	8(1)	-2(1)	-1(1)
C(27)	32(1)	22(1)	29(1)	7(1)	6(1)	-4(1)
C(28)	23(1)	19(1)	25(1)	4(1)	7(1)	0(1)
C(29)	15(1)	16(1)	19(1)	-3(1)	2(1)	3(1)
C(30)	21(1)	18(1)	19(1)	-1(1)	4(1)	2(1)
C(31)	24(1)	17(1)	28(1)	-4(1)	3(1)	0(1)
C(32)	27(1)	27(1)	24(1)	-10(1)	-3(1)	4(1)
C(33)	29(1)	28(1)	18(1)	-2(1)	2(1)	8(1)
C(34)	21(1)	20(1)	18(1)	0(1)	4(1)	6(1)
C(35)	18(1)	11(1)	18(1)	0(1)	6(1)	0(1)
C(36)	20(1)	20(1)	20(1)	-2(1)	4(1)	0(1)
C(37)	27(1)	30(1)	14(1)	-4(1)	3(1)	1(1)
C(38)	23(1)	28(1)	21(1)	2(1)	10(1)	2(1)
C(39)	18(1)	23(1)	23(1)	3(1)	8(1)	-1(1)
C(40)	20(1)	20(1)	17(1)	2(1)	2(1)	1(1)
C(41)	21(1)	16(1)	16(1)	-2(1)	4(1)	1(1)
C(42)	35(1)	35(1)	16(1)	2(1)	8(1)	10(1)
C(43)	23(1)	26(1)	30(1)	-7(1)	10(1)	-1(1)
C(44)	36(1)	19(1)	26(1)	-4(1)	6(1)	6(1)
Cl11	40(1)	57(1)	38(1)	14(1)	14(1)	12(1)
Cl21	56(1)	23(1)	57(1)	1(1)	19(1)	3(1)

C11	38(2)	24(1)	39(2)	8(1)	12(1)	3(1)

3.2.5 Crystal Structure Determination of $(Y_{CN})_3P$

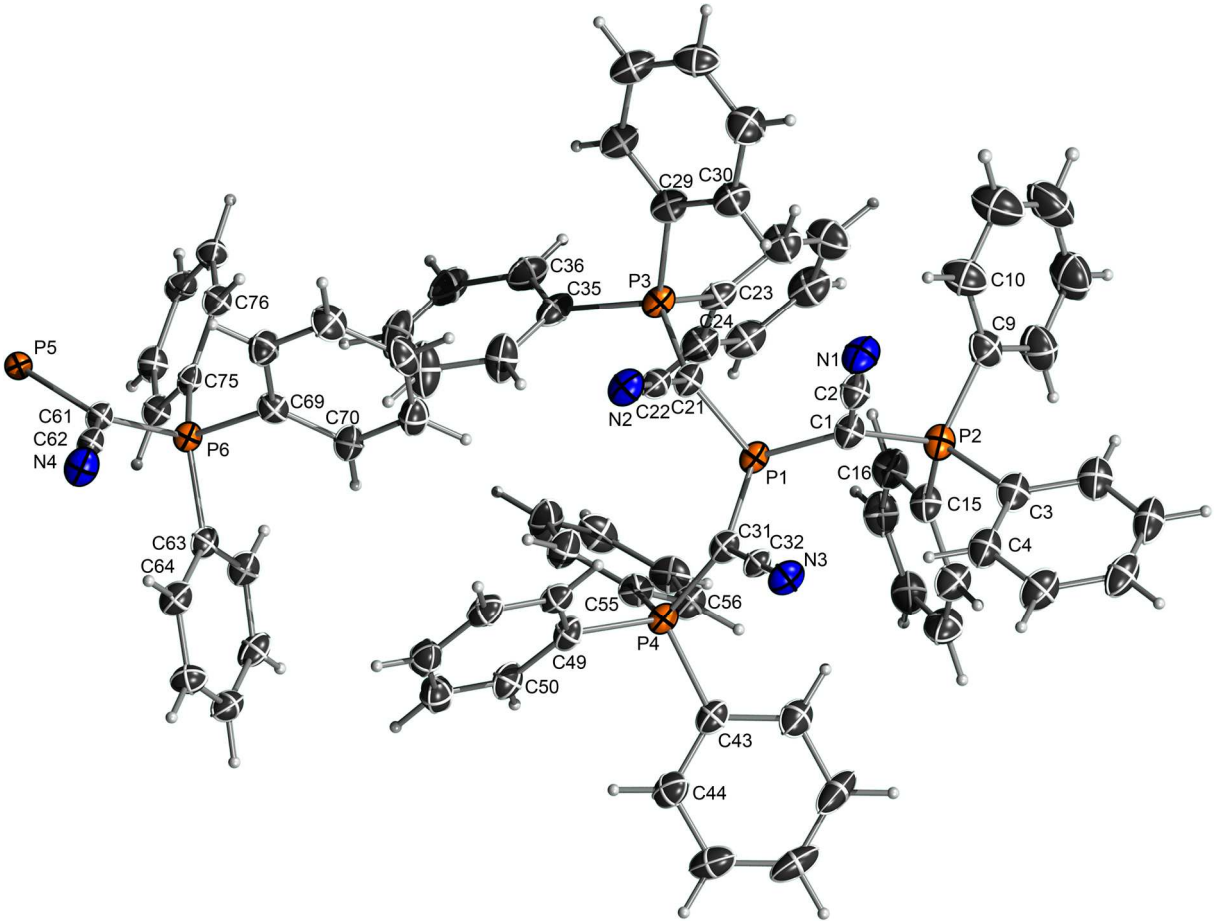


Figure S45 ORTEP Plot of **$(Y_{CN})_3P$**. Ellipsoids are drawn at the 50% probability level.

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_3P$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	3381(1)	3195(1)	7959(1)	21(1)
P(2)	3196(1)	2240(1)	8008(1)	26(1)
P(3)	2583(1)	3321(1)	8090(1)	24(1)
P(4)	4310(1)	4011(1)	7883(1)	21(1)
P(5)	3333	6667	6030(1)	17(1)
P(6)	3624(1)	5983(1)	6067(1)	19(1)
N(1)	2841(1)	2464(1)	4765(3)	35(1)
N(2)	3146(1)	3705(1)	4792(2)	31(1)
N(3)	4089(1)	3333(1)	4796(2)	29(1)
N(4)	3922(1)	6606(1)	2793(2)	30(1)
C(1)	3206(1)	2670(1)	7140(3)	26(1)
C(2)	3016(1)	2566(1)	5824(3)	28(1)
C(3)	3449(1)	1992(1)	7000(3)	31(1)
C(4)	3788(1)	2267(1)	6105(3)	35(1)
C(5)	4001(1)	2094(1)	5349(3)	41(1)
C(6)	3875(1)	1653(1)	5472(3)	39(1)
C(7)	3544(1)	1387(1)	6346(3)	40(1)
C(8)	3328(1)	1553(1)	7118(3)	37(1)
C(9)	2652(1)	1798(1)	8484(3)	34(1)

C(10)	2289(1)	1746(1)	7748(4)	45(1)
C(11)	1871(1)	1416(2)	8105(5)	62(1)
C(12)	1810(2)	1144(1)	9203(5)	67(1)
C(13)	2170(2)	1194(1)	9948(5)	60(1)
C(14)	2594(1)	1523(1)	9583(4)	48(1)
C(15)	3496(1)	2426(1)	9600(3)	29(1)
C(16)	3303(1)	2519(1)	10718(3)	34(1)
C(17)	3526(1)	2656(1)	11948(3)	35(1)
C(18)	3934(1)	2692(1)	12089(3)	35(1)
C(19)	4122(1)	2603(1)	11009(3)	41(1)
C(20)	3903(1)	2468(1)	9749(3)	35(1)
C(21)	3014(1)	3353(1)	7169(3)	23(1)
C(22)	3083(1)	3538(1)	5866(3)	25(1)
C(23)	2480(1)	2995(1)	9639(3)	27(1)
C(24)	2732(1)	3186(1)	10818(3)	33(1)
C(25)	2653(1)	2938(1)	11992(3)	35(1)
C(26)	2327(1)	2501(1)	12010(3)	40(1)
C(27)	2086(1)	2312(1)	10834(4)	45(1)
C(28)	2162(1)	2562(1)	9654(3)	39(1)
C(29)	2079(1)	3060(1)	7082(3)	28(1)
C(30)	2031(1)	2741(1)	6144(3)	34(1)
C(31)	1641(1)	2513(1)	5404(3)	41(1)
C(32)	1308(1)	2612(1)	5586(3)	40(1)
C(33)	1360(1)	2936(1)	6516(3)	38(1)
C(34)	1749(1)	3160(1)	7269(3)	32(1)
C(35)	2672(1)	3851(1)	8655(3)	30(1)
C(36)	2459(1)	3894(1)	9808(3)	37(1)
C(37)	2561(1)	4309(1)	10261(3)	41(1)
C(38)	2870(1)	4678(1)	9591(3)	43(1)
C(39)	3076(2)	4637(1)	8425(3)	49(1)
C(40)	2981(1)	4227(1)	7980(3)	38(1)
C(41)	3901(1)	3547(1)	7106(3)	23(1)
C(42)	4002(1)	3436(1)	5833(3)	22(1)
C(43)	4815(1)	3985(1)	8033(3)	26(1)
C(44)	5230(1)	4354(1)	8109(3)	35(1)
C(45)	5601(1)	4308(1)	8171(3)	42(1)
C(46)	5560(1)	3900(1)	8167(3)	43(1)
C(47)	5154(1)	3538(1)	8076(4)	47(1)
C(48)	4777(1)	3574(1)	8010(3)	36(1)
C(49)	4464(1)	4525(1)	6994(3)	25(1)
C(50)	4740(1)	4927(1)	7617(3)	30(1)
C(51)	4866(1)	5315(1)	6920(3)	35(1)
C(52)	4708(1)	5301(1)	5596(3)	35(1)
C(53)	4432(1)	4902(1)	4987(3)	32(1)
C(54)	4307(1)	4512(1)	5687(3)	28(1)
C(55)	4128(1)	4067(1)	9570(3)	25(1)
C(56)	4142(1)	3819(1)	10660(3)	29(1)
C(57)	3971(1)	3839(1)	11929(3)	33(1)
C(58)	3784(1)	4105(1)	12098(3)	34(1)
C(59)	3766(1)	4345(1)	11009(3)	38(1)
C(60)	3939(1)	4330(1)	9729(3)	32(1)
C(61)	3584(1)	6384(1)	5197(2)	19(1)
C(62)	3764(1)	6498(1)	3872(3)	22(1)
C(63)	4176(1)	6130(1)	6605(3)	23(1)
C(64)	4268(1)	5982(1)	7822(3)	26(1)
C(65)	4701(1)	6112(1)	8151(3)	28(1)
C(66)	5039(1)	6381(1)	7260(3)	30(1)
C(67)	4945(1)	6521(1)	6037(3)	29(1)
C(68)	4516(1)	6403(1)	5727(3)	27(1)
C(69)	3445(1)	5501(1)	4997(3)	23(1)
C(70)	3588(1)	5203(1)	5238(3)	28(1)
C(71)	3427(1)	4826(1)	4440(3)	32(1)
C(72)	3131(1)	4752(1)	3390(3)	33(1)
C(73)	2996(1)	5051(1)	3135(3)	35(1)
C(74)	3151(1)	5426(1)	3935(3)	30(1)
C(75)	3276(1)	5831(1)	7571(2)	20(1)
C(76)	3436(1)	6054(1)	8808(3)	24(1)
C(77)	3160(1)	5958(1)	9931(3)	25(1)
C(78)	2718(1)	5642(1)	9801(3)	26(1)

C(79)	2557(1)	5429(1)	8570(3)	28(1)
C(80)	2835(1)	5519(1)	7448(3)	25(1)
O1A1	1503(12)	1359(9)	4470(30)	273(17)
C1A1	1371(11)	899(9)	4490(30)	203(10)
C2A1	1318(12)	763(10)	2970(30)	215(9)
C3A1	1125(13)	1032(12)	2350(30)	218(11)
C4A1	1309(14)	1439(10)	3270(30)	221(10)
O1C1	788(6)	166(7)	650(30)	168(10)
C1C1	727(17)	95(17)	2110(30)	270(30)
C2C1	481(18)	325(17)	2620(30)	310(30)
C3C1	295(11)	406(14)	1290(50)	310(30)
C4C1	646(13)	470(13)	230(30)	238(19)
O1B1	1587(5)	1261(6)	3210(20)	179(9)
C1B1	1466(7)	808(7)	3440(40)	188(9)
C2B1	963(8)	533(7)	3370(40)	213(10)
C3B1	828(7)	878(11)	3670(40)	320(30)
C4B1	1192(7)	1278(8)	2910(30)	190(9)

Table S19. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_3P$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{\cdot 2}U^{11} + ... + 2\ h\ k\ a{\cdot}b{\cdot}U^{12}]$.

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
P(1)	26(1)	26(1)	16(1)	1(1)	1(1)	17(1)
P(2)	34(1)	28(1)	21(1)	-2(1)	-3(1)	18(1)
P(3)	28(1)	32(1)	18(1)	0(1)	1(1)	19(1)
P(4)	26(1)	27(1)	15(1)	1(1)	1(1)	17(1)
P(5)	18(1)	18(1)	13(1)	0	0	9(1)
P(6)	22(1)	22(1)	14(1)	1(1)	2(1)	12(1)
N(1)	43(2)	43(2)	27(1)	-5(1)	-9(1)	27(1)
N(2)	36(1)	39(1)	22(1)	5(1)	2(1)	23(1)
N(3)	32(1)	38(1)	22(1)	-1(1)	4(1)	21(1)
N(4)	39(1)	36(1)	21(1)	6(1)	8(1)	23(1)
C(1)	33(2)	29(1)	21(1)	0(1)	1(1)	20(1)
C(2)	36(2)	31(1)	24(1)	-2(1)	-1(1)	20(1)
C(3)	43(2)	35(2)	21(1)	-9(1)	-10(1)	23(1)
C(4)	44(2)	37(2)	32(2)	-2(1)	-4(1)	26(2)
C(5)	50(2)	53(2)	31(2)	-3(2)	0(2)	34(2)
C(6)	54(2)	50(2)	30(2)	-9(1)	-9(1)	39(2)
C(7)	62(2)	38(2)	32(2)	-8(1)	-12(2)	35(2)
C(8)	50(2)	37(2)	26(1)	-3(1)	-6(1)	25(2)
C(9)	38(2)	32(2)	31(2)	-6(1)	0(1)	16(1)
C(10)	39(2)	49(2)	39(2)	0(2)	-2(2)	15(2)
C(11)	44(2)	62(3)	61(2)	0(2)	-8(2)	12(2)
C(12)	51(2)	45(2)	77(3)	3(2)	16(2)	4(2)
C(13)	63(3)	44(2)	65(3)	17(2)	16(2)	22(2)
C(14)	53(2)	39(2)	48(2)	10(2)	7(2)	20(2)
C(15)	39(2)	30(2)	20(1)	1(1)	-2(1)	19(1)
C(16)	42(2)	39(2)	27(1)	2(1)	3(1)	24(2)
C(17)	52(2)	34(2)	22(1)	0(1)	4(1)	23(2)
C(18)	49(2)	34(2)	24(1)	-2(1)	-6(1)	22(2)
C(19)	43(2)	45(2)	39(2)	-9(2)	-14(2)	25(2)
C(20)	41(2)	43(2)	28(2)	-7(1)	-4(1)	26(2)
C(21)	30(1)	29(1)	17(1)	0(1)	0(1)	20(1)
C(22)	26(1)	30(1)	25(1)	-3(1)	-3(1)	18(1)
C(23)	28(1)	42(2)	19(1)	3(1)	5(1)	22(1)
C(24)	36(2)	42(2)	24(1)	-1(1)	0(1)	23(1)
C(25)	41(2)	55(2)	19(1)	-3(1)	-1(1)	31(2)
C(26)	44(2)	55(2)	25(1)	12(1)	5(1)	29(2)
C(27)	42(2)	45(2)	37(2)	11(2)	-1(2)	15(2)
C(28)	45(2)	42(2)	27(2)	0(1)	-9(1)	21(2)
C(29)	31(2)	38(2)	18(1)	3(1)	-2(1)	19(1)
C(30)	35(2)	40(2)	28(1)	1(1)	-1(1)	21(1)
C(31)	46(2)	46(2)	34(2)	-7(2)	-8(2)	24(2)
C(32)	32(2)	52(2)	33(2)	1(2)	-7(1)	18(2)
C(33)	33(2)	60(2)	30(2)	4(2)	2(1)	30(2)
C(34)	35(2)	46(2)	23(1)	-1(1)	1(1)	26(2)
C(35)	37(2)	42(2)	22(1)	-5(1)	-6(1)	28(1)

C(36)	36(2)	50(2)	31(2)	-7(1)	-1(1)	27(2)
C(37)	43(2)	56(2)	36(2)	-20(2)	-7(1)	35(2)
C(38)	70(2)	47(2)	31(2)	-11(2)	-12(2)	43(2)
C(39)	83(3)	42(2)	29(2)	3(1)	5(2)	36(2)
C(40)	62(2)	38(2)	24(1)	5(1)	7(1)	32(2)
C(41)	28(1)	30(1)	17(1)	4(1)	2(1)	18(1)
C(42)	24(1)	25(1)	20(1)	1(1)	-1(1)	15(1)
C(43)	32(1)	34(2)	18(1)	0(1)	-1(1)	22(1)
C(44)	35(2)	40(2)	35(2)	12(1)	5(1)	22(1)
C(45)	31(2)	62(2)	37(2)	15(2)	6(1)	27(2)
C(46)	43(2)	81(3)	29(2)	-6(2)	-3(1)	48(2)
C(47)	62(2)	69(2)	41(2)	-21(2)	-21(2)	56(2)
C(48)	42(2)	41(2)	34(2)	-12(1)	-11(1)	28(2)
C(49)	31(1)	30(1)	21(1)	6(1)	4(1)	20(1)
C(50)	38(2)	34(2)	25(1)	-2(1)	2(1)	24(1)
C(51)	39(2)	31(2)	37(2)	-1(1)	4(1)	19(1)
C(52)	36(2)	32(2)	42(2)	9(1)	10(1)	20(1)
C(53)	33(2)	40(2)	30(1)	8(1)	1(1)	23(1)
C(54)	28(1)	33(2)	27(1)	4(1)	1(1)	19(1)
C(55)	28(1)	31(1)	18(1)	-2(1)	1(1)	15(1)
C(56)	34(2)	36(2)	22(1)	-3(1)	-2(1)	22(1)
C(57)	36(2)	43(2)	18(1)	2(1)	-1(1)	18(1)
C(58)	38(2)	38(2)	20(1)	-6(1)	6(1)	13(1)
C(59)	48(2)	40(2)	34(2)	-2(1)	13(1)	28(2)
C(60)	41(2)	37(2)	26(1)	6(1)	10(1)	26(1)
C(61)	23(1)	23(1)	14(1)	-1(1)	0(1)	14(1)
C(62)	26(1)	24(1)	21(1)	0(1)	-1(1)	17(1)
C(63)	26(1)	25(1)	19(1)	-2(1)	1(1)	14(1)
C(64)	31(1)	31(1)	19(1)	2(1)	4(1)	18(1)
C(65)	36(2)	38(2)	21(1)	0(1)	-4(1)	25(1)
C(66)	28(1)	37(2)	32(1)	-4(1)	-4(1)	21(1)
C(67)	24(1)	35(2)	29(1)	2(1)	4(1)	14(1)
C(68)	31(1)	34(2)	20(1)	5(1)	4(1)	20(1)
C(69)	25(1)	25(1)	16(1)	0(1)	4(1)	10(1)
C(70)	33(1)	27(1)	26(1)	1(1)	1(1)	17(1)
C(71)	39(2)	30(2)	34(2)	-1(1)	4(1)	21(1)
C(72)	39(2)	26(1)	31(2)	-6(1)	4(1)	13(1)
C(73)	40(2)	36(2)	29(2)	-11(1)	-7(1)	19(1)
C(74)	35(2)	30(2)	28(1)	-5(1)	-2(1)	19(1)
C(75)	25(1)	21(1)	19(1)	4(1)	4(1)	15(1)
C(76)	27(1)	26(1)	22(1)	0(1)	0(1)	15(1)
C(77)	34(1)	27(1)	17(1)	-1(1)	-1(1)	18(1)
C(78)	27(1)	31(1)	25(1)	8(1)	10(1)	18(1)
C(79)	27(1)	27(1)	31(1)	4(1)	5(1)	14(1)
C(80)	28(1)	27(1)	21(1)	-2(1)	0(1)	16(1)
O1A1	410(40)	232(17)	185(18)	30(16)	-80(20)	170(20)
C1A1	173(19)	210(16)	217(18)	40(16)	-42(19)	89(16)
C2A1	168(18)	224(15)	231(19)	22(15)	-35(19)	83(14)
C3A1	200(20)	260(20)	187(17)	30(16)	-35(16)	111(19)
C4A1	240(20)	240(20)	179(18)	52(16)	-25(18)	116(19)
O1C1	69(10)	82(11)	320(30)	-13(16)	31(15)	11(8)
C1C1	320(60)	290(50)	310(30)	-20(30)	20(30)	250(50)
C2C1	450(60)	360(60)	310(30)	-60(40)	-10(40)	340(60)
C3C1	340(50)	420(70)	330(40)	-10(40)	20(30)	310(50)
C4C1	220(40)	230(40)	320(30)	-30(30)	-10(30)	160(40)
O1B1	170(12)	188(13)	200(20)	59(15)	-54(14)	108(11)
C1B1	157(14)	194(13)	230(20)	56(16)	-45(17)	102(11)
C2B1	160(15)	210(15)	250(20)	30(19)	-50(20)	78(12)
C3B1	220(20)	330(30)	460(70)	150(40)	110(40)	190(30)
C4B1	186(15)	237(19)	189(18)	43(17)	-51(14)	137(16)

3.3 Crystal structures of metal complexes

3.3.1 Crystal Structure Determination of $Y_{CN}P^tBu_2 \cdot AuCl$

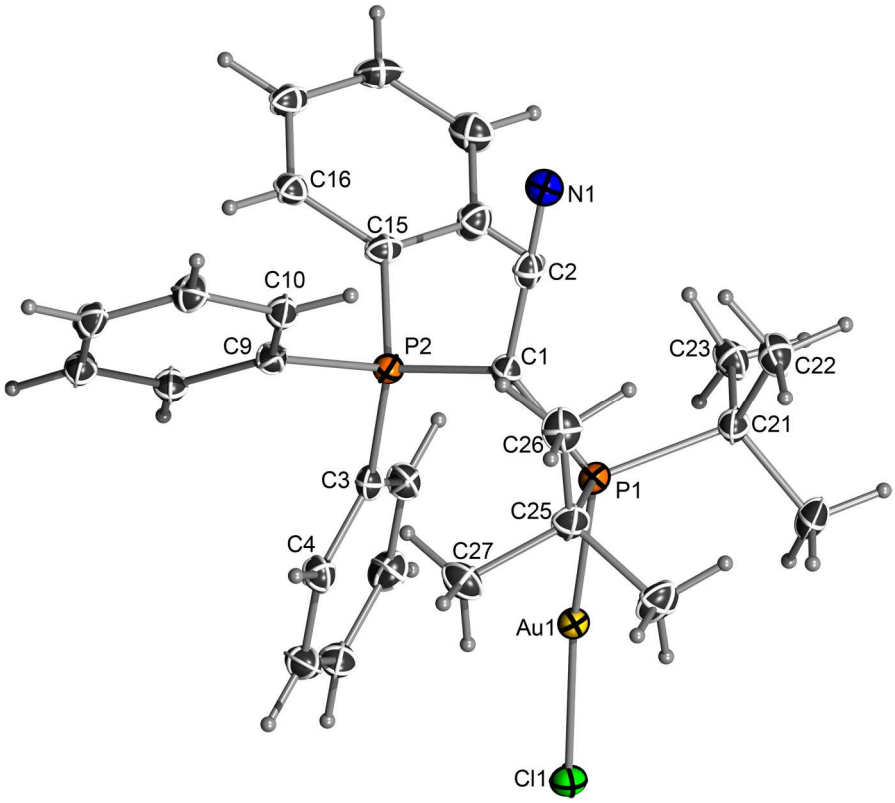


Figure S46 ORTEP Plot of **$Y_{CN}P^tBu_2$·AuCl**. Ellipsoids are drawn at the 50% probability level.

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$Y_{CN}P^tBu_2$·AuCl**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	9025(1)	4718(1)	3586(1)	15(1)
P(1)	7974(1)	2753(1)	3296(1)	14(1)
P(2)	6370(1)	3227(1)	4157(1)	13(1)
N(1)	5970(2)	-220(2)	3527(1)	20(1)
Cl(1)	10204(1)	6685(1)	3797(1)	22(1)
C(1)	6944(2)	2240(3)	3689(1)	15(1)
C(2)	6411(2)	882(3)	3596(1)	15(1)
C(3)	7193(2)	4802(3)	4393(1)	15(1)
C(4)	6931(2)	6088(3)	4103(1)	19(1)
C(5)	7551(2)	7310(3)	4292(1)	23(1)
C(6)	8439(2)	7255(3)	4766(1)	22(1)
C(7)	8703(2)	5997(3)	5053(1)	21(1)
C(8)	8081(2)	4764(3)	4868(1)	18(1)
C(9)	4878(2)	3775(3)	3891(1)	15(1)
C(10)	4183(2)	2988(3)	3464(1)	18(1)
C(11)	2997(2)	3303(3)	3300(1)	21(1)
C(12)	2524(2)	4410(3)	3553(1)	20(1)
C(13)	3220(2)	5211(3)	3966(1)	20(1)
C(14)	4389(2)	4887(3)	4140(1)	18(1)
C(21)	9014(2)	1204(3)	3336(1)	19(1)
C(20)	7267(2)	1286(3)	4988(1)	21(1)
C(19)	7265(3)	473(3)	5461(1)	24(1)
C(18)	6306(3)	510(3)	5704(1)	21(1)
C(17)	5348(2)	1344(3)	5475(1)	21(1)
C(16)	5348(2)	2151(3)	5001(1)	18(1)
C(15)	6314(2)	2133(3)	4758(1)	16(1)
C(22)	8533(3)	-70(3)	2967(1)	24(1)
C(23)	9315(2)	715(3)	3947(1)	22(1)
C(24)	10147(2)	1706(3)	3181(1)	28(1)
C(25)	7144(2)	3113(3)	2567(1)	19(1)
C(26)	6223(2)	1989(3)	2340(1)	22(1)

C(27)	6521(3)	4542(3)	2598(1)	24(1)
C(28)	7997(3)	3281(3)	2180(1)	27(1)

Table S21. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **$Y_{CN}P^tBu_2$·AuCl**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{\cdot 2}U^{11} + ... + 2\ h\ k\ a{\cdot}b{\cdot}U^{12}]$.

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
Au(1)	14(1)	14(1)	19(1)	1(1)	6(1)	0(1)
P(1)	14(1)	15(1)	15(1)	0(1)	5(1)	0(1)
P(2)	12(1)	14(1)	13(1)	0(1)	3(1)	0(1)
N(1)	20(1)	18(1)	22(1)	1(1)	5(1)	0(1)
Cl(1)	18(1)	16(1)	32(1)	0(1)	7(1)	-2(1)
C(1)	14(1)	16(1)	16(1)	0(1)	4(1)	0(1)
C(2)	15(1)	18(1)	13(1)	1(1)	3(1)	3(1)
C(3)	15(1)	15(1)	16(1)	-1(1)	6(1)	1(1)
C(4)	17(1)	19(1)	20(1)	1(1)	3(1)	2(1)
C(5)	21(1)	16(1)	30(1)	2(1)	4(1)	0(1)
C(6)	21(1)	18(1)	27(1)	-5(1)	6(1)	-3(1)
C(7)	17(1)	26(1)	19(1)	-2(1)	1(1)	-2(1)
C(8)	19(1)	17(1)	18(1)	0(1)	3(1)	1(1)
C(9)	14(1)	15(1)	17(1)	1(1)	4(1)	0(1)
C(10)	15(1)	19(1)	19(1)	1(1)	5(1)	2(1)
C(11)	17(1)	22(1)	23(1)	1(1)	1(1)	-1(1)
C(12)	13(1)	24(1)	23(1)	6(1)	4(1)	2(1)
C(13)	18(1)	22(1)	21(1)	1(1)	8(1)	3(1)
C(14)	18(1)	19(1)	19(1)	0(1)	5(1)	2(1)
C(21)	17(1)	19(1)	22(1)	-2(1)	7(1)	2(1)
C(20)	20(1)	24(1)	19(1)	2(1)	6(1)	0(1)
C(19)	24(1)	24(1)	22(1)	3(1)	0(1)	-1(1)
C(18)	28(2)	20(1)	15(1)	1(1)	5(1)	-9(1)
C(17)	27(1)	18(1)	20(1)	-3(1)	12(1)	-5(1)
C(16)	20(1)	14(1)	20(1)	-2(1)	7(1)	-3(1)
C(15)	20(1)	16(1)	14(1)	0(1)	5(1)	-3(1)
C(22)	22(1)	21(1)	27(1)	-4(1)	3(1)	2(1)
C(23)	20(1)	20(1)	24(1)	1(1)	1(1)	4(1)
C(24)	18(1)	29(2)	39(2)	-2(1)	14(1)	1(1)
C(25)	20(1)	22(1)	16(1)	5(1)	5(1)	2(1)
C(26)	22(1)	26(1)	16(1)	-1(1)	0(1)	2(1)
C(27)	27(2)	21(1)	22(1)	4(1)	1(1)	4(1)
C(28)	28(2)	35(2)	20(1)	5(1)	11(1)	-1(1)

3.3.2 Crystal Structure Determination of $(Y_{CN})_2PPh{\cdot}AuCl$

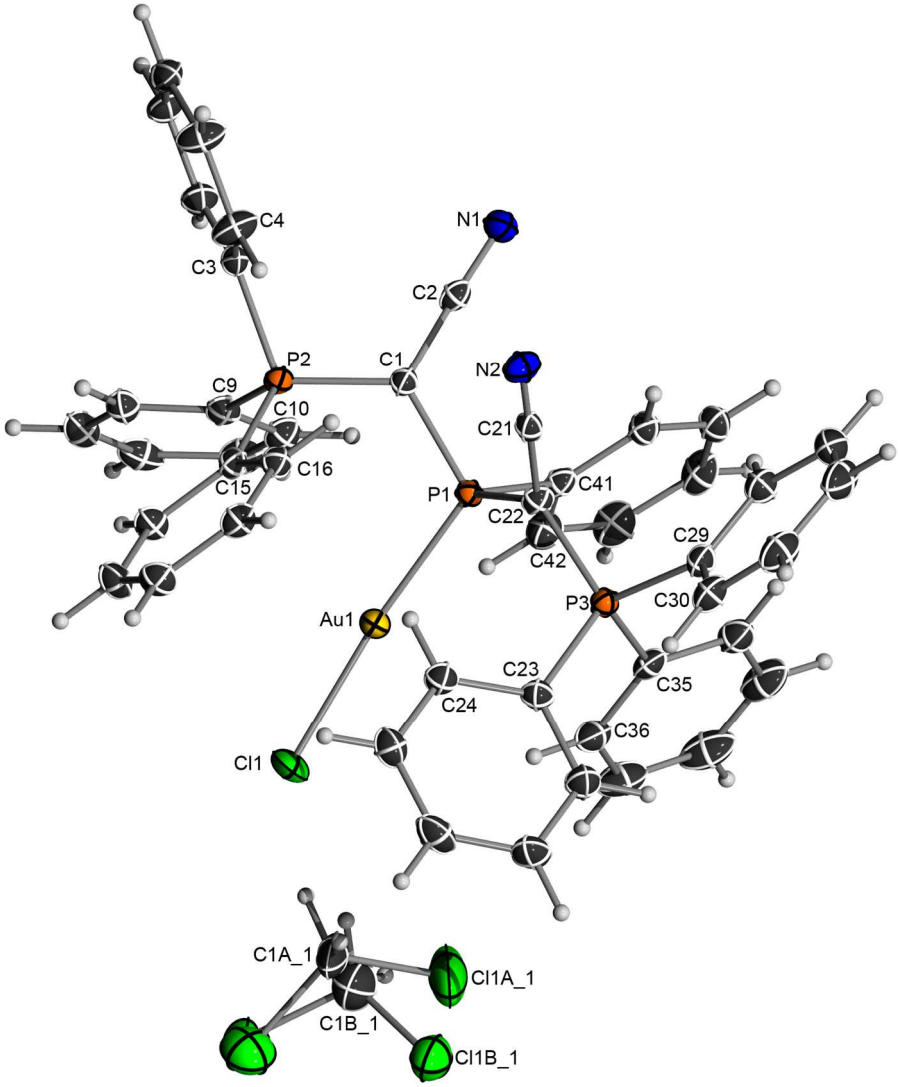


Figure S47 ORTEP Plot of **$(Y_{CN})_2PPh{\cdot}AuCl$**. Ellipsoids are drawn at the 50% probability level.

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2PPh{\cdot}AuCl$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	1599(1)	3951(1)	2527(1)	18(1)
Cl(1)	299(1)	5505(1)	2159(1)	35(1)
P(1)	2928(1)	2501(1)	2982(1)	14(1)
P(2)	2329(1)	2107(1)	1031(1)	15(1)
P(3)	4415(1)	3753(1)	3615(1)	16(1)
N(1)	4057(2)	-293(2)	2897(2)	26(1)
N(2)	5805(2)	2291(2)	1839(2)	22(1)
C(1)	3060(2)	1678(2)	2163(2)	16(1)
C(2)	3610(2)	594(2)	2546(2)	18(1)
C(3)	2859(2)	1264(2)	227(2)	18(1)
C(4)	3808(2)	1429(2)	-376(2)	28(1)
C(5)	4218(3)	789(2)	-1001(2)	32(1)
C(6)	3677(3)	-11(2)	-1032(2)	27(1)
C(7)	2740(2)	-177(2)	-431(2)	27(1)
C(8)	2325(2)	454(2)	203(2)	24(1)
C(9)	908(2)	2015(2)	1252(2)	19(1)
C(10)	494(2)	1650(2)	2278(2)	22(1)
C(12)	-1269(2)	1845(2)	1611(3)	27(1)
C(11)	-595(2)	1564(2)	2457(2)	26(1)

C(13)	-852(2)	2195(2)	588(2)	26(1)
C(14)	236(2)	2271(2)	408(2)	21(1)
C(15)	2441(2)	3493(2)	275(2)	16(1)
C(18)	2718(2)	5573(2)	-999(2)	24(1)
C(17)	1696(2)	5290(2)	-866(2)	24(1)
C(16)	1552(2)	4259(2)	-234(2)	21(1)
C(19)	3596(2)	4824(2)	-492(2)	21(1)
C(20)	3467(2)	3783(2)	144(2)	18(1)
C(21)	4222(2)	2865(2)	2984(2)	16(1)
C(22)	5089(2)	2547(2)	2361(2)	17(1)
C(23)	4144(2)	5176(2)	2836(2)	20(1)
C(24)	3873(2)	5485(2)	1788(2)	21(1)
C(25)	3694(2)	6579(2)	1176(2)	26(1)
C(26)	3780(2)	7357(2)	1619(2)	29(1)
C(27)	4024(2)	7061(2)	2672(2)	29(1)
C(28)	4209(2)	5967(2)	3286(2)	26(1)
C(29)	5827(2)	3407(2)	3954(2)	21(1)
C(30)	6526(2)	4152(2)	3567(2)	25(1)
C(31)	7629(2)	3812(3)	3756(3)	31(1)
C(32)	8026(2)	2751(3)	4346(3)	34(1)
C(33)	7335(3)	2006(2)	4744(3)	32(1)
C(34)	6239(2)	2325(2)	4535(2)	25(1)
C(35)	3514(2)	3653(2)	4753(2)	20(1)
C(36)	2496(2)	4337(2)	4622(2)	26(1)
C(37)	1747(3)	4212(3)	5461(3)	35(1)
C(38)	2013(3)	3422(3)	6427(3)	40(1)
C(39)	3020(3)	2762(3)	6560(2)	36(1)
C(40)	3773(3)	2868(2)	5727(2)	26(1)
C(41)	2706(2)	1614(2)	4315(2)	18(1)
C(42)	1668(2)	1681(2)	4780(2)	24(1)
C(43)	1500(3)	1020(3)	5814(2)	31(1)
C(44)	2364(3)	313(2)	6381(2)	29(1)
C(45)	3390(2)	230(2)	5921(2)	24(1)
C(46)	3562(2)	871(2)	4886(2)	20(1)
C1A1	990(12)	7900(13)	2049(9)	51(4)
Cl2A1	-59(7)	9018(8)	1565(8)	51(2)
Cl1A1	1181(4)	7460(4)	3393(3)	90(2)
C1B1	761(6)	7969(7)	2460(7)	53(2)
Cl1B1	1486(1)	8740(1)	2885(1)	42(1)
Cl2B1	-281(4)	8824(4)	1633(3)	51(1)

Table S23. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_2$PPh·AuCl**. The anisotropic displacement factor exponent takes the form: $–2\pi^2$ [$h^2a^{\cdot 2}U^{11}$ + ... + 2 h k a·b·U^{12}].

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
Au(1)	18(1)	16(1)	18(1)	-7(1)	-3(1)	0(1)
Cl(1)	34(1)	30(1)	35(1)	-12(1)	-12(1)	16(1)
P(1)	16(1)	13(1)	14(1)	-4(1)	0(1)	-3(1)
P(2)	17(1)	14(1)	14(1)	-4(1)	-1(1)	-4(1)
P(3)	20(1)	14(1)	15(1)	-5(1)	-2(1)	-4(1)
N(1)	36(1)	18(1)	21(1)	-6(1)	-3(1)	1(1)
N(2)	21(1)	24(1)	25(1)	-11(1)	1(1)	-6(1)
C(1)	19(1)	15(1)	14(1)	-5(1)	-2(1)	-4(1)
C(2)	22(1)	20(1)	15(1)	-6(1)	2(1)	-8(1)
C(3)	22(1)	16(1)	15(1)	-5(1)	-4(1)	-1(1)
C(4)	32(1)	30(1)	31(2)	-18(1)	8(1)	-13(1)
C(5)	37(2)	32(2)	32(2)	-18(1)	12(1)	-11(1)
C(6)	41(2)	22(1)	18(1)	-9(1)	-4(1)	0(1)
C(7)	36(2)	20(1)	29(1)	-11(1)	-8(1)	-6(1)
C(8)	27(1)	20(1)	26(1)	-9(1)	-2(1)	-6(1)
C(9)	18(1)	16(1)	23(1)	-7(1)	0(1)	-5(1)
C(10)	26(1)	21(1)	23(1)	-8(1)	1(1)	-9(1)
C(12)	18(1)	18(1)	45(2)	-11(1)	1(1)	-6(1)
C(11)	27(1)	24(1)	28(1)	-10(1)	8(1)	-11(1)
C(13)	22(1)	20(1)	36(2)	-6(1)	-7(1)	-6(1)
C(14)	23(1)	18(1)	23(1)	-4(1)	-4(1)	-5(1)
C(15)	21(1)	15(1)	13(1)	-4(1)	0(1)	-5(1)
C(18)	29(1)	18(1)	23(1)	-4(1)	1(1)	-8(1)

C(17)	25(1)	18(1)	26(1)	-2(1)	-4(1)	-2(1)
C(16)	19(1)	18(1)	25(1)	-6(1)	-2(1)	-6(1)
C(19)	21(1)	22(1)	21(1)	-8(1)	2(1)	-8(1)
C(20)	21(1)	18(1)	16(1)	-6(1)	-1(1)	-4(1)
C(21)	19(1)	14(1)	17(1)	-5(1)	0(1)	-6(1)
C(22)	21(1)	13(1)	16(1)	-3(1)	-5(1)	-4(1)
C(23)	22(1)	16(1)	21(1)	-5(1)	-2(1)	-4(1)
C(24)	21(1)	21(1)	20(1)	-7(1)	-1(1)	-4(1)
C(25)	27(1)	24(1)	23(1)	-3(1)	-3(1)	-4(1)
C(26)	29(1)	17(1)	36(2)	-1(1)	-5(1)	-3(1)
C(27)	34(2)	18(1)	37(2)	-10(1)	-8(1)	-4(1)
C(28)	34(2)	20(1)	25(1)	-7(1)	-6(1)	-5(1)
C(29)	22(1)	24(1)	20(1)	-11(1)	-4(1)	-4(1)
C(30)	27(1)	28(1)	25(1)	-13(1)	-2(1)	-8(1)
C(31)	28(1)	39(2)	35(2)	-19(1)	0(1)	-13(1)
C(32)	22(1)	46(2)	41(2)	-26(1)	-8(1)	-2(1)
C(33)	32(2)	29(1)	36(2)	-14(1)	-12(1)	3(1)
C(34)	27(1)	23(1)	28(1)	-9(1)	-6(1)	-4(1)
C(35)	26(1)	20(1)	19(1)	-10(1)	1(1)	-7(1)
C(36)	28(1)	26(1)	27(1)	-15(1)	0(1)	-4(1)
C(37)	32(2)	40(2)	43(2)	-26(1)	10(1)	-9(1)
C(38)	49(2)	41(2)	36(2)	-22(1)	21(2)	-20(2)
C(39)	58(2)	31(2)	22(1)	-10(1)	9(1)	-17(1)
C(40)	38(2)	22(1)	20(1)	-8(1)	0(1)	-8(1)
C(41)	24(1)	17(1)	14(1)	-6(1)	2(1)	-7(1)
C(42)	23(1)	28(1)	23(1)	-9(1)	1(1)	-7(1)
C(43)	32(2)	37(2)	24(1)	-8(1)	9(1)	-15(1)
C(44)	45(2)	27(1)	16(1)	-2(1)	3(1)	-17(1)
C(45)	35(2)	18(1)	18(1)	-2(1)	-4(1)	-7(1)
C(46)	24(1)	19(1)	18(1)	-5(1)	0(1)	-5(1)
C1A1	40(7)	74(9)	44(8)	-39(8)	-24(6)	20(6)
Cl2A1	44(3)	54(3)	51(2)	-18(2)	6(2)	-2(2)
Cl1A1	83(3)	126(4)	53(2)	-48(2)	-38(2)	52(2)
C1B1	53(4)	58(4)	53(5)	-26(4)	-14(4)	-3(3)
Cl1B1	39(1)	50(1)	40(1)	-20(1)	-6(1)	-6(1)
Cl2B1	56(2)	63(2)	38(2)	-28(1)	-20(2)	11(1)

3.3.3 Crystal Structure Determination of $(Y_{CN})_2PCy{\cdot}AuCl$

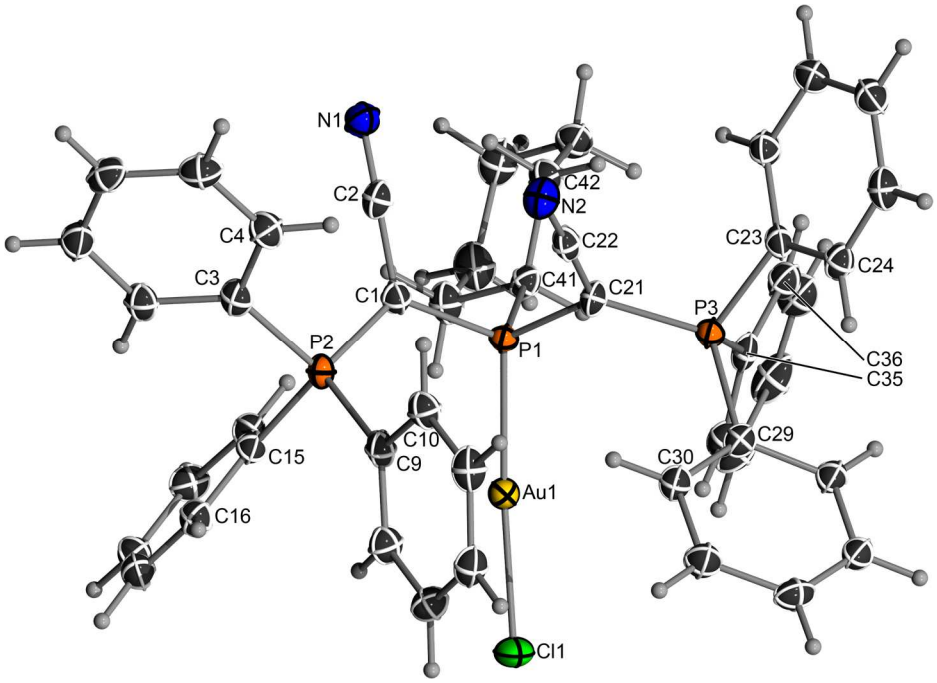


Figure S48 ORTEP Plot of **$(Y_{CN})_2PCy{\cdot}AuCl$**. Ellipsoids are drawn at the 50% probability level.

Table S24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2$PCy·AuCl.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	6214(1)	6838(1)	7410(1)	20(1)
Cl(1)	7522(1)	6908(1)	7461(1)	33(1)
N(1)	3078(2)	5670(2)	6683(2)	27(1)
N(2)	3584(2)	5873(2)	8747(2)	26(1)
P(1)	4940(1)	6893(1)	7375(1)	16(1)
P(2)	5025(1)	4565(1)	7109(1)	18(1)
P(3)	4891(1)	8126(1)	8890(1)	18(1)
C(1)	4518(2)	5715(2)	7054(2)	20(1)
C(2)	3722(2)	5684(2)	6859(2)	20(1)
C(3)	4327(2)	3534(2)	6952(2)	22(1)
C(4)	3724(2)	3418(3)	7430(2)	27(1)
C(5)	3180(2)	2660(3)	7281(2)	30(1)
C(6)	3205(2)	2022(3)	6653(2)	29(1)
C(7)	3793(2)	2145(3)	6172(2)	29(1)
C(8)	4355(2)	2898(3)	6315(2)	24(1)
C(9)	5577(2)	4390(2)	8001(2)	22(1)
C(10)	5197(2)	4259(3)	8667(2)	24(1)
C(11)	5617(2)	4115(3)	9352(2)	27(1)
C(12)	6412(2)	4095(3)	9380(2)	26(1)
C(13)	6789(2)	4254(3)	8722(2)	29(1)
C(14)	6369(2)	4414(3)	8035(2)	26(1)
C(15)	5693(2)	4393(2)	6380(2)	20(1)
C(16)	6197(2)	3562(3)	6402(2)	24(1)
C(17)	6669(2)	3401(3)	5816(2)	27(1)
C(18)	6627(2)	4059(3)	5194(2)	27(1)
C(19)	6120(2)	4888(3)	5169(2)	25(1)
C(20)	5657(2)	5061(3)	5765(2)	22(1)
C(21)	4564(2)	7158(2)	8275(2)	19(1)
C(22)	4025(2)	6463(2)	8545(2)	20(1)
C(23)	4120(2)	8445(2)	9480(2)	21(1)
C(24)	4219(2)	8405(2)	10269(2)	22(1)
C(25)	3598(2)	8567(3)	10702(2)	28(1)
C(26)	2889(2)	8784(3)	10360(2)	28(1)
C(27)	2786(2)	8835(3)	9577(2)	28(1)
C(28)	3399(2)	8652(3)	9137(2)	24(1)
C(29)	5705(2)	7817(3)	9522(2)	19(1)
C(30)	5958(2)	6805(2)	9593(2)	22(1)
C(31)	6534(2)	6559(3)	10143(2)	28(1)
C(32)	6847(2)	7331(3)	10612(2)	27(1)
C(33)	6606(2)	8342(3)	10532(2)	24(1)
C(34)	6039(2)	8600(3)	9985(2)	23(1)
C(35)	5190(2)	9231(2)	8362(2)	22(1)
C(36)	4687(2)	10041(3)	8157(2)	27(1)
C(37)	4912(2)	10799(3)	7671(2)	34(1)
C(38)	5624(2)	10762(3)	7379(2)	36(1)
C(39)	6139(2)	9973(3)	7593(2)	32(1)
C(40)	5926(2)	9227(3)	8100(2)	26(1)
C(41)	4619(2)	7957(2)	6726(2)	20(1)
C(42)	3774(2)	8250(3)	6739(2)	23(1)
C(43)	3606(2)	9212(3)	6256(2)	28(1)
C(44)	3829(2)	9052(3)	5447(2)	33(1)
C(45)	4661(2)	8722(3)	5425(2)	33(1)
C(46)	4833(2)	7757(3)	5914(2)	26(1)

Table S25. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_2$PCy·AuCl**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{\cdot 2}U^{11}$ + ... + 2 h k a·b·U^{12}].

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
Au(1)	18(1)	19(1)	22(1)	-2(1)	2(1)	1(1)
Cl(1)	17(1)	34(1)	47(1)	-7(1)	3(1)	0(1)
N(1)	26(1)	25(1)	29(1)	-1(1)	-6(1)	1(1)
N(2)	31(1)	24(1)	24(1)	1(1)	2(1)	-4(1)

P(1)	17(1)	16(1)	16(1)	-1(1)	0(1)	0(1)
P(2)	21(1)	16(1)	17(1)	0(1)	1(1)	0(1)
P(3)	20(1)	16(1)	17(1)	-1(1)	-1(1)	1(1)
C(1)	22(1)	17(1)	20(1)	-1(1)	1(1)	2(1)
C(2)	26(2)	16(1)	18(1)	2(1)	0(1)	-3(1)
C(3)	27(2)	16(1)	21(2)	2(1)	-2(1)	2(1)
C(4)	28(2)	28(2)	25(2)	0(1)	3(1)	0(1)
C(5)	25(2)	32(2)	33(2)	4(2)	2(1)	-2(1)
C(6)	25(2)	21(2)	39(2)	3(1)	-5(1)	-3(1)
C(7)	32(2)	23(2)	31(2)	-6(1)	-3(1)	0(1)
C(8)	27(2)	20(2)	26(2)	1(1)	1(1)	2(1)
C(9)	27(2)	18(1)	20(1)	0(1)	-1(1)	4(1)
C(10)	28(2)	20(2)	24(2)	1(1)	2(1)	2(1)
C(11)	40(2)	21(2)	21(2)	2(1)	2(1)	0(1)
C(12)	35(2)	21(2)	22(2)	1(1)	-4(1)	1(1)
C(13)	25(2)	34(2)	28(2)	-2(1)	-4(1)	3(1)
C(14)	27(2)	29(2)	21(2)	-1(1)	2(1)	-1(1)
C(15)	21(1)	20(2)	20(1)	-3(1)	2(1)	-3(1)
C(16)	26(2)	22(2)	24(2)	1(1)	0(1)	0(1)
C(17)	28(2)	26(2)	27(2)	-4(1)	1(1)	3(1)
C(18)	24(2)	33(2)	24(2)	-4(1)	5(1)	-1(1)
C(19)	24(2)	30(2)	20(2)	5(1)	1(1)	-2(1)
C(20)	21(1)	22(2)	24(2)	-2(1)	0(1)	-1(1)
C(21)	23(1)	19(1)	15(1)	-3(1)	-1(1)	-2(1)
C(22)	25(2)	19(2)	15(1)	-2(1)	1(1)	3(1)
C(23)	25(2)	16(1)	22(2)	-5(1)	3(1)	1(1)
C(24)	25(2)	17(1)	23(2)	0(1)	0(1)	-1(1)
C(25)	36(2)	25(2)	22(2)	-3(1)	3(1)	0(1)
C(26)	28(2)	25(2)	32(2)	-3(1)	7(1)	2(1)
C(27)	24(2)	27(2)	32(2)	-4(1)	-1(1)	5(1)
C(28)	27(2)	24(2)	21(2)	-4(1)	-1(1)	3(1)
C(29)	20(1)	20(2)	18(1)	0(1)	0(1)	-2(1)
C(30)	24(2)	21(2)	21(2)	-1(1)	0(1)	-1(1)
C(31)	28(2)	25(2)	30(2)	0(1)	-5(1)	4(1)
C(32)	21(2)	34(2)	23(2)	3(1)	-3(1)	1(1)
C(33)	22(2)	27(2)	23(2)	-4(1)	0(1)	-3(1)
C(34)	23(2)	21(2)	24(2)	-2(1)	-2(1)	-1(1)
C(35)	30(2)	14(1)	21(1)	-3(1)	-4(1)	-2(1)
C(36)	29(2)	23(2)	28(2)	-1(1)	-7(1)	0(1)
C(37)	39(2)	20(2)	40(2)	6(1)	-12(2)	1(1)
C(38)	47(2)	26(2)	35(2)	9(2)	-7(2)	-14(2)
C(39)	34(2)	30(2)	31(2)	5(2)	-1(1)	-12(2)
C(40)	28(2)	22(2)	26(2)	-1(1)	-4(1)	-4(1)
C(41)	21(2)	17(1)	22(2)	1(1)	-2(1)	-2(1)
C(42)	23(2)	20(2)	26(2)	2(1)	0(1)	1(1)
C(43)	29(2)	21(2)	31(2)	1(1)	-6(1)	4(1)
C(44)	46(2)	26(2)	26(2)	4(1)	-7(2)	1(2)
C(45)	46(2)	27(2)	26(2)	6(1)	3(2)	2(2)
C(46)	34(2)	21(2)	23(2)	2(1)	2(1)	2(1)

3.3.4 Crystal Structure Determination of $(Y_{CN})_2P^tBu{\cdot}AuCl$

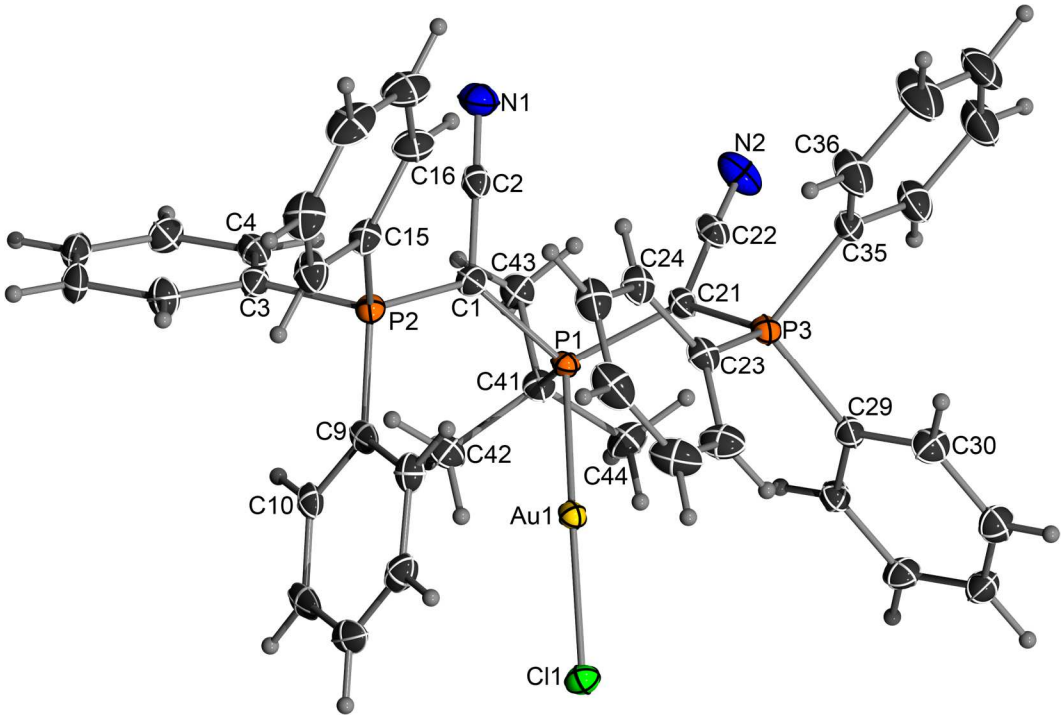


Figure S49 ORTEP Plot of **$(Y_{CN})_2P^tBu{\cdot}AuCl$**. Ellipsoids are drawn at the 50% probability level.

Table S26. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2P^tBu{\cdot}AuCl$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	4082(1)	3171(1)	602(1)	14(1)
Cl(1)	5081(1)	2786(1)	-429(1)	19(1)
P(1)	2896(1)	3462(1)	1581(1)	14(1)
P(2)	5520(1)	3748(1)	3862(1)	16(1)
P(3)	1798(1)	3993(1)	-787(1)	16(1)
N(1)	2440(3)	4157(1)	3937(3)	27(1)
N(2)	-585(3)	3910(1)	771(3)	30(1)
C(1)	3805(3)	3741(1)	2989(3)	17(1)
C(2)	3049(3)	3969(1)	3500(3)	19(1)
C(3)	5926(3)	3578(1)	5470(3)	18(1)
C(4)	4925(3)	3436(1)	5836(3)	21(1)
C(5)	5249(4)	3285(1)	7046(3)	23(1)
C(6)	6571(4)	3275(1)	7899(3)	24(1)
C(7)	7584(4)	3414(1)	7545(3)	23(1)
C(8)	7267(3)	3565(1)	6335(3)	23(1)
C(9)	6423(3)	3429(1)	3220(3)	17(1)
C(10)	6652(3)	3038(1)	3653(3)	19(1)
C(11)	7340(3)	2786(1)	3169(4)	24(1)
C(12)	7826(3)	2923(1)	2288(4)	26(1)
C(13)	7618(3)	3310(1)	1878(3)	24(1)
C(14)	6901(3)	3565(1)	2326(3)	21(1)
C(15)	6268(4)	4238(1)	4024(3)	21(1)
C(16)	5489(4)	4574(1)	3915(4)	26(1)
C(17)	6081(4)	4946(1)	4095(4)	34(1)
C(18)	7443(5)	4985(1)	4379(4)	36(1)
C(19)	8213(4)	4651(1)	4470(4)	34(1)
C(20)	7640(4)	4279(1)	4305(4)	27(1)
C(21)	1629(3)	3774(1)	511(3)	17(1)
C(22)	424(3)	3853(1)	670(3)	21(1)
C(23)	3515(3)	4140(1)	-443(3)	20(1)
C(24)	4162(4)	4389(1)	582(3)	23(1)
C(25)	5450(4)	4525(1)	817(4)	28(1)
C(26)	6095(4)	4404(1)	48(4)	32(1)

C(27)	5471(4)	4149(1)	-950(4)	35(1)
C(28)	4174(4)	4018(1)	-1212(4)	29(1)
C(29)	1261(3)	3698(1)	-2225(3)	18(1)
C(30)	1120(4)	3878(1)	-3365(3)	25(1)
C(31)	699(4)	3658(1)	-4476(4)	26(1)
C(32)	395(4)	3261(1)	-4453(3)	24(1)
C(33)	531(4)	3082(1)	-3320(3)	23(1)
C(34)	968(3)	3299(1)	-2204(3)	19(1)
C(35)	739(4)	4426(1)	-1274(3)	21(1)
C(36)	1254(4)	4801(1)	-1245(4)	37(1)
C(37)	392(5)	5123(1)	-1654(5)	51(1)
C(38)	-979(5)	5069(1)	-2067(5)	45(1)
C(39)	-1499(4)	4695(1)	-2137(4)	39(1)
C(40)	-647(4)	4373(1)	-1745(4)	31(1)
C(41)	2038(3)	3047(1)	2065(3)	18(1)
C(42)	3133(4)	2752(1)	2818(3)	23(1)
C(43)	1316(3)	3178(1)	2913(3)	20(1)
C(44)	1037(4)	2843(1)	878(3)	24(1)
Au(1)	4082(1)	3171(1)	602(1)	14(1)
Cl(1)	5081(1)	2786(1)	-429(1)	19(1)

Table S27. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_2P^tBu{\cdot}AuCl$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{\cdot 2}U^{11} + ... + 2\ h\ k\ a{\cdot}b{\cdot}U^{12}]$.

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
Au(1)	14(1)	13(1)	15(1)	0(1)	5(1)	0(1)
Cl(1)	19(1)	21(1)	20(1)	-2(1)	11(1)	0(1)
P(1)	14(1)	12(1)	16(1)	0(1)	6(1)	0(1)
P(2)	16(1)	13(1)	16(1)	0(1)	4(1)	-2(1)
P(3)	17(1)	12(1)	18(1)	0(1)	4(1)	-1(1)
N(1)	27(2)	20(1)	33(2)	-4(1)	12(1)	2(1)
N(2)	24(2)	27(2)	43(2)	10(1)	16(2)	6(1)
C(1)	15(2)	15(1)	20(2)	-2(1)	6(1)	-2(1)
C(2)	18(2)	16(2)	19(2)	0(1)	2(1)	-2(1)
C(3)	21(2)	16(2)	16(2)	0(1)	5(1)	-1(1)
C(4)	17(2)	20(2)	24(2)	1(1)	6(1)	1(1)
C(5)	25(2)	26(2)	21(2)	1(1)	12(2)	-1(1)
C(6)	31(2)	23(2)	15(2)	2(1)	6(2)	2(1)
C(7)	17(2)	29(2)	16(2)	0(1)	0(1)	0(1)
C(8)	17(2)	26(2)	23(2)	2(1)	6(1)	-3(1)
C(9)	12(1)	16(2)	21(2)	-1(1)	2(1)	-1(1)
C(10)	14(2)	20(2)	18(2)	1(1)	0(1)	-1(1)
C(11)	12(2)	19(2)	31(2)	-3(1)	-1(1)	1(1)
C(12)	11(2)	32(2)	30(2)	-11(2)	3(1)	1(1)
C(13)	19(2)	34(2)	20(2)	-4(1)	7(1)	-3(1)
C(14)	16(2)	24(2)	20(2)	2(1)	5(1)	-4(1)
C(15)	24(2)	17(2)	19(2)	0(1)	5(1)	-4(1)
C(16)	30(2)	20(2)	29(2)	-4(1)	14(2)	-3(1)
C(17)	46(2)	19(2)	39(2)	-6(2)	20(2)	-5(2)
C(18)	49(3)	22(2)	37(2)	-8(2)	18(2)	-17(2)
C(19)	29(2)	31(2)	37(2)	-2(2)	9(2)	-13(2)
C(20)	23(2)	26(2)	28(2)	1(1)	3(2)	-4(1)
C(21)	15(2)	14(1)	20(2)	2(1)	5(1)	1(1)
C(22)	22(2)	13(2)	26(2)	3(1)	7(1)	1(1)
C(23)	19(2)	16(2)	24(2)	4(1)	6(1)	-2(1)
C(24)	25(2)	18(2)	24(2)	4(1)	7(1)	-2(1)
C(25)	26(2)	21(2)	31(2)	4(1)	4(2)	-7(1)
C(26)	22(2)	24(2)	47(2)	7(2)	11(2)	-4(1)
C(27)	29(2)	26(2)	55(3)	-5(2)	23(2)	-4(2)
C(28)	27(2)	21(2)	40(2)	-6(2)	15(2)	-4(1)
C(29)	17(2)	18(2)	18(2)	1(1)	4(1)	1(1)
C(30)	30(2)	19(2)	26(2)	1(1)	12(2)	-2(1)
C(31)	26(2)	29(2)	23(2)	3(1)	12(2)	1(2)
C(32)	24(2)	28(2)	20(2)	-5(1)	7(2)	0(1)
C(33)	24(2)	18(2)	26(2)	-5(1)	8(2)	-3(1)
C(34)	20(2)	17(2)	18(2)	1(1)	6(1)	0(1)
C(35)	23(2)	16(2)	18(2)	1(1)	3(1)	4(1)

C(36)	31(2)	18(2)	45(2)	3(2)	-1(2)	-2(2)
C(37)	48(3)	18(2)	65(3)	2(2)	-2(2)	3(2)
C(38)	41(3)	28(2)	51(3)	4(2)	2(2)	18(2)
C(39)	27(2)	36(2)	43(2)	6(2)	4(2)	8(2)
C(40)	26(2)	22(2)	35(2)	4(2)	2(2)	2(2)
C(41)	18(2)	13(1)	21(2)	0(1)	6(1)	-3(1)
C(42)	24(2)	17(2)	27(2)	4(1)	11(2)	0(1)
C(43)	16(2)	23(2)	23(2)	0(1)	9(1)	-3(1)
C(44)	29(2)	20(2)	23(2)	-3(1)	11(2)	-8(1)

3.3.5 Crystal Structure Determination of $(Y_{CN})_2$PCy·Rh(CO)(acac)

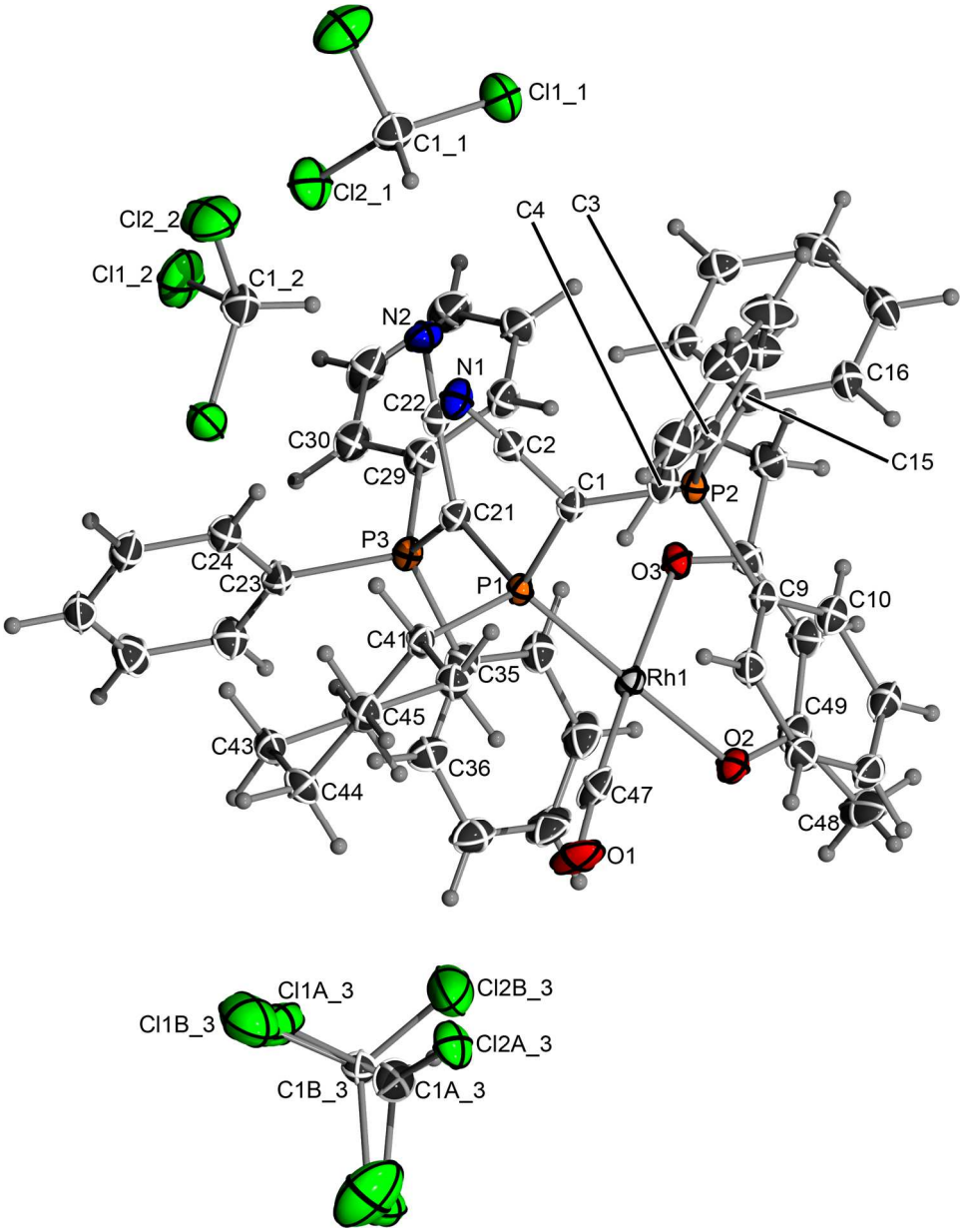


Figure S50 ORTEP Plot of **$(Y_{CN})_2$PCy·Rh(CO)(acac)**. Ellipsoids are drawn at the 50% probability level.

Table S28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$(Y_{CN})_2$PCy·Rh(CO)(acac)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	2444(1)	1877(1)	3891(1)	16(1)
P(1)	4022(1)	2536(1)	4128(1)	15(1)
P(2)	5802(1)	1433(1)	4132(1)	16(1)
P(3)	2678(1)	3457(1)	3177(1)	16(1)
O(1)	1786(2)	1963(1)	5011(1)	42(1)
O(2)	963(1)	1268(1)	3643(1)	23(1)
O(3)	2883(1)	1756(1)	3102(1)	20(1)
N(1)	7472(2)	2860(1)	4576(1)	25(1)
N(2)	6007(2)	3353(1)	3263(1)	23(1)
C(1)	5533(2)	2191(1)	4239(1)	17(1)
C(2)	6604(2)	2556(1)	4419(1)	18(1)
C(3)	7338(2)	1258(1)	4568(1)	20(1)
C(4)	7618(2)	1419(1)	5146(1)	25(1)
C(5)	8779(2)	1285(1)	5490(1)	29(1)
C(6)	9672(2)	1001(1)	5255(1)	33(1)
C(7)	9420(2)	856(1)	4685(1)	35(1)
C(8)	8245(2)	980(1)	4340(1)	27(1)
C(9)	4684(2)	931(1)	4345(1)	19(1)
C(10)	3849(2)	580(1)	3951(1)	23(1)
C(11)	3002(2)	201(1)	4134(1)	27(1)
C(12)	2977(2)	177(1)	4707(1)	28(1)
C(13)	3809(2)	523(1)	5100(1)	27(1)
C(14)	4662(2)	897(1)	4923(1)	24(1)
C(15)	5883(2)	1248(1)	3404(1)	18(1)
C(16)	5959(2)	653(1)	3208(1)	24(1)
C(17)	6110(2)	553(1)	2659(1)	29(1)
C(18)	6223(2)	1042(1)	2307(1)	29(1)
C(19)	6160(2)	1630(1)	2500(1)	26(1)
C(20)	5976(2)	1734(1)	3046(1)	21(1)
C(21)	3972(2)	3072(1)	3553(1)	17(1)
C(22)	5089(2)	3233(1)	3401(1)	18(1)
C(23)	2571(2)	4229(1)	3432(1)	19(1)
C(24)	3661(2)	4502(1)	3738(1)	22(1)
C(25)	3621(2)	5087(1)	3950(1)	26(1)
C(26)	2500(2)	5399(1)	3861(1)	28(1)
C(27)	1419(2)	5133(1)	3551(1)	29(1)
C(28)	1449(2)	4548(1)	3336(1)	25(1)
C(29)	2807(2)	3532(1)	2444(1)	20(1)
C(30)	2341(2)	4040(1)	2116(1)	24(1)
C(31)	2425(2)	4072(1)	1550(1)	29(1)
C(32)	2962(2)	3602(1)	1306(1)	30(1)
C(33)	3434(2)	3098(1)	1632(1)	26(1)
C(34)	3363(2)	3062(1)	2198(1)	23(1)
C(35)	1204(2)	3100(1)	3175(1)	21(1)
C(36)	575(2)	3217(1)	3608(1)	25(1)
C(37)	-549(2)	2932(1)	3604(1)	31(1)
C(38)	-1052(2)	2539(1)	3167(1)	36(1)
C(39)	-453(2)	2425(1)	2729(1)	33(1)
C(40)	678(2)	2707(1)	2729(1)	25(1)
C(41)	4252(2)	3028(1)	4772(1)	17(1)
C(42)	3102(2)	3413(1)	4790(1)	19(1)
C(43)	3378(2)	3870(1)	5282(1)	23(1)
C(44)	3867(2)	3550(1)	5852(1)	24(1)
C(45)	5000(2)	3158(1)	5830(1)	22(1)
C(46)	4718(2)	2696(1)	5342(1)	20(1)
C(47)	2070(2)	1947(1)	4576(1)	27(1)
C(48)	-391(2)	546(1)	3111(1)	41(1)
C(49)	711(2)	973(1)	3180(1)	26(1)
C(50)	1338(2)	1009(1)	2736(1)	26(1)
C(51)	2341(2)	1389(1)	2714(1)	21(1)
C(52)	2852(2)	1370(1)	2184(1)	27(1)
Cl11	6779(1)	3217(1)	1664(1)	45(1)
Cl21	5891(1)	4345(1)	2041(1)	41(1)
Cl31	8534(1)	4106(1)	2241(1)	50(1)

C11	7051(2)	3784(1)	2195(1)	28(1)
Cl12	6950(1)	4847(1)	3540(1)	52(1)
Cl22	9238(1)	4498(1)	4320(1)	58(1)
Cl32	6901(1)	4432(1)	4670(1)	37(1)
C12	7633(2)	4347(1)	4098(1)	32(1)
Cl1A3	56(1)	3718(1)	5680(1)	49(1)
Cl2A3	788(1)	2515(1)	6103(1)	33(1)
Cl3A3	-1681(1)	2948(1)	6096(1)	38(1)
C1A3	-455(3)	2963(2)	5741(1)	29(1)
Cl1B3	353(10)	3873(6)	5835(5)	68(3)
Cl2B3	495(6)	2662(3)	5494(4)	76(3)
Cl3B3	-1236(12)	3009(6)	6254(5)	82(3)
C1B3	-446(17)	3197(9)	5674(8)	21(5)

Table S29. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$(Y_{CN})_2$PCy·Rh(CO)(acac)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{\cdot 2}U^{11} + ... + 2\ h\ k\ a{\cdot}b{\cdot}U^{12}]$.

	U^{11}	U^{22}	U^{22}	U^{23}	U^{13}	U^{12}
Rh(1)	18(1)	15(1)	15(1)	-1(1)	3(1)	-3(1)
P(1)	17(1)	13(1)	12(1)	0(1)	3(1)	-2(1)
P(2)	18(1)	14(1)	15(1)	0(1)	2(1)	0(1)
P(3)	18(1)	15(1)	14(1)	1(1)	2(1)	-1(1)
O(1)	54(1)	56(1)	21(1)	-8(1)	20(1)	-27(1)
O(2)	22(1)	24(1)	25(1)	-5(1)	6(1)	-7(1)
O(3)	21(1)	20(1)	17(1)	-4(1)	3(1)	-3(1)
N(1)	24(1)	22(1)	27(1)	-1(1)	2(1)	-3(1)
N(2)	24(1)	22(1)	23(1)	5(1)	7(1)	-1(1)
C(1)	20(1)	15(1)	15(1)	0(1)	3(1)	-1(1)
C(2)	22(1)	17(1)	16(1)	1(1)	4(1)	2(1)
C(3)	20(1)	17(1)	20(1)	4(1)	1(1)	-2(1)
C(4)	28(1)	21(1)	23(1)	1(1)	1(1)	0(1)
C(5)	32(1)	27(1)	24(1)	4(1)	-5(1)	-4(1)
C(6)	21(1)	38(1)	34(1)	11(1)	-4(1)	-2(1)
C(7)	21(1)	49(1)	34(1)	7(1)	7(1)	6(1)
C(8)	23(1)	36(1)	22(1)	3(1)	4(1)	2(1)
C(9)	22(1)	14(1)	22(1)	2(1)	6(1)	2(1)
C(10)	24(1)	19(1)	24(1)	1(1)	4(1)	-1(1)
C(11)	25(1)	20(1)	35(1)	2(1)	4(1)	-3(1)
C(12)	27(1)	18(1)	42(1)	7(1)	15(1)	1(1)
C(13)	37(1)	21(1)	28(1)	4(1)	16(1)	4(1)
C(14)	31(1)	18(1)	23(1)	0(1)	8(1)	1(1)
C(15)	17(1)	20(1)	17(1)	-2(1)	2(1)	-1(1)
C(16)	23(1)	20(1)	26(1)	-2(1)	3(1)	2(1)
C(17)	28(1)	28(1)	29(1)	-11(1)	4(1)	5(1)
C(18)	24(1)	42(1)	20(1)	-7(1)	5(1)	4(1)
C(19)	25(1)	33(1)	20(1)	1(1)	5(1)	-3(1)
C(20)	21(1)	22(1)	19(1)	-2(1)	3(1)	-2(1)
C(21)	18(1)	17(1)	15(1)	1(1)	3(1)	-1(1)
C(22)	22(1)	15(1)	15(1)	2(1)	1(1)	1(1)
C(23)	25(1)	17(1)	16(1)	2(1)	5(1)	0(1)
C(24)	23(1)	21(1)	22(1)	0(1)	4(1)	-1(1)
C(25)	30(1)	20(1)	28(1)	-2(1)	5(1)	-5(1)
C(26)	40(1)	18(1)	28(1)	-1(1)	12(1)	1(1)
C(27)	32(1)	24(1)	32(1)	2(1)	7(1)	7(1)
C(28)	24(1)	23(1)	26(1)	0(1)	2(1)	2(1)
C(29)	21(1)	20(1)	16(1)	0(1)	1(1)	-2(1)
C(30)	25(1)	22(1)	21(1)	2(1)	1(1)	-2(1)
C(31)	35(1)	26(1)	21(1)	5(1)	-3(1)	-6(1)
C(32)	38(1)	34(1)	16(1)	-1(1)	3(1)	-13(1)
C(33)	31(1)	28(1)	20(1)	-6(1)	7(1)	-6(1)
C(34)	26(1)	22(1)	19(1)	0(1)	2(1)	-3(1)
C(35)	18(1)	19(1)	22(1)	3(1)	1(1)	0(1)
C(36)	21(1)	29(1)	25(1)	3(1)	4(1)	-1(1)
C(37)	23(1)	35(1)	38(1)	5(1)	10(1)	0(1)
C(38)	19(1)	35(1)	53(2)	3(1)	6(1)	-7(1)
C(39)	24(1)	29(1)	43(1)	-6(1)	-2(1)	-5(1)
C(40)	22(1)	23(1)	29(1)	-2(1)	1(1)	0(1)
C(41)	21(1)	16(1)	15(1)	-2(1)	4(1)	-2(1)

C(42)	21(1)	19(1)	17(1)	-2(1)	4(1)	0(1)
C(43)	27(1)	20(1)	23(1)	-4(1)	7(1)	0(1)
C(44)	29(1)	26(1)	17(1)	-5(1)	7(1)	-1(1)
C(45)	26(1)	24(1)	16(1)	-3(1)	2(1)	-2(1)
C(46)	25(1)	20(1)	14(1)	0(1)	4(1)	0(1)
C(47)	27(1)	23(1)	27(1)	0(1)	0(1)	-13(1)
C(48)	36(1)	51(2)	40(1)	-22(1)	16(1)	-25(1)
C(49)	22(1)	27(1)	28(1)	-7(1)	4(1)	-7(1)
C(50)	25(1)	28(1)	24(1)	-8(1)	4(1)	-6(1)
C(51)	21(1)	22(1)	19(1)	-2(1)	3(1)	2(1)
C(52)	31(1)	31(1)	21(1)	-6(1)	6(1)	-6(1)
Cl11	53(1)	39(1)	46(1)	-11(1)	17(1)	-3(1)
Cl21	41(1)	35(1)	46(1)	6(1)	6(1)	10(1)
Cl31	32(1)	59(1)	53(1)	11(1)	-2(1)	-10(1)
C11	32(1)	28(1)	26(1)	4(1)	7(1)	0(1)
Cl12	78(1)	39(1)	39(1)	9(1)	12(1)	-5(1)
Cl22	37(1)	72(1)	68(1)	-14(1)	16(1)	-15(1)
Cl32	45(1)	33(1)	37(1)	0(1)	16(1)	4(1)
C12	37(1)	28(1)	33(1)	-4(1)	10(1)	-5(1)
Cl1A3	38(1)	39(1)	74(1)	22(1)	20(1)	6(1)
Cl2A3	27(1)	31(1)	39(1)	-2(1)	1(1)	8(1)
Cl3A3	32(1)	38(1)	48(1)	6(1)	15(1)	4(1)
C1A3	26(1)	30(2)	30(2)	4(1)	3(1)	2(1)
Cl1B3	46(5)	77(7)	82(6)	-17(4)	19(4)	4(4)
Cl2B3	57(3)	46(3)	136(7)	-25(4)	47(4)	-6(3)
Cl3B3	98(8)	85(6)	57(5)	26(4)	6(5)	-25(6)
C(51)	21(1)	22(1)	19(1)	-2(1)	3(1)	2(1)

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