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Supplementary Information

Borylation, silylation and selenation of C-H bonds in metal sandwich compounds by applying a directing group strategy

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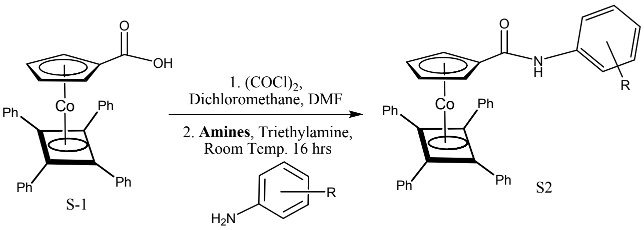
Contents

A. General information:

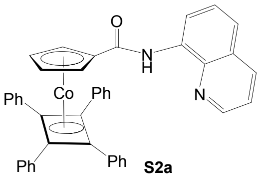
All reactions were carried out under pure nitrogen following Schlenck-line techniques. Solvents were dried under suitable drying agents such as toluene on sodium/ benzophenone, and CH_2Cl_2 on dry phosphorus pentoxide. All compounds were purified by column chromatography using silica-gel of 60-120 mesh. ^1H and ^{13}C {^1H} spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.4 MHz respectively. $CDCl_3$ was the solvent utilized for NMR studies unless otherwise specified. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Suitable crystals of the compounds were obtained by slow evaporation of their saturated solutions in suitable solvent mixtures and using diffusion method. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer and Bruker D8 Quest CMOS diffractometer with a Mo Kα (λ=0.71073 Å) sealed tube. The data frames were collected using the program APEX3 and processed using the program SAINT routine in APEX3. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL-2014/7 program.[1-3] All hydrogen atoms were included in idealized positions, and a riding model was used. Hydrogen atoms on hetero-atoms were located using Fourier map, except for **2b** and **9**. In these two cases we could not locate the H-atoms on hetero-atoms using Fourier map and had to affix them at their calculated positions using riding model following the common practice. Non-hydrogen atoms were refined with anisotropic displacement parameters. All reactions were standardized first on the cobalt sandwich derivative (η^5-Cp)Co(C_4Ph_4). Only fruitful reactions were extended to ferrocene derivatives.

B. General procedure for introducing different directing groups on the cobalt sandwich compound (η^5-Cp)Co(C_4Ph_4) with carboxamide linkers:



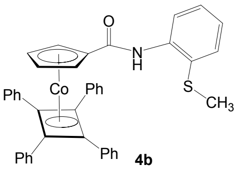
Scheme S1: Introduction of directing groups on cobalt sandwich compounds

{(η^5-C_5H_4)-COOH}Co(η^4-C_4Ph_4) 1g (1.9 mmol) was dissolved in dichloromethane. Oxalyl chloride (1.21g, 0.817mL, 9.53 mmol, 5 equiv) was added to it. 2 drops of *N,N*-dimethylformamide was added as catalyst. The reaction mixture was stirred for 1 hour at room temperature. The acid chloride formed was evaporated under reduced pressure under a nitrogen atmosphere. The acid chloride solution was added to a solution of amine along with triethylamine (10mL) and DCM, by solubilising it in DCM. This reaction mixture was stirred for 16 hours at room temperature. The product formed was washed with saturated $NaHCO_3$ solution followed by brine using a separatory funnel; the organic part was dried over anhydrous Na_2SO_4 and was purified by column chromatography using active neutral alumina.



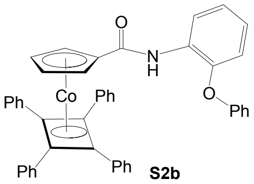
S2a

S2a: Prepared according to known literature procedure.**4** The characterization data exactly matches with the literature values.



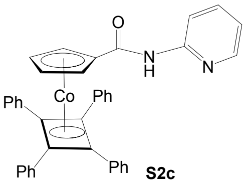
4b

4b: M.P.:201°-203°C, Yield (73%). Anal. Found: C, 76.15; H, 5.18; N, 2.11. Calcd for $C_{41}H_{32}CoNOS$: C, 76.26; H, 5.00; N, 2.17. ^{1}HNMR ($CDCl_3$): δ 8.33 [1H, s, N-*H*], δ 8.14-8.12 [1H, d, Ph-*H*], δ 7.45-7.41 [10H, m, Ph-*H*], δ 7.35-7.13 [12H, m, Ph-*H*], δ 6.99-6.95 [1H, d, Ph-*H*], δ 5.21 [2H, Cp*H*], δ 4.82 [2H, Cp*H*], δ 2.20 [3H, SC*H*3]. ^{13}C{1H}($CDCl_3$): δ 162.80 (*C*=O), δ 138.99-119.86 (Ph*C*), 91.11-82.54 (Cp*C*), 76.62 (Cb*C*), 19.25 (S*C*H3). HRMS: Calc. m/z for $C_{41}H_{33}CoNOS$ $[M+H]^+$ 646.1609; Found: 646.1608.



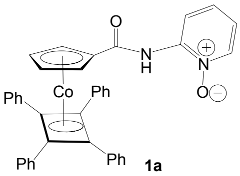
S2b

S2b: M.P.:177˚-181˚C, Yield (78%). Anal. Found: C, 79.75; H, 5.02; N, 2.07. Calcd for $C_{46}H_{34}CoNO_2$: C, 79.87; H, 4.95; N, 2.02. ^{1}HNMR ($CDCl_3$): δ 8.23 [1H, s, N-*H*], δ 7.58-7.27 [12H, m, Ph-*H*], δ 7.17-7.01 [13H, m, Ph-*H*], δ 6.98-6.79 [5H, m, Ph-*H*], δ 5.05 [2H, Cp*H*], δ 4.80 [2H, Cp*H*]. ^{13}C{1H}($CDCl_3$): δ 162.75 (*C*=O), δ 144.87-117.36 (Ph*C*), 85.87-82.66 (Cp*C*), 76.50 (Cb*C*). HRMS: Calc. m/z for $C_{46}H_{34}CoNNaO_2$ $[M+Na]^+$ 714.1813; Found: 714.1814



S2c

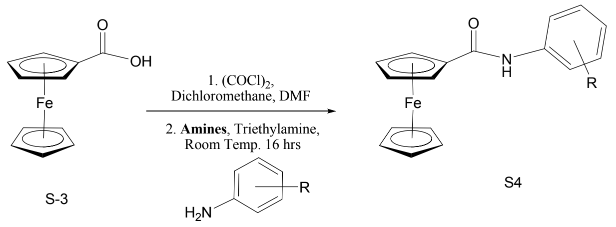
S2c: M.P.: Decomp. above 155˚C, Yield (65%). Anal. Found: C, 78.10; H, 4.82; N, 4.60. Calcd for $C_{39}H_{29}CoN_2O$: C, 77.99; H, 4.87; N, 4.66. ^{1}HNMR ($CDCl_3$): δ 8.21-8.19 [1H, s, N-*H*], δ 7.93-7.90 [1H, m, Ph-*H*], δ 7.61 [1H, m, Ph-*H*], δ 7.48-7.41 [8H, m, Ph-*H*], δ 7.25-6.98 [14H, m, Ph-*H*], δ 5.25 [2H, Cp*H*], δ 4.87 [2H, Cp*H*]. ^{13}C{1H}($CDCl_3$): δ 162.59 (*C*=O), δ 151.46-113.96 (Ph*C*), 89.83-82.67 (Cp*C*), 76.64 (Cb*C*). HRMS: Calc. m/z for $C_{39}H_{30}CoN_2O$ $[M+H]^+$ 601.1684; Found: 601.1671



1a

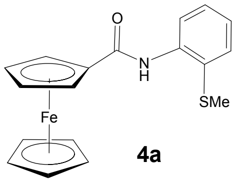
1a: M.P.: Above 220˚C, Yield (75%). Anal. Found: C, 75.90; H, 4.78; N, 4.57. Calcd for $C_{39}H_{29}CoN_2O_2$: C, 75.97; H, 4.74; N, 4.54. ^{1}HNMR ($CDCl_3$): δ 9.85 [1H, s, N-*H*], δ 8.19-8.16 [1H, dd, Ph-*H*], δ 8.06-8.02 [1H, m, Ph-*H*], δ 7.52-7.42 [8H, m, Ph-*H*], δ 7.52-7.42 [8H, m, Ph-*H*], δ 7.25-7.11 [13H, m, Ph-*H*], δ 5.30-5.29 [2H, Cp*H*], δ 4.91-4.90 [2H, Cp*H*]. ^{13}C{1H}($CDCl_3$): δ 163.22 (*C*=O), δ 144.18-114.59 (Ph*C*), 89.06, 86.84, 83.09 (Cp*C*), 76.61 (Cb*C*), 19.25 (S*C*H_3). HRMS: Calc. m/z for $C_{39}H_{29}CoN_2NaO_2$ $[M+Na]^+$ 639.1453; Found: 639.1473.

C. General procedure for introducing different directing groups on ferrocene with carboxamide linkers:



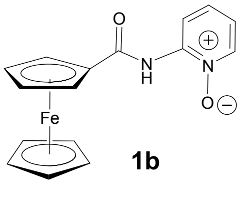
Scheme S2: Introduction of directing groups on ferrocene.

[{(η^5-C_5H_4)-COOH}Fe(C_5H_5)] 1g (4.34 mmol) was dissolved in dichloromethane, Oxalyl chloride 1.65g , 1.19 mL (13.04 mmol, 3 equiv) was added to it. 2 drops of *N,N*-dimethylformamide was added as catalyst. The reaction mixture was stirred for 1 hour at room temperature. The acid chloride formed was evaporated under reduced pressure under nitrogen atmosphere. The acid chloride solution was added to a solution of amine with triethylamine 10mL and DCM, by solubilising it in DCM. This reaction mixture was stirred for 16 hours at room temperature. The product formed was washed with saturated $NaHCO_3$ solution followed by brine using a separatory funnel and the organics were dried over anhydrous Na_2SO_4 and was purified by column chromatography using active neutral alumina.



4a

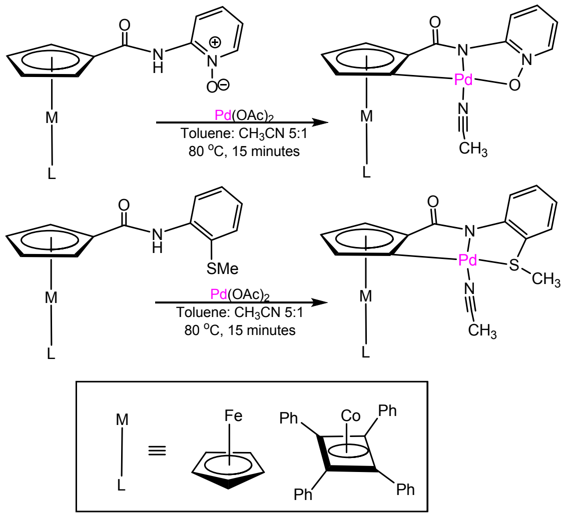
4a: M.P.: Decomp. at 132°C, Yield (71%). Anal. Found: C, 62.70; H, 4.78; N, 3.93. Calcd for $C_{39}H_{29}CoN_2O$: C, 61.55; H, 4.88; N, 3.99. ^{1}HNMR ($CDCl_3$): δ 8.81 [1H, s, N-*H*], δ 8.48-8.46 [1H, d, Ph-*H*], δ 7.56-7.53 [1H, m, Ph-*H*], δ 7.35 [1H, m, Ph-*H*], δ 7.10-7.09 [1H, m, Ph-*H*], δ 4.85 [2H, Cp*H*], δ 4.46 [2H, Cp*H*], δ 4.29-4.23 [5H, Cp*H*], δ 2.48 [3H, SC*H*$_3$]. ^{13}C{1H}($CDCl_3$): δ 168.75 (*C*=O), δ 139.27-114.05 (Ph*C*), 71.01-68.34 (Cp*C*)*,* 19.14 (S*C*H$_3$). HRMS: Calc. m/z for $C_{18}H_{18}FeNOS$ $[M+H]^+$ 352.0453; Found: 352.0452.



1b

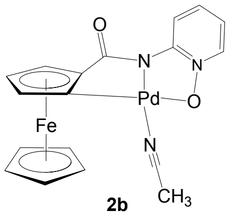
1b: M. P. 164°-167°C. Yield (72%). Anal. Found: C, 59.81; H, 4.30; N, 8.78. Calcd for $C_{16}H_{14}FeN_2O_2$: C, 59.65; H, 4.38; N, 8.70. ^{1}HNMR ($CDCl_3$): δ 10.38 [1H, s, N-*H*], δ 8.49-8.46 [1H, d, Ph-*H*], δ 8.27-8.25 [1H, dd, Ph-*H*], δ 7.37-7.24 [1H, dd, Ph-*H*], δ 6.99-6.95 [1H, d, Ph-*H*], δ 4.89 [2H, Cp of Fc], δ 4.49 [2H, Cp of Fc], δ 4.26 [5H, Cp of Fc]. ^{13}C{1H}($CDCl_3$): δ 169.59 (*C*=O), δ 144.43-114.48 (Ph*C*), 71.80-68.84 Cp*C*. HRMS: Calc. m/z for $C_{16}H_{14}FeN_2NaO_2$ $[M+Na]^+$ 345.0295; Found: 345.0296.

D. General procedures for the formation of Palladacycles:



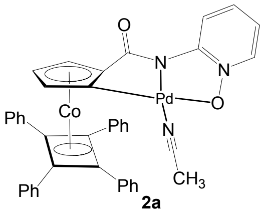
Scheme S3: Synthesis of palladacycles **2a**, **2b** and **5b**

Metal sandwich carboxamides were dissolved in toluene (1.5 mL) in a 5 mL reaction vial charged with a magnetic stir bar. $Pd(OAc)_2$ (1 equiv) was added to it and stirred at 80 ˚C for 5 to 10 minutes. A gradual colour change from deep red to dark brown was observed. The co solvent acetonitrile (0.3 mL) was added then and a colour change to deep red occurred instantly. The reaction was allowed to stir for further 10 minutes. The reaction mixture was cooled. It was directly put in the refrigerator resulting in the crystallization of the product.



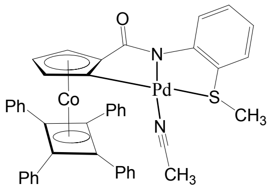
2b

2b: Yield (80%). Anal. Found: C, 45.98; H, 3.41; N, 9.06. Calcd for $C_{18}H_{15}FeN_3O_2Pd$: C, 46.23; H, 3.23; N, 8.99. ^{1}HNMR ($CDCl_3$): δ 8.78-8.72 [1H, d, Ph-*H*], δ 7.93-7.90 [1H, d, Ph-*H*], δ 7.22-7.18 [1H, dd, Ph-*H*], δ 6.71-6.66 [1H, dd, Ph-*H*], δ 4.71-4.64 [1H, Cp of Fc], δ 4.43-4.30 [7H, Cp of Fc], δ 2.36 [3H, s, C*H*$_3$ of acetonitrile]. ^{13}C{1H}($CDCl_3$): δ 181.29 (*C*=O), δ 152.91 (*C*N),δ 136.95-114.45 (Ph*C*), 71.91-67.05 Cp*C*, 3.51 [*C*H3 of AN]. HRMS: Calc. m/z for $C_{17}H_{16}FeNO_3Pd$ [M (-CH_3CN)+CH_3OH (in CH_3OH solvent)]$^+$ 443.9518; found: 443.9415.



2a

2a: Yield (92%). Anal. Found: C, 64.55; H, 3.93; N, 5.60. Calcd for $C_{41}H_{30}CoPdN_3O_2$: C, 64.62; H, 3.97; N, 5.51. ^{1}HNMR ($CDCl_3$): δ 8.33-8.30 [1H, d, Ph-*H*], δ 7.83-7.80 [1H, d, Ph-*H*], δ 7.64-7.62 [8H, m, Ph-*H*], δ 7.23-7.02 [13H, m, Ph-*H*], δ 6.60 [1H, m, Ph-*H*], δ 4.94-4.93 [1H, Cp*H*], δ 4.64 [1H, Cp*H*], δ 4.40-4.39 [1H, Cp*H*], δ 2.15 [3H, s, C*H*$_3$ of acetonitrile]. ^{13}C{1H}($CDCl_3$): δ 174.67 (*C*=O), 152.75 (*C*N), 137.88-114.13 (Ph*C*), 98.58, 92.56, 85.97, 84.77, 83.04 (Cp*C*), 75.59 (Cb*C*), 3.51 (*C*H$_3$ of acetonitrile). HRMS: Calc. m/z for $C_{39}H_{28}N_2CoO_2Pd$ $[M(-CH_3CN)+H]^+$ 721.0526; found: 721.0541

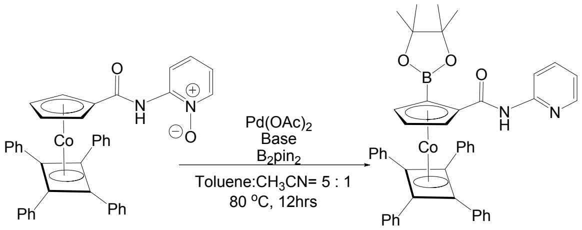


5b

5b: Yield (81%) ^{1}HNMR ($CDCl_3$): Repeated attempts for obtaining ^{1}H & ^{13}C NMR was unsuccessful for **5b** due to decomposition of the palladacycle in various dry deuterated solvents. HRMS: Calc. m/z for $C_{41}H_{30}CoNOSPd$ $[M(-CH_3CN)+H]^+$ 750.0502; found: 750.0496.

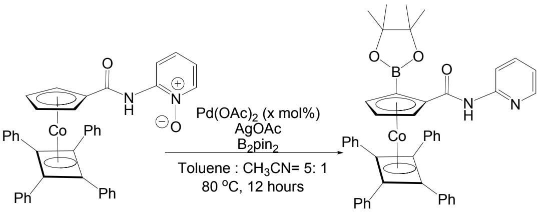
E. Optimization of standard conditions for C-H borylation:

Table S1: Optimization of Base:



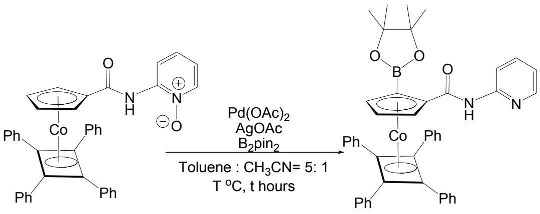
Sr No	Base Used	Yield (%)
1	NaOAc	nil
2	K_2CO_3	nil
3	Li_2CO_3	nil
4	Na_2CO_3	nil
5	$NaHCO_3$	nil
6	Ag_2CO_3	10
7	Cs_2CO_3	nil
8	AgOAc	43
9	-	5

Table S2: Optimization of Pd-catalyst loading:



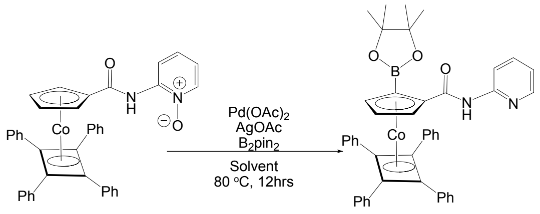
Sr No	Catalyst loading (mol%)	Yield	TON
1	20	43	2.15
2	15	40	2.66
3	10	37	3.7
4	5	32	6.4
5	2	trace	-

Table S3: Optimization of temperature & time:



Sr. No.	Temperature (˚C)	Time (hours)	Yield (%)
1	100	12	18
2	80	12	43
3	80	24	40
4	70	12	35
5	70	24	33
5	60	12	8

Table S4: Optimization of solvent & co-solvent:

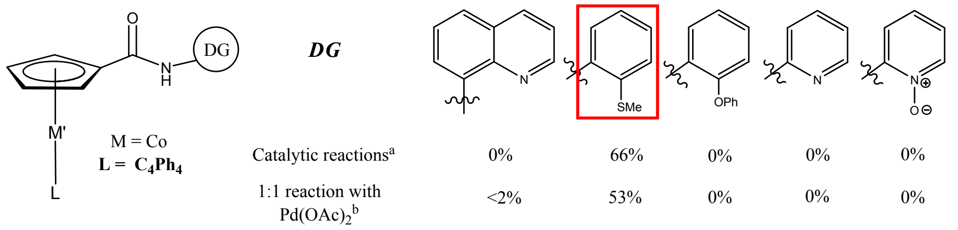


Sr No	Solvent (1.5 mL)	Co-solvent (0.3 mL)	Yield (%)
1	DMF	Nil	nil
2	THF	Nil	nil
3	Xylene	Nil	nil
4	Xylene	CH_3CN	<5
5	DMSO	Nil	nil
6	tBuOH	Nil	nil
7	t-amyl alcohol	Nil	nil
8	DCE	Nil	nil
9	Toluene	Nil	10
10	Toluene	CH_3CN	43

Table S5: Borylating agent and its equivalents:

Sr. No.	Borylation reagent	No. of equivalents	Yield (%)
1	H-Bpin	0.5	nil
2	H-Bpin	1	nil
3	H-Bpin	2	nil
4	B_2pin_2	0.5	5
5	B_2pin_2	1	20
6	B_2pin_2	2	43
7	B_2pin_2	4	41
8	B_2pin_2	8	38
9	B_2pin_2	16	40

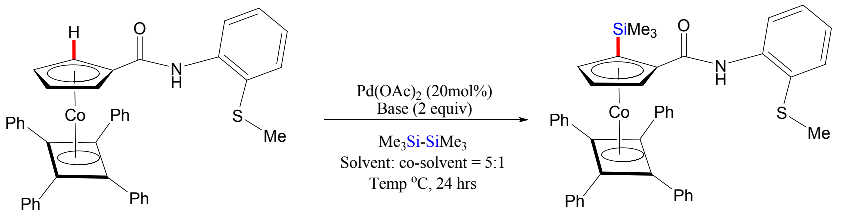
C-H silylation studies



Screening of directing groups for C-H silylation

Conditions: **a**. $Pd(OAc)_2$ (20mol%), AgOAc (2equiv), $Me_3Si\text{-}SiMe_3$ (2 equiv), in Toluene (1.5mL), acetonitrile (0.3 mL) as co-solvent. **b**. $Pd(OAc)_2$ (1 equiv), $Me_3Si\text{-}SiMe_3$ (2 equiv), in Toluene (1.5mL), acetonitrile (0.3 mL) as co-solvent.

Scheme S4: Determination of suitable directing groups for C-H silylation.



Scheme S5: C-H silylation reaction.

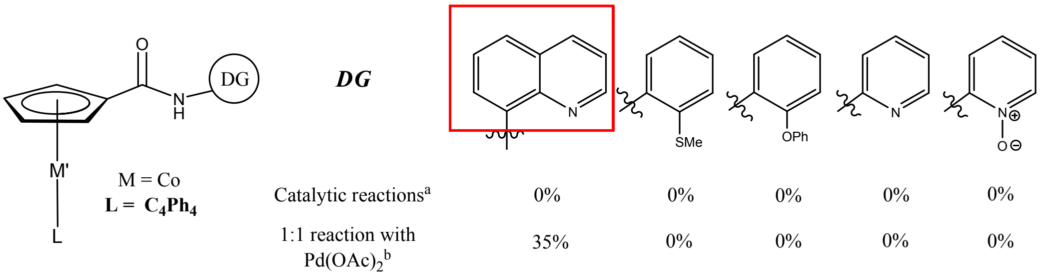
Table S6: Optimization of the catalytic silylation reaction conditions:

Entry No	Base	Solvent	co-solvent	Temp(˚C)	Yield[a] (%)
1	Li_2CO_3	Toluene	-	80	nil
2	Na_2CO_3	Toluene	-	80	nil
3	$NaHCO_3$	Toluene	-	80	nil
4	Ag_2CO_3	Toluene	-	80	nil
5	Cs_2CO_3	Toluene	-	80	nil
6	NaOAc	Toluene	-	80	nil
7	AgOAc	Toluene	-	80	16
8	AgOAc	1,4 dioxane	-	80	nil
9	AgOAc	tBuOH	-	80	nil
10	AgOAc	DMF	-	80	5
11	AgOAc	DMSO	-	130	nil
12	AgOAc	THF	-	67	nil
13	AgOAc	Toluene	CH_3CN	100	35
14	**AgOAc**	**Toluene**	$\mathbf{CH_3CN}$	**80**	**66**
15	-	Toluene	CH_3CN	80	18
16	AgOAc	Toluene	CH_3CN	80	51[b]

[a]Isolated yields, [b]5mol% $Pd(OAc)_2$ was used.

C-H selenation Studies

Sceening of the directing group



Catalytic reactions[a]	0%	0%	0%	0%	0%
1:1 reaction with $Pd(OAc)_2$[b]	35%	0%	0%	0%	0%

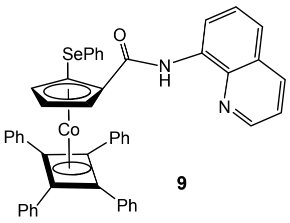
Screening of directing groups for C-H selenation

Conditions: **a**. $Pd(OAc)_2$ (20mol%), AgOAc (2equiv), PhSe-SePh (2 equiv), in Toluene (1.5mL), acetonitrile (0.3 mL) as co-solvent. **b**. $Pd(OAc)_2$ (1 equiv), PhSe-SePh (2 equiv), in DCE (2mL).

Scheme S6: Determination of suitable directing groups for C-H selenation.

F. Synthesis of the alpha mono C-H Selenated cobalt sandwich compound (9):

A 5 mL catalytic vial was charged with a magnetic stir bar. Palladacycle of 8-aminoquinoline based cobalt sandwich carboxamide **8** was treated with diphenyldiselenide at 80 °C in dichloroethane. The reaction mixture was allowed to stir for 24 hrs. Then it was cooled to room temperature and was purified by column chromatography using silica gel using hexane: ethylacetate (9: 1) as eluent.

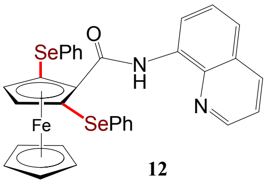


9

9: Yellow solid. MP: decomp. above 155˚-157˚C. Yield (35%). Anal. Found: C, 73.21; H, 4.44; N, 3.29. Calcd for $C_{49}H_{35}N_2OCoSe$: C, 73.04; H, 4.38; N, 3.48. ^{1}HNMR ($CDCl_3$): δ 10.72 [1H, s, N-*H*], δ 8.65 [1H, d, Ph-*H*], δ 8.42 [1H, d, Ph-*H*], δ 8.11-8.09 [1H, d, Ph-*H*], δ 7.60-7.44 [12H, m, Ph-*H*], δ 7.19-7.07 [15H, m, Ph-*H*], δ 5.57 [1H, Cp*H*], δ 4.92-4.90 [2H, s, Cp*H*]. ^{13}C{1H}($CDCl_3$): δ 163.51 (*C*=O), δ 147.95-117.86 (Ph*C*), 90.86-85.24 (Cp*C*), 77.83 (Cb*C*). HRMS: Calc. m/z for $C_{49}H_{35}N_2OCoSeNa$ $[M+Na]^+$ 829.1144; found: 829.1113

G. Synthesis of the alpha, alpha bis C-H selenated ferrocene derivative (12)*:*

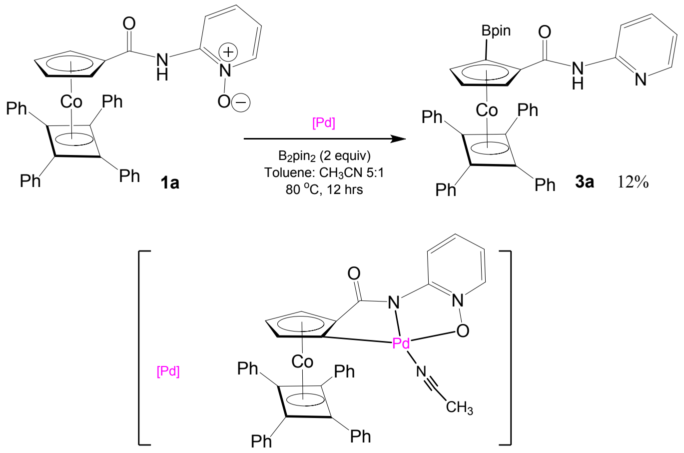
A 5 mL reaction vial was charged with a magnetic stir bar. Palladacycle of 8-aminoquinoline based ferrocene carboxamide **11** (50 mg, 0.099 mmol) was treated with diphenyldiselenide (30.9 mg, 0.099 mmol) at 80 °C in dichloroethane (2 mL). The reaction mixture was allowed to stir for 24 hrs. Then it was cooled to room temperature and was purified by column chromatography using silica gel using hexane: ethylacetate (9: 1) as eluent.



12

12: Yellow solid. MP: decomp. above 133˚C. Yield (60%). Anal. Found: C, 58.06; H, 3.43; N, 4.11. Calcd for $C_{32}H_{24}FeN_2OSe_2$: C, 57.68; H, 3.63; N, 4.20. ^{1}HNMR ($CDCl_3$): δ 11.57 [1H, s, N-*H*], δ 8.95-8.93 [1H, Ph-*H*], δ 8.73 [1H, Ph-*H*], δ 8.16-8.14 [1H, Ph-*H*], δ 7.59-7.51 [6H, m, Ph-*H*], δ 7.44-7.19 [7H, m, Ph-*H*], δ 4.41-4.36 [2H, Cp*H*], δ 4.36-4.30 [5H, s, Cp*H*]. ^{13}C{1H}($CDCl_3$): δ 168.78 (*C*=O), δ 148.04-117.61 (Ph*C*), 76.58, 76.17, 73.18 (Cp*C*).

Catalytic activity of palladacycles:



A catalytic reaction vial was charged with a magnetic stir bar. Ligand **1a** (50 mg, 0.08mmol), palladacycle **2a** (6.1 mg, 0.008 mmol), AgOAc (26.7 mg, 0.16 mmol) and B_2pin_2 (40.6 mg, 0.016 mmol) were added to it. The mixture was dissolved in 5:1 mixture of toluene and acetonitrile. The reaction mixture was stirred for 12 hours at 80 ^{o}C. The progress of the reaction was checked using TLC. The reaction mixture was cooled to room temperature. It was purified by column chromatography using silica gel 60-120 mesh using hexane : ethyl acetate (13 : 7) as eluent. Yield of **3a** 12%.

H. Table-S7: X-ray crystallographic data for compounds 1a, 1b, 2a:[5]

Identification code	**1a**	**1b**	**2a**
Empirical formula	C39 H29 Co N2 O2	C16 H14 Fe N2 O2	C41 H30 Co N3 O2 Pd
Formula weight	616.57	322.14	762.01
Temperature	273(2) K	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 21/c	P n a 21	P 21/n
Unit cell dimensions	a = 12.92(4) Å b = 14.34(4) Å c = 17.16(6) Å α= 90°. β= 93.61(3)° γ = 90°.	a = 13.66(3) Å b = 19.02(4) Å c = 10.88(2) Å α= 90°. β= 90°. γ = 90°.	a = 11.024(11) Å b = 20.65(2) Å c = 14.762(11) Å α= 90°. β= 97.10(3)°. γ = 90°.
Volume	3173(17) Å^3	2825(9) Å^3	3334(6) Å^3
Z	4	8	4
Density (calculated)	1.291 Mg/m^3	1.515 Mg/m^3	1.518 Mg/m^3
Absorption coefficient	0.577 mm^{-1}	1.072 mm^{-1}	1.078 mm^{-1}
F(000)	1280	1328	1544
Crystal size	0.324 x 0.251 x 0.146 mm^3	0.354 x 0.251 x 0.164 mm^3	0.345 x 0.255 x 0.165 mm^3
Theta range for data collection	1.579 to 28.316°.	1.836 to 28.298°.	2.107 to 28.283°.
Index ranges	-12<=h<=12, -19<=k<=18, -22<=l<=18	-12<=h<=18, -25<=k<=24, -13<=l<=14	-13<=h<=14, -8<=k<=27, -19<=l<=19
Reflections collected	17820	17776	16351
Independent reflections	6419 [R(int) = 0.0701]	6214 [R(int) = 0.0659]	7700 [R(int) = 0.0939]
Completeness to theta	98.0 % (theta max=28.316°)	100.0 % (theta_max=28.298°)	99.8 %(theta_max=28.283°)
Max. and min. transmission	0.945 and 0.816	0.853 and 0.713	0.849 and 0.711
Data / restraints / parameters	6419 / 0 / 401	6214 / 1 / 387	7700 / 0 / 434
Goodness-of-fit on F^2	0.882	0.921	0.724
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0849	R1 = 0.0445, wR2 = 0.0822	R1 = 0.0498, wR2 = 0.0634
R indices (all data)	R1 = 0.0754, wR2 = 0.0924	R1 = 0.0653, wR2 = 0.0898	R1 = 0.1168, wR2 = 0.0749
Largest diff. peak and hole	0.310 and -0.472 e.Å^{-3}	0.382 and -0.295 e.Å^{-3}	0.577 and -0.704 e.Å^{-3}

$R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\ (|F_o|^2 - |F_c|^2)^2]\}^{½}$

H. Table-S8: X-ray crystallographic data for compounds 2b, 3a, 4a:[5]

Identification code	**2b**	**3a**	**4a**
Empirical formula	C36 H32 Fe2 N6 O5 Pd2	C45 H40 B Co N2 O3	C18 H17 Fe N O S
Formula weight	953.18	726.53	351.23
Temperature	293(2) K	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P -1	P -1	P 21 21 21
Unit cell dimensions	a = 10.80(3) Å b = 11.71(3) Å c = 15.37(4) Å α= 95.62(4)°. β= 101.53(4)°. γ = 103.73(4)°.	a = 11.64(5) Å b = 13.37(5) Å c = 13.68(6) Å α= 65.93(10)°. β= 78.53(7)°. γ = 77.94(7)°.	a = 9.91(3) Å b = 12.38(3) Å c = 14.01(4) Å α= 90°. β= 90°. γ = 90°.
Volume	1828(9) Å^3	1886(14) Å^3	1719(8) Å^3
Z	2	2	4
Density (calculated)	1.731 Mg/m^3	1.279 Mg/m^3	1.357 Mg/m^3
Absorption coefficient	1.795 mm^{-1}	0.498 mm^{-1}	0.999 mm^{-1}
F(000)	948	760	728
Crystal size	0.365 x 0.245 x 0.115 mm^3	0.364 x 0.286 x 0.199 mm^3	0.398 x 0.287 x 0.176 mm^3
Theta range for data collection	1.368 to 28.303°.	1.851 to 28.231°.	2.195 to 28.121°.
Index ranges	-14<=h<=14, -15<=k<=12, -19<=l<=16	-12<=h<=15, -17<=k<=17, -18<=l<=14	-9<=h<=11, -3<=k<=16, -10<=l<=18
Reflections collected	11198	11692	3606
Independent reflections	8081 [R(int) = 0.1188]	8470 [R(int) = 0.0585]	2951 [R(int) = 0.0390]
Completeness to theta	98.6 %(theta_max=28.303°)	98.2 %(theta_max=28.231°)	98.0 %(theta_max=28.121°)
Max. and min. transmission	0.831 and 0.569	0.921 and 0.823	0.858 and 0.699
Data / restraints / parameters	8081 / 0 / 465	8470 / 0 / 477	2951 / 1 / 205
Goodness-of-fit on F^2	0.931	0.832	0.864
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1147	R1 = 0.0529, wR2 = 0.0901	R1 = 0.0377, wR2 = 0.0643
R indices (all data)	R1 = 0.0816, wR2 = 0.1340	R1 = 0.0960, wR2 = 0.1025	R1 = 0.0533, wR2 = 0.0687
Largest diff. peak and hole	1.113 and -1.391 e.Å^{-3}	0.384 and -0.398 e.Å^{-3}	0.372 and -0.274 e.Å^{-3}

$R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\ (|F_o|^2 - |F_c|^2)^2]\}^{1/2}$

H. Table-S9: X-ray crystallographic data for compounds 4b, 5b, 6b:[5]

Identification code	**4b**	**5b**	**6b**
Empirical formula	C41 H32 Co N O S	C46 H39 Cl2 Co N2 O3 Pd S	C48 H44 B Cl3 Co N O3 S
Formula weight	645.66	936.08	890.99
Temperature	304(2) K	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 21/c	P -1	P -1
Unit cell dimensions	a = 11.255(6) Å b = 22.409(10) Å c = 12.599(6) Å α= 90°. β= 90.186(16)°. γ = 90°.	a = 11.285(19) Å b = 13.21(2) Å c = 15.82(3) Å α= 98.50(2)°. β= 97.19(4)°. γ = 107.13(3)°.	a = 10.257(2) Å b = 11.746(2) Å c = 18.873(4) Å α= 96.25(3)°. β= 92.91(3)°. γ = 94.13(3)°.
Volume	3178(3) Å^3	2192(6) Å^3	2250.4(8) Å^3
Z	4	2	2
Density (calculated)	1.350 Mg/m^3	1.418 Mg/m^3	1.315 Mg/m^3
Absorption coefficient	0.640 mm^{-1}	0.999 mm^{-1}	0.647 mm^{-1}
F(000)	1344	952	924
Crystal size	0.388 x 0.298 x 0.211 mm^3	0.351 x 0.268 x 0.148 mm^3	0.355 x 0.275 x 0.195 mm^3
Theta range for data collection	2.565 to 26.433°.	1.645 to 24.534°.	2.162 to 28.466°.
Index ranges	-14<=h<=11, -28<=k<=28, -11<=l<=15	-12<=h<=12, -10<=k<=15, -17<=l<=18	-10<=h<=13, -15<=k<=15, -25<=l<=21
Reflections collected	13462	8928	14974
Independent reflections	6363 [R(int) = 0.0338]	6500 [R(int) = 0.0241]	10383 [R(int) = 0.1101]
Completeness to theta	98.9 %(theta_max=26.433°)	98.9 %(theta_max=24.534°)	98.7 %(theta_max=28.466°)
Max. and min. transmission	0.889 and 0.777	0.887 and 0.711	0.908 and 0.781
Data / restraints / parameters	6363 / 0 / 412	6500 / 0 / 509	10383 / 0 / 532
Goodness-of-fit on F^2	1.025	1.005	0.776
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1073	R1 = 0.0426, wR2 = 0.1035	R1 = 0.0626, wR2 = 0.1201
R indices (all data)	R1 = 0.0869, wR2 = 0.1237	R1 = 0.0566, wR2 = 0.1112	R1 = 0.1639, wR2 = 0.1506
Largest diff. peak and hole	0.224 and -0.388 e.Å^{-3}	0.595 and -0.439 e.Å^{-3}	0.420 and -0.422 e.Å^{-3}

$R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\ (|F_o|^2 - |F_c|^2)^2]\}^{½}$

H. Table-S10: X-ray crystallographic data for compounds 7, 9:[5]

Identification code	**7**	**9**
Empirical formula	C44 H40 Co N O S Si	C49 H35 Co N2 O Se
Formula weight	717.85	805.68
Temperature	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic
Space group	P -1	P 21 21 21
Unit cell dimensions	a = 13.00(3) Å b = 13.25(3) Å c = 23.77(5) Å α= 84.63(2)°. β= 86.64(2)°. γ = 72.88(3)°.	a = 10.27(2) Å b = 16.50(3) Å c = 23.24(5) Å α= 90°. β= 90°. γ = 90°.
Volume	3895(13) Å^3	3936(14) Å^3
Z	4	4
Density (calculated)	1.224 Mg/m^3	1.360 Mg/m^3
Absorption coefficient	0.558 mm^{-1}	1.400 mm^{-1}
F(000)	1504	1648
Crystal size	0.368 x 0.246 x 0.152 mm^3	0.388 x 0.278 x 0.196 mm^3
Theta range for data collection	1.767 to 24.999°.	1.514 to 27.910°.
Index ranges	-15<=h<=15, -7<=k<=15, -28<=l<=28	-12<=h<=12, -21<=k<=10, -30<=l<=30
Reflections collected	20295	20113
Independent reflections	13544 [R(int) = 0.0566]	8682 [R(int) = 0.1003]
Completeness to theta	98.6 %(theta_max=24.999°)	98.6 %(theta_max=27.910°)
Max. and min. transmission	0.934 and 0.832	0.779 and 0.615
Data / restraints / parameters	13544 / 0 / 899	8682 / 0 / 488
Goodness-of-fit on F^2	0.916	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.1212	R1 = 0.0940, wR2 = 0.1256
R indices (all data)	R1 = 0.0966, wR2 = 0.1339	R1 = 0.1529, wR2 = 0.1426
Largest diff. peak and hole	0.802 and -0.347 e.Å^{-3}	1.047 and -0.459 e.Å^{-3}

$R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\ (|F_o|^2 - |F_c|^2)^2]\}\ ^{1/2}$

I. Selected Bond-lengths and bond-angles:[5]

1a

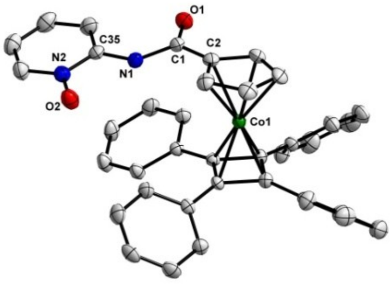


Table-S11 (1a)

Bond lengths (Å)	
O(1)-C(1)	1.243(4)
O(2)-N(2)	1.345(4)
N(1)-C(35)	1.397(4)
N(1)-C(1)	1.401(4)
C(1)-C(2)	1.499(4)
Bond Angles (deg)	
O(1)-C(1)-N(1)	122.9(2)
O(1)-C(1)-C(2)	123.6(3)
N(1)-C(1)-C(2)	113.5(3)
O(2)-N(2)-C(35)	118.9(2)
C(35)-N(1)-C(1)	128.5(3)

1b

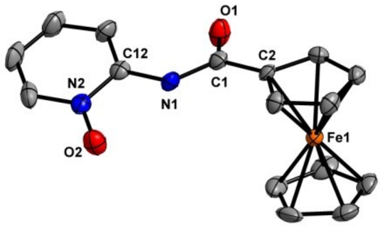


Table-S12 (1b)

Bond lengths (Å)	
O(1)-C(1)	1.213(6)
O(2)-N(2)	1.329(5)
N(1)-C(12)	1.380(6)
N(1)-C(1)	1.390(7)
C(1)-C(2)	1.491(7)
Bond Angles (deg)	
O(1)-C(1)-N(1)	123.6(5)
O(1)-C(1)-C(2)	123.5(5)
N(1)-C(1)-C(2)	112.9(4)
O(2)-N(2)-C(12)	118.2(4)
C(16)-N(2)-C(12)	120.1(4)

2a

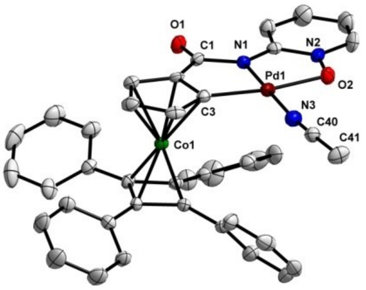


Table-S13 (2a)

Bond lengths (Å)	
Pd(1)-C(3)	1.960(4)
Pd(1)-N(1)	1.972(3)
Pd(1)-N(3)	2.005(4)
Pd(1)-O(2)	2.090(3)
O(2)-N(2)	1.357(4)
Bond Angles (deg)	
C(3)-Pd(1)-N(1)	83.06(16)
C(3)-Pd(1)-N(3)	97.94(16)
N(1)-Pd(1)-N(3)	178.75(15)
C(3)-Pd(1)-O(2)	163.58(14)
N(1)-Pd(1)-O(2)	80.55(13)

2b

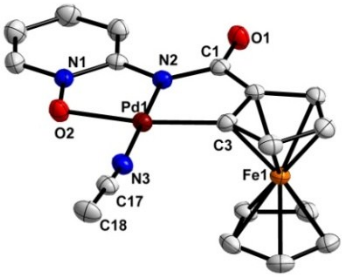


Table-S14 (2b)

Bond lengths (Å)	
Pd(1)-C(3)	2.006(6)
Pd(1)-N(1)	2.024(5)
Pd(1)-N(3)	2.055(6)
Pd(1)-O(2)	2.149(5)
O(2)-N(1)	1.373(6)
Bond Angles (deg)	
C(3)-Pd(1)-N(3)	96.7(3)
N(1)-Pd(1)-N(3)	179.46(16)
C(3)-Pd(1)-O(2)	162.99(17)
N(1)-Pd(1)-O(2)	79.9(3)
N(3)-Pd(1)-O(2)	100.3(3)

3a

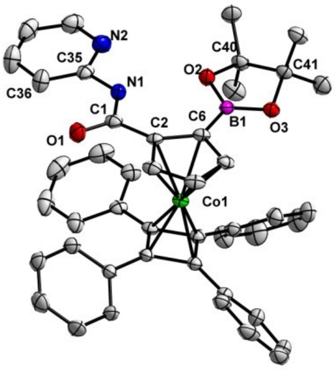


Table-S15 (3a)

Bond lengths (Å)

O(2)-B(1)	1.394(5)
O(3)-B(1)	1.374(7)
C(6)-B(1)	1.562(6)
N(1)-C(1)	1.377(5)
O(1)-C(1)	1.243(5)

Bond Angles (deg)

B(1)-O(2)-C(40)	106.9(3)
B(1)-O(3)-C(41)	106.8(2)
O(3)-B(1)-O(2)	113.6(3)
O(3)-B(1)-C(6)	123.3(3)
O(2)-B(1)-C(6)	123.0(4)

4a

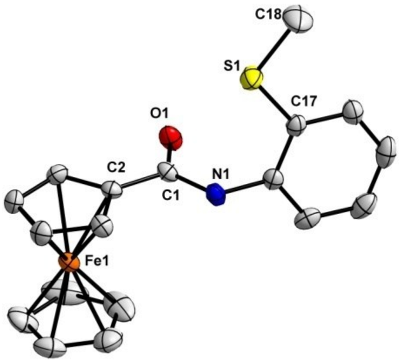


Table-S16 (4a)

Bond lengths (Å)

O(1)-C(1)	1.238(6)
N(1)-C(1)	1.391(7)
S(1)-C(17)	1.801(6)
S(1)-C(18)	1.808(7)
N(1)-C(12)	1.464(6)

Bond Angles (deg)

O(1)-C(1)-N(1)	122.5(5)
O(1)-C(1)-C(2)	122.6(5)
N(1)-C(1)-C(2)	114.9(5)
C(16)-C(17)-S(1)	123.7(4)
C(12)-C(17)-S(1)	117.2(3)

4b

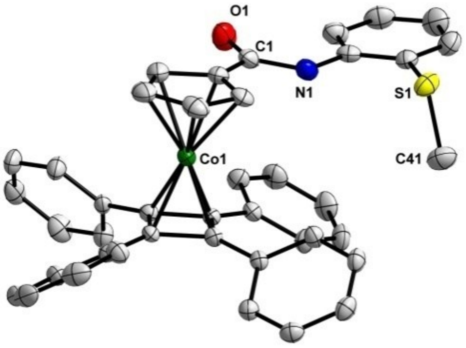


Table-S17 (4b)

Bond lengths (Å)

O(1)-C(1)	1.212(4)
N(1)-C(1)	1.367(4)
N(1)-C(35)	1.395(4)
S(1)-C(40)	1.767(4)
S(1)-C(41)	1.779(4)

Bond Angles (deg)

O(1)-C(1)-N(1)	123.4(3)
O(1)-C(1)-C(2)	121.6(3)
N(1)-C(1)-C(2)	115.0(3)
C(39)-C(40)-S(1)	118.7(3)
C(35)-C(40)-S(1)	120.8(2)

5b

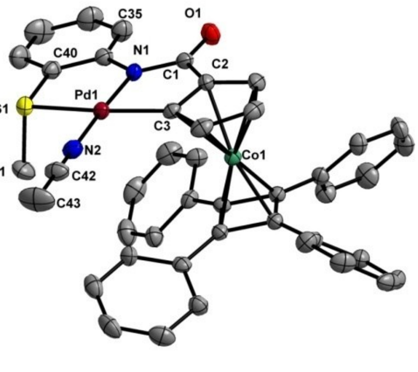


Table-S18 (5b)

Bond lengths (Å)	
Pd(1)-C(3)	2.006(5)
Pd(1)-N(2)	2.040(5)
Pd(1)-N(1)	2.050(5)
Pd(1)-S(1)	2.410(4)
S(1)-C(41)	1.847(5)
Bond Angles (deg)	
C(3)-Pd(1)-N(1)	83.29(16)
N(2)-Pd(1)-N(1)	176.69(15)
C(3)-Pd(1)-S(1)	168.09(11)
N(2)-Pd(1)-S(1)	98.03(14)
N(1)-Pd(1)-S(1)	85.26(13)

6b

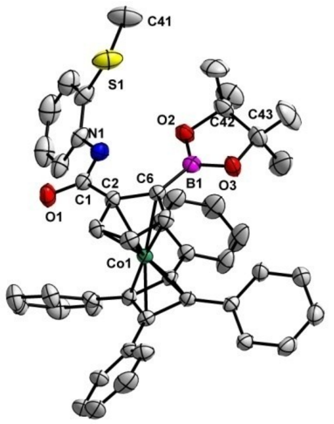


Table-S19 (6b)

Bond lengths (Å)	
O(2)-B(1)	1.381(6)
O(3)-B(1)	1.367(5)
N(1)-C(1)	1.357(5)
C(6)-B(1)	1.552(6)
S(1)-C(41)	1.814(5)
Bond Angles (deg)	
O(3)-B(1)-O(2)	112.9(4)
O(3)-B(1)-C(6)	122.1(4)
O(2)-B(1)-C(6)	125.0(4)
O(1)-C(1)-N(1)	124.2(4)
O(1)-C(1)-C(2)	118.5(4)

7

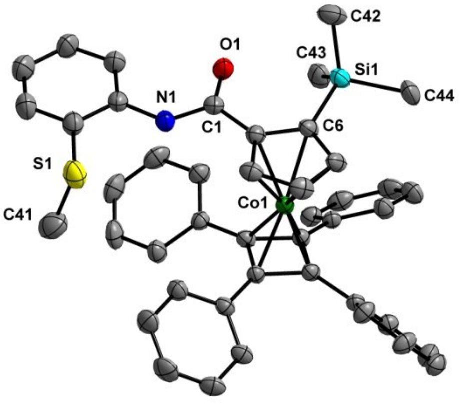


Table-S20 (7)

Bond lengths (Å)	
S(1)-C(40)	1.803(5)
S(1)-C(41)	1.805(6)
Si(1)-C(43)	1.876(5)
Si(1)-C(6)	1.919(5)
O(1)-C(1)	1.231(4)
Bond Angles (deg)	
C(43)-Si(1)-C(44)	110.6(2)
C(43)-Si(1)-C(42)	108.7(2)
C(44)-Si(1)-C(42)	106.8(2)
C(43)-Si(1)-C(6)	115.86(16)
C(44)-Si(1)-C(6)	108.37(18)

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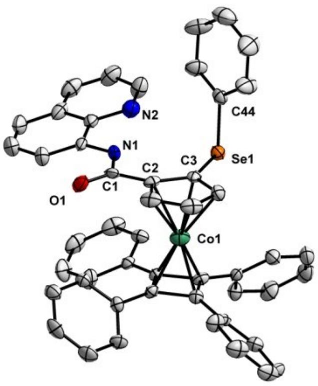

Table-S21 (9)

Bond lengths (Å)

Se(1)-C(3)	1.934(10)
Se(1)-C(44)	1.958(10)
O(1)-C(1)	1.221(11)
N(1)-C(1)	1.365(12)
N(1)-C(35)	1.427(12)

Bond Angles (deg)

C(3)-Se(1)-C(44)	97.7(4)
C(41)-N(2)-C(42)	116.0(10)
O(1)-C(1)-N(1)	123.6(11)
O(1)-C(1)-C(2)	118.0(11)
N(1)-C(1)-C(2)	118.3(9)

J. References:

1. *Bruker (2015). APEX3 and SAINT. Bruker–Nonius AXS Inc., Madison, Wisconsin, USA.*
2. G. M. Sheldrick, SHELXTL Version 2014/7. http://shelx.uni-ac.gwdg.de/SHELX/index.php.
3. B. Klaus, *Diamond*, Version 3.2; University of Bonn: Germany, 1999.
4. J. Singh, M. Deb and A. J. Elias, *Organometallics*, 2015, **34**, 4946.
5. **CCDC** 1579963, 1523199-1523208 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures