Supporting Information

Reactivity of scandium terminal imido complexes towards metal halides

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Contents

General. All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. Toluene, hexane, C_6D_6, and d_8-toluene were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. CuI (A.R.) was purchased from SCRC (Sinopharm Chemical Reagent Co., Ltd), dried under vacuum at 50 ^oC for 12 hours, and stored in the glovebox in darkness. $[Rh(COD)Cl]_2$ (99%) and $[Ir(COD)Cl]_2$ (99%) were purchased from Shanghai Boka-Chem Tech Inc., stored in the freezer of glovebox, and used without further purification. Pinacolborane was purchased from Alfa-Aesar, dried over activated 4 Å molecule sieve, distilled under vacuum, degassed by freeze-thaw-vacuum, and stored in the glovebox. 3-Hexyne and prop-1-ynylbenzene were purchased from Acros, dried over activated 4 Å molecule sieve, distilled under vacuum, degassed by freeze-thaw-vacuum, and stored in the freezer of glovebox. The scandium terminal imido complexes **1** and **2** were synthesized as we previously reported.[1] ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or a Varian 400 MHz spectrometer. Low temperature ^1H NMR spectra were recorded on a Bruker AV 500 MHz spectrometer in d_8-toluene. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

3: **1** (100 mg, 0.149 mmol) and CuI (56.8 mg, 0.298 mmol) were mixed in 3 mL of toluene and stirred at room temperature in dark. After 1.5 hours, the reaction mixture was filtrated, the filtrate was concentrated to approximately 0.5 mL, and to which 0.1 mL of hexane was added. The above solution was cooled to -35 ^oC to afford **3** as a dark red crystalline solid (97 mg, 0.113 mmol, 76% yield). Anal. Calcd for $C_{40}H_{61}CuIN_6Sc$: C, 55.78; H, 7.14; N, 9.76. Found: C, 54.95; H, 6.93; N, 9.10. ^1H NMR (400 MHz, C_6D_6, 25 ^oC): δ = 8.26 (br, d, $^3J_{H-H}$ = 5.2 Hz, 2H; *orthoH* of DMAP), 7.29-7.26 (m, 4H; Ar*H*), 7.21 (dd, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 2.4 Hz, 1H; Ar*H*), 6.97 (t, $^3J_{H-H}$ = 7.6 Hz, 1H; Ar*H*), 5.51 (br, d, $^3J_{H-H}$ = 6.0 Hz, 2H; *meta H* of DMAP), 5.14 (s, 1H; MeC(N)C*H*); 4.46 (br, 1H; ArC*H*Me_2), 4.03 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H; ArC*H*Me_2), 3.59 (m, 1H; NCH_2), 3.01-2.85 (m, 3H; NCH_2), 2.89 (s, 3H; CH_2NMe_2), 2.16 (s, 3H; CH_2NMe_2), 1.89 (br, s, 6H; $CNMe_2$), 1.80 (s, 3H; *Me*C), 1.72 (s, 3H; *Me*C), 1.71 (d, $^3J_{H-H}$ = 6.8 Hz, 3H; ArCHMe_2), 1.54 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; ArCHMe_2), 1.49 (d, $^3J_{H-H}$ = 6.8 Hz, 3H; ArCHMe_2), 1.47 (br, d, $^3J_{H-H}$ = 6.8 Hz, 6H; ArCHMe_2), 1.37 (d, $^3J_{H-H}$ = 6.8 Hz, 3H; ArCHMe_2), 1.11 (d, $^3J_{H-H}$ = 6.8 Hz, 3H; ArCHMe_2). ^{13}C NMR (100 MHz, C_6D_6, 25 ^oC): δ = 166.3, 165.4 (imine *C*), 158.1, 153.8, 150.8, 148.6, 143.2, 142.2, 125.7, 124.3, 123.9, 123.1, 122.4, 116.8, 106.5 (Ar*C* and DMAP's aromatic *C*), 99.6 (MeC(N)*C*H), 57.5, 51.4, 46.9, 42.4, 38.0 (N*C*H_2, CH_2NMe_2 and $CNMe_2$), 28.9, 28.3, 27.8, 26.0, 25.7, 25.4, 25.3, 25.1, 24.3, 23.1, 22.5 (^iPr and *Me*C).

4: **2** (100 mg, 0.165 mmol) in 1 mL of toluene was added to $[Rh(COD)Cl]_2$ (40.7 mg, 0.083mmol) in 1 mL of toluene at room temperature. The reaction solution gradually changed from red into yellow. After standing at room temperature for 1 hour, the volatiles of the reaction solution were removed under vacuum to give a red viscous oil. The oil was extracted by 2 mL of hexane, the extraction was concentrated to approximately 1 mL and cooled to -35 ^{o}C to afford **4** as a yellow crystalline solid (107 mg, 0.126 mmol, 76% yield). Anal. Calcd for $C_{44}H_{70}ClN_5RhSc$·(0.5 hexane): C, 63.04; H, 8.67; N, 7.82. Found: C, 63.10; H, 8.34; N, 8.04. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 7.25-7.17 (m, 3H; Ar*H*), 5.77(d, $^3J_{H-H}$ = 6.0 Hz, 0.5H; 3, 5-*H* of η^4 2,6-DIPP), 5.74 (d, $^3J_{H-H}$ = 6.0 Hz, 0.5H; 3, 5-*H* of η^4 2,6-DIPP), 5.72 (d, $^3J_{H-H}$ = 6.0 Hz, 0.5H; 3, 5-*H* of η^4 2,6-DIPP), 5.68 (d, $^3J_{H-H}$ = 6.0 Hz, 0.5H; 3, 5-*H* of η^4 2,6-DIPP), 5.04 (s, 0.5H; MeC(N)C*H*), 5.00 (s, 0.5H; MeC(N)C*H*), 3.88 (t, $^3J_{H-H}$ = 6.0 Hz, 0.5H; 4-*H* of η^4 2,6-DIPP), 3.87 (t, $^3J_{H-H}$ = 6.0 Hz, 0.5H; 4-*H* of η^4 2,6-DIPP), 3.72 (br, 2H; $CH_2CHCHCH_2$), 3.67 (br, 2H; $CH_2CHCHCH_2$), 3.63-3.37 (m, 5H; NCH_2 and $ArCHMe_2$), 3.30-3.13 (m, 2H; NCH_2 or $ArCHMe_2$), 3.10-3.02 (m, 1.5H; NCH_2 or $ArCHMe_2$), 2.90 (m, 0.5H; NCH_2 or $ArCHMe_2$), 2.68 (s, 1.5H; N*Me*), 2.58 (m, 1H; NCH_2), 2.50 (s, 1.5H; N*Me*), 2.30 (t, $^3J_{H-H}$ = 6.4 Hz, 1H; NCH_2), 2.21-2.18 (m, 5H; 4Hs of $CH_2CHCHCH_2$, 1H of NCH_2), 2.05 (s, 3H; NMe_2), 2.00 (s, 3H; NMe_2), 1.94-1.82 (m, 5H; 4Hs of $CH_2CHCHCH_2$, 1H of NCH_2), 1.89 (s, 1.5H; *Me*C), 1.84 (s, 1.5H; *Me*C), 1.72 (s, 1.5H; *Me*C), 1.71 (s, 1.5H; *Me*C), 1.64 (d, $^3J_{H-H}$ = 6.4 Hz, 1.5H; $ArCHMe_2$), 1.54 (d, $^3J_{H-H}$ = 6.8 Hz, 1.5H; $ArCHMe_2$), 1.49 (d, $^3J_{H-H}$ = 6.8 Hz, 1.5H; $ArCHMe_2$), 1.45 (d, $^3J_{H-H}$ = 6.8 Hz, 1.5H; $ArCHMe_2$), 1.41-1.35 (m, 12H; $ArCHMe_2$), 1.30 (d, $^3J_{H-H}$ = 6.8 Hz, 1.5H; $ArCHMe_2$), 1.26 (d, $^3J_{H-H}$ = 6.4 Hz, 1.5H; $ArCHMe_2$), 1.18 (d, $^3J_{H-H}$ = 6.8 Hz, 3H; $ArCHMe_2$), 0.89 (t, $^3J_{H-H}$ = 6.4 Hz, 3H; CH_3 of hexane). ^{13}C NMR (100 MHz, C_6D_6, 25 ^{o}C): δ =166.3, 166.1, 164.9, 164.4 (imine *C*), 148.5, 148.2, 143.8, 143.2, 142.8, 142.3, 142.0, 125.3, 125.2, 124.3, 124.0, 123.9, 123.5, 123.4, 123.1, 122.3, 100.4, 100.3, 100.2, 100.0, 98.7, 98.2 (Ar*C* and MeC(N)*C*H), 73.5, 73.3, 72.1(br), 71.4(br), 71.1(br) ($CH_2CHCHCH_2$ of COD), 55.9, 55.3, 54.2, 53.8, 53.0, 50.2, 47.8, 47.7, 46.0, 45.6, 45.0, 39.7,32.4, 32.3, 32.1, 32.0, 31.9, 28.6, 28.4, 28.3, 28.2, 26.7, 26.5, 26.4, 26.3, 25.5, 25.3, 24.8, 24.7, 24.6, 24.4, 24.2, 23.9, 23.3, 23.1, 23.0, 22.9 (NCH_2, N*Me*, C*Me*, ^{i}*Pr*, CH_2 of COD and CH_2 of hexane), 14.3 (CH_3 of hexane).

5: Following the procedure described for **4**, but with **2** (100 mg, 0.165 mmol) and $[Ir(COD)Cl]_2$ (55.4 mg, 0.083mmol), and the reaction time was 12 hours. **5** was obtained as a brownish yellow crystalline solid (96.8 mg, 0.103 mmol, 63% yield). Anal. Calcd for $C_{44}H_{70}ClN_5IrSc$: C, 56.12; H, 7.49; N, 7.44. Found: C, 56.35; H, 7.60; N, 7.47. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.26-7.21 (m, 3H; Ar*H*), 5.45 (d, $^3J_{H-H}$ = 5.7 Hz, 0.5H; 3, 5-*H* of η^3-η^5 2, 6-DIPP), 5.40 (d, $^3J_{H-H}$ = 5.7 Hz, 0.5H; 3, 5-*H* of η^3-η^5 2, 6-DIPP), 5.35 (d, $^3J_{H-H}$ =5.7 Hz, 0.5H; 3, 5-*H* of η^3-η^5 2, 6-DIPP), 5.03 (s, 0.5H; MeC(N)C*H*), 4.98 (s, 0.5H; MeC(N)C*H*), 4.43 (t, $^3J_{H-H}$ = 5.7 Hz, 1H; 4-*H* of η^3-η^5 2, 6-DIPP), 3.70 (br, 4H; $CH_2CHCHCH_2$), 3.53-

3.44 (m, 1.5H; NC*H*$_2$ or ArC*H*Me$_2$), 3.38-3.07 (m, 7.5H; NC*H*$_2$ or ArC*H*Me$_2$), 2.96 (m, 1H; NC*H*$_2$ or ArC*H*Me$_2$), 2.72 (s, 1.5H; N*Me*), 2.67 (m, 0.5H; NC*H*$_2$ or ArC*H*Me$_2$), 2.57 (m, 0.5H; NC*H*$_2$ or ArC*H*Me$_2$), 2.54 (s, 1.5H; N*Me*), 2.28 (t, $^3J_{H-H}$ = 6.3 Hz, 1H; NC*H*$_2$), 2.22 (t, $^3J_{H-H}$ = 6.3 Hz, 1H; NC*H*$_2$), 2.16-2.12 (m, 4H; C*H*$_2$CHCHC*H*$_2$), 2.06 (s, 3H; N*Me*$_2$), 2.01 (s, 3H; N*Me*$_2$), 1.91-1.82 (m, 5H; 4*H*s of C*H*$_2$CHCHC*H*$_2$, 1H of NC*H*$_2$), 1.88 (s, 1.5H; *Me*C), 1.82 (s, 1.5H; *Me*C), 1.73 (s, 1.5H; *Me*C), 1.72 (s, 1.5H; *Me*C), 1.59 (d, $^3J_{H-H}$ = 6.6 Hz, 1.5H; ArCH*Me*$_2$), 1.53 (d, $^3J_{H-H}$ = 6.6 Hz, 1.5H; ArCH*Me*$_2$), 1.52 (d, $^3J_{H-H}$ = 6.6 Hz, 1.5H; ArCH*Me*$_2$), 1.42-1.39 (m, 4.5H; ArCH*Me*$_2$),1.30 (d, $^3J_{H-H}$ = 6.6 Hz, 6H; ArCH*Me*$_2$), 1.28 (d, $^3J_{H-H}$ = 6.6 Hz, 3H; ArCH*Me*$_2$), 1.20 (d, $^3J_{H-H}$ = 6.6 Hz, 6H; ArCH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 ^oC): δ =166.5, 166.4, 165.3, 165.0 (imine *C*), 148.4, 148.1, 146.0, 145.3, 143.0, 142.4, 142.1, 125.5, 125.4, 123.9, 123.8, 123.7, 110.9, 110.5, 107.6, 106.9, 98.6, 98.2, 93.9, 93.6, 93.4, 92.9 (Ar*C*, CH$_2$*C*H*C*HCH$_2$ of COD,and MeC(N)*C*H), 75.2, 75.1 (CH$_2$*C*H*C*HCH$_2$ of COD), 55.2, 55.1, 54.5, 54.3, 54.2, 54.0, 53.4, 53.1, 50.9, 47.9, 47.7, 46.0, 45.6, 44.8, 39.8, 33.9, 33.8, 33.6, 33.5, 31.9, 28.5, 28.4, 28.3, 27.2, 27.1, 26.9, 26.8, 25.6, 25.6, 25.5, 25.4, 25.0, 24.9, 24.8, 24.7, 24.0, 23.7, 23.6, 23.1, 23.0, 23.0, 22.8, 22.7, 22.6, 22.5 (N*C*H$_2$, N*Me*, C*Me*, ^{i}*Pr* and *C*H$_2$ of COD).

Variable-temperature ^{1}H NMR spectra of 4 and 5 in C_6D_6 or d_8-toluene:

The ^{1}H NMR spectra of **4** and **5** in C_6D_6 at room temperature are similar to each other, both of which features two sets of signals in a ratio of 1:1. For example, the hydrogen at the β-diketiminato backbone appears as two signals at δ = 5.04 and 5.00 ppm for **4**, and at δ = 5.03 and 4.98 ppm for **5**. Increasing the temperature results in the coalescence of the two sets of signals (see Figures S1 and S3 for **4** and **5** in C_6D_6, respectively). When the complexes were brought back to room temperature, they return to their orginal state without any observable decomposition (for **4**, Figure S1), or with a small amount of decomposition (for **5**, Figure S3).

In d_8-toluene, the similar ^{1}H NMR dynamical behavior as that in C_6D_6 was observed for both of the complexes (**4**: Figure S2; **5**: Figure S4), with the temperature ranges from -23 ^{o}C to 60 ^{o}C (the low-end of the temperature range is -23 ^{o}C due to the restriction of the our NMR facility, for which a temperature lower than -23 ^{o}C is inaccessible).

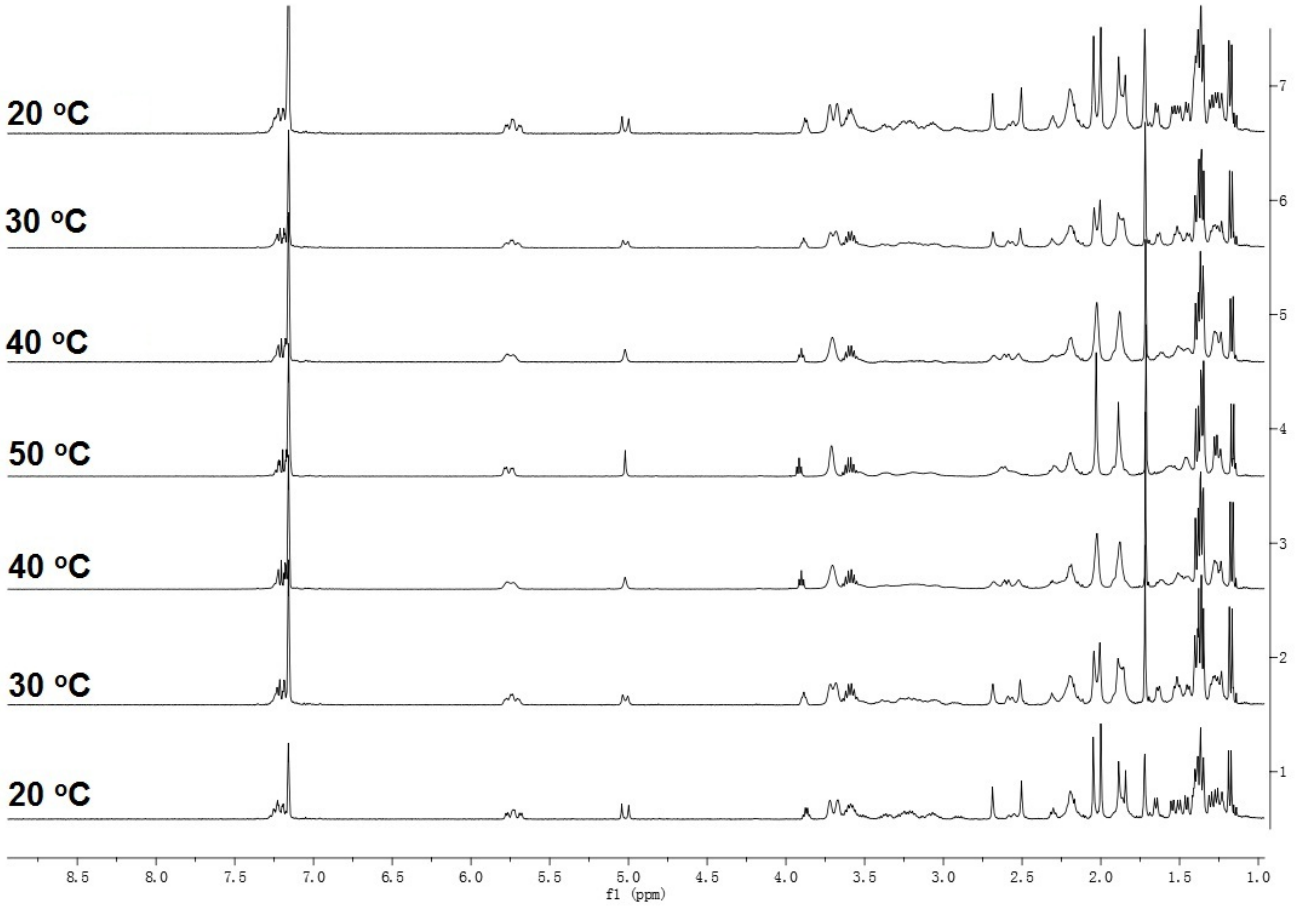


Figure S1. Variable-temperature ^{1}H NMR spectra of **4** (C_6D_6, 400 MHz). The temperature was varied from 20 ^{o}C→30 ^{o}C→40 ^{o}C→50 ^{o}C→40 ^{o}C→30 ^{o}C→20 ^{o}C.

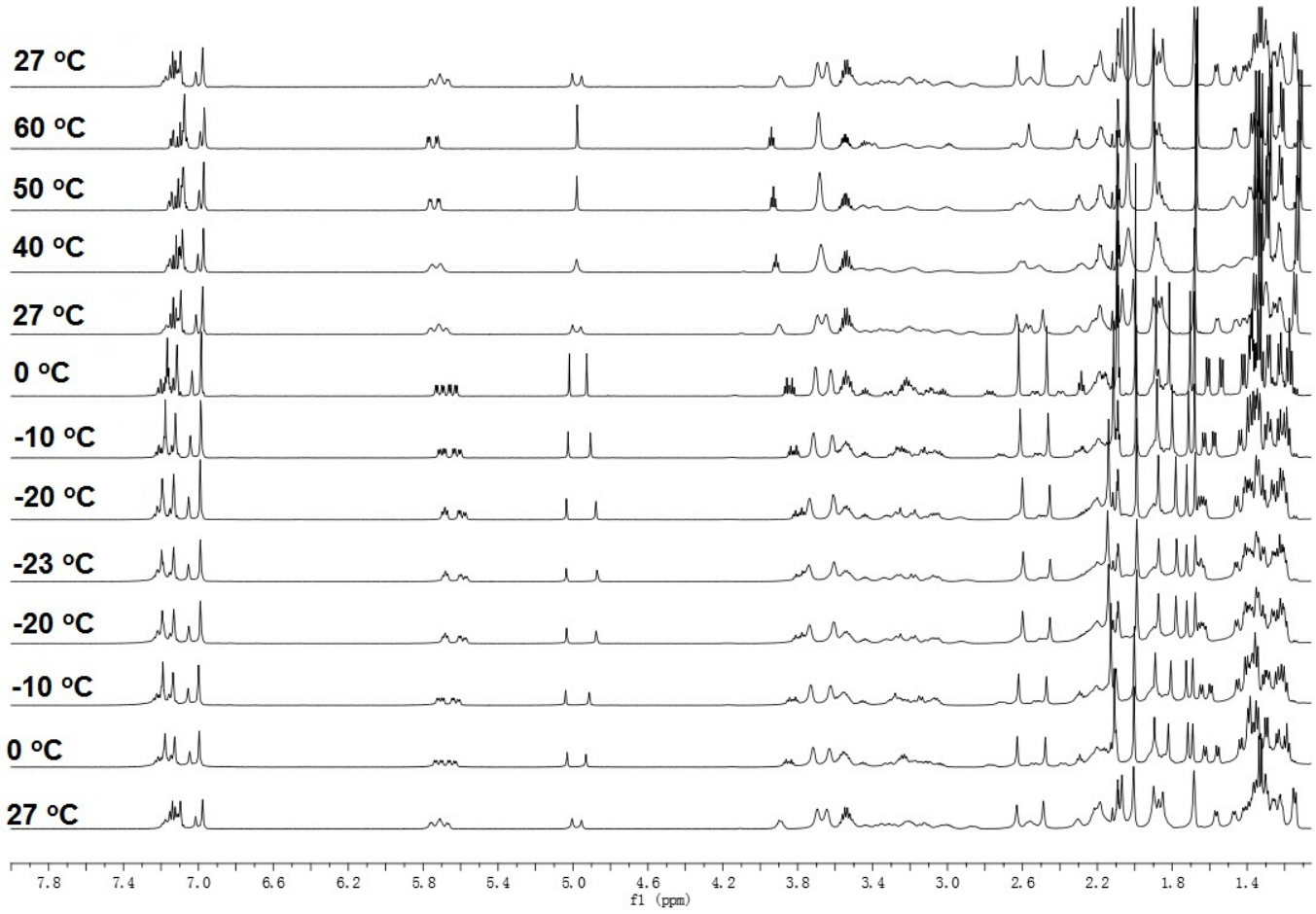


Figure S2. Variable-temperature ^{1}H NMR spectra of **4** (d_8-toluene, 500 MHz). The temperature was varied from 27 °C→0 °C→-10 °C→-20 °C→-23 °C→-20 °C→-10 °C→0 °C→27 °C→40 °C→50 °C→60 °C→27 °C.

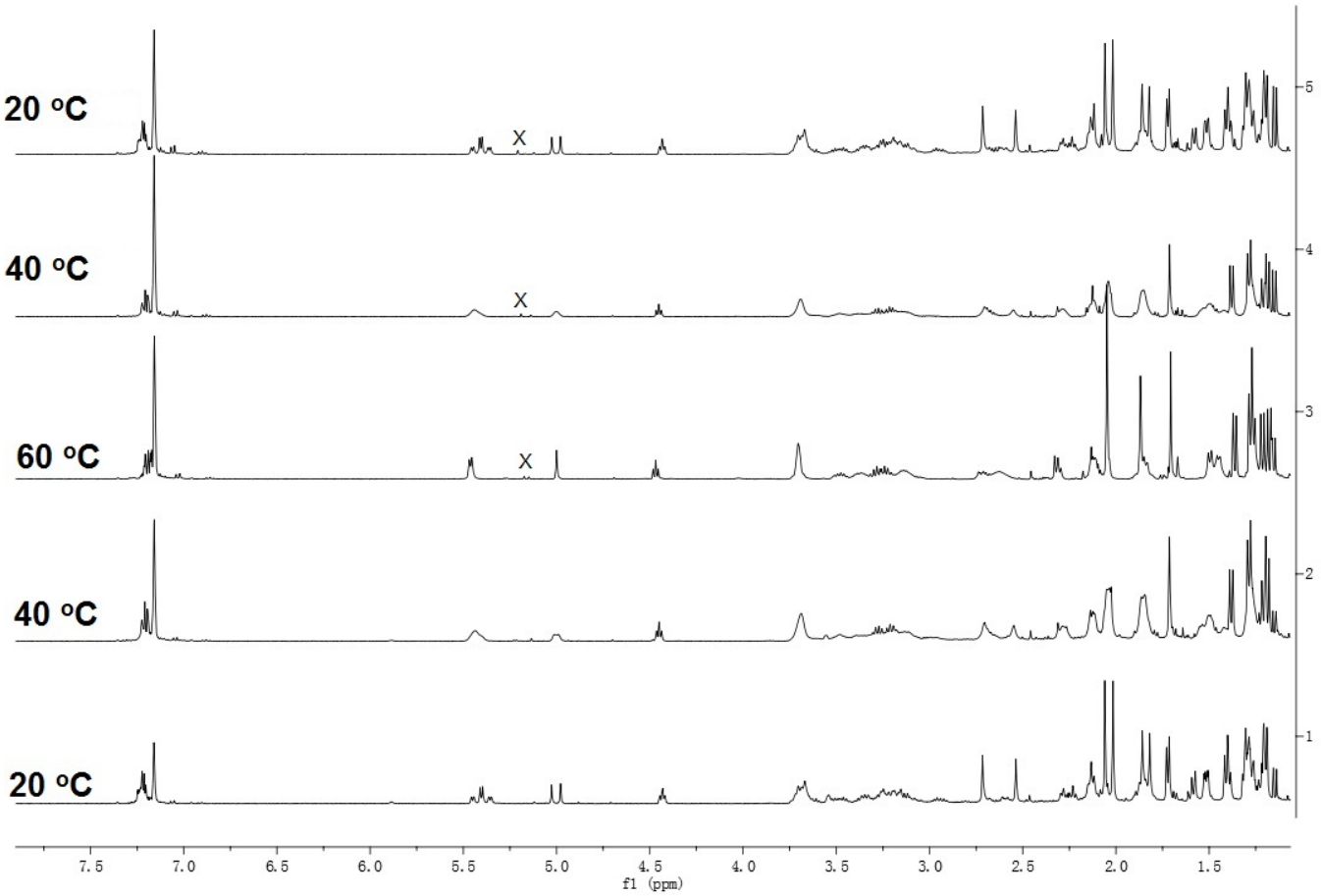


Figure S3. Variable-temperature ^{1}H NMR spectra of **5** (C_6D_6, 400 MHz). The temperature was varied from 20 $^{o}C \rightarrow 40\ ^{o}C \rightarrow 60\ ^{o}C \rightarrow 40\ ^{o}C \rightarrow 20\ ^{o}C$.

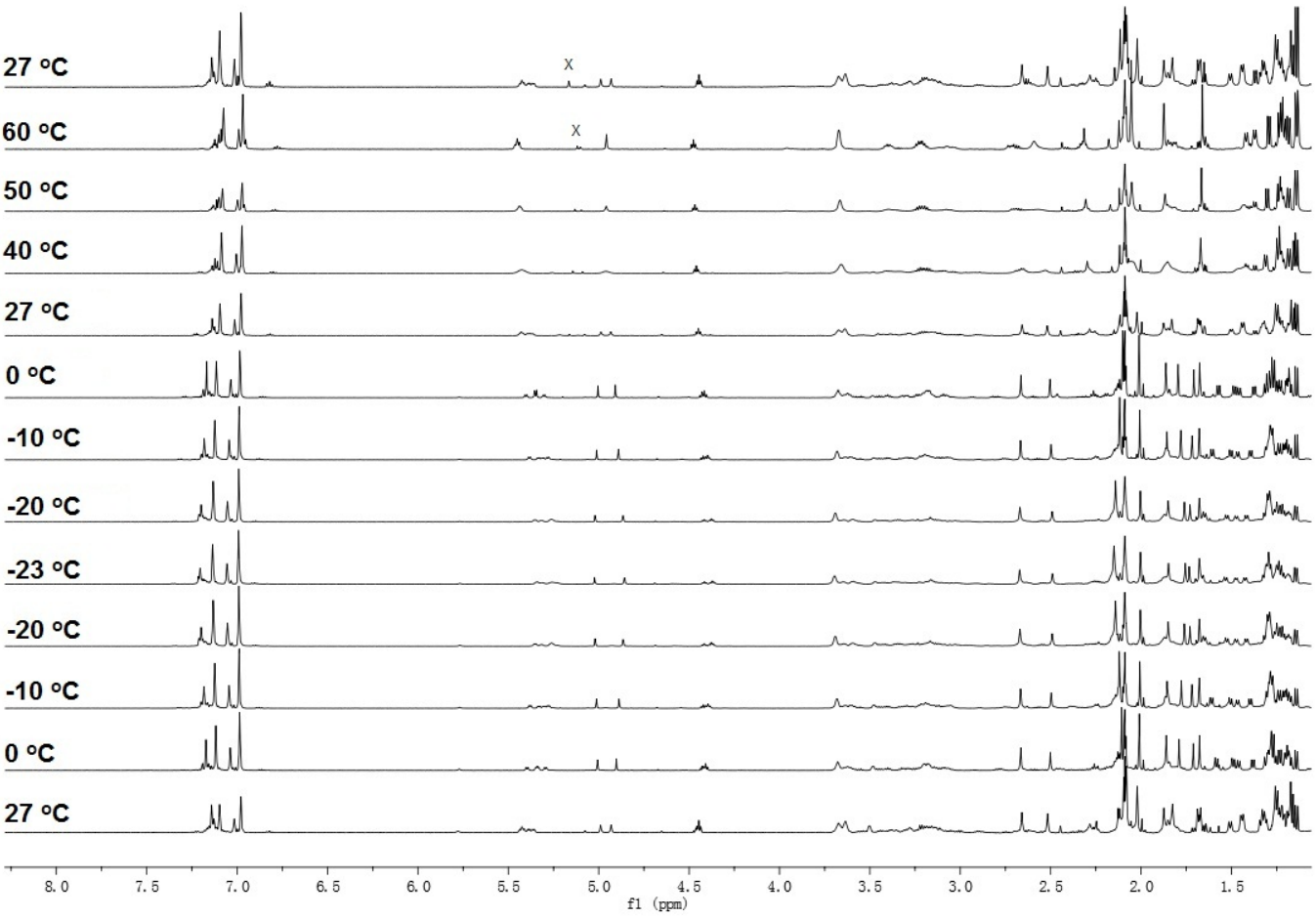
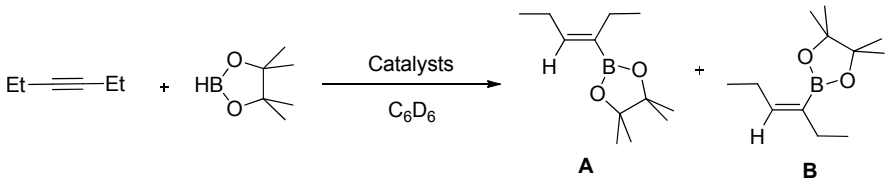


Figure S4. Variable-temperature ^{1}H NMR spectra of **5** (d_8-toluene, 500 MHz). The temperature was varied from 27 ^{o}C→0 ^{o}C→-10 ^{o}C→-20 ^{o}C→-23 ^{o}C→-20 ^{o}C→-10 ^{o}C→0 ^{o}C→27 ^{o}C→40 ^{o}C→50 ^{o}C→60 ^{o}C→27 ^{o}C.

General procedure for hydroboration of alkynes. Alkyne (0.352 mmol) and pinacolborane (0.352 mmol) were disolved in 200 mg (0.210 mL) of C_6D_6. **4**, **5**, $[Rh(COD)Cl]_2$, or $[Ir(COD)Cl]_2$ (0.00352 mmol for **4** and $[Rh(COD)Cl]_2$; 0.00176 mmol for **5** and $[Ir(COD)Cl]_2$) in 275 mg of C_6D_6 (0.290 mL) was added to the substrates' C_6D_6 solution by one portion at room temperature. The $[Sub.]_0$ is 0.704 mmol L^{-1}. The process of the reaction was monitored by ^1H NMR spectroscopy.

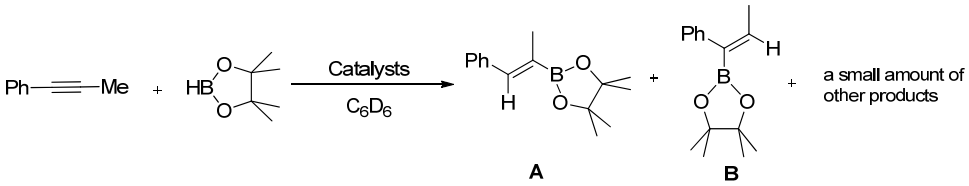
Table S1. Hydroboration of 3-hexyne



Entry	[Cat] (mol%)	Temp. (°C)	Time	Selectivity (%) [a]		Conv. (%) [b]
				A	**B**	
1	**4** (1)	50 °C	10 h	83	17	>95
2	$[Rh(COD)Cl]_2$ (1)	50 °C	10 h	83	17	90
3	**5** (0.5)	R. T.	50 mins	93	7	>95
4	$[Ir(COD)Cl]_2$ (0.5)	R. T.	12 h	85	15	95

[a] Selectivity of products were determinated by ^1H NMR spectrum, and the *Z*- and *E*- isomers were determinated by ^1H-^1H 1D NOESY spectrum. [b] conversions were determinated by ^1H NMR spectrum.

Table S2. Hydroboration of prop-1-ynylbenzene



Entry	[Cat] (mol %)	Temp. (°C)	Time	Selectivity (%) [a]		Conv. (%) [b]
				A	**B**	
1	**4** (1)	50 °C	11 h	40	60	60
2	$[Rh(COD)Cl]_2$ (1)	50 °C	11 h	40	60	80
3	**5** (0.5)	50 °C	2.5 h	67	33	>95
4	$[Ir(COD)Cl]_2$ (0.5)	50 °C	9 h	56	44	60

[a] Selectivity of products were determinated by ^1H NMR spectrum. [b] conversions were determinated by ^1H NMR spectrum.

X-ray Crystallography.

Data collection of **3** was performed on a Bruker SMART diffractometer at 293(2) K; data collection of **4** and **5** were performed on a Bruker SMART APEXII diffractometer at 133(2) K. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using the SHELXL-97 program.[2] Hydrogen atoms were placed at calculated positions and were included in the structure calculation.

Table S3. Crystal data and refinement parameters for **3-5**.

Compound	**3**	**4**	**5**
Empirical formula	$C_{40}H_{61}CuIN_6Sc$	$C_{44}H_{70}ClN_5RhSc$	$C_{44}H_{70}ClIrN_5Sc$
Formula weight	861.35	852.37	941.66
Crystal size, mm	0.31 × 0.25 × 0.17	0.15 × 0.10 × 0.05	0.35 × 0.18 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	Cc
Unit cell dimensions:			
a [Å]	11.2772(9)	13.2520(12)	23.527(3)
b [Å]	36.002(3)	22.398(2)	12.3238(13)
c [Å]	14.1324(12)	15.4942(14)	15.6154(16)
α [°]	90	90	90
β [°]	104.966(2)	110.3550(10)	105.940(2)
γ [°]	90	90	90
Volume [Å^3]	5543.2(8)	4311.8(7)	4353.4(8)
Z	4	4	4
Density (calculated) [g·cm^3]	1.032	1.313	1.437
Abosrption coefficient [mm^{-1}]	1.089	0.638	3.306
F(000)	2184	1808	1936
θ range [°]	1.87 to 26.00	1.64 to 26.00	1.80 to 27.00
	$-13 \le h \le 11$	$-16 \le h \le 16$	$-26 \le h \le 30$
Index ranges	$-41 \le k \le 44$	$-20 \le k \le 27$	$-14 \le k \le 15$
	$-16 \le l \le 17$	$-19 \le l \le 19$	$-19 \le l \le 19$
Refelections collected/unique	30198/10864	28282/8452	15211/8417
	[R_{int} = 0.053]	[R_{int} = 0.089]	[R_{int} = 0.026]
Flack parameter			-0.001(5)
Su [max / min]	0.001 / 0.000	0.001 / 0.000	0.005 / 0.000
Completeness [%]	99.7	99.8	99.7
Observed refelections $I > 2\sigma(I)$	5683	5731	7851
Min. and Max. transmission	0.728 and 0.832	0.910 and 0.969	0.391 and 0.637
Data/restrains/parameters	10864 / 0 / 456	8452 / 0 / 470	8417/40/492
Goodness-of-fit on F^2	0.946	0.985	1.010
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0496	R_1 = 0.0450	R_1 = 0.0272
	wR_2 = 0.1005	wR_2 = 0.0996	wR_2 = 0.0626
R indices (all data)	R_1 = 0.0847	R_1 = 0.0855	R_1 = 0.0311
	wR_2 = 0.1049	wR_2 = 0.1194	wR_2 = 0.0645
Largest diff. peak and hole [e·Å^{-3}]	0.633 and -0.331	0.616 and -0.763	1.314 and -0.393

Table S4. Selected bonds lengths (Å) and angles (deg) for **3**–**5**

	3	**4** (M = Rh)	**5** (M = Ir)
Sc–N^{imido}	1.920(3)	1.928(4)	1.937(4)
N^{imido}–C^{ipso}	1.411(4)	1.300(5)	1.286(6)
Sc–N1	2.183(3)	2.233(3)	2.220(4)
Sc–N2	2.188(3)	2.206(3)	2.188(5)
Sc–N3	2.372(3)	2.360(3)	2.328(5)
Sc–Cu	2.926(8)	-	-
Cu–I	2.409(5)	-	-
Sc–Cl	-	2.453(1)	2.435(2)
M–C25	-	2.568(4)	2.700(4)
M–C26	-	2.497(4)	2.317(4)
M–C27	-	2.344(4)	2.245(5)
M–C28	-	2.184(4)	2.245(6)
M–C29	-	2.254(4)	2.213(5)
M–C30	-	2.340(4)	2.347(4)
Sc–N^{imido}–C^{ipso}	152.5(2)	174.5(3)	161.8(4)
Sc–N6–Cu	100.6(1)	-	-
Cu–N^{imido}–C^{ipso}	106.9(2)	-	-
N^{imido}–Sc–Cu	39.2(8)	-	-
N^{imido}–Cu–Sc	40.2(9)	-	-
Sc–Cu–I	146.0(3)	-	-
I–Cu–N^{imido}	173.6(9)	-	-

Theoretical Calculation. Density functional theory (DFT)[3] studies have been performed with the Gaussian 09 program[4] using the B3LYP method[5]. The 6-311G* basis set was used for C, H, N, and Cl, and the Lanl2DZ basis set with Effective Core Potential (ECP)[6] was used for Cu, I, Sc, Rh, and Ir. The NBO charges and the Wiberg bond order were calculated by NBO natural bonding analysis.[7] The structures of the complexes **3–5** obtained by the X-ray diffraction were used as the initial structures to do the optimization. The molecule orbitals were depicted using isodensity at 0.02 au.

The optimized structure of 3

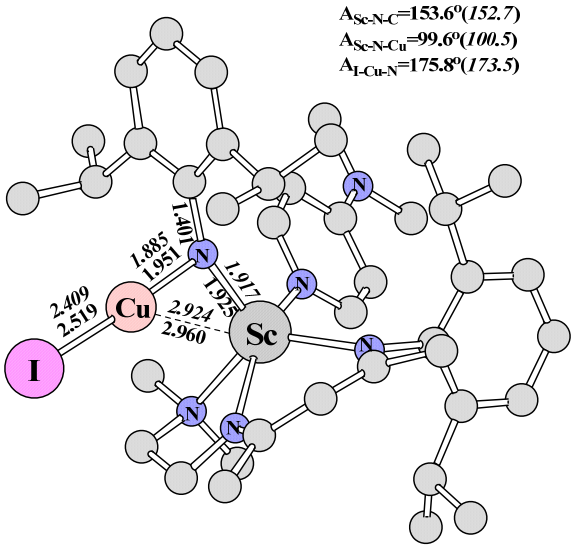
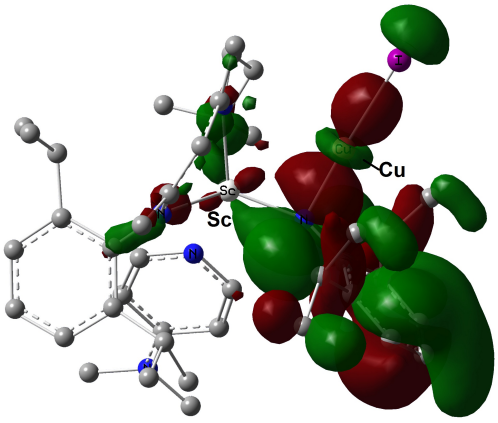
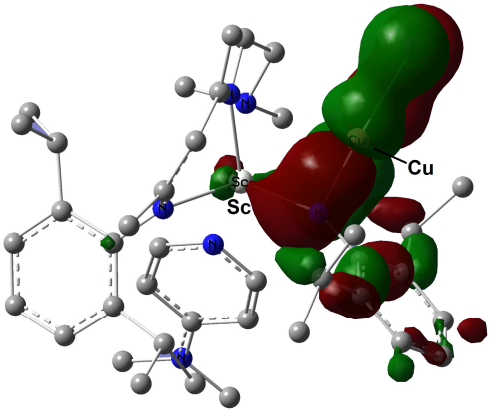


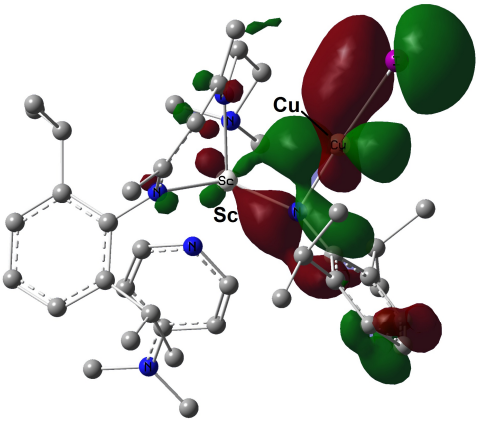
Figure S5. The optimized structure of **3** with selected bond lengths and bond angles (the data in italic are obtained from X-ray diffraction). Hydrogen atoms have been omitted for clarity.



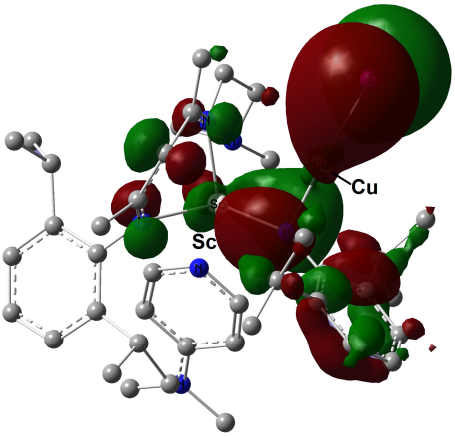
MO-170



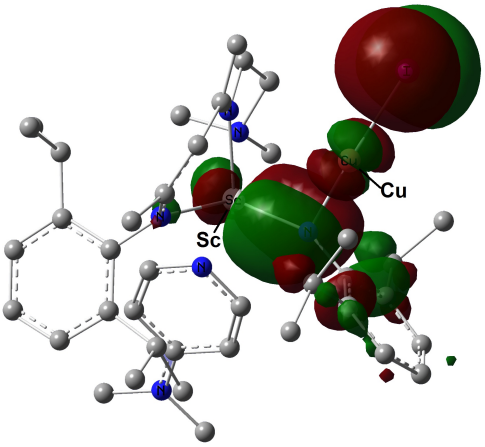
MO-176



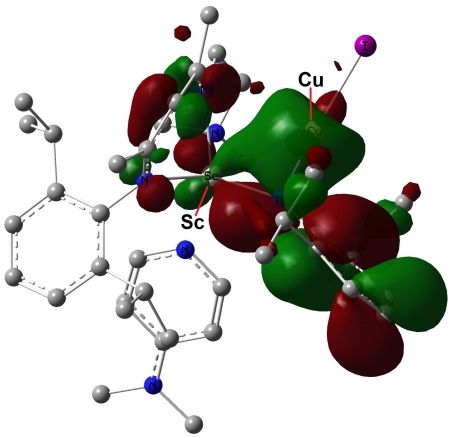
MO-180



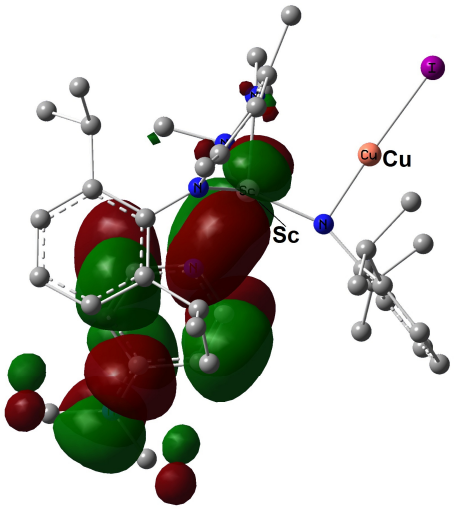
MO-187



MO-189



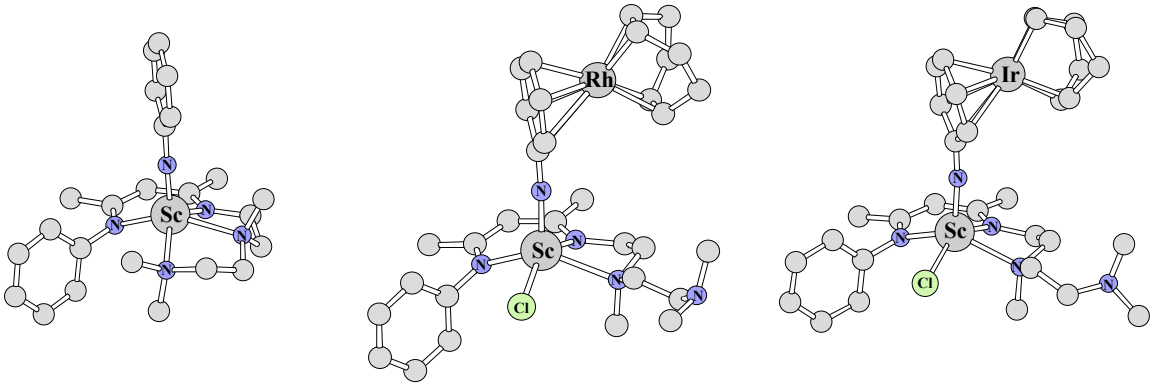
MO-190(HOMO)



MO-191(LUMO)

Figure S6. Selected molecule orbitals of **3,** showing some overlaps between the empty 3*d* orbitals of Sc(III) and the filled 3*d* orbitals of Cu(I) in **MO-170**, **MO-176**, **MO-180** and **MO-190** (HOMO).

The optimized structures of 2, 4 and 5



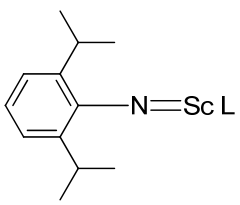
2 **4** **5**

Figure S7. The optimized structures of **2**, **4** and **5**. Isopropyl groups at the DIPP substituents and hydrogen atoms have been omitted for clarity.

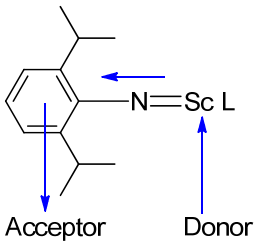
Table S5. Selected bond lengths (Å) and bond angles (deg) obtained from X-ray diffraction and theoretical calculations for **1**, **2**, **4**, and **5**. The calculated Wiberg bond orders (WBO) are also given.

	Sc–Nimido (Å)			Nimido–C (Å)			Sc–Nimido–C (°)	
Complex	X-ray	DFT	WBO	X-ray	DFT	WBO	X-ray	DFT
1*	1.881	1.854	1.33	1.357	1.363	1.23	169.6	170.3
2	1.859	1.850	1.35	1.360	1.368	1.22	167.9	170.5
4	1.928	1.947	0.95	1.300	1.292	1.58	174.5	179.2
5	1.937	1.951	0.94	1.286	1.289	1.60	161.8	173.1

*See ref 1 a).



2



4/5

Complex	Donated Charges	Accepted Charges	Charges on **Sc**	Charges on $\mathbf{N^{imido}}$
2			+1.308	-1.020
4	Cl^-: -0.529	$[Rh(COD)]^+$: -0.822	+1.145	-0.884
5	Cl^-: -0.532	$[Ir(COD)]^+$: -0.841	+1.146	-0.886

Scheme S1. Some NBO charges for **2**, **4**, and **5**.

The calculated NBO charges indicate that the charge donation from the chloride ion to the Sc center in **4** and **5** are -0.529 and -0.532, respectively; and the charge donation from the imido ligand to the Rh or Ir center in **4** and **5** are -0.822 and -0.841, respectively. The charge donation from the imido ligand to the Sc center in **4** and **5** (-0.652 and -0.643) are much less than that in **2** (-0.955). The NBO charges on the Sc centers in **2**, **4** and **5** are 1.308, 1.145 and 1.146, respectively, indicating that the Sc centers in **4** and **5** are less electron-deficient than that in **2**.

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Calculated total energies and geometrical coordinates calculated at B3LYP/6-311G*/Lanl2DZ level.

3

E(RB3LYP) = -2144.16670472 Hartree

Sc	0.0314167100	-0.4286638866	-0.4726078827
Cu	-2.8271322499	0.2495162387	-0.1103945527
I	-5.1357902868	-0.4285707998	-0.8570880119
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N	-0.2553585329	-0.3153804793	-2.9216887950
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2

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H	-2.2681372894	2.9411745418	-1.1665619536
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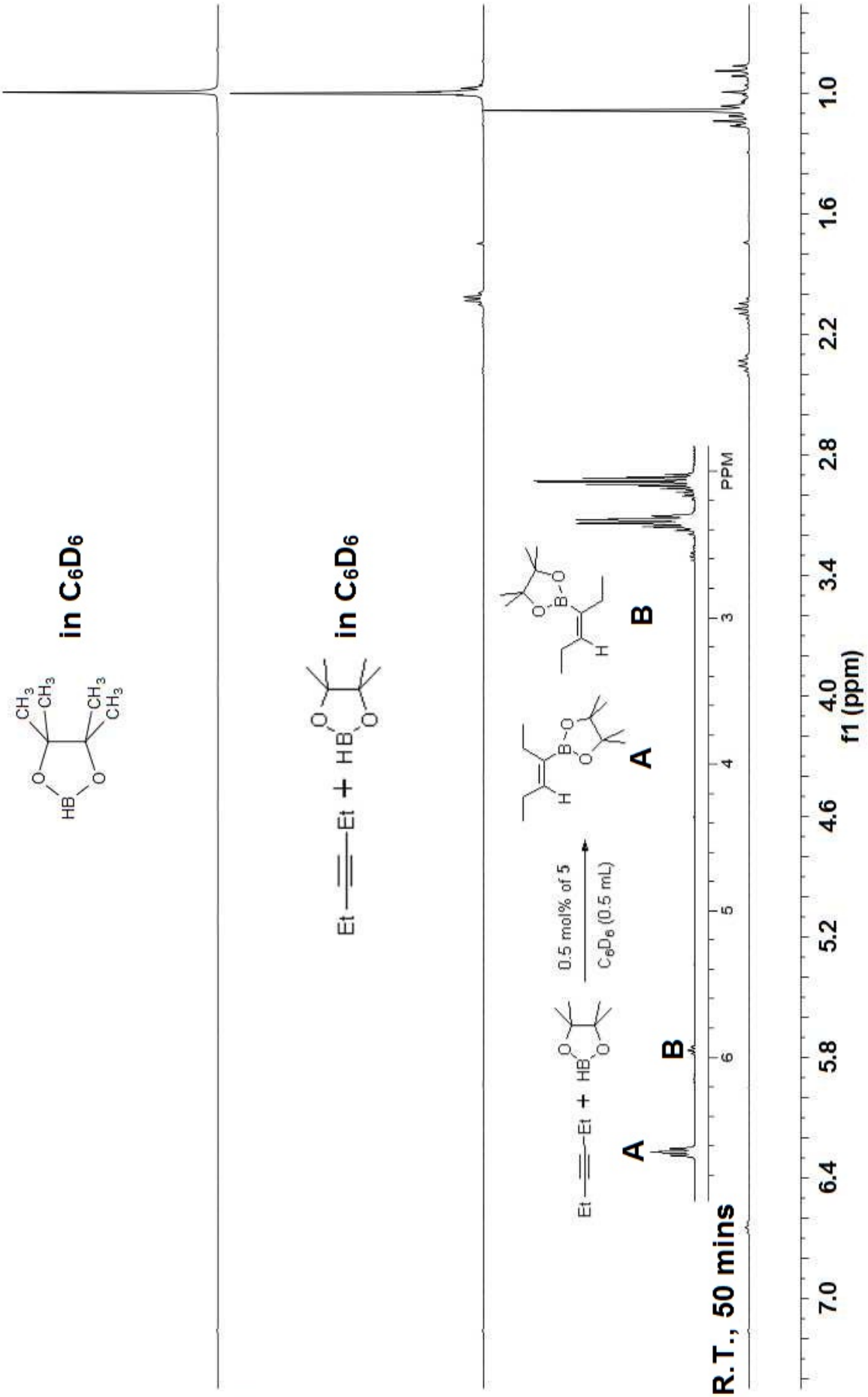

Figure S8. ^{1}H NMR spectra showing the hydroboration of 3-hexyne and pinacolboran catalyzed by 0.5 mol% of **5**.

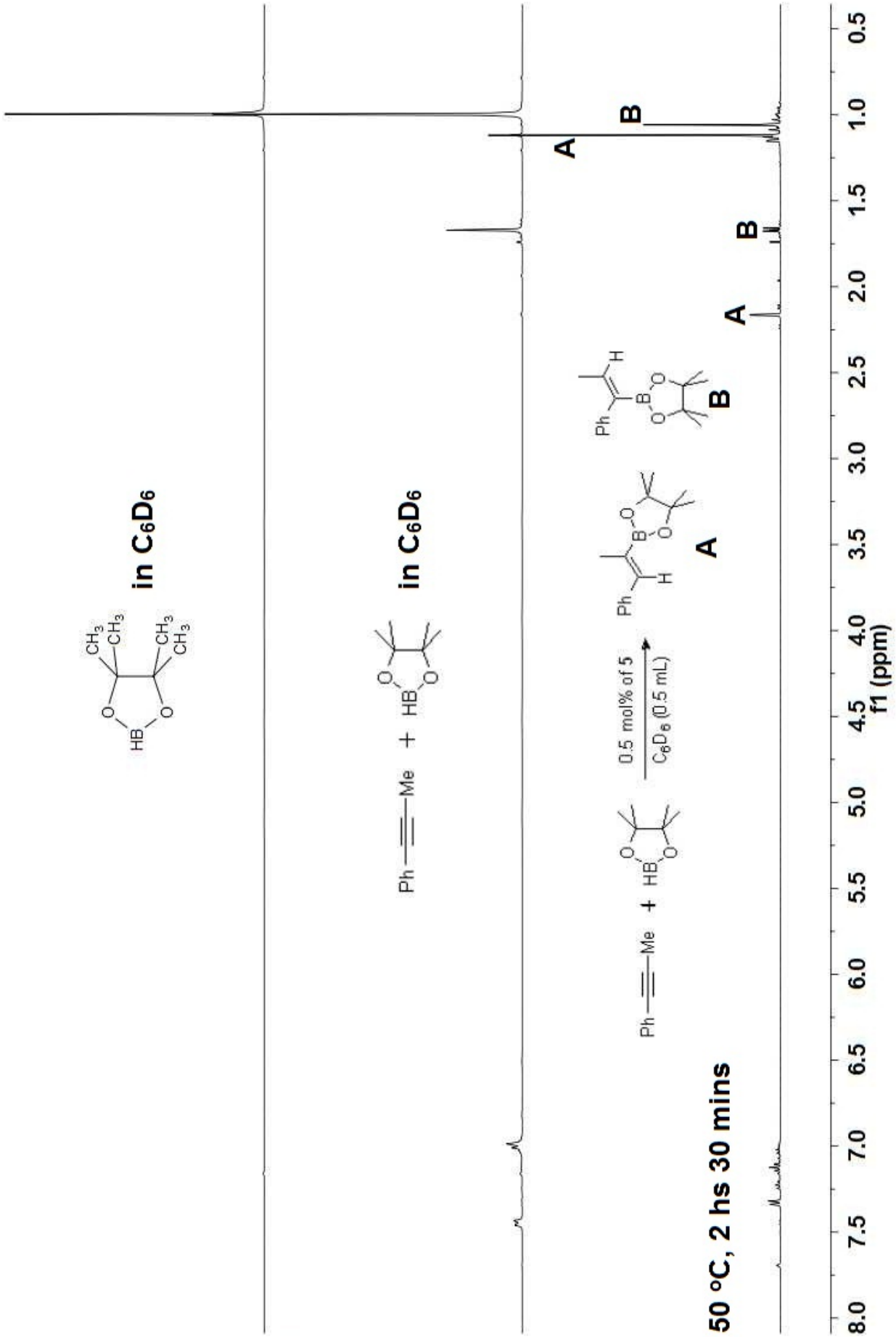

Figure S9. ^{1}H NMR spectra showing the hydroboration of prop-1-ynylbenzene and pinacolboran catalyzed by 0.5 mol% of **5**.