Isolation and Reaction of (Indolin-3-ylidene)pentacarbonyltungsten Generated from Tungsten-containing Azomethine Ylide

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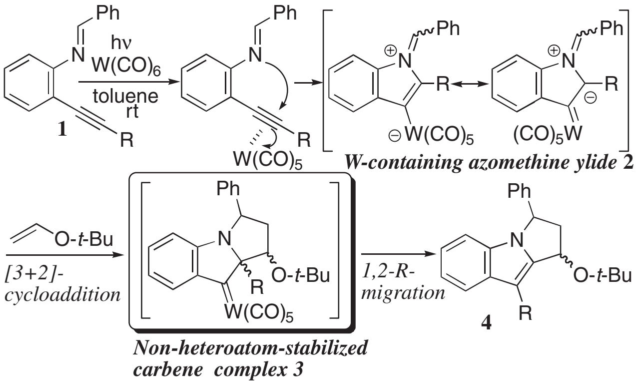
(Indolin-3-ylidene)pentacarbonyltungsten, a non-heteroatom-stabilized carbene complex of group 6 metal, was successfully isolated by the reaction of *N*-(*o*-alkynylphenyl)imine derivative, vinyl ether and tungstenhexacarbonyl under photoirradiation. This complex was moderately stable and fully characterized by spectroscopic analysis.

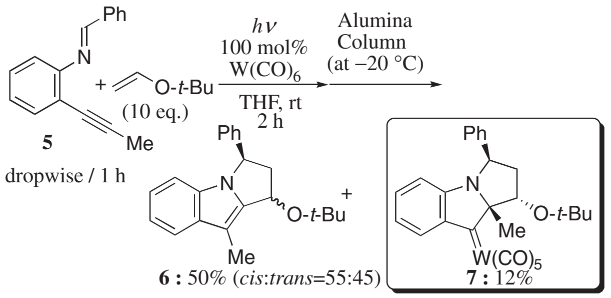
Fischer-type carbene complexes of group 6 metal pentacarbonyl have long been employed as a useful reagent in synthetic organic reactions. High utility of these complexes is partly due to their stability caused by electron-donation from the heteroatom on the carbene carbon.[1] On the contrary, although non-heteroatom-stabilized carbene complexes of group 6 metal pentacarbonyl have appeared as a key intermediate in various reactions,[2,3] the isolation of such complexes has rarely been achieved due to their high instability.[4,5]

We recently reported a novel method for the construction of polycyclic indole skeletons by the tungstenpentacarbonyl catalyzed reaction of *N*-(*o*-alkynylphenyl)imine derivatives (**1**) and electron-rich alkenes (Scheme 1).[6] It was postulated that novel tungsten-containing azomethine ylide species were generated by the reaction of **1** and tungstenpentacarbonyl, and they underwent [3+2]-cycloaddition reaction with electron-rich alkenes to afford non-heteroatom-stabilized tungsten carbene complexes (**3**), from which 1,2-migration of the substituent R (R = H, alkyl, aryl) occured to afford polycyclic indole derivatives. Such 1,2-migration of alkyl or aryl group is quite rare in group 6 metal carbene complexes and isolation of the intermediate carbene complex is highly desirable not only for the chemistry of non-heteroatom-stabilized carbene complexes but also for the establishment of the mechanism of this reaction. Herein we wish to report the successful isolation and characterization of the intermediate carbene complex **3** (R = Me, Scheme 1) and the unique reactivity of this non-heteroatom-stabilized carbene complex.



Scheme 1.

When Me-substituted alkyne **5** and *t*-butyl vinyl ether were treated with a stoichiometric amount of $W(CO)_6$ in THF under photoirradiation at room temperature, the reaction mixture immediately became deep blue and the color remained even after removal of the solvent. Further careful investigation revealed that the deep blue oil could be separated in 12% yield by alumina column chromatography with hexane-toluene (2:1) as an eluent at −20 °C without remarkable decomposition, along with the Me-migrated tricyclic indole derivatives **6** (50% yield, *cis*:*trans* = 55:45, Scheme 2).

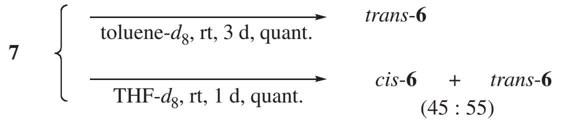


Scheme 2.

Extensive spectroscopic analysis (NMR (^1H, ^{13}C, DEPT, HMBC, HMQC, NOE), IR, high resolution mass spectrometry (FAB) and elemental analyses) revealed that this blue material was the (indolin-3-ylidene)pentacarbonyltungsten **7**.[7] The absorption of the pentacarbonyl was observed at 2053 and 1909 cm^{-1} in IR spectra and the carbene carbon was detected at 310.9 ppm by ^{13}C NMR, which was reasonable as compared with the values of the reported non-heteroatom-stabilized carbene complexes.[8] This carbene complex is rather stable and can be stored for several weeks at −20 °C under Ar without decomposition. This unexpected stability of **7** can be explained by considering the existence of a homologous conjugating effect from the nitrogen through the aromatic ring. This is a quite rare example of the isolation of non-heteroatom-stabilized group 6 metal pentacarbonyl carbene complex possessing alkyl substituent.[9]

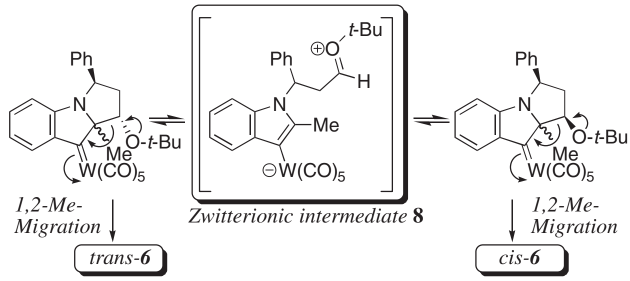
Interestingly, although the 1,2-Me-migrated product **6** was obtained as a mixture of *cis*- and *trans*-stereroisomers with low diastereoselectivity (55:45), the isolated carbene complex **7** was obtained as a single stereoisomer whose stereochemistry was determined by the measurement of the differential NOE spectrum as shown in Scheme 2.[10] We believe that the carbene complex **7** is most stable among the possible four isomers as this has the least steric repulsion between substituents (Me, Ph, and *t*-BuO).

Next, we investigated the reactivity of (indolin-3-ylidene)-pentacarbonyltungsten **7**. After several investigations, it was found that **7** slowly decomposed in toluene at room temperature to give the Me-migrated tricyclic indole derivative quantitatively after 3 days. The product was obtained as a single stereoisomer, which was confirmed to have the same *trans* relationship between the phenyl and *t*-BuO groups as shown in Scheme 3. This result strongly supports that, in the W(CO)$_5$ catalyzed preparation of polycyclic indole derivatives, a very rare 1,2-alkyl-migration is really occurring through the non-heteroatom stabilized carbene intermediate **7** as proposed previously.[11]



Scheme 3.

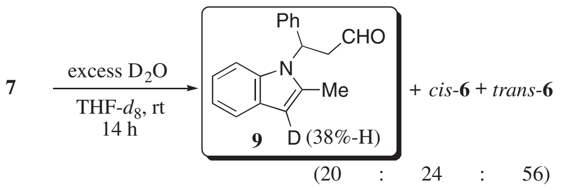
Very interestingly, when **7** was left at rt in THF instead of toluene, decomposition occurred within 1 day and the product was obtained *as a mixture of cis and trans 1,2-Me-migrated products (cis-**6**:trans-**6** = 45:55) quantitatively* (Scheme 3). This result indicates the existence of the equilibrium between the carbene complex **7** and a zwitterionic intermediate **8** through ring opening and closing reactions (retro-aldol and aldol type reactions) (Scheme 4). We propose that, in THF, recyclization from **8** proceeds in low stereoselectivity to afford up to four stereoisomeric carbene complexes, which undergo 1,2-Me-migration to give the mixture of *cis* and *trans*-**6** finally.[12] Difference of the reactivity in toluene and THF can be explained by considering the stability of the zwitterionic intermediate **8**, which is expected to be stabilized in a more polar solvent like THF.



Scheme 4.

The existence of the zwitterionic intermediate **8** was further confirmed by the experiment in the presence of D$_2$O. By the treatment of **7** in THF containing an excess amount of D$_2$O, aldehyde **9**, which is the hydrolyzed product of **8**, was obtained along with the 1,2-Me-migrated indoles (**9**:*cis*-**6**:*trans*-**6** = 20:24:56, Scheme 5). Formation of the aldehyde moiety and incorporation of a deuterium at the 3-position of the indole skeleton also support the existence of the zwitterionic intermediate **8**, and thus, the existence of ring opening and closing equilibrium by retro-aldol and aldol type reactions.

In summary, we have succeeded in isolating the non-heteroatom-stabilized tungsten carbene complex, (indolin-3-ylidene)-pentacarbonyltungsten, possessing aryl and *tert*-alkyl substituents on the carbene carbon. This non-heteroatom-stabilized tungsten carbene complex easily undergoes the 1,2-Me-migration to afford a tricyclic indole derivative and this result strongly supports the proposed reaction mechanism of the tungsten-containing azomethine ylides.



Scheme 5.

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References and Notes

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2 M. J. Winter, in “Comprehensive Organometallic Chemistry II,” ed. by E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon, New York (1995), Vol. 5, pp 168–172. See also ref 1a.

3 Examples for the catalytic process including a non-heteroatom-stabilized carbene complex as the key intermediate, see; a) N. Iwasawa, M. Shido, and H. Kusama, *J. Am. Chem. Soc.*, **123**, 5814 (2001). b) K. Miki, F. Nishino, K. Ohe, and S. Uemura, *J. Am. Chem. Soc.*, **124**, 5260 (2002).

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5 There are several reports on the synthesis and isolation of diarylcarbene complexes. a) C. P. Casey, T. J. Burkhardt, and C. A. Bunnell, *J. Am. Chem. Soc.*, **99**, 2127 (1977). b) K. H. Dötz and J. Preiffer, *Chem. Commun.*, **1996**, 895. Other examples for the isolation of non-heteroatom-stabilized carbene complexes, see; c) H. Fischer, S. Zeuner, and K. Ackermann, *J. Chem. Soc., Chem. Commun.*, **1984**, 684. d) K. Miki, T. Yokoi, F. Nishino, K. Ohe, and S. Uemura, *J. Organomet. Chem.*, **645**, 228 (2002).

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7 Spectroscopic data of **7**; IR (neat) 2917, 2053, 1909, 1607 cm^{-1}; ^{1}H NMR (500 MHz) $\delta = 1.16$ (s, 9H), 1.78 (s, 3H), 2.67 (ddd, $J = 13.8$, 10.7, 2.8 Hz, 1H), 3.12 (dd, $J = 13.8$, 7.8 Hz, 1H), 4.73 (dd, $J = 10.7$, 7.8 Hz, 1H), 4.91 (d, $J = 2.8$ Hz, 1H), 6.70 (brd, $J = 8.5$ Hz, 1H), 7.00 (ddd, $J = 8.5$, 8.1, 1.0 Hz, 1H), 7.35–7.38 (m, 3H), 7.41–7.46 (m, 2H), 7.63 (ddd, $J = 8.5$, 8.1, 1.2 Hz, 1H), 8.10 (brd, $J = 8.5$ Hz, 1H); ^{13}C NMR (125 MHz) $\delta = 24.1$, 29.2, 46.2, 61.4, 74.5, 77.6, 103.1, 113.2, 121.9, 125.4, 127.4, 128.8, 136.2, 141.8, 142.1, 151.7, 160.1, 199.2, 207.0, 310.9; HRMS Calcd for $C_{27}H_{25}NO_6W$, M 643.1191. Found m/z 643.1164.; Anal. Calcd for $C_{27}H_{25}NO_6W$: C, 50.41; H, 3.92; N, 2.18. Found: C, 50.67; H, 4.12; N, 2.13.

8 See Ref 1a, 4b, 5c.

9 There are few reports on the synthesis and isolation of alkylcarbene complexes of group 6 metal pentacarbonyl; see for examples; a) J. Preiffer and K. H. Dötz, *Organometallics*, **17**, 1353 (1998). b) K. H. Dötz, M. Papall, G. Müller, and K. Ackermann, *J. Organomet. Chem.*, **383**, 93 (1990).

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11 1,2-Alkyl migration of group 6 metal carbene intermediates is reported in a few, specific cases. See; a) M. Zora, J. W. Herndon, Y. Li, and J. Rossi, *Tetrahedron*, **57**, 5097 (2001). b) K. Nagao, M. Chiba, and S.-W. Kim, *Synthesis*, **1983**, 197.

12 No isomeric carbene complexes were observed during this NMR study.

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