A novel ylide-stabilized carbene; formation and electron donating ability of an amino(sulfur-ylide)carbene†

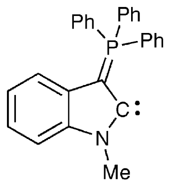
Junji Kobayashi, Shin-ya Nakafuji, Atsushi Yatabe and Takayuki Kawashima*

Received (in Cambridge, UK) 5th August 2008, Accepted 11th September 2008
First published as an Advance Article on the web 14th October 2008
DOI: 10.1039/b813454e

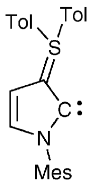
A novel *N*-heterocyclic carbene, amino(sulfur-ylide)carbene, which is stabilized by electron donation from the carbanion of a sulfur ylide as well as a nitrogen atom, was generated and its Rh complex was synthesized; the electron donating properties of the amino(sulfur-ylide)carbene were investigated using the IR carbonyl stretching frequencies of the Rh complex, indicating a relatively strong electron-donating ability among reported carbenes.

The synthesis of a stable carbene, in which the carbene center is stabilized by two adjacent nitrogen atoms, (*N*-heterocyclic carbene; NHC) was a very important landmark,[1] because the utilization of NHCs as a new class of ligands for transition metals and their application to catalytic systems has been widely investigated since their isolation in 1991.[2]

In NHCs, the carbene center is in an sp^2 hybrid state with a localized lone pair and a vacant *p*-orbital. The lone pair of the carbene center has similar properties to those of the phosphine ligand, and NHCs can coordinate to transition metals. The vacant *p*-orbital is stabilized by the mesomeric effect from the lone pair of the nitrogen atom, and at the same time, this electronic donation also contributes to the prevention of back donation from the *d*-orbital of the transition metal when it coordinates to the transition metal. For these reasons, NHCs usually show strong σ-donating ability to the transition metal and NHC-transition metal complexes achieve high catalytic activity.[2] From such a viewpoint, the σ-donating ability of NHCs should be more and more improved. The most successful strategy for enhancing the σ-donating ability of NHCs is modification of the NHC scaffold, especially replacement of the nitrogen atom by other main group elements.[3] Recently, we reported a novel NHC (amino(phosphorus-ylide)carbene; APYC), in which a phosphorus ylide moiety is at the position adjacent to the carbene center instead of another nitrogen atom, and showed that APYC has the strongest electron-donating ability among known carbenes to date.[4–6] Because phosphorus ylides have a resonance structure with both a carbanion and a phosphonium cation, the ylide carbon can function as an electron donor, and the carbon has a much lower electronegativity than the nitrogen atom. These characteristics are the main features giving the strong electron-donating property of APYC. On the other hand, ylide species of sulfur have also been well known since the 19th century as well as phosphorus ylides, the ylide stability being higher in sulfur ylides than in phosphorus ylides.[7] For these reasons, we expected that the sulfur ylide would also be a good candidate for a substituent to enhance the electron-donating ability of carbenes. Herein we report the generation of a novel sulfur ylide-substituted carbene (amino(sulfur-ylide)carbene; ASYC) and the electron-donating properties of ASYC.



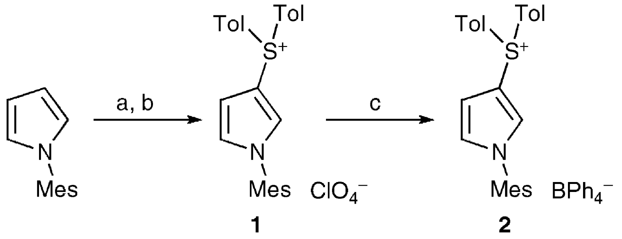
APYC



ASYC

The precursor **2** of ASYC was synthesized by modification of the reported procedure. In the literature procedure, unsubstituted pyrrole was used as a starting material, and the reaction gave a mixture of 2- and 3-sulfoniopyrrole (Scheme 1). However, introduction of the sterically hindered mesityl group on the nitrogen atom prevented substitution at the 2-position and gave the desired product **1** in moderate yield. After counter-anion exchange, **2** was isolated as a colorless solid. The structure of **2** was confirmed by X-ray crystallographic analysis. An ORTEP drawing of **2** is shown in Fig. 1.[8]

In the previous report, we confirmed the generation of APYC by the reaction of the corresponding precursor with MesLi and succeeded in trapping APYC with elemental sulfur and in synthesizing its transition metal complexes. ASYC was also generated from **2** using MesLi as a base and trapped by elemental sulfur at −40 °C (Scheme 2). The formation of thioamide **3** was suggested by mass spectroscopy, but its isolation by GPC or PTLC failed due to decomposition. However, subsequent treatment of thioamide **3** with MeI led



Scheme 1 Synthesis of carbene precursor **2**. *Reagents and conditions*: (a) $(CF_3CO)_2O$, $Tol_2S{=}O$, CH_2Cl_2; (b) aq. $LiClO_4$ (22% yield for 2 steps); (c) $NaBPh_4$, MeOH (83%).

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, 113-0033 Tokyo, Japan.
E-mail: takayuki@chem.s.u-tokyo.ac.jp; Fax: +81-3-5800-6899;
Tel: +81-3-5841-4338

† Electronic supplementary information (ESI) available: Synthesis of the compounds. CCDC 695652 and 695653. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b813454e

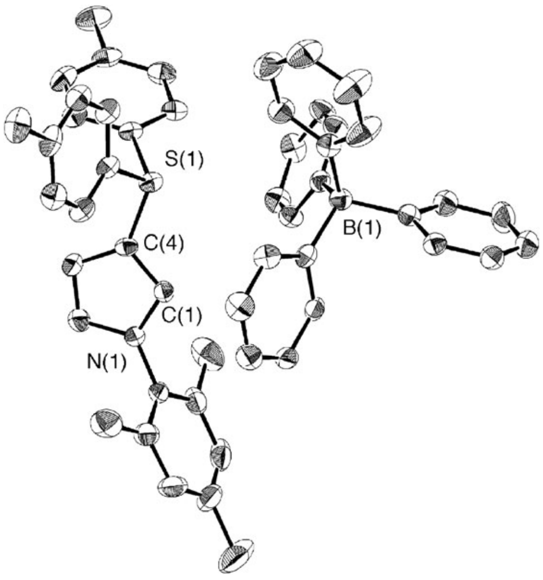
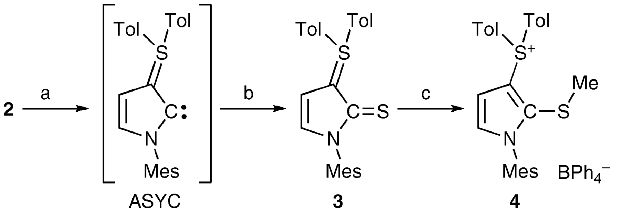


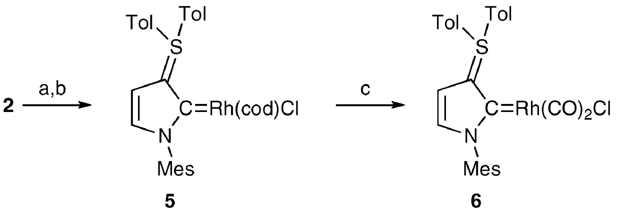
Fig. 1 ORTEP drawing of carbene precursor **2** (50% probability). Selected bond lengths and angles: C(1)–C(4) 1.371(3) Å; C(1)–N(1) 1.355(2) Å; S(1)–C(4) 1.730(2) Å; N(1)–C(1)–C(6) 107.24(17) Å.



Scheme 2 Generation and trapping of ASYC. *Reagents and conditions*: (a) MesLi, THF, −40 °C; (b) S_8, THF, −40 °C (not isolated); (c) MeI (90% yield for 3 steps).

to the isolation of methyl thioether **4** in 90% yield. These results indicate that ASYC can certainly be generated in good yield and has sufficient stability to be trapped by appropriate reagents at low temperature. We have also attempted the direct observation of ASYC at a lower temperature (−40 °C). Although we could observe the signal assignable to the carbene carbon by ^{13}C NMR (δ_C 198.9), unambiguous identification of ASYC failed because it was observed as a mixture with the starting material and an unidentified product (probably due to the decomposition of ASYC).

To elucidate the coordination properties of ASYC, the synthesis of the Rh complex of ASYC was examined. ASYC was generated by the method described above, and subsequent treatment with $[Rh(cod)Cl]_2$ afforded [(ASYC)Rh(cod)Cl] **5** (Scheme 3). In the ^{13}C NMR spectrum, the carbene carbon was observed at 179.7 ppm as a doublet ($^1J_{CRh}$ = 37.1 Hz) and the signal was shifted upfield compared with [(APYC)Rh(cod)Cl] (δ_C 200.6, $^1J_{CRh}$ = 40.3 Hz). **5** was converted to dicarbonyl complex **6** by reaction with carbon monoxide. **6** was characterized by ^{1}H and ^{13}C NMR and its structure was finally determined by X-ray crystallographic analysis. The ^{13}C NMR showed a chemical shift corresponding to the carbene center at 172.5 ppm with one-bond coupling to the Rh center ($^1J_{CRh}$ = 37.1 Hz). The chemical shift of the carbene center of **6** is also shifted upfield compared with that of $[(APYC)Rh(CO)_2Cl]$ (δ_C 187.8, $^1J_{CRh}$ = 35.7 Hz). However, it is very close to that of the $[(NHC)Rh(CO)_2Cl]$ complex **7** (δ_C 170.2, $^1J_{CRh}$ = 43 Hz).[9]



Scheme 3 Formation of ASYC–Rh complexes **5** and **6**. *Reagents and conditions*: (a) MesLi, THF, −40 °C; (b) $[Rh(cod)Cl]_2$, THF, −40 °C (40% yield for 2 steps); (c) CO(gas), THF (70%).

Single crystals of **6** were obtained by slow evaporation of an Et_2O–THF solution of **6**. The ORTEP drawing of **6** is shown in Fig. 2.[8] The Rh center has a square-planar structure (Σ_{Rh} = 359.88°) and the heterocyclic moiety is also planar (Σ_{ring} = 540.0°). These two planes are twisted relative to each other by 63.88°. The Rh–$C_{carbene}$ bond length (2.058(4) Å) is a normal value. The Rh–C_{CO} bond lengths are 1.912(5) Å for *trans* CO against ASYC and 1.816(5) Å for *cis* CO, indicating the *trans* influence of the ASYC ligand. The $C_{carbene}$–C_{ylide} bond length (1.397(6) Å) lies between those of single and double bonds, whereas $C_{carbene}$–N (1.382(5) Å) is slightly longer than those in the $[(NHC)Rh(CO)_2Cl]$ complex (1.349–1.350 Å). These tendencies were also observed in APYC–Rh complexes, meaning

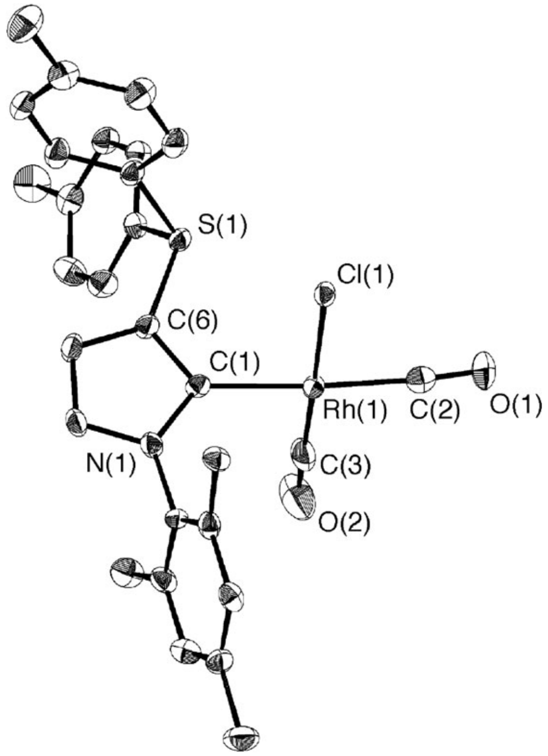
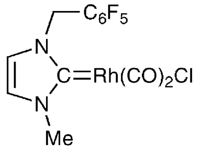


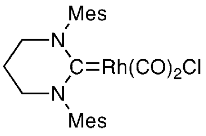
Fig. 2 ORTEP drawing of $[(ASYC)Rh(CO)_2Cl]$ **6** (50% probability). Selected bond lengths and angles: C(1)–C(6) 1.397(6) Å; C(1)–N(1) 1.382(5) Å; C(1)–Rh(1) 2.058(4) Å; S(1)–C(6) 1.727(4) Å; Rh(1)–C(2) 1.912(5) Å; Rh(1)–C(3) 1.816(5) Å; N(1)–C(1)–C(6) 102.9(3)°.

that π-donation from the ylide carbon to the carbene center is working effectively and π-donation from the nitrogen atom to the carbene center is smaller than observed in other NHC complexes.

The carbonyl stretching frequencies of *cis*-[LRh(CO)$_2$Cl] complexes are recognized as an index of the electron-donating properties of the ligand L. The average carbonyl stretching frequency of **6** (2019 cm^{-1}) was observed in the very low wavenumber region compared with IR data for known *cis*-[(carbene)Rh(CO)$_2$Cl] complexes (see, Table 1 of ref. 4), although the wavenumber is slightly higher than those of [(APYC)Rh(CO)$_2$Cl] (2012 cm^{-1}) and **8** (2018 cm^{-1}).[10] Taking the result of the APYC complex into consideration, it is suggested that ylide-stabilized carbenes generally show very strong σ-donating ability.



7



8

In summary, we have designed ASYC, a novel ylide-stabilized carbene, and succeeded in the generation of ASYC as well as the synthesis of Rh complexes containing ASYC. The high electron-donating ability of ASYC was demonstrated by comparison of the IR stretching frequencies of [LRh(CO)$_2$Cl] complexes. These results indicated that stabilization of the carbene center by the ylide moiety is a general and remarkable strategy for enhancement of the electron-donating ability of singlet carbene ligands. Such strong electron-donating abilities of ylide-stabilized carbenes promise an enhancement of the catalytic activity of transition metal complexes. The catalytic activity of ASYC–transition metal complexes is now under investigation.

This work was supported by the Global COE program for Chemical Innovation and for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (T.K.). We thank Tosoh Finechem Corp. for the generous gifts of alkyllithiums.

Notes and references

1 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.

2 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*b*) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247; (*c*) N. M. Scott and S. P. Nolan, *Eur. J. Inorg. Chem.*, 2005, 1815; (*d*) L. Cavallo, A. Correa, C. Costabile and H. Jacobsen, *J. Organomet. Chem.*, 2005, **690**, 5407; (*e*) R. H. Crabtree, *J. Organomet. Chem.*, 2005, **690**, 5451; (*f*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768.

3 (*a*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; (*b*) Y. Canac, M. Soleilhavoup, S. Conejero and G. Bertrand, *J. Organomet. Chem.*, 2004, **689**, 3857; (*c*) F. E. Hahn, *Angew. Chem., Int. Ed.*, 2006, **45**, 1348.

4 S.-y. Nakafuji, J. Kobayashi and T. Kawashima, *Angew. Chem., Int. Ed.*, 2008, **47**, 1141.

5 APYC–transition metal complexes have been synthesized by alternative intramolecular cyclization methods, see: (*a*) G. Facchin, R. Campostrini and R. A. Michelin, *J. Organomet. Chem.*, 1985, **294**, C21; (*b*) R. A. Michelin, G. Facchin, D. Braga and P. Sabatino, *Organometallics*, 1986, **5**, 2265; (*c*) R. A. Michelin, M. Mozzon, G. Facchin, D. Braga and P. Sabatino, *J. Chem. Soc., Dalton Trans.*, 1988, 1803; (*d*) G. Facchin, M. Mozzon, R. A. Michelin, M. T. A. Ribeiro and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 1992, 2827; (*e*) M. Tamm and F. E. Hahn, *Coord. Chem. Rev.*, 1999, **182**, 175; (*f*) A. J. L. Pombeiro, *J. Organomet. Chem.*, 2005, **690**, 6021.

6 The studies on aminoylidecarbene have been reported, see: M. Asay, B. Donnadieu, A. Baceiredo, M. Soleilhavoup and G. Bertrand, *Inorg. Chem.*, 2008, **47**, 3949.

7 V. Aggarwal and J. Richardson, in *Science of Synthesis*, ed. A Padwa, Georg Thieme, Stuttgart and New York, 2004, ch. 1, vol. 27, p. 21.

8 CCDC-695653 (**2**) and CCDC-695652 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. **Crystal data of 2**. $C_{51}H_{48}BNS{\cdot}CH_3OH$, M = 749.82, orthorhombic, a = 18.673(5), b = 23.053(7), c = 19.701(6) Å, U = 8481(4) Å^3, T = 120 K, space group *Pbca* (no. 61), Z = 852 084 reflections measured, 7364 unique (R_{int} = 0.0390) which were used in all calculations. The final $wR(F_2)$ was 0.1369 (all data). **Crystal data of 6**. $C_{29}H_{27}ClNO_2RhS$, M = 591.94, triclinic, a = 9.903(5), b = 11.130(5), c = 13.844(7) Å, α = 88.329(19), β = 77.738(17), γ = 66.558(14) deg, U = 1365.5(12) Å^3, T = 120 K, space group *P*–1 (no. 2), Z = 28 442 reflections measured, 4640 unique (R_{int} = 0.0315) which were used in all calculations. The final $wR(F_2)$ was 0.1242 (all data).

9 S. Burling, M. F. Mahon, S. P. Reade and M. K. Whittlesey, *Organometallics*, 2006, **25**, 3761.

10 M. Mayr, K. Wurst, K.-H. Ongania and M. R. Buchmeiser, *Chem.–Eur. J.*, 2004, **10**, 1256.