## Supplementary Material (ESI) for Chemical Communication

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## Intramolecular Heterocyclization Assisted Oxidative Addition:

# Synthesis of Octahedral Cycloplatinated (IV) Methyl

## Complexes

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## **General Techniques:**

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen. Chemicals were purchased from Aldrich and used as it is unless mentioned otherwise. All the solvents used for the reaction were dried before use. The product purification by column chromatography was accomplished using silica gel 60-120 mesh. The technical grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded in Fourier transform mode. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker-Avance (300 MHz); Inova (400 MHz) and Avance (500 MHz) spectrophotometer using CDCl<sub>3</sub> and TMS as the internal standard. Multiplicities in the <sup>1</sup>H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were recorded on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units. All the melting point is uncorrected. Electrochemical measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. The optical thin layer electrochemical studies were carried on Maya 2000 Ocean Optics software using DT-MINI-2-GS, UV-VIS-NIR LIGHTSOURCE. Steady-state fluorescence spectra were recorded using a Fluorolog-3 spectrofluorometer (Spex model, Jobin Yvon) for solutions with optical density at the wavelength of excitation ( $\lambda_{ex}$ )  $\approx 0.05$  Electrochemical measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. The optical thin layer electrochemical studies were carried on Maya 2000 Optics Ocean software using DT-MINI-2-GS, UV-VIS-NIR

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General procedure for the preparation of N-aryl perfluoroalkyl propargl imines. (1a, 1b, 1c, 1d):



### Scheme 1:

To a stirred mixture of  $PdCl_2(PPh_3)_2$  (2mol%) and CuI (4mol%) in Et<sub>3</sub>N (4mL), 2-(methylthio/methylseleno)phenylacetylene(1 mmol) and *N*-aryl trifluoromethylimidoyl iodide(1mmol) were added successively under N<sub>2</sub> atmosphere. The mixture was stirred at room temperature until the starting materials were consumed. The reaction mixture was then filtered and from the filtrate the solvent was evaporated under reduced pressure. The crude product obtained was purified by column chromatography using hexane/EtOAc(90:10) mixture.

## **Ligand data:**



(4-Methoxy-phenyl)-[3-(2-methylthio-phenyl)-1-trifluoromethyl-prop-2-ynylidene]amine (1a) :

Yield: 88% (307 mg), Yellow liquid, 1H NMR (500 MHz, CDCl3): 7.66 (m, 2H), 7.46-7.34 (m, 2H), 7.22-7.08 (m, 1H), 7.12 (m, 1H), 6.98-6.92 (dd, *J* = 2.07 Hz and 6.98 Hz, 2H), 3.86 (s, 3H), 2.50 (s, 3H). 13C -NMR (125 MHz CDCl<sub>3</sub>):159.9, 143.8, 140.2, 133.9, 131.0, 125.2, 124.8, 124.5, 122.2, 118.6, 114.4, 113.9, 97.7, 85.9, 55.1, 15.3; IR (Neat): v(cm<sup>-1</sup>): 2930, 2841, 2198,1612, 1252, 1161, 1138, 1095, 836, 756, 578; ESI-MS:m/z = 350 [M + H]<sup>+</sup>.



(4-Methoxy-phenyl)-[3-(2-methylthio-phenyl)- 1-nonafluorobutyl-prop-2-

### ynylidene]-amine (1b):

Yield: 84% (394 mg), Yellow liquid, <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ 7.67 (dd, J = 2.136 and 6.866 Hz 2H), 7.39 (m, 2H), 7.19 (m, 1H), 7.11 (m, 1H), 6.95 (m, 2H), 3.85 (s, 3H), 2.48 (s, 3H) <sup>13</sup>C -NMR (125 MHz CDCl3): 150.5, 144.0,141.6, 141.2,140.9, 137.7, 133.9, 133.4, 131.0, 129.5, 127.9, 124.3, 124.2, 120.3, 118.0, 111.8, 97.9, 85.5, 55.6,

14.7; IR (Neat): v(cm<sup>-1</sup>): 2925, 2841, 2190, , 1610, 1573,1503, 1463, 1353, 1300, 1234, 1135, 1091, 751; ESI-MS:m/z = 522 [M + Na]<sup>+</sup>.



(4-Methoxy-phenyl)-[3-(2-methylseleno-phenyl)-1-trifluoromethyl-prop-2-

### ynylidene]-amine(1c)

The product was obtained as a yellowish oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ7.65 (m, 2H), 7.35 -7.45 (m, 2H), 7.10 -7.25 (m, 2H), 6.95 (m, 2H), 3.85 (s, 3H), 2.5 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.9, 143.8, 140.2, 133.9, 131.9, 131.0, 125.2, 124.6, 124.9, 118.5, 113.9, 97.7, 85.9, 55.5, 15.2; IR (Neat): v(cm<sup>-1</sup>): 2930, 2845, 2198, 1612,1584, 1490, 1462, 1331, 1165, 985, 758; ESI-MS:m/z = 398 [M + H]<sup>+</sup>.



(4-Methoxy-phenyl)-[3-(2-methylseleno-phenyl)-1-pentafluoroethyl-prop-2-

### ynylidene]-amine(1d)

The product was obtained as a yellowish oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ7.65 (m, 2H), 7.35 -7.45 (m, 2H), 7.10 -7.25 (m, 2H), 6.95 (m, 2H), 3.85 (s, 3H), 2.5 (s, 3H); <sup>13</sup>C NMR

(125 MHz, CDCl<sub>3</sub>) δ 160.0, 143.8, 140.2, 135.4, 133.8, 131.0, 125.2, 124.5, 124.4, 118.6, 113.9, 97.9, 86.2, 55.3, 14.9; IR (Neat): v(cm<sup>-1</sup>) 2926, 2839, 2195, 1584, 1461, 1434, 1254, 1204, 1161, 1097, 1026, 965, 749; ESI-MS:m/z = 449[M + H]<sup>+</sup>.

# 2. General procedure for the preparation of platinacylces (2a, 2b, 2c, 2d):

To a solution of PtCl<sub>2</sub> (67 mg, 0.25 mol) in dry toluene (5 mL) at 0° C, ligand 1(0.25 mol) was added. The mixture was stirred for overnight at room temperature. On the completion of reaction (monitored by TLC), the mixture was concentrated to half volume. The addition of n-hexane to mixture affords dark reddish colour precipitation. The mixture was filtered and residue was washed with diethyl ether (10 mL). The crude product was subjected to column chromatography and purified using hexane/EtOAc (80:20) mixture.



X=S or Se;  $R_f = CF_3, C_2F_5, C_4F_9$ ; Ar= 4-OCH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>



### Synthesis of 2a :

The product was obtained as a reddish solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 ( d, *J* = 8.3 Hz, 1H), 8.0 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* =7.3 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.3Hz, 1H), 7.08 (m, 2H), 6.97 (dd, *J* = 2.6 and 8.7Hz, 1H), 6.83-6.91 (m, 3H), 6.64 (m, 1H), 6.20 (d, *J* = 8.2 Hz, 1H), 6.06 (d, *J* = 8.5 Hz, 1H), 5.50 (m, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.03 (s with satellites, *J* (Pt-CH<sub>3</sub>) = 33.7 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 158.9, 153.1, 147.2, 138.2, 136.1, 128.6, 127.9, 127.3, 125.4, 125.4, 125.3, 124.5, 123.9, 123.0, 122.6, 121.8, 114.3, 113.6, 112.7, 55.7, 55.3, 31.5, 30.9, 29.7, 29.0, 22.6, 14.1, -7.0; IR (Neat) v(cm<sup>-1</sup>): 3064, 2997, 2923, 2834, 1603, 1578, 1501, 1445, 1413, 1327, 1294, 1243, 1182, 1028, 992, 840, 760, 729, 625, 584, 524, 499, 405; Elemental analysis Calculated for C<sub>35</sub>H<sub>25</sub>ClF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>PtS<sub>2</sub>: C, 45.98; H, 2.76; N, 3.06; S, 7.01. Found C, 46.00; H, 2.73; N 2.97; S, 6.94.



Synthesis of 2b :

The compound **2b** was isolated by column chromatographic technique repeatedly however all the attempts were failed to purify the compound.

The product was obtained as a reddish solid, <sup>1</sup>H- NMR (500 MHz, CDCl<sub>3</sub>) ):  $\delta$  9.60 ( d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.76(m, 1H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.48 (m, 1H),7.36 (m, 2H), 6.99 (dd, *J* = 2.7 and 8.7Hz, 1H), 6.93 (m, 1H), 6.88 (m, 1H), 6.80 (dd, *J* = 2.7 and 8.7 Hz, 1H), 6.61 (dd, *J* = 2.7 and 8.8 Hz, 1H), 6.08 (m, 2H), 5.31 (d, *J*=9.3Hz,1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.18 (m, 3H); <sup>13</sup>C- NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  : 207.0, 158.8, 128.7, 128.2, 127.4, 127.3, 125.2, 125.1, 124.4, 123.6, 122.8, 122.3, 121.2, 114.1, 112.9, 112.7, 112.2, 112.1, 55.7, 55.2, 30.9, 29.6, -6.1; IR (Neat): v(cm<sup>-1</sup>) 3447, 3050, 2958, 2839, 1605, 1564, 1525, 1438, 1408, 1348,

analysis Calculated for C<sub>41</sub>H<sub>25</sub>ClF<sub>18</sub>N<sub>2</sub>O<sub>2</sub>PtS<sub>2</sub> (**2b**): C, 4.52; H, 2.08; N, 2.31; S, 5.27. Found C, 40.52; H 2.06; N 2.30; S, 5.16.

1298, 1240, 1201, 1165, 1134, 1030, 989, 851, 815, 739, 633, 554, 527, 495; Elemental



#### Synthesis of 2c:

The product was obtained as a reddish solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.52(t, J = 7.5 and 7.6 Hz, 1H), 7.39 (t, J = 7.3 and 8.1 Hz, 1H), 7.31(m, 2H),7.13 (m, 1H), 7.05 (d, J = 8.1Hz, 1H),

6.91 (t, J = 7.3 and 8.1 Hz, 2H), 6.83 (t, J = 7.5 and 7.6 Hz, 1H ), 6.59 (m, 1H), 6.14 (d, J = 8.4 Hz, 1H), 5.93 (m, 1H), 4.79 (m, 1H), 3.83 (s, 3H), 3.61 (s, 3H), 2.20 (s with satellites, J (Pt-CH<sub>3</sub>) = 34.7 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.5, 128.7, 128.2, 127.3, 125.3, 125.1, 124.4, 123.6, 122.8, 122.4, 121.2, 114.1, 112.9, 112.3, 112.1, 55.7, 55.2, 29.7, -6.1; IR (Neat) v(cm<sup>-1</sup>): 3449, 2961, 2835, 1600, 1580, 1549, 1499, 1444, 1416, 1337, 1298, 1250, 1169, 1106, 982, 840, 781, 761, 718, 651, 576, 525; Elemental analysis Calculated for C<sub>35</sub>H<sub>25</sub>ClF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>PtSe<sub>2</sub>: C, 41.70; H, 2.50; N, 2.78. Found C, 41.66; H, 2.48; N, 2.77.



### Synthesis of 2d :

The product was obtained as a reddish solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 ( d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.31 (m, 2H), 6.97 (m, 3H), 6.84 (t, *J* = 7.3Hz, 1H), 6.77 (m, 2H), 6.55 (dd, *J* = 2.9 and 8.8 Hz, 1H), 6.01 (d, *J* = 8.4 Hz, 1H), 5.85 (d, *J* = 8.7 Hz, 1H), 5.22(d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 1.97 (s with satellites, *J* (Pt-CH<sub>3</sub>)= 33.7 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  207.0, 158.8, 158.5, 147.6, 144.9, 139.0, 138.1, 136.3, 128.7, 128.1, 127.3, 125.2, 125.1, 124.4, 123.6, 122.3, 121.3, 121.2, 114.0, 112.9, 112.7, 112.2, 112.0, 55.7, 55.2, 30.9, 29.7, 22.6, -6.2; IR (Neat) v(cm<sup>-1</sup>) 3423, 2957, 2836, 1603, 1547, 1502, 1448, 1333, 1304, 1253, 1180, 1143, 1032, 993, 839, 779, 755, 721, 657, 588, 534, 404;

Elemental analysis calculated for C37H25ClF10N2O2PtSe2: C, 40.77; H, 2.27; N, 2.52.

Found C, 40.77; H, 2.25; N, 2.52.

### In-situ ESI-MS Study



Fig: 1. a) Positive ion ESI mass spectrum recorded for the reaction mixture of propargyl imine 1a and platinum dichloride (12 h), b) Expanded spectrum of the sample showing the experimental isotopic pattern of the ion m/z 878, c) Simulated (theoretical) isotopic pattern for the formula  $C_{35}H_{25}F_6N_2O_2S_2Pt$ .

**Table 1.** HRMS data for Pt containing species detected for the reaction mixture of propargyl imine **1a** and platinum dichloride (12 h).

lon ( <i>m/z</i> )	Formula	Measured mass (m/z)	Exact mass (m/z)	Error (in ppm)
877	$C_{35}H_{25}F_6N_2O_2S_2^{(194)}Pt$	877.0877	877.0888	-1.2
878	$C_{35}H_{25}F_6N_2O_2S_2^{(195)}Pt$	878.0898	878.0912	-1.5
601	$C_{20}H_{18}F_3N_2O_2S^{(194)}Pt$	601.0659	601.0668	-1.5
602	$C_{20}H_{18}F_3N_2O_2S^{(195)}Pt$	602.0682	602.0691	-1.4

UV/Vis spectral changes in ligands 1a, 1b, 1c and 1d in  $CH_2Cl_2$  Solution (2.4 x 10 <sup>-4</sup> M)



In situ UV-Visible absorption changes of Pt-complex 2b at an applied potential of -1.25V.



In situ UV-Visible absorption changes of Pt-complex 2b at an applied potential of +1.4V.



DPV for Ligands 1 and Complexes 2.



## **Electrochemical data**

Compounds	Oxi <sub>1</sub>	Oxi <sub>2</sub>	Red <sub>1</sub>	Red <sub>2</sub>
1a	1.68	1.28	-1.03	-1.47
1b	1.70	1.10	-1.03	-1.45
1c	1.68	1.02	-1.06	-1.47
1d	1.68	1.30	-1.04	-1.48
2a	1.75	1.39	-1.06	-1.54
2b	1.79	1.41	-1.06	-1.47
2c	1.75	1.38	-1.03	-1.52
2d	1.60	1.18	-1.07	-1.51

CyclicVoltamogram of ligand 1a.



CyclicVoltamogram of Complex 2a.



Insertion of diphenyl acetylene into platinum complex 2b:



**Procedure:** - Diphenyl acetylene (89 mg, 0.5 mmol) was added into a solution of platinum complex 3b (47 mg, 0.05 mmol) in dry toluene (5 ml), Mixture was refluxed overnight (12 Hrs.). The solvent was removed under vaccum. The resulting solid was dissolved in DCM (10 ml). The black palladium formed was removed by filtration; solution was concentrated to small volume (up to 2 ml). Addition of diethyl ether (5 ml) caused precipitation of green colour solid, which was washed with additional diethyl ether. The product was obtained as a greenish solid, <sup>1</sup>H -NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (m, 1H), 7.41(m, 1H), 7.23 (m, 6H), 7.05 (d, J = 8.87 Hz, 3H), 6.93 (m, 5H), 6.74 (d, J = 8.87, 2H), 6.63 (m, 1H), 3.72 (s, 3H)<sup>13</sup>C -NMR (125 MHz, CDCl<sub>3</sub>): 160.8, 154.6, 149.8, 145.4, 139.0, 137.8, 135.8, 133.5, 132.9, 131.5, 131.2, 131.5, 131.5, 130.8, 130.2, 129.2, 129.1, 129.0, 128.5, 127.5, 126.2, 122.6, 113.4, 55.5; ESI-MS:m/z = 662[M]<sup>+</sup>

Reaction of platinacycle 2a with triphenyl phosphine:



**Procedure:** - Triphenyl phosphine (17.6 mg, 6.7 x  $10^{-5}$  Mol) was added to solution formed by (62.6 mg,  $6.7x10^{-5}$ Mol) of Platinum complex 2a and 0.5 ml of CDCl<sub>3</sub>. During the addition of triphenylphosphine, the colour of mixture changed from orange to bright yellow. The resulting solution was stirred for 2 hours in nitrogen atmosphere at room temperature. Solvent was allowed to evaporate. The pale yellow residue was then treated with 5 ml of n-hexane; solid was collected by filtration, washed with n-hexane and airdried. ESI-MS of product shows removal of p-methoxy imidoyl chloride (C<sub>9</sub>H<sub>7</sub>ClF<sub>3</sub>NO mol. Wt. 237). The product was obtained as a Yellowish solid, <sup>1</sup>H -NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.98 (d, J = 7.93 Hz 1H), 7.71(dd, J = 5.64, 12.35 Hz 1H), 7.45 (m, 12H), 7.39 (m,2H), 7.29 (t, *J* = 7.32Hz 6H), 7.15 (m, 12H), 7.07 (m, 1H), 6.88(m, 2H), 6.80 (m, 1H), 6.58 (m, 2H), 3.90 (s, 3H)<sup>13</sup>C -NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  179.6, 156.1, 143.7, 142.8, 140.9, 135.0, 134.2, 133.7, 133.6, 131.0, 130.8, 130.6, 130.4, 129.8, 129.7, 129.5, 129.3, 128.6, 128.5, 128.4, 128.0, 127.7, 125.6, 122.8, 121.0, 120.0, 117.6, 113.6, 96.0, 60.0, 55.6, 45.7, 8.6.

ESI-MS:  $m/z = 852 [M - 237]^+$ 

<sup>1</sup>H NMR and <sup>13</sup>C NMR

<sup>1</sup>H NMR of (4-Methoxy-phenyl)-[3-(2-methylthio-phenyl)-1-trifluoromethyl-prop-2-ynylidene]-amine (1a):



<sup>13</sup> C NMR of (4-Methoxy-phenyl)-[3-(2-methylthio-phenyl)-1-trifluoromethyl-prop-2-ynylidene]-amine (1a):



<sup>1</sup>H NMR of (4-Methoxy-phenyl)-[3-(2-methylthio-phenyl) - 1-nonafluorobutyl-prop-2-ynylidene]-amine (1b):



<sup>13</sup>C NMR of (4-Methoxy-phenyl)-[3-(2-methylthio-phenyl) - 1-nonafluorobutyl-prop-2-ynylidene]-amine (1b):



<sup>1</sup>H NMR of (4-Methoxy-phenyl)-[3-(2-methylseleno-phenyl)-1-trifluoromethyl-prop-2-ynylidene]-amine (1c):





### <sup>13</sup>C NMR of (4-Methoxy-phenyl)-[3-(2-methylseleno-phenyl)-1-trifluoromethyl-prop-2-ynylidene]-amine (1c):

<sup>1</sup>H NMR of (4-Methoxy-phenyl)-[3-(2-methylseleno-phenyl)-1-pentafluoroethyl-prop-2-ynylidene]-amine (1d):



<sup>13</sup>C NMR of (4-Methoxy-phenyl)-[3-(2-methylseleno-phenyl)-1-pentafluoroethyl-prop-2-ynylidene]-amine (1d):



# <sup>1</sup>H NMR of *platinum complex 2a*





<sup>1</sup>H NMR of platinum complex 2b



## <sup>13</sup>C NMR of platinum complex 2b:



<sup>1</sup>H NMR of platinum complex 2c



# <sup>13</sup>C NMR of platinum complex 2c



<sup>1</sup>H NMR of platinum complex 2d



# <sup>13</sup>C NMR of platinum complex 2d



<sup>1</sup>H NMR of Alkyne (diphenyl acetylene) insertion into Pt (IV) complex 2b





<sup>1</sup>H NMR of reaction of Pt (IV) Complex 2a with triphenyl phosphine





<sup>13</sup>C NMR of reaction of Pt (IV) Complex 2a with triphenyl phosphine











