

Supporting Information

A Novel Ylide-stabilized Carbene; Formation and Electron Donating Ability of Amino(sulfur-ylide)carbene

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Experimental Section

General Remarks. General chemicals were used as received. All manipulations were carried out under an argon atmosphere unless otherwise noted. Solvents were purified by MBRAUN MB-SPS system. Preparative thin-layer chromatography (PTLC) was performed using Merck silica gel 60 PF₂₅₄. Gel permeation liquid chromatography (GPC) was performed using LC-918 or LC-908 with JAIGEL 1H+2H columns (Japan Analytical Industry) using chloroform or toluene as solvents, respectively. NMR spectra were recorded by a JEOL AL-400 spectrometer (¹H, 400 MHz; ¹³C, 100 MHz). Chemical shifts are reported in δ . ¹H NMR spectra are referenced to residual protons in deuterated solvent; ¹³C NMR spectra are referenced to carbon-13 in the deuterated solvent. Low resolution mass spectra were obtained with a JEOL JMS-700P using *m*-nitrobenzyl alcohol as a matrix. High resolution mass spectra were recorded by a JEOL JMS-700P using PEG600 or Ultramark® as internal standards. Infrared spectra were recorded with a JASCO Irtron IRT-30. All melting points were measured with a Yanaco MP-S3 and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

N-Mesitylpyrrole was synthesized according to the literature.¹

(1) Y. Fang, D. Leysen and H. C. J. Ottenheijm, *Synth. Commun.*, 1995, **25**, 1857.

Synthesis of sulfonium salt **2**.

To a solution of ditolyl sulfoxide (1.24 g, 5.4 mmol) and *N*-mesitylpyrrole (1.00 g, 5.4 mmol) in CH₂Cl₂ (30 cm³) was added a solution of trifluoroacetic anhydride (0.76 cm³, 5.4 mmol) in CH₂Cl₂ (5.0 cm³) at 0 °C over 30 min. The reaction mixture was gradually warmed up to room temperature and then treated with saturated aq. LiClO₄ (20 cm³). The aqueous layer was extracted by CHCl₃ and organic layer was combined and dried over anhydrous CaCl₂. After the removal of solvent under reduced pressure, the resulting material was subjected to GLPC to give sulfonium perchlorate **1** (602 mg, 22%). A solution of sulfonium salt **1** (250 mg, 0.50 mmol) and NaBPh₄ (206 mg, 0.60 mmol) in MeOH (30 cm³) was stirred for 30 min at room temperature. The resulting white solid was collected by suction filtration and recrystallized by THF/methanol to give sulfonium salt **2** as a white solid (300 mg, 83%). mp 135-136 °C; δ (400 MHz; CDCl₃) 1.92 (6H, s, 2,6-CH₃(Mes)), 2.36 (3H, s, 4-CH₃(Mes)), 2.41 (6H, s, 4-CH₃(Tol)), 6.14-6.16 (1H, m, CH(pyrrole)), 6.21-6.22 (1H, m, CH(pyrrole)), 6.69-6.71 (1H, m, CH(pyrrole)), 6.78 (4H, t, *J* 7.0, 4-*H*(BPh)), 6.88 (8H, t, *J* 7.4, 3,5-*H*(BPh)), 6.98 (6H, m, 3,5-*H*(Mes), 3,5-*H*(Tol)), 7.27 (4H, m, 2,6-*H*(Tol)), 7.39 (8H, br s, 2,6-*H*(BPh)); δ_c (100 MHz; CDCl₃) 17.8 (q, 2,6-CH₃(Mes)), 21.6 (q, 4-CH₃(Mes)), 22.0 (q, 4-CH₃(Tol)), 100.5 (s, 3-*C*(pyrrole)), 110.3 (d, *C*(pyrrole)), 122.2 (d, 4-*C*(BPh)), 124.5 (s, 1-*C*(Tol)), 125.9 (dq, *J* 5.8, 3,5-*C*(BPh)), 127.5 (d, *C*(pyrrole)), 129.5 (d, 3,5-*C*(Mes)), 129.7 (d, 2,6-*C*(Tol)), 130.6 (d, *C*(pyrrole)), 132.1 (d, 3,5-*C*(Tol)), 135.0 (s, 2,6-*C*(Mes)), 135.3 (s, 1-*C*(Mes)), 136.8 (d, 2,6-*C*(BPh)), 140.0 (s, 4-*C*(Mes)), 145.3 (s, 4-*C*(Tol)), 164.4 (q, *J*_{BC} 98.1, 1-*C*(BPh)); *m/z* (FAB⁺) 398.1959 (M⁺-BPh₄. C₂₇H₂₈NS requires 398.1942); Anal. Found: C, 83.44; H, 6.76; N, 1.96%. C₅₁H₄₈BNS·H₂O requires C, 83.25; H, 6.85; N, 1.90%.

Trapping ASYC by elemental sulfur and methylation of trapping product with MeI.

Sulfonium salt **2** (100 mg, 0.139 mmol) was dissolved in THF (10 cm³). The solution was cooled to -40 °C and a solution of MesLi (26 mg, 0.21 mmol) in Et₂O (ca. 5 cm³) was added to the cooled solution. The reaction mixture was stirred for 1 h at -40 °C and a THF solution (ca. 5 cm³) of elemental sulfur (18 mg, 0.070 mmol) was added to the reaction mixture. The temperature was gradually warmed up to room temperature. This reaction mixture was monitored by low-resolution mass spectroscopy showing *m/z* 428 (corresponding to thioamide **3**). The reaction mixture was treated with excess amount of MeI. The volatile material was removed under reduced pressure and the resulting yellow solid was purified by PTLC (solvent: CHCl₃/EtOH = 8:1) to give thioether **4** (95 mg, 90%). mp 124-125 °C; δ (400 MHz; CDCl₃) 1.85 (3H, s, SCH₃), 1.92 (6H, s, 2,6-CH₃(Mes)), 2.37 (3H, s, 4-CH₃(Mes)), 2.41 (6H, s, 4-CH₃(Tol)), 6.05 (1H, d, *J* 3.2, CH(pyrrole)), 6.72 (1H, d, *J* 3.6, CH(pyrrole)), 6.81 (4H, t, *J* 7.0, 4-*H*(BPh)), 6.94 (8H, t, *J* 7.2, 3,5-*H*(BPh)), 7.00 (2H, s, 3,5-*H*(Mes)), 7.13 (4H, m, 3,5-*H*(Tol)), 7.28 (4H, m, 2,6-*H*(Tol)), 7.39 (8H, br s, 2,6-*H*(BPh)); δ_c (100 MHz; CDCl₃) 17.8 (q, 2,6-CH₃(Mes)), 19.4 (q, SCH₃), 21.4 (q, 4-CH₃(Mes)), 21.8 (q, 4-CH₃(Tol)), 108.4 (s, 3-*C*(pyrrole)), 111.2 (d, *C*(pyrrole)), 121.7 (d, 4-*C*(BPh)), 123.0 (s, 1-*C*(Tol)), 125.6 (dq, *J*_{BC} 5.4, 3,5-*C*(BPh)), 129.2 (d, 3,5-*C*(Mes)), 129.5 (d, 2,6-*C*(Tol)), 131.4 (d, *C*(pyrrole)), 131.7 (s, *C*(pyrrole)), 132.3 (d, 3,5-*C*(Tol)), 133.7 (s, 2,6-*C*(Mes)), 135.1 (s, 1-*C*(Mes)), 136.4 (d, 2,6-*C*(BPh)), 140.2 (s, 4-*C*(Mes)), 145.8 (s, 4-*C*(Tol)), 164.3 (q, *J*_{BC} 98.5,

1-C(BPh)); m/z (FAB⁺) 444.1820 (M^+ -BPh₄. C₂₈H₃₀NS₂ requires 444.1820)

Attempted direct observation of ASYC

In a 5 mm diameter NMR tube, to the mixture of sulfonium salt **2** (@@ mg, @@ mmol) and MesLi (@@mg, @@ mmol) was added THF-*d*₈ (@@ mmol) in liquid N₂ bath. The NMR tube was flame-sealed and the reaction mixture was warmed to -40 °C. The reaction mixture was observed by ¹³C NMR keeping the temperature as -40 °C.

Synthesis of ASYC-Rh complex **6**

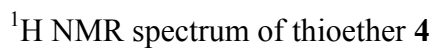
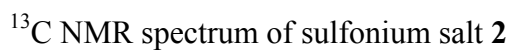
To a solution of sulfonium salt **2** (100 mg, 0.139 mmol) in THF (10 cm³) was added a solution of MesLi (26 mg, 0.21 mmol) in Et₂O (ca. 5 cm³) at -40 °C. After 1 h stirring at -40 °C, a solution of [Rh(cod)Cl]₂ (41 mg, 0.084 mmol) in THF was added to the mixture at -40 °C. The reaction mixture was gradually warmed up to room temperature for 1.5 h. After the removal of solvents under reduced pressure, the resulting solid was subjected to GLPC to give [(ASYC)Rh(cod)Cl] **5** as a yellow solid (182 mg, 58%). To a solution of **5** (50 mg, 0.078 mmol) in THF (3.0 cm³), CO gas was bubbled via gas inlet tube for 1 min. The volatile material was removed under reduced pressure and the resulting pale yellow solid was extracted by hexane. After the removal of solvent, pure [(ASYC)Rh(CO)₂Cl] **6** was obtained as a yellow solid (32.2 mg, 70%). mp 101-102 °C (dec.); δ (400 MHz; CDCl₃) 2.11 (6H, s, 2,6-CH₃(Mes)), 2.34 (3H, s, 4-CH₃(Mes)), 2.42 (6H, s, 4-CH₃(Tol)), 6.25 (1H, d, *J* 3.0, CH(pyrrole)), 6.85 (1H, d, *J* 3.0, CH(pyrrole)), 6.93 (2H, s, 3,5-*H*(Mes)), 7.33 (4H, m, 3,5-*H*(Tol)), 7.51 (4H, m, 2,6-*H*(Tol)); δ_c (126 MHz; CDCl₃) 18.5 (q, 2,6-CH₃(Mes)), 21.2 (q, 4-CH₃(Mes)), 21.5 (q, 4-CH₃(Tol)), 104.7 (s, 3-C(pyrrole)), 108.7 (d, C(pyrrole)), 128.4 (s, 1-C(Tol)), 128.5 (d, 3,5-C(Mes)), 128.8 (d, C(pyrrole)), 129.3 (d, 2,6-C(Tol)), 130.8 (d, 3,5-C(Tol)), 135.6 (s, 2,6-C(Mes)), 137.5 (s, 1-C(Mes)), 140.1 (s, 4-C(Mes)), 142.7 (s, 4-C(Tol)), 172.5 (d, *J*_{CRh} 37.2, 2-C(pyrrole)), 183.8 (d, *J*_{CRh} 78.4, *cis*-CO), 186.4 (d, *J*_{CRh} 51.1, *trans*-CO); m/z (FAB⁺) 556.0815 (M^+ -Cl. C₂₉H₂₇NO₂SRh requires 556.0818), 535 (100, M^+ -(CO)₂), 500 (44, M^+ -(CO)₂Cl); $\nu_{\max}/\text{cm}^{-1}$ 2057 (CO) and 1981 (CO).

X-ray crystallographic analyses.

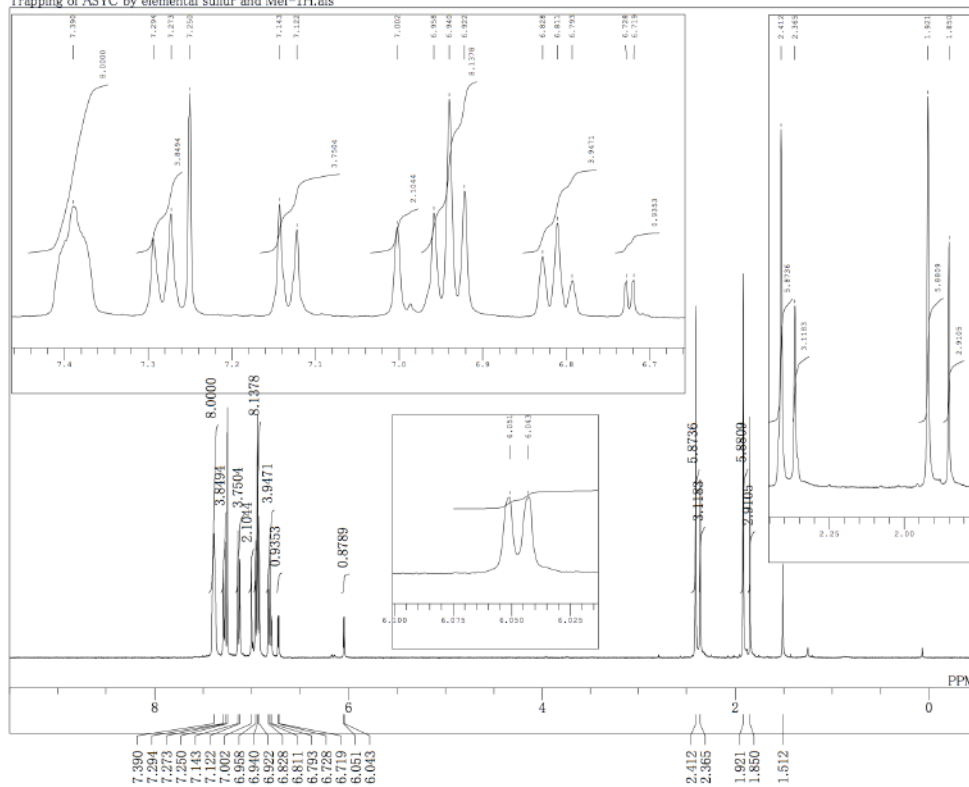
Single crystals of **2** and **6** were grown from a CHCl₃ solution for **2** and Et₂O/THF solution for **6**. The intensity data were collected on Rigaku/MSM Mercury CCD with Mo/K α radiation ($\lambda = 0.71069$ Å). The structures were solved by the direct method and refined by full-matrix least squares on F² using SHELXS97. The structures were refined anisotropically except for hydrogen atoms. Hydrogen atoms were idealized by using the riding models.

NMR spectra of new compounds.

¹H NMR spectrum of sulfonium salt **2**



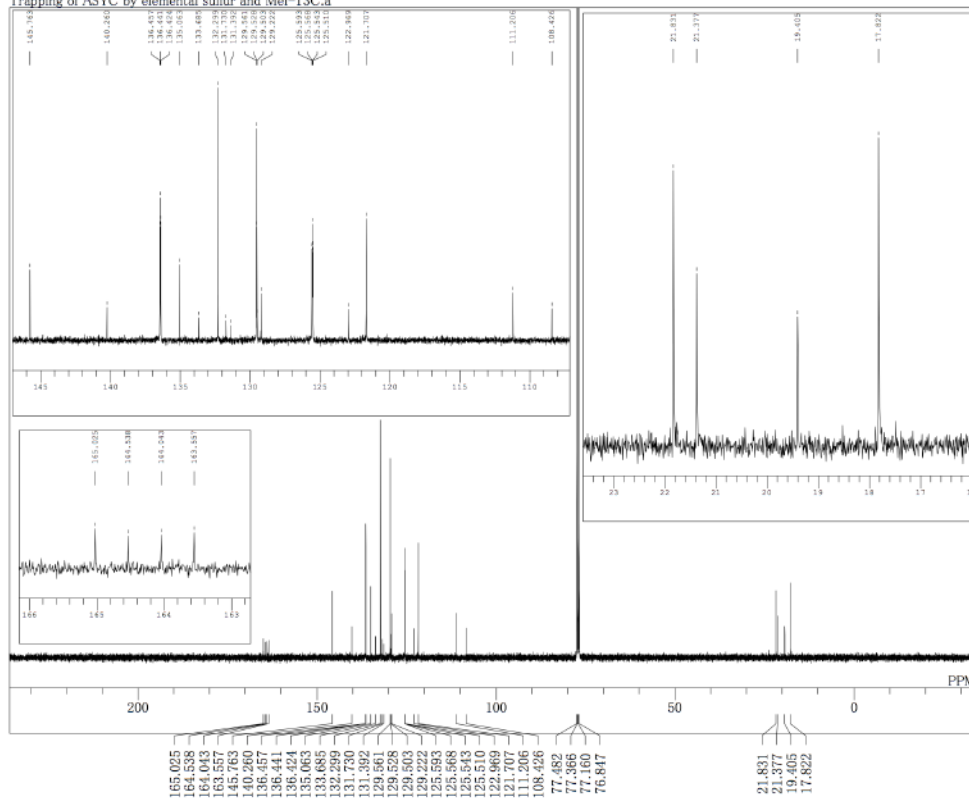
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Trapping of ASYC by elemental sulfur and MeI-1H.als



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¹³C NMR spectrum of thioether 4

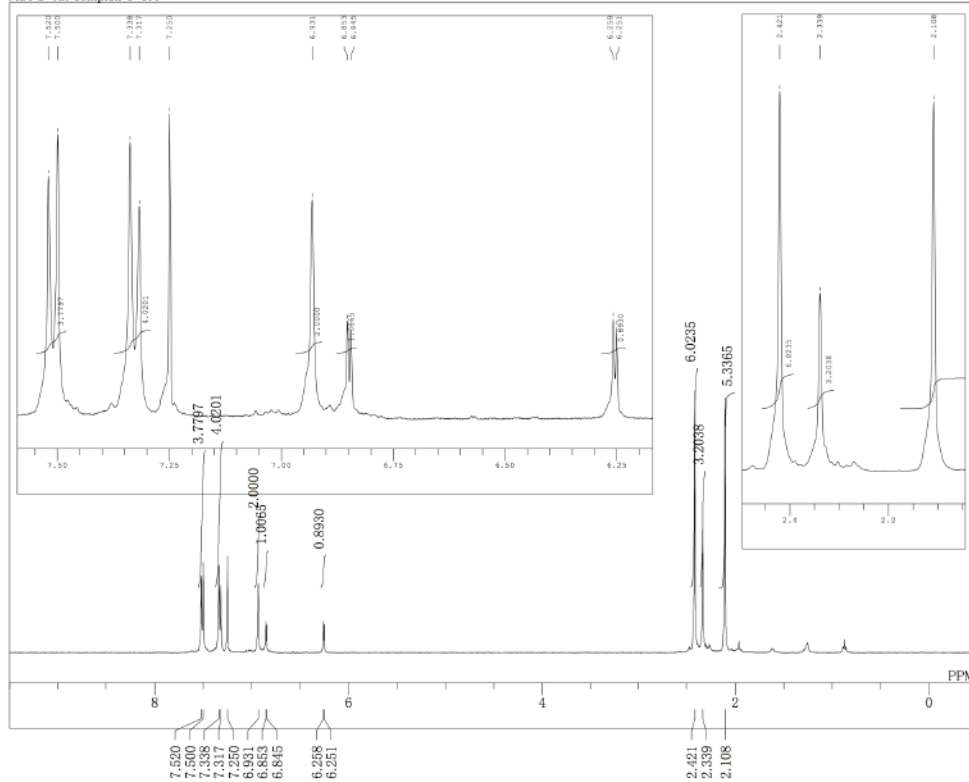
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Trapping of ASYC by elemental sulfur and MeI-13C.als



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¹H NMR spectrum of Rh complex 6

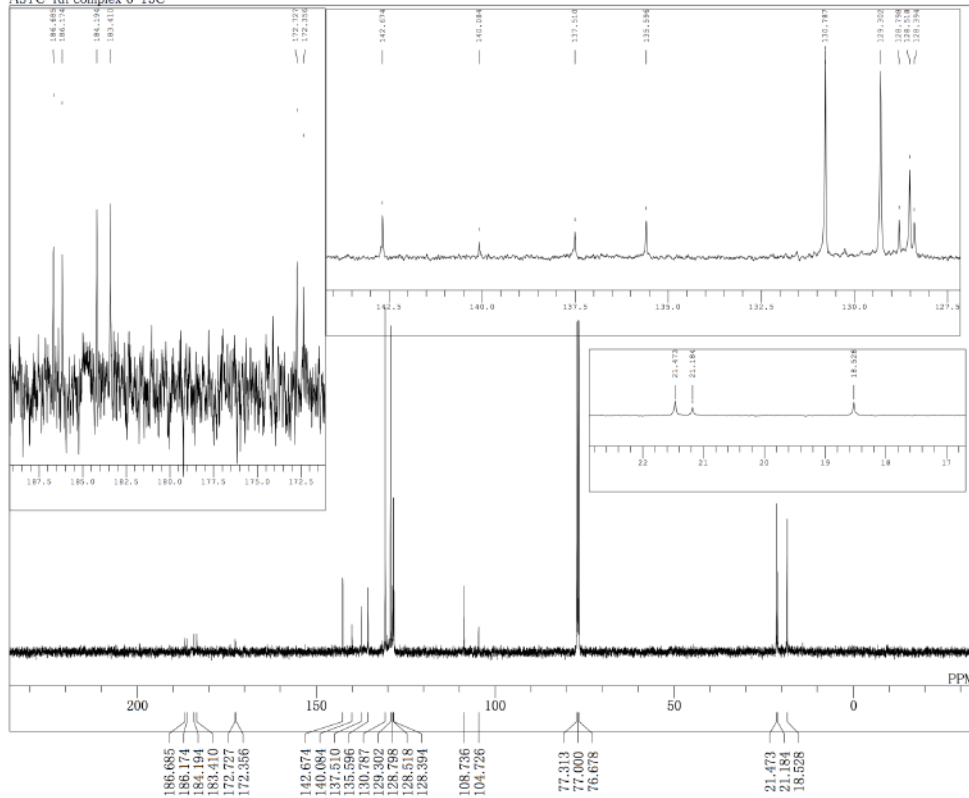
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ASYC-Rh complex 6-1H



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^{13}C NMR spectrum of Rh complex 6

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ASYC-Rh complex 6-13C



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