Supporting Information for:

Cobalt(-I) triphos dinitrogen complexes: activation and silyI-functionalisation of N₂

Samantha L. Apps, Philip W. Miller* and Nicholas J. Long*

Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, Wood Lane, London W12 0BZ, UK

Email: philip.miller@imperial.ac.uk; n.long@imperial.ac.uk;

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General considerations

All manipulations were performed in an MBraun glovebox under an N₂ atmosphere. Dry solvents were obtained from an MBraun MB-SPS 800 Solvent Purification system, degassed by thoroughly sparging with nitrogen and stored over activated 3 Å molecular sieves. Deuterated solvents were purchased from Goss-Scientific, freeze-pump-thaw degassed, and stored over 3 Å molecular sieves. C₆D₆ was additionally dried over CaH₂ before storage. ¹⁵N₂ gas was donated by Dr Andrew Ashley, Imperial College London (purchased from Cambridge Isotope Laboratories, 98% ¹⁵N) and was transferred from a breakseal flask using a Toepler pump. NP₃^{Ph} was synthesised according to known literature procedures.^{1–3} KC₈ was donated by the Ashley group and prepared according to known literature procedures by Mr. Adam Piascik of Imperial College London. SiMe₃Cl was bought as the anhydrous reagent and immediately transferred to a J.Y. flask under an N₂ atmosphere for storage. All other reagents were commercially available and were used as received.

¹H, ³¹P{¹H}, ¹⁵N{¹H} and ²⁹Si NMR spectra were recorded on Bruker AV-400, AV-500 or DRX-400 spectrometers. Chemical shifts are reported in ppm, using the residual proton impurities in the solvents for ¹H NMR spectroscopy, and ³¹P{¹H}, ¹⁵N{¹H} and ²⁹Si were externally referenced ($\delta = 0$) to 85% H₃PO₄ (aq), CH₃NO₂ and SiMe₄, respectively. Mass spectrometry analyses were conducted by the Mass Spectrometry Service, Imperial College London. Infrared spectra were recorded on a Perkin-Elmer Spectrum FT-IR spectrometer; solution phase spectroscopy was performed using a Specac Omni-cell solution cell with NaCl plates and a 50µm PTFE spacer. Elemental analyses were carried out by Mr. Stephen Boyer at London Metropolitan University. X-ray diffraction analysis was carried out by S. L. Apps, with assistance and useful discussions from Dr. Andrew J. P. White of the Department of Chemistry at Imperial College London.

Isolated complexes:

[CoCI(NP₃^{Ph})] (1): To a flask charged with CoCl₂ (50 mg, 0.385 mmol), NP₃^{Ph} (235 mg, 0.385 mmol) and Zn powder (130 mg, 1.99 mmol, excess) was added THF (5 mL). The mixture was stirred for 1 d at room temperature, resulting in the formation of an orange suspension. The mixture was filtered to remove unreacted Zn and ZnCl₂ impurities, and the orange THF solution was concentrated to a half *in vacuo*. Vapour diffusion of hexane into the THF solution resulted in the formation of orange/brown crystals (needles), which were isolated by decanting

the supernatant, and washing with hexane (3 x 1 mL), before drying *in vacuo*. Yield = 151 mg (55 %). ES-MS (positive ion): *m/z* calcd. for $C_{40}H_{40}NOP_3Co$ ([(M-CI).MeOH]⁺) 702.1655, found 702.1655; for $C_{41}H_{40}CIN_2P_3Co$ ([(M+H+MeCN]⁺) 747.1419, found 747.1689. Anal. Calcd. for $C_{39}H_{36}CoCINP_3$ (found): C, 66.35 (66.50); H, 5.14 (5.28); N, 1.98 (2.05). Single crystals suitable for X-ray diffraction were grown by vapour diffusion of hexane into a THF solution.

[{(NP₃^{Ph})Co(μ -N₂)}₂Mg(THF)₄] (2): To a flask charged with [CoCl(NP₃^{Ph})] (1) (72 mg, 0.10 mmol) was added THF (3 mL) and Mg powder (~ 20 mg, excess). A colour change from orange to deep red was initially observed after 3 h stirring at room temperature, and the mixture was stirred for a total of 2 d to ensure reaction completion and full reduction. The mixture was filtered through a Teflon syringe filter and brought to dryness *in vacuo*. The red residue was redissolved in THF (2 mL), filtered again, and brought to dryness *in vacuo*. Yield = 82 mg (47 %). IR (solution cell, THF, cm⁻¹): 1878 (v_{NN}). ¹H NMR (C₆D₆, 298 K, 400 MHz) δ : 7.38 (m, 24H, phenyl), 6.96 (m, 12H, phenyl), 6.86 (t, 24H, ³J_{HH} = 7.0 Hz, phenyl), 3.86 (s, 12H, CH₂), 3.79 (s, THF), 1.45 (s, THF). ³¹P{¹H} NMR (*d*₈-THF, 200 K, 202 MHz) δ : 14.3 (br s). Accurate elemental analysis could not be obtained, due to the extreme air and moisture sensitivity of this complex.

[{(MeCP₃^{Ph})Co(μ-N₂)}₂Mg(THF)4] (5): To a flask charged with CoCl₂ (25 mg, 0.19 mmol), MeCP₃^{Ph} (120 mg, 0.19 mmol) and Zn powder (60 mg, excess) was added THF (3 mL). The mixture was left to stir for 1 d at 298 K, generating [CoCl(MeCP₃^{Ph})] *in situ*, as an orange solution within the suspension. The mixture was filtered into a new flask, containing Mg powder (~30 mg, excess), and the resulting mixture was stirred for 2 d at room temperature, resulting in a colour change to deep red. The mixture was filtered through a Teflon syringe filter and brought to dryness *in vacuo*. The red residue was redissolved in THF (2 mL), filtered again, and brought to dryness *in vacuo*. Yield = 138 mg (42 %). IR (solution cell, THF, cm⁻¹): 1872 (v_{NN}). ¹H NMR (C₆D₆, 298 K, 400 MHz) δ: 7.80 - 7.61 (m, 12H, phenyl), 7.47 - 7.42 (m, 18H, phenyl), 7.02 - 6.89 (m, 12H, phenyl), 6.86 - 6.76 (m, 18H, phenyl), 3.75 (s, THF), 2.13 - 2.04 (m, 12H, CH₂) 1.38 (THF), 1.23 - 1.16 (m, 6H, C-CH₃). ³¹P{¹H} NMR (C₆D₆, 298 K, 162 MHz) δ: 31.2 (s). Accurate elemental analysis could not be obtained, due to the extreme air and moisture sensitivity of this complex.

Additional procedures (non-isolated complexes)

Preparation of 2 with side-products [{(NP₃^{Ph})Co}₂{ μ -N₂}] (3) and [Co₂(NP₃^{Ph})₂] (4): To a flask charged with an equimolar amount of CoCl₂ (10 mg, 0.077 mmol) and NP₃^{Ph} (47 mg, 0.077 mmol) was added THF (3 mL). The mixture was stirred at room temperature for 15 minutes until fully dissolved, before the addition of Mg powder (excess, > 0.50 mmol, 15 mg). The resulting mixture was stirred for 2 d, resulting in the formation of a deep red solution. An aliquot of the resulting solution was characterised by IR spectroscopy (solution IR in THF), indicating the formation of **2** (v_{NN} = 1878 cm⁻¹). The mixture was filtered, reduced to a half *in vacuo*, and set up for crystallisation by vapour diffusion with hexane. Resulting deep red crystals were obtained for multiple experimental attempts, which were characterised by XRD and gave crystals structures of either **3** or **4** (in unknown quantities).

[{(NP₃^{Ph})Co(μ -¹⁵N₂)}₂Mg(THF)₄] (2-¹⁵N): To a flask charged with [CoCl(NP₃^{Ph})] (1) (35 mg, 0.050 mmol) was added THF (5 mL) and Mg powder (20 mg, excess). The mixture was freeze-pump-thaw-degassed (4 x) and the flask was backfilled with ¹⁵N₂ gas atmosphere (1 atm, ~1 mmol). The mixture was stirred for 2 d at room temperature, resulting in a colour change to a deep red solution. An aliquot of the solution was characterized by IR spectroscopy, indicating the formation of 2-¹⁵N. IR (solution cell, THF, cm⁻¹): 1816 (v_{15N15N}).

[(NP₃^{Ph})Co{ μ -N₂}Li(THF)_x] (2-Li): To a solution of 2, [{(NP₃^{Ph})Co(μ -N₂)}₂Mg(THF)₄] (20 mg, 0.012 mmol) in THF (5 mL) was added ^{*n*}BuLi (2.5 M in hexanes, 0.1 mL, > 2 eq, excess). The mixture was stirred for 1 d, and the solution was characterised by IR spectroscopy, indicating the conversion of 2 to 2-Li. The solution was dried *in vacuo*, and redissolved in *d*₈-THF for NMR characterisation. IR (solution, THF, cm⁻¹): 1885 (v_{NN}). ¹H NMR (*d*₈-THF, 298 K, 400 MHz) δ : 7.15 (m, 12H, phenyl), 6.75 - 6.68 (m, 18H, phenyl), 3.46 (s, 6H, CH₂), 3.79. ³¹P{¹H} NMR (*d*₈-THF, 200 K, 202 MHz) δ : 8.6 (s).

[(NP₃^{Ph})Co{ μ -N₂}Na(THF)_x] (2-Na): A solution of 2, [{(NP₃^{Ph})Co(μ -N₂)}₂Mg(THF)₄] (20 mg, 0.012 mmol) in THF (5 mL) was decanted into a Schlenk flask containing a freshly prepared Na mirror (20 mg, excess). The mixture was stirred for 1 d, and the resulting darker red/purple solution was characterised by IR spectroscopy, indicating the conversion of 2 to 2-Na. IR (solution, THF, cm⁻¹): 1904 (v_{NN}). NMR spectroscopic characterisation was ambiguous and could not be assigned.

[(NP₃^{Ph})Co{ μ -N₂}K(THF)_x] (2-K): To a flask charged with 2, [{(NP₃^{Ph})Co(μ -N₂)}₂Mg(THF)₄], (20 mg, 0.012 mmol) and KC₈ (4 mg, 0.030 mmol, 2.5 eq) was added THF (2 mL). The mixture was stirred for 1 d at room temperature, resulting in the formation of a darker red/purple solution. An aliquot of the solution was characterised by IR spectroscopy, indicating the conversion of **2** to **2-K**. The solution was dried *in vacuo*, and redissolved in *d*₈-THF for NMR characterisation. IR (solution, THF, cm⁻¹): 1856 (v_{NN}). ³¹P{¹H} NMR (*d*₈-THF, 200 K, 202 MHz) δ : 12.2 (br s). [(NP₃^{Ph})Co{ μ -N₂}K(18-crown-6)] (2-K(18C6)): To a mixture of complex 2-K ([(NP₃^{Ph})Co{ μ -N₂}K(THF)_x]) generated by the above procedure, was added 18-crown-6 (1.5 eq), and the mixture was stirred for 2 h at room temperature. An aliquot of the solution was characterised by IR spectroscopy, indicating the conversion of 2-K to 2-K(18C6). The solution was dried *in vacuo*, and redissolved in *d*₈-THF for NMR characterisation. IR (solution, THF, cm⁻¹): 1932 (v_{NN}). ³¹P{¹H} NMR (*d*₈-THF, 200 K, 202 MHz) δ: 4.8 (s).

[$(MeCP_3^{Ph})Co\{\mu-N_2\}K(THF)_x$] (5-K): To a flask charged with 5, [$((MeCP_3^{Ph})Co(\mu-N_2)\}_2Mg(THF)_4$] (20 mg, 0.012 mmol) and KC₈ (4 mg, 0.030 mmol, 2.5 eq) was added THF (2 mL). The mixture was stirred for 1 d at room temperature, before an aliquot of the solution was taken for IR spectroscopy, confirming the conversion of 5 to 5-K. The solution was dried *in vacuo*, and redissolved in *d*₈-THF for NMR characterisation. IR (solution cell, THF, cm⁻¹): 1850 (v_{NN}). ³¹P{¹H} NMR (*d*₈-THF, 200 K, 202 MHz) δ : 30.2 (s).

[MeCP₃^{Ph})Co{μ-N₂}K(18-crown-6)] (5-K(18C6)): To a mixture of complex 5-K ([(MeP₃^{Ph})Co{μ-N₂}K(THF)_x]) generated by the above procedure, was added 18-crown-6 (1.5 eq), and the mixture was stirred for 2 h at room temperature. An aliquot of the solution was taken for IR spectroscopic characterisation, confirming the conversion of 5-K to 5-K(18C6). The solution was dried *in vacuo*, and redissolved in *d*₈-THF for NMR characterisation. IR (solution cell, THF, cm⁻¹): 1922 (v_{NN}). ³¹P{¹H} NMR (*d*₈-THF, 200 K, 202 MHz) δ: 22.3 (s).

[(NP₃^{Ph})Co(NNSiMe₃)] (6): To a solution of [{(NP₃^{Ph})Co(μ -N₂)}₂Mg(THF)₄] (2) (20 mg, 0.012 mmol) in THF was added Me₃SiCl (4 μ L, 0.030 mmol, 2.5 eq). The resulting brown solution was stirred for 1 h at room temperature before an aliquot was taken for IR spectroscopic characterisation, indicating the formation of **6**. The solution was dried *in vacuo*, and redissolved in *d*₈-THF for NMR characterisation. IR (solution cell, THF, 298 K, cm⁻¹): 1678 (v_{N=N}). ¹H NMR (*d*₈-THF, 298 K, 400 MHz) δ : 7.34 (m, 12H, phenyl), 6.96 - 6.86 (m, 18H, phenyl), 3.68 (s, 6H, C*H*₂), 0.28 (s, 9H, -Si*Me*₃). ²⁹Si NMR (*d*₈-THF, 79 MHz, 298 K) δ : -7.6 (s).

[(NP₃^{Ph})Co(¹⁵N¹⁵NSiMe₃)] (6-¹⁵N): To a solution of [{(NP₃^{Ph})Co(μ -¹⁵N₂)}₂Mg(THF)₄] (2-¹⁵N) (generated *in situ via* above method, ~0.010 mmol) in THF was added Me₃SiCl (4 μ L, 0.030 mmol, 3 eq) under an Ar atmosphere. The resulting brown solution was stirred for 1 h at room temperature before an aliquot was taken for IR spectroscopic characterisation, indicating the formation of 6-¹⁵N. IR (solution cell, THF, 298 K, cm⁻¹): 1622 (v_{15N=15N}).

brown solution was stirred for 1 h at room temperature before an aliquot was taken for IR spectroscopic characterisation, indicating the formation of **7**. IR (solution cell, THF, cm⁻¹): 1672 ($v_{N=N}$).

IR Spectra



Fig. S1. Solution IR spectrum (THF) of complex 5

Table S1. IR stretching frequencies of triphos N₂ complexes with various stabilising metal interactions, compared to parent Mg system (**2** or **5**) (+ve Δv_{NN} = stronger and less-activated N₂ stretch).

	Complex	∨ № (ст ⁻¹)	Δv _{NN} from Mg (cm ⁻¹)
N-triphos	2	1878	n/a
	2-Li	1885	+ 8
	2-Na	1904	+ 26
	2-K	1856	- 22
	2-K(18C6)	1932	+ 54
C-triphos	5	1872	n/a
	5-K	1850	-22
	5-K(18C6)	1922	+ 50



Fig. S2: Solution IR spectra (THF) of alkali metal exchanges, from 2 to form 2-M.



Fig. S3: Solution IR spectra (THF) of alkali metal exchange, from 5 to form 5-K and 5-K(18C6).

NMR spectra:



Fig. S4: ¹H NMR spectrum of 2 (C_6D_6 , 400 MHz, 298 K). *hexane



Fig. S5: Variable temperature ${}^{31}P{}^{1}H$ NMR spectra of **2** (d_8 -THF, 202 MHz). *minor impurity signals.



Fig. S6: ¹⁵N{¹H} NMR spectrum recorded for preparation of **2-**¹⁵N (C₆D₆, 51 MHz, 298 K). Broad resonance at -12.1 ppm possibly corresponds to **2-**¹⁵N.



Fig. S7: ¹H NMR spectrum of 5 (C₆D₆, 400 MHz, 298 K).



Fig. S8: ${}^{31}P{}^{1}H$ NMR spectrum of 5 (C₆D₆, 162 MHz, 298 K).



Fig. S9: ¹H NMR spectra of **2-Li** (*d*₈-THF, 400 MHz, 298 K). Signals between 1.5 and 0.5 ppm relate to ⁿBuLi and hexane impurities.



Fig. S10: ³¹P{¹H} NMR spectra of **2-Li** (*d*₈-THF, 162 MHz, 200 K). *uncoordinated NP₃^{Ph}, **minor impurity.



Fig. S11: ¹H NMR spectra of **2-K** (*d*₈-THF, 400 MHz, 298 K). Starred signals (*) are tentatively assigned to **2-K**.



Fig. S12: ³¹P{¹H} NMR spectra of **2-K** (*d*₈-THF, 162 MHz, 200 K).



Fig. S13: ¹H NMR spectra of **2-K(18C6)** (*d*₈-THF, 400 MHz, 298 K).



Fig. S14: ³¹P{¹H} NMR spectra of **2-K(18C6)** (*d*₈-THF, 162 MHz, 200 K). *signal corresponds to unreacted **2-K**.



Fig. S15: ¹H NMR spectra of **5-K** (*d*₈-THF, 400 MHz, 298 K).



Fig. S16: ³¹P{¹H} NMR spectra of **5-K** (*d*₈-THF, 162 MHz, 200 K). *signal corresponds to unreacted **5**.



Fig. S17: ¹H NMR spectra of **5-K(18C6)** (*d*₈-THF, 400 MHz, 298 K).



Fig. S18: ³¹P{¹H} NMR spectra of **5-K(18C6)** (*d*₈-THF, 162 MHz, 200 K). *signal corresponds to unreacted **5-K**.



Fig. S19: ¹H NMR spectra of **6** (*d*₈-THF, 400 MHz, 298 K). *minor impurities, **excess SiMe₃Cl, ***THF solvent.



Fig. S20: 2D NMR spectrum (¹H/²⁹Si HMBC) of 6 (*d*₈-THF, 400/79 MHz, 298 K).

Crystallographic details:

Crystallographic data were collected using Agilent Xcalibur PX Ultra A (Cu radiation) and Agilent Xcalibur 3E (Mo radiation) diffractometers. The structures were refined using Olex 2, SHELXTL and SHELX-2013 program systems, with refinement against $F^{2,4,5}$

[CoCl(NP₃^{Ph})] (1):

Crystal data for **1**: $C_{39}H_{36}CICoNP_3$, M = 705.98, monoclinic, $P2_1/n$ (no. 14), a = 10.2110(4) Å, b = 20.2536(5) Å, c = 16.7695(5) Å, $\beta = 99.940(3)^\circ$, V = 3416.04(18) Å³, Z = 4, $D_c = 1.373$ g cm⁻³, μ (Mo-K α) = 0.750 mm⁻¹, T = 173 K, orange needles, Agilent Xcalibur 3E diffractometer; 12346 independent measured reflections ($R_{int} = 0.0231$), F² refinement,^[4,5] R_1 (obs) = 0.0423, wR_2 (all) = 0.1039, 6786 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full} = 50^\circ$], 406 parameters. CCDC 1897365.



Fig. S21. X-ray crystal structure with 50% thermal ellipsoids

$[{(NP_3^{Ph})Co(\mu-N_2)}_2Mg(THF)_4] (2):$

Crystal data for **2**: C₉₄H₁₀₄Co₂MgN₆O₄P₆, *M* = 1709.82, orthorhombic, Pna2₁ (no. 33), *a* = 35.2041(4) Å, *b* = 18.5349(2) Å, *c* = 13.28584(19) Å, *V* = 8669.08(18) Å³, *Z* = 4, *D*_c = 1.310 g cm⁻³, μ (Cu-K α) = 4.543 mm⁻¹, T = 173 K, dark red blocks, Agilent Xcalibur PX Ultra A diffractometer; 18064 independent measured reflections (*R_{int}* = 0.0390), F² refinement,^[4,5]*R*₁(obs) = 0.0455, *wR*₂(all) = 0.1235, 12435 independent observed absorptioncorrected reflections [|*F*_o| > 4 σ (|*F*_o|), 2 θ _{full} = 50°], 1099 parameters. CCDC 1897366.

The four included magnesium-coordinated thf solvent molecules in the structure of **2** were found to be disordered. Two orientations were identified for each thf solvent molecule of *ca*. 56 % and 44 % occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).



Fig. S22. X-ray crystal structure with 50% thermal ellipsoids

[{(NP₃^{Ph})Co}₂{µ-N₂}] (3):

Crystal data for **3**: $C_{78}H_{72}Co_2N_4P_6$, M = 1369.07, cubic, Pa-3 (no. 205), *a* = 18.92580(10) Å, V = 6778.95(11) Å³, Z = 4, $D_c = 1.341$ g cm⁻³, μ (Cu-K α) = 5.537 mm⁻¹, T = 173 K, dark red blocks, Agilent Xcalibur PX Ultra A diffractometer; 4814 independent measured reflections ($R_{int} = 0.0274$), F² refinement,^[4,5] R_1 (obs) = 0.0375, wR_2 (all) = 0.1002, 2193 independent observed absorption-corrected reflections [$|F_o| > 4\sigma$ ($|F_o|$), 2 $\theta_{full} = 50^{\circ}$], 136 parameters. CCDC 1897367.



Fig. S23. X-ray crystal structure with 50% thermal ellipsoids

[Co₂(NP₃^{Ph})₂] (4):

Crystal data for **4**: C₆₆H₆₂Co₂N₂P₆, 2(C₄H₈O), *M* = 1331.06, triclinic, P-1 (no. 2), *a* = 11.2875(8) Å, *b* = 11.4069(8) Å, *c* = 13.6863(8) Å, α = 66.762(6) °, β = 87.116(5) °, γ = 88.787(6) °, *V* = 1617.2(2) Å³, *Z* = 1, *D*_c = 1.367 g cm⁻³, μ (Mo-K α) = 0.710 mm⁻¹, T = 173 K, dark red blocks, Agilent Xcalibur 3E diffractometer; 9470 independent measured reflections (*R_{int}* = 0.0383), F² refinement,^[4,5] *R*₁(obs) = 0.0534, *wR*₂(all) = 0.1445, 6404 independent observed absorption-corrected reflections [|*F*_o| > 4 σ (|*F*_o|), 2 θ _{full} = 50°], 409 parameters. CCDC 1897368. The included thf solvent molecule (one per asymmetric unit) in the structure of **4** was found to be disordered. Two orientations were identified of *ca.* 64 % and 36 % occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).



Fig. S24. X-ray crystal structure with 50% thermal ellipsoids

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