

Supporting Information

Mechanistic Studies of Si-CN and C-NC Bond Activation of Silylnitriles and Alkyl Isonitriles by Rhodium Porphyrin Radical: Novel Cyanide Transfer

Lirong Zhang, Chun Wah Fung and Kin Shing Chan*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Email: ksc@cuhk.edu.hk

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Figure S1. Saturation kinetics on pyridine.

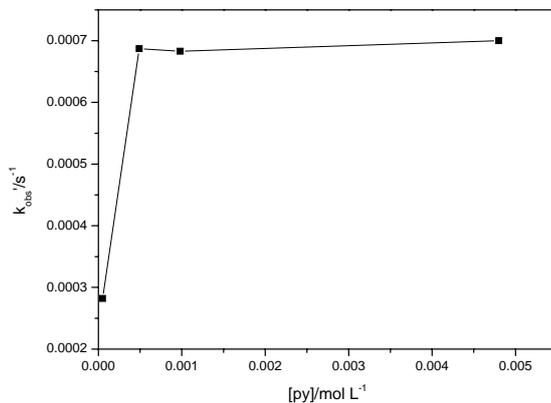


Table S1. Saturation kinetics on pyridine

Entry	[Rh(tmp)] $\times 10^5$ (M)	[Me ₃ SiCN] $\times 10^2$ (M)	[py] $\times 10^3$ (M)	$k'_{\text{obs}} \times 10^4$ (s ⁻¹)	error $\times 10^5$	$k_{\text{obs}} \times 10^2$ (M ⁻¹ s ⁻¹)
1	9.81	1.26	0.98	7.45	± 1.95	5.91
2	9.61	1.28	0.49	6.83	± 1.00	5.34
3	9.61	1.28	0.05	6.87	± 0.59	5.37
4	9.61	1.28	0.01	2.82	± 0.52	2.20

Table S2. k_{obs} ' of reaction 20

entry	[Rh(tmp)]*10 ⁴ (M)	[BuNC]*10 ² (M)	k_{obs}' *10(M ⁻¹ s ⁻¹)	error*10 ⁵	k_{obs} *10 ⁻³ (M ⁻² s ⁻¹)
1	1.11	1.43	14.91	±9.34	7.30
2	1.11	1.43	15.80	±4.47	7.73
3	0.56	1.43	11.30	±5.61	5.53
4	1.11	0.71	3.82	±1.32	7.51
5	1.11	2.15	34.40	±1.12	7.39
6	1.11	0.36	0.94	±3.74	7.36
7	1.11	0.18	0.25	±6.35	7.41

Derivation of pseudo-second order fitting equation

$$r = k_{\text{obs}}[\text{Rh}(\text{tmp})]^m[\text{BuNC}]^n$$

if $[\text{BuNC}] \gg [\text{Rh}(\text{tmp})]$

then, pseudo m order reaction

$$r = k_{\text{obs}}'[\text{Rh}(\text{tmp})]^m$$

where, $k_{\text{obs}}' = k_{\text{obs}}[\text{BuNC}]^n$

if m = 2



a

p

s

$$A_{\lambda} = a\varepsilon_{a,\lambda}d + p\varepsilon_{p,\lambda}d + s\varepsilon_{s,\lambda}d$$

$$= a_0\varepsilon_{a,\lambda}d + d[\varepsilon_{p,\lambda} + \varepsilon_{s,\lambda} - 2\varepsilon_{a,\lambda}]x \quad (\text{x is absorbance changing})$$

in it, $q_{\lambda} = d[\varepsilon_{p,\lambda} + \varepsilon_{s,\lambda} - 2\varepsilon_{a,\lambda}]$

so, $A_{\lambda} - A_{\lambda,0} = q_{\lambda}x$ $x = (A_{\lambda} - A_{\lambda,0}) / q_{\lambda}$ (1)

$$dx/dt = k_{\text{obs}}' [a_0 - 2x]^2$$
 (2)

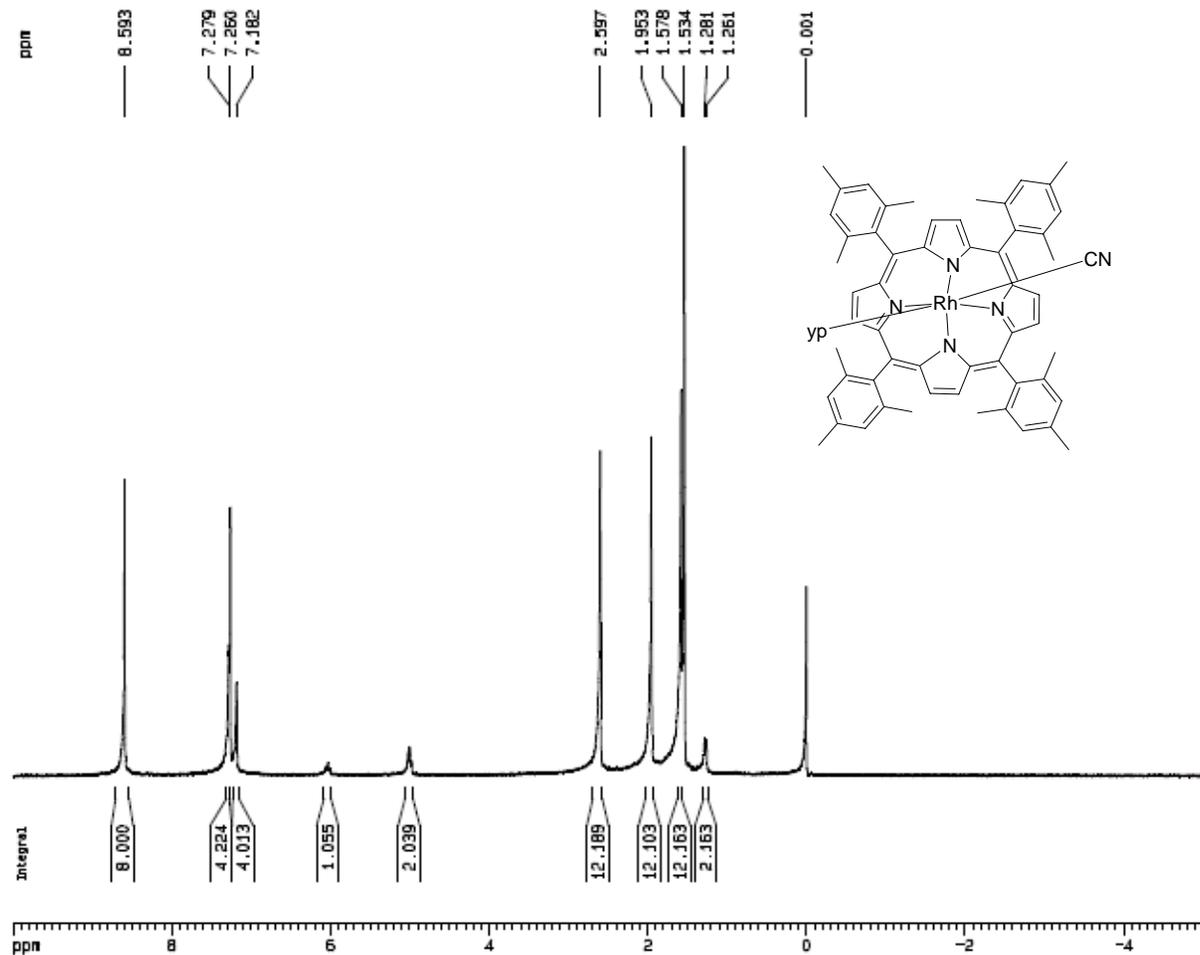
introducing (1) to (2): $dA_{\lambda}/dt = 4k_{\text{obs}}'/q_{\lambda} (A_{\lambda,\infty} - A_{\lambda})^2$

integrated rate law: $1/(A_{\lambda,\infty} - A_{\lambda}) - 1/(A_{\lambda,\infty} - A_{\lambda,0}) = 4k_{\text{obs}}'/q_{\lambda} t$

$$(A_{\lambda} - A_{\lambda,0}) / t = 2k_{\text{obs}}' a_0 A_{\lambda,\infty} - 2k_{\text{obs}}' a_0 A_{\lambda}$$

$$(A_{\lambda} - A_{\lambda,0}) / t \sim A_{\lambda}$$

^1H NMR of pyRh(tmp)CN



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 PROCNO 1

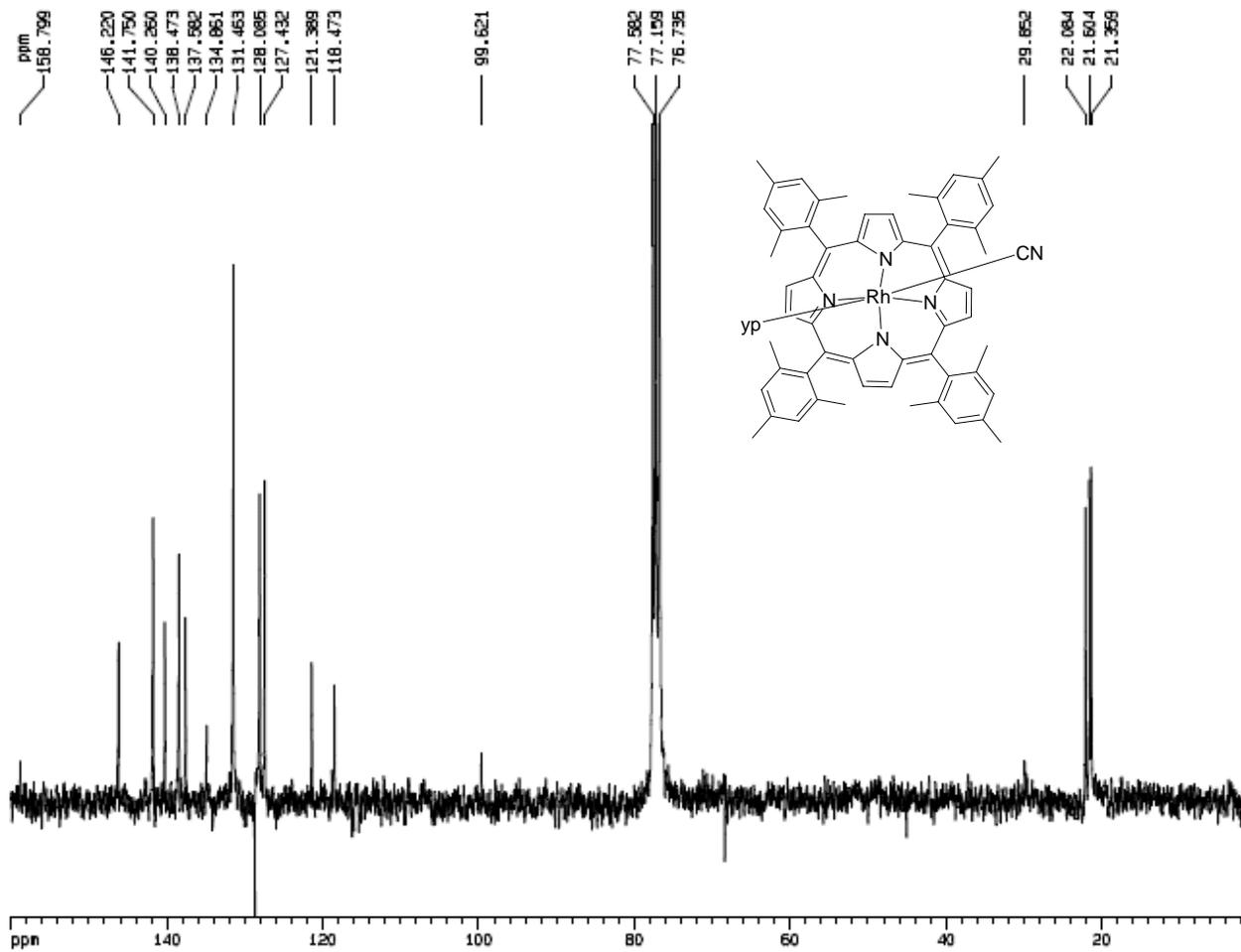
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 DS 0
 SWH 8002.806 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219008 sec
 RG 812.7
 CW 55.000 usec
 DE 79.49 usec
 TE 0.0 K
 DJ 1.0000000 sec
 NCREST 0.0000000 sec
 NCMK 0.0150000 sec

CHANNEL F1
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 PL1 -2.00 dB
 SF01 300.1312000 MHz

F2 - Processing parameters
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 SF 300.1300052 MHz
 WDW EN
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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 CY 12.00 cm
 FJP 10.000 ppm
 F1 9001.30 Hz
 F2P -5.000 ppm
 F2 -1500.65 Hz
 PPMCN 0.68182 ppm/cm
 HZCM 204.63409 Hz/cm

¹³C NMR of pyRh(tmp)CN



```

Current Data Parameters
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PROCNO   1

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PULPROG  zgpg
TD        65536
SOLVENT  CDCl3
NS        7878
DS        0
SWH       22678.738 Hz
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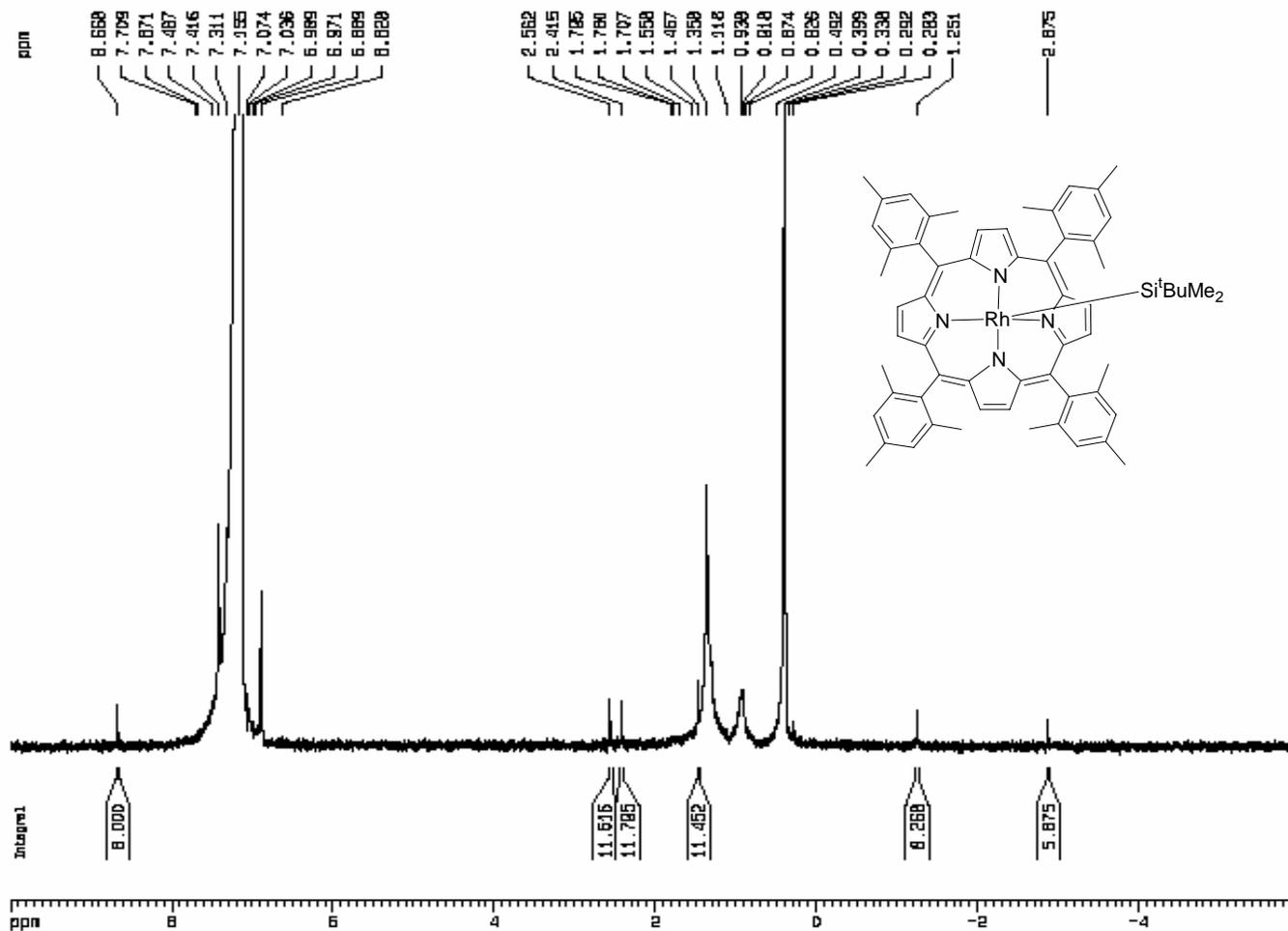
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NUC2      1H
PCPD2     100.00 usec
PL2       120.00 dB
PL12      19.00 dB
SFO2      300.1315007 MHz

F2 - Processing parameters
SI        65536
SF        75.4877382 MHz
WDW       EM
SSB       0
LB        3.00 Hz
GB        0
PC        1.40

F2 NMR plot parameters
CX        23.00 cm
CY        30.00 cm
F1P       160.000 ppm
F1        12074.84 Hz
F2P       -0.000 ppm
F2        -0.00 Hz
PPMCH     6.95652 ppm/cm
HZCM      524.99298 Hz/cm
    
```

¹H NMR of Rh(tmp)Si^tBuMe₂



Current Data Parameters
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 PROCNO 1

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 NS 32
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CHANNEL F1 ---
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F2 - Processing parameters
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1D NMR plot parameters
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 CY 800.00 cm
 F1P 10.000 ppm
 F1 9001.30 Hz
 F2P -6.000 ppm
 F2 -1800.78 Hz
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