Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for the Paper Entitled:

Dinitrogen Binding, P_4-Activation and Aza-Büchner Ring Expansions Mediated by an Isocyano Analogue of CpCo(CO).

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S1. Selected FTIR Spectra

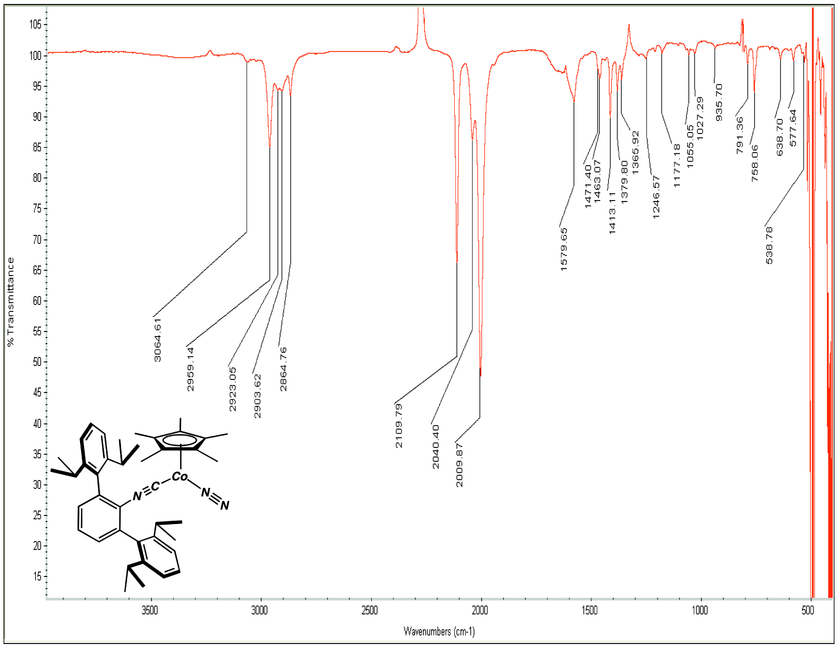

Figure S1.1. Baseline-corrected, solution-state transmittance FTIR Spectrum (C_6D_6) of Cp*Co(N_2)(CNAr^{Dipp2}) (**4**). Solvent background (C_6D_6) for subtraction was obtained immediately prior to experiment.

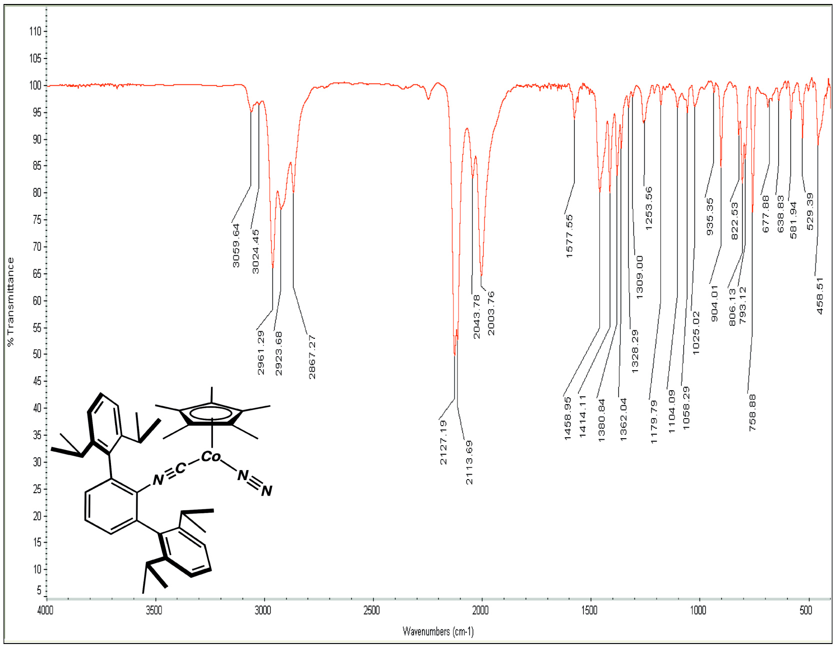

Figure S1.2. Baseline–corrected, solid-state transmittance FTIR Spectrum (KBr) of crystalline Cp*Co(N_2)(CNAr^{Dipp2}) (**4**).

S3. Selected NMR Spectra

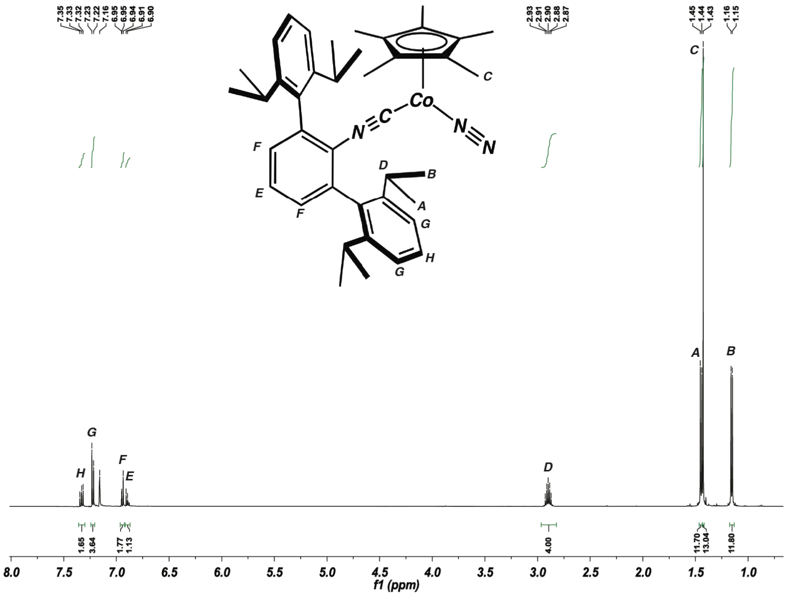

Figure S2.1. ^{1}H NMR spectrum of Cp*Co(N_2)(CNAr^{Dipp2}) (**4**) (C_6D_6, 500.1 MHz, 20 ˚C).

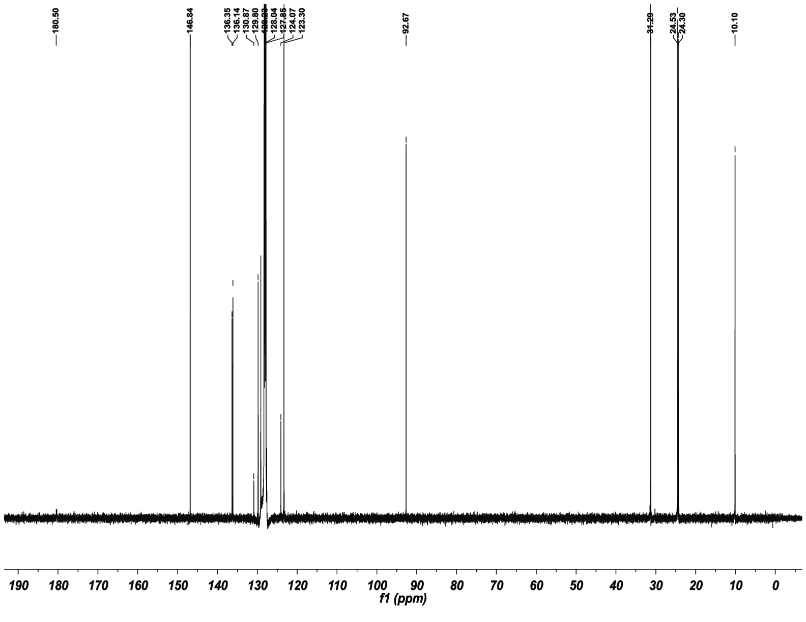

Figure S2.2. ^{13}C{^{1}H} NMR spectrum of Cp*Co(N_2)(CNAr^{Dipp2}) (**4**) (C_6D_6, 128.1 MHz, 20 ˚C).

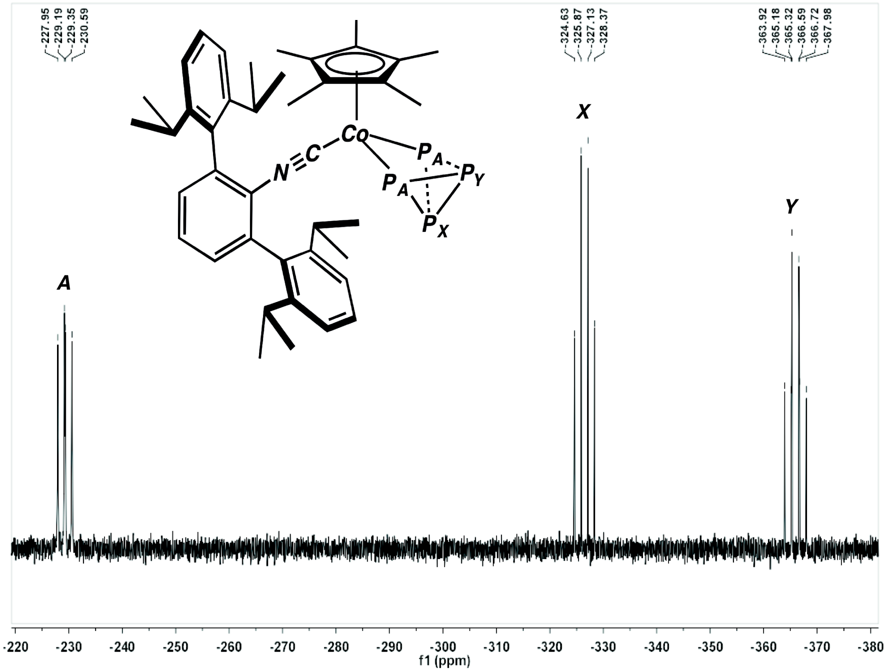

Figure S2.3. $^{31}P\{^1H\}$ NMR spectrum of Cp*Co(κ^2-P_4)(CNAr^{Dipp2}) (**8**) (C_6D_6, 202.7 MHz) displaying an A_2XY spin system.[1]

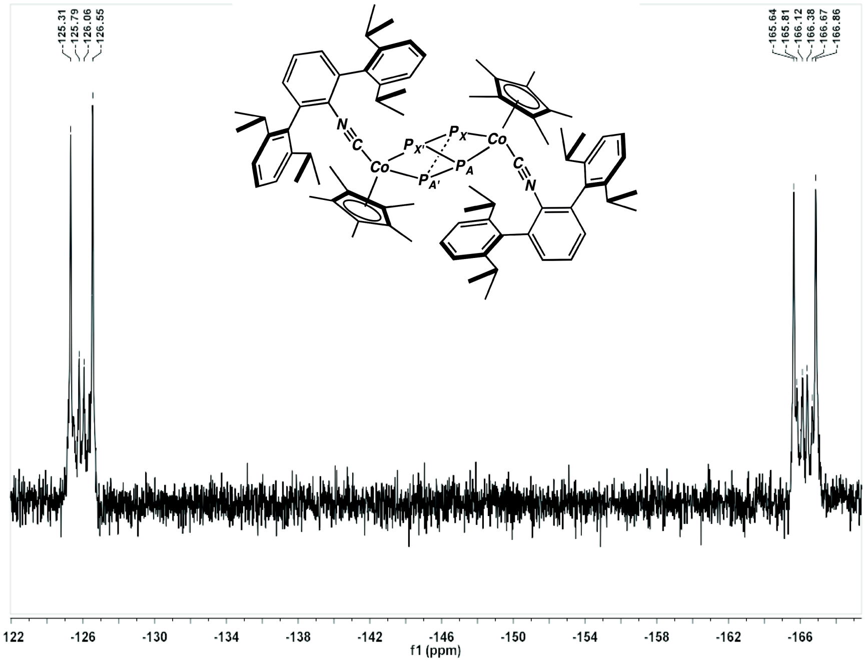

Figure S2.4. $^{31}P\{^1H\}$ NMR spectrum of [Cp*Co(CNAr^{Dipp2})]$_2$(μ_2:κ^2:κ^2-P_4) (**9**) (C_6D_6, 202.7 MHz) displaying an AA'XX' spin system.[1]

S3. Crystallographic Structure Determinations

S3.1. General Information. Single crystal X-ray structure determinations were carried out at low temperature on Bruker Kappa diffractometers equipped with a Mo sealed tube or rotating anode or Cu rotating anode radiation source and a Bruker APEX-II, APEX-I, or Proteum Pt135 detector. All structures were solved via direct methods with SHELXS[2] and refined by full-matrix least squares procedures using SHELXL[2] within the Olex2 small-molecule solution, refinement and analysis software package.[3] Crystallographic data collection and refinement information are listed in table S3.1.

S3.2. CCDC Deposition. All crystal structures reported herein have been deposited with the Cambridge Crystallographic Data Center (CCDC) and have been assigned the following CCDC deposition numbers:

$(\eta^5\text{-Cp})\text{CoI}_2\text{CNAr}^{\text{Dipp2}}$ (**1**): **1482918**
$(\eta^5\text{-Cp})_2\text{Co}_2(\mu^2\text{-CNAr}^{\text{Dipp2}})_2{\bullet}(\text{Et}_2\text{O})$; (**2**•$\text{Et}_2\text{O}$): **1482914**
$(\eta^5\text{-Cp*})\text{CoI}_2(\text{CNAr}^{\text{Dipp2}})$ (**3**): **1482913**
$(\eta^5\text{-Cp*})\text{Co}(\text{N}_2)(\text{CNAr}^{\text{Dipp2}})$ (**4**): **1482912**
$(\eta^5\text{-Cp*})\text{Co}(\text{Azabenz}[b]\text{azulene}^{\text{Dipp}})$ (**5**): **1482910**
$(\eta^5\text{-Cp*})\text{Co}(\text{CNAr}^{\text{Dipp2}})_2{\bullet}(\text{Et}_2\text{O})$; (**6**• Et_2O): **1482915**
$(\eta^5\text{-Cp*})\text{Co}(\eta^2\text{-PhCCPh})(\text{CNAr}^{\text{Dipp2}})$ (**7**): **1482919**
$(\eta^5\text{-Cp*})\text{Co}(\kappa^2\text{-P}_4)(\text{CNAr}^{\text{Dipp2}})$ (**8**): **1482911**
$[(\eta^5\text{-Cp*})\text{Co}(\text{CNAr}^{\text{Dipp2}})]_2(\mu^2{:}\kappa^2{;}\kappa^2\text{-P}_4)$ (**9**): **1482917**

S3.3. Information on Crystallographic Disorder. The following molecules contained positionally disordered components that were modeled and refined anisotropically. They are listed along with their respective disordered components:

$\text{Cp*CoI}_2(\text{CNAr}^{\text{Dipp2}})$ (**3**): Two site positional disorder *i*-Pr Methyl groups on flanking DIPP rings.

$\text{Cp*Co}(\text{CNAr}^{\text{Dipp2}})_2{\bullet}(\text{Et}_2\text{O})$; (**6**• Et_2O): Two site positional disorder in one Et_2O molecule of solvation.

$\text{Cp*Co}(\eta^2\text{-PhCCPh})(\text{CNAr}^{\text{Dipp2}})$ (**7**): Two site positional disorder *i*-Pr Methyl groups on flanking DIPP rings. $\text{Cp*Co}(\eta^2\text{-PhCCPh})(\text{CNAr}^{\text{Dipp2}})$ contains one TMS_2O molecule of solvation that was severely disordered. The Platon routine SQUEEZE[4] was used to account for this disordered molecule as a diffuse contribution to the overall scattering pattern without specific atom positions.

$[\text{Cp*Co}(\text{CNAr}^{\text{Dipp2}})]_2(\mu^2{:}\kappa^2{;}\kappa^2\text{-P}_4)$ (**9**): Two site positional disorder *i*-Pr Methyl groups. Two site rotational and translational disorder in one Cp* ring that was modeled using the AFIX 106 command to generate an idealized Cp* ring that is set to approximately 30% occupancy. $[\text{Cp*Co}(\text{CNAr}^{\text{Dipp2}})]_2(\mu^2{:}\kappa^2{;}\kappa^2\text{-P}_4)$ also contains severe compositional solvent disorder. The Platon routine SQUEEZE[4] was used to account for these disordered molecules as a diffuse contribution to the overall scattering pattern without specific atom positions.

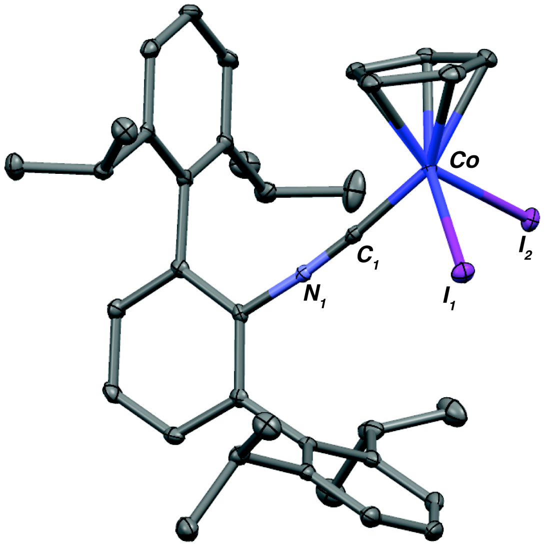

Figure S3.1. Molecular structure of $CpCoI_2CNAr^{Dipp2}$ **(1)**. Hydrogen atoms omitted for clarity. Selected Bond Distance (Å): Co-I_1 = 2.5716(3), Co-I_2 = 2.5786(3), Co-C_1 = 1.8232(19), C_1-N_1 = 1.159(2).

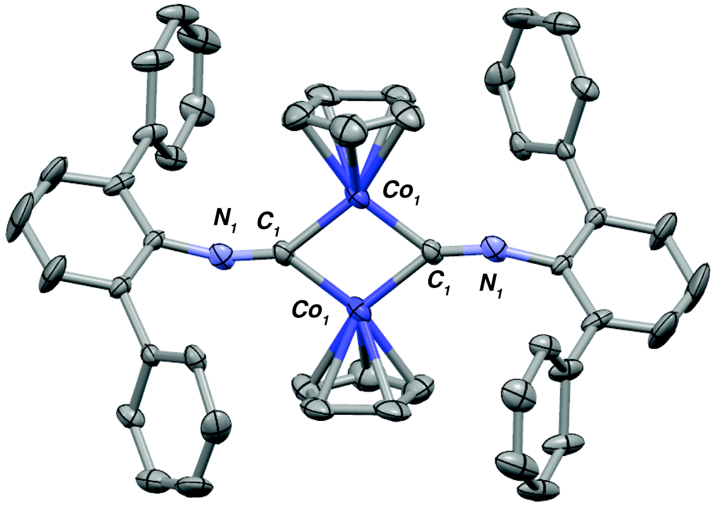

Figure S3.2. Molecular structure of $[CpCo(\mu^2\text{-}CNAr^{Dipp2})]_2$ (**2**). $[CpCo(\mu^2\text{-}CNAr^{Dipp2})]_2$ lies on a crystallographic mirror plane resulting in one half of $[CpCo(\mu^2\text{-}CNAr^{Dipp2})]_2$ to be symmetry generated. Hydrogen atoms and flanking *i*-Pr groups omitted for clarity. Selected bond distances (Å): Co-Co = 2.321(1), Co-C_1 = 1.857(7), C_1-N_1 = 1.222(9). Selected bond angles (˚): C_1-N_1-C_2 = 157.6(7), C_1-Co_1-C_1-Co_1 = 180.0.

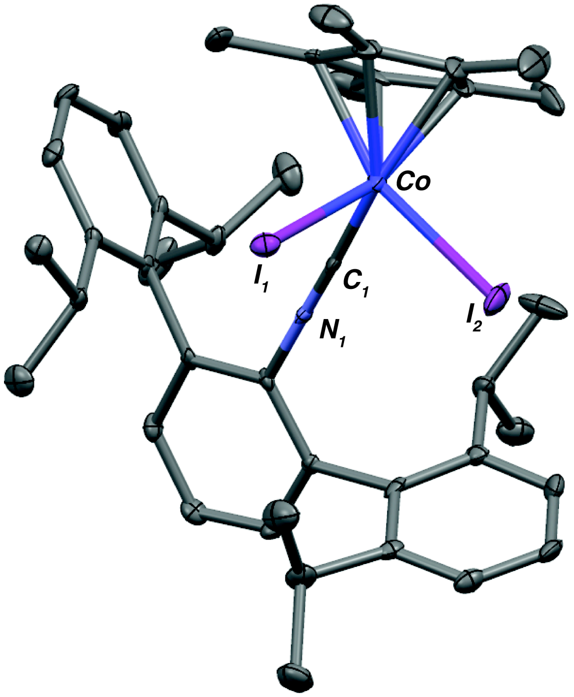

Figure S3.3. Molecular structure of Cp*CoI_2($CNAr^{Dipp2}$) (**3**). Hydrogen atoms, and positionally disordered *i*-Pr methyl groups omitted for clarity. Selected bond distances (Å): Co-C_1 = 1.832(5), Co-I_1 = 2.5963(6), Co-I_2 = 2.5739(6), C_1-N_1 = 1.161(5).

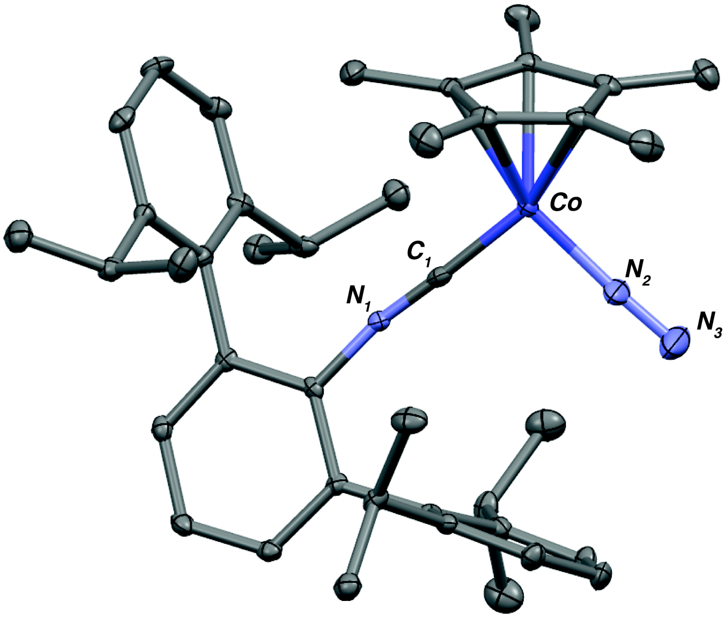

Figure S3.4. Molecular Structure of Cp*Co(N_2)($CNAr^{Dipp2}$) **(4)**. Hydrogen atoms omitted for clarity. Selected bond distances (Å): Co-C_1 = 1.766(2), C_1-N_1 = 1.179(3), Co-N_2 = 1.781(2), N_2-N_3 = 1.116(3). Selected bond angles (˚): C_1-N_1-C_2 = 166.1(2), Co-N_2-N_3 = 177.1(2), C_1-Co-N_2 = 96.49(9).

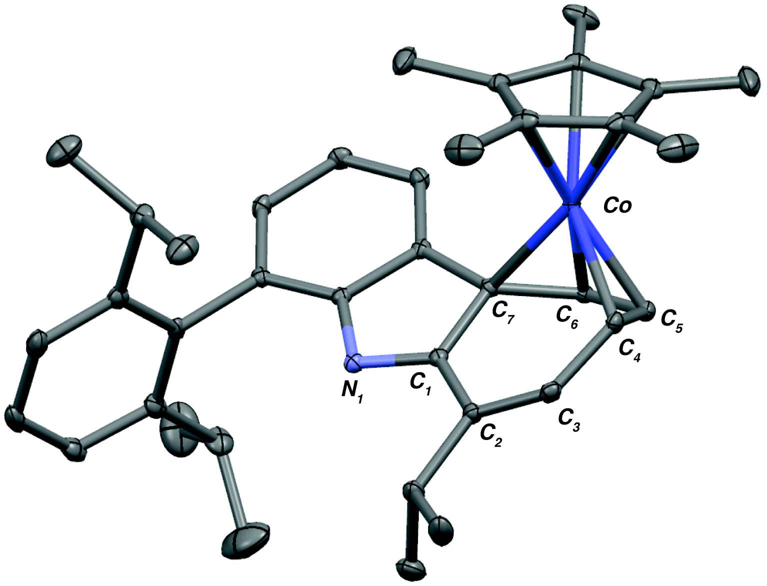

Figure S3.5. Molecular structure of Cp*Co(η^4-1-azabenz[b]azulene$^{\mathrm{Dipp2}}$) (**5**). Hydrogen atoms and one *i*-Pr group at C_6 omitted for clarity. Selected bond distances (Å): C_1-N_1 = 1.3196(19), C_1-C_2 = 1.463(2), C_2-C_3 = , C_3-C_4 = 1.466(2), C_4-C_5 = 1.441(2), C_5-C_6 = 1.409(2), C_6-C_7 = 1.470(2), C_1-C_7 = , Co-C_7 = 2.0778(15), Co-C_6 = 2.0187(15), Co-C_5 = 1.9800(15), Co-C_4 = 2.0441(15). Selected bond angles (˚): C_1-N_1-C_{19} = 106.60(12), C_1-C_2-C_3 = 119.73(13), C_2-C_3-C_4 = 127.71(14), C_3-C_4-C_5 = 124.77(14), C_4-C_5-C_6 = 120.02(13), C_5-C_6-C_7 = 117.07(13), C_6-C_7-C_1 = 126.20(13).

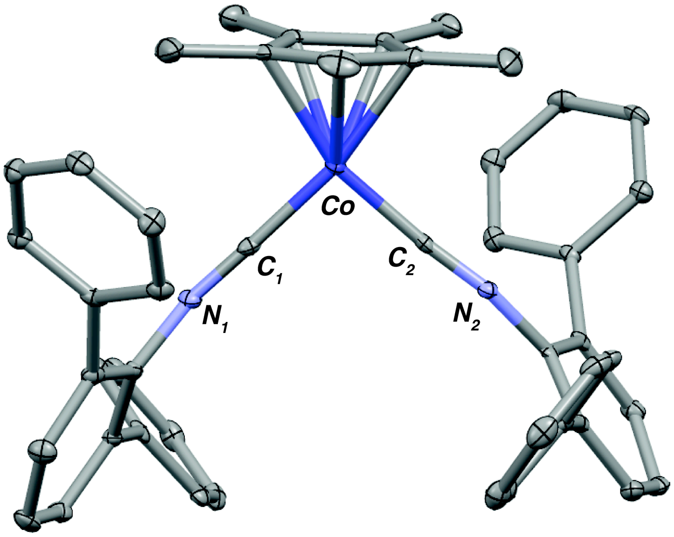

Figure S3.6. Molecular structure of Cp*Co(CNAr$^{\mathrm{Dipp2}}$)$_2$•Et_2O (**6**•Et_2O). Flanking *i*-Pr groups, Hydrogen atoms and one Et_2O molecule of solvation omitted for clarity. Selected bond distances (Å): Co-C_1 = 1.766(13), Co-C_2 = 1.780(2), C_1-N_1 = 1.207(3), C_2-N_2 = 1.187(3). Selected bond angles (˚): C_1-N_1-C_3 = 153.4(2), C_2-N_2-C_{33} = 163.3(2). C_1-Co-C_2 = 96.85(11).

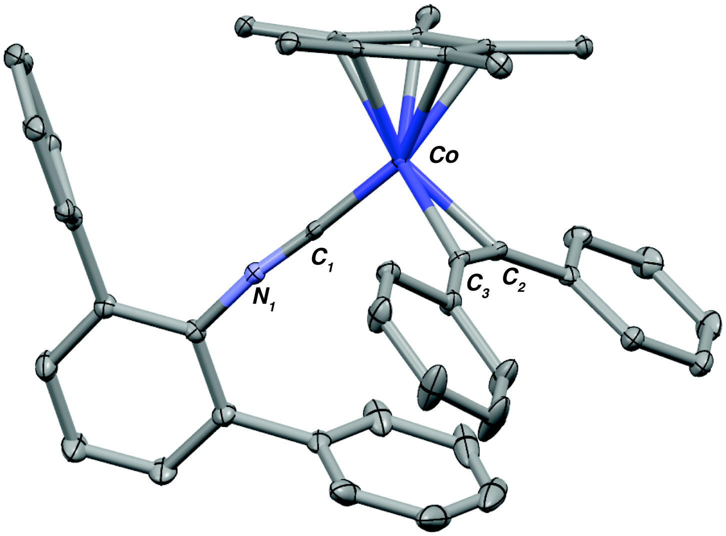

Figure S3.7. Molecular structure of Cp*Co(η^2-PhCCPh)(CNAr$^{\mathrm{Dipp2}}$) (**7**). Flanking *i*-Prmethyl groups and hydrogen atoms omitted for clarity. Selected bond distances (Å): Co-C_1 = 1.782(2), Co-C_2 = 1.9668(19), Co-C_3 = 19819(19), C_1-N_1 = 1.176(3), C_3-C_2 = 1.269(3). Selected bond angles (°): C_1-N_1-C_4 = 170.77(19), C_3-C_2-C_{34} = 151.3(2), C_2-C_3-C_{40} = 148.7(2).

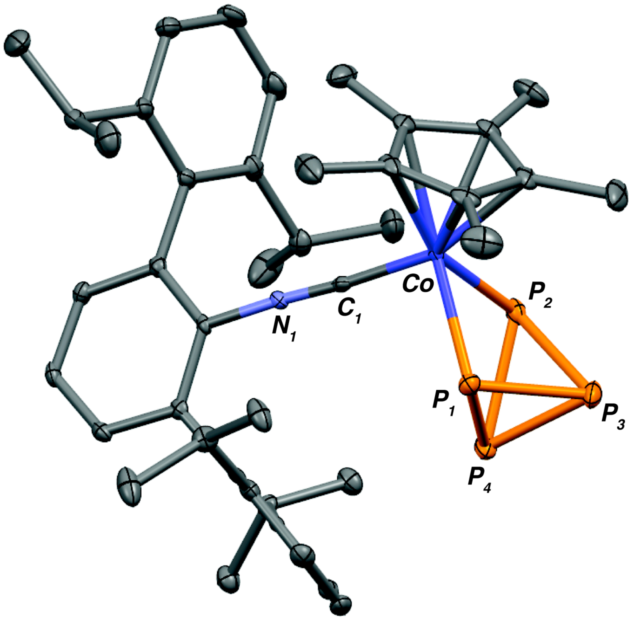

Figure S3.8. Molecular structure of Cp*Co(κ^2-P_4)(CNAr$^{\mathrm{Dipp2}}$) (**8**). Hydrogen atoms omitted for clarity. Selected bond distances (Å): Co-C_1 = 1.7913(17), C_1-N_1 = 1.170(2), Co-P_1 = 2.2462(5), Co-P_2 = 2.2523(5), P_1-P_2 = 2.6065(8), P_1-P_3 = 2.2235(7), P_1-P_4 = 2.2096(7), P_2-P_3 = 2.2174(7), P_2-P_4 = 2.2201(7), P_3-P_4 = 2.1872(7). Selected bond angles (°): C_1-N_1-C_2 = 175.24(16), P_1-Co-P_2 = 70.817(18), Co-P_1-P_3 = 99.74(2), Co-P_2-P_3 = 99.74(2), Co-P_1-P_4 = 101.49(2), Co-P_2-P_4 = 100.97(2), P_2-P_3-P_1 = 71.88(2), P_2-P_4-P_1 = 72.09(2),.

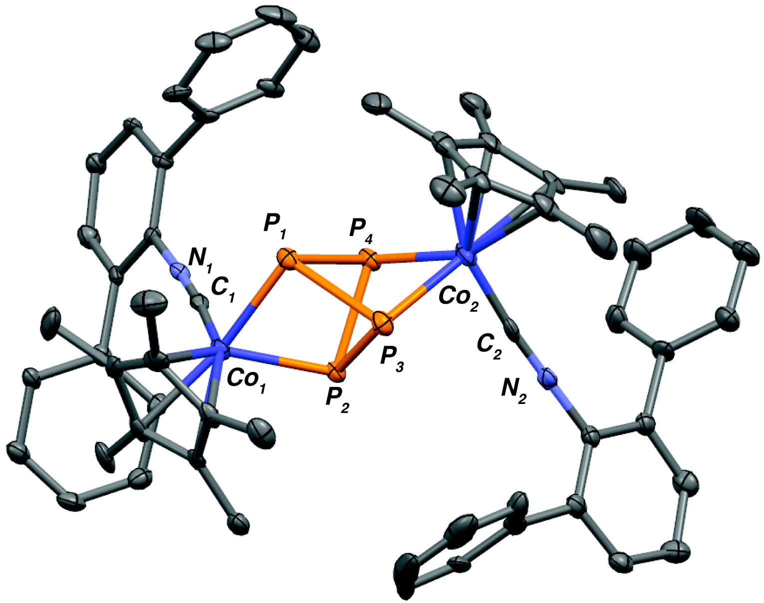

Figure S3.9 Molecular structure of $[Cp^*Co(CNAr^{Dipp2})]_2(\mu_2{:}\kappa^2{:}\kappa^2\text{-}P_4)$ (**9**). Disordered Cp*, flanking *i*-Pr methyl groups, and hydrogen atoms omitted for clarity. Selected bond distances (Å): $Co_1\text{-}C_1 = 1.794(5)$, $C_1\text{-}N_1 = 1.181(5)$, $Co_1\text{-}P_1 = 2.2565(14)$, $Co_1\text{-}P_2 = 2.2727(15)$, $Co_2\text{-}C_2 = 1.765(6)$, $C_2\text{-}N_2 = 1.193(6)$, $Co_2\text{-}P_3 = 2.2614(13)$, $Co_2\text{-}P_4 = 2.2635(15)$, $P_1\text{-}P_4 = 2.2462(18)$, $P_1\text{-}P_3 = 2.2581(19)$, $P_2\text{-}P_3 = 2.2478(17)$, $P_2\text{-}P_4 = 2.2207(17)$, $P_1\text{-}P_2 = 2.5663(18)$, $P_3\text{-}P_4 = 2.5951(18)$.

Table S3.1

Name	$CpCoI_2CNAr^{Dipp2}$ (**1**)	$[CpCo(\mu^2\text{-}CNAr^{Dipp2})]_2$•$(Et_2O)$; (**2**•$Et_2O$)
Formula	$C_{36}H_{42}CoI_2N$	$C_{72}H_{84}Co_2N_2$
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/c$	C2/c
a, Å	11.2236(3)	29.1006(17)
b, Å	18.3864(4)	10.4530(7)
c, Å	17.5003(4)	21.8596(13)
α, deg	90	90
β, deg	108.6110(10)	102.775(4)
γ, deg	90	90
V, $Å^3$	3422.54(14)	6484.8(7)
Z	4	4
Radiation (λ, Å)	Mo-K_α, 0.71073	Cu-K_α, 1.54178
ρ (calcd.), g/cm^3	1.555	1.122
μ (Mo Ka), mm^{-1}	2.329	4.298
Temp, K	100	100
θ max, deg	50.756	100.862
data/parameters	6278/369	3378/351
R_1	0.0183	0.0776
wR_2	0.0453	0.1991
GOF	1.036	1.063

Table S3.1. Continued.

Name	Cp*CoI$_2$(CNAr^{Dipp2}) (**3**)	Cp*Co(N$_2$)(CNAr^{Dipp2}) (**4**)	Cp*Co(η^4-1-azabenz[b]azulene^{Dipp2}) (**5**)
Formula	$C_{41}H_{52}CoI_2N$	$C_{41}H_{52}CoN_3$	$C_{41}H_{53}CoN$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	10.1747(2)	18.1976(8)	12.3600(4)
b, Å	21.3662(5)	10.5931(5)	14.5680(4)
c, Å	17.6111(4)	18.9124(8)	19.8481(6)
α, deg	90	90	90
β, deg	96.1823(13)	92.5640(19)	97.9218(15)
γ, deg	90	90	90
V, Å^3	3806.29(15)	3642.1(13)	3539.75(18)
Z	4	4	4
Radiation (λ, Å)	Mo-K$_\alpha$, 0.71073	Mo-K$_\alpha$, 0.71073	Mo-K$_\alpha$, 0.71073
ρ (calcd.), g/cm^3	1.521	1.178	1.161
μ (Mo Ka), mm^{-1}	2.101	0.502	0.512
Temp, K	100	100	100
θ max, deg	51.002	52.054	56.62
data/parameters	7028/428	7156/419	8774/401
R_1	0.0392	0.0408	0.0369
wR_2	0.0672	0.0772	0.0813
GOF	1.054	1.022	1.013

Table S3.1. Continued.

Name	Cp*Co(CNAr^{Dipp2})$_2$ •(Et$_2$O); (**6**• Et$_2$O)	Cp*Co(η^2-PhCCPh)(CNAr^{Dipp2}) (**7**)	Cp*Co(κ^2-P$_4$) (CNAr^{Dipp2}) (**8**)
Formula	$C_{74}H_{92.5}CoN_2O_{0.5}$	$C_{55}H_{62}CoN$	$C_{41}H_{52}CoNP_4$
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/c$	C2/c	P-1
a, Å	21.222(3)	39.4977(15)	10.5024(5)
b, Å	14.0788(17)	10.7818(4)	11.2267(5)
c, Å	21.829(3)	25.7877(9)	17.5316(7)
α, deg	90	90	91.4990(10)
β, deg	96.131(7)	110.826(3)	90.424(2)
γ, deg	90	90	110.691(2)
V, Å^3	6484.6(14)	10624.3(7)	1932.81(15)
Z	4	8	2
Radiation (λ, Å)	Mo-K$_\alpha$, 0.71073	Mo-K$_\alpha$, 0.71073	Mo-K$_\alpha$, 0.71073
ρ (calcd.), g/cm^3	1.143	1.030	1.274
μ (Mo Ka), mm^{-1}	0.310	0.366	0.639
Temp, K	100	100	100
θ max, deg	50.768	52.058	50.728
data/parameters	11827/731	10126/554	7084/437
R_1	0.0513	0.0427	0.0284
wR_2	0.1247	0.1019	0.0670
GOF	1.039	1.031	1.020

Table S3.1. Continued.

Name	$[Cp^*Co(CNAr^{Dipp2})]_2$ $(\mu_2{:}\kappa^2{:}\kappa^2\text{-}P_4)$ (**9**)
Formula	$C_{82}H_{104}Co_2N_2P_4$
Crystal System	Triclinic
Space Group	P-1
a, Å	12.0968(7)
b, Å	12.4201(7)
c, Å	29.0162(18)
α, deg	94.200(3)
β, deg	93.812(2)
γ, deg	108.525(2)
V, $Å^3$	4103.9(4)
Z	2
Radiation (λ, Å)	Mo-K_α, 0.71073
ρ (calcd.), g/cm^3	1.100
μ (Mo Ka), mm^{-1}	0.522
Temp, K	100
θ max, deg	50.676
data/parameters	14930/890
R_1	0.0677
wR_2	0.1526
GOF	1.004

S4. References

1. S. Dürr, D. Ertler, U. Radius, *Inorg. Chem*, **2012**, *51*, 3904-3909.
2. G. M. Sheldrick, *Acta Crystallogr. A.*, **2008**, *64*, 112.
3. O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
4. P. van der Sluis and A. L. Spek, *Acta Crystallogr.* **1990,** *A46***,** 194.