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Acid-Promoted Isomerization of a Tungsten−η^1-2,5-Dihydropyrrolyl Complex to Its Tungsten−η^1-2,3-Dihydropyrrolyl Isomer

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*Summary: Treatment of the tungsten−η^1-2,5-dihydropyrrolyl complex **3** with a mixture of Ph_3CBF_4 and water in cold CH_2Cl_2 produced the tungsten−η^1-2,3-dihydropyrrolium cation **7**; this cation gradually lost one proton in CH_2Cl_2 at 23 °C, to yield the tungsten−η^1-2,3-dihydropyrrolyl species **5**.*

Transition-metal five-membered η^1-heterocyclics such as η^1-pyrrolyl, η^1-furyl, and η^1-thienyl complexes[1−3] have attracted considerable attention due to their interesting reaction chemistry. Most of them are prepared with the heterocyclic ring linked to the metal center at the C(2) carbon; few η^1-3-metalated heterocyclics have been reported.[1a,2b,3] Previously, we reported an unusual acid-catalyzed isomerization of tungsten−η^1-3-furyl to η^1-2-furyl species;[3] the reaction was proposed to proceed via a ring-opening mechanism involving a tungsten−η^2-alkyne tungsten−η^1-allenylidene rearrangement. In this paper, we report another atypical isomerization of a tungsten−η^1-2,5-dihydropyrrolyl complex to its η^1-2,3-dihydropyrrolyl isomer; the reaction intermediate has been successfully isolated in order to elucidate the isomerization mechanism.

Shown in Scheme 1 is the reaction between $CpW(CO)_3Na$ and bromopropargyl amine **1** in cold THF (0 °C, 4 h) to afford the tungsten−η^1-propargyl species **2** in 88% isolated yield; slight warming of a THF solution of **2** at 40 °C for 8 h led to intramolecular cyclization to give η^1-2,5-dihydropyrrole **3** and η^3-*anti*-γ-lactam **4** in 51 and 14% yields, respectively, after separation on a silica column. Complex **4** has an *anti* configuration, as characterized by the coupling constant $J_{34} = 0$ Hz. The *syn* isomer is expected to have the coupling constant value $J_{34} = 4-5$ Hz according to the NMR data for tungsten−η^3-γ-lactonyl species.[4]

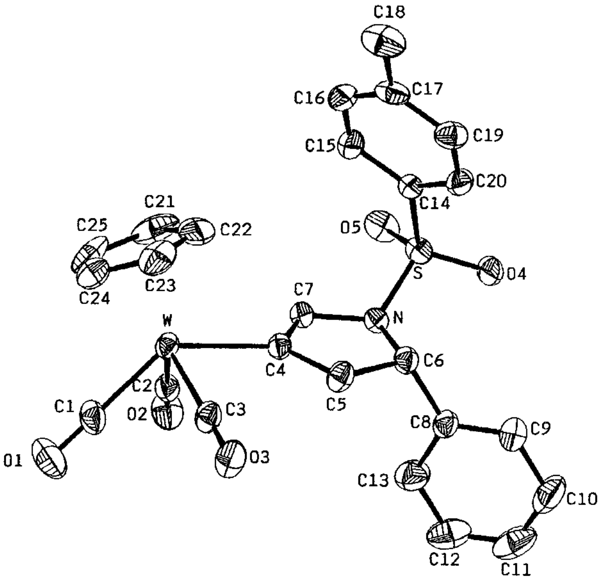

Figure 1. ORTEP drawing of tungsten−η^1-pyrrolyl complex **5**. Pertinent distances (Å): W−C(4) = 2.236(4), C(4)−C(7) = 1.327(6), C(7)−N = 1.446(6), C(6)−N = 1.490(6), C(4)−C(5) = 1.327(6).

Treatment of **3** with 1 equiv of CF_3CO_2H in CH_2Cl_2 (23 °C) effected the isomerization of **3** to its η^1-2,5-dihydropyrrolyl isomer **5** (Scheme 1, eq ii). The reaction, however, required a prolonged time (ca. 96 h) for completion, giving a 55% yield of **5** with some insoluble demetalated species persisting. The crystal structure of **5** is shown in Figure 1[5] to confirm the isomerization, which involves a 1,2-shift of the double bond of the pyrrolyl ring. We employed the stronger acid CF_3SO_3H to increase the reaction rate in an attempt to isolate the reaction intermediate; unfortunately, we obtained the tungsten−η^1(N)-2,3-dihydropyrrole **6** salt exclusively (92% yield), which was fully characterized by IR, ^1H and ^{13}C NMR, and elemental analyses. We later discovered that treatment of **3** with a mixture of purified Ph_3CBF_4 (1.5 equiv) and water (1.0 equiv) in cold CH_2Cl_2 (0 °C, 2 h) generated the cationic tungsten species **7**, which was purified by rapid crystallization twice in cold CH_2Cl_2/diethyl ether (−30 °C); the yield was 56%. This salt could also be prepared from unpurified Ph_3CBF_4 (2.0 equiv) in 46% yield. Attempts to grow single crystals of **7** were hampered by its kinetic instability as well as its poor crystallinity. If the NMR sample ($CDCl_3$) was allowed to stand at 23 °C for 36 h, species **7** gradually

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(1) For transition-metal−η^1-furyl compounds, see: (a) Jones, W. D.; Dong, L.; Myers, A. W. *Organometallics* **1995**, *14*, 855. (b) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583. (c) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 3800. (d) Pannell, K. H.; Cea-Olivares, R.; Toscano, R. A.; Kapoor, R. N. *Organometallics* **1987**, *6*, 1821.

(2) For transition metal−η^1-pyrrolyl and −η^1-thienyl compounds, see: (a) Johnson, T. D.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728. (b) Robertson, M. J.; White, C. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1994,** *116*, 5190. (c) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (d) Ng, M. M. P.; Roper, W. R.; Wright, L. J. *Organometallics* **1994**, *13*, 2563. (e) Erker, G.; Petrenz, R.; Kruger, C.; Lutz, F.; Weiss, A.; Werner, S. *Organometallics* **1992**, *11*, 1646.

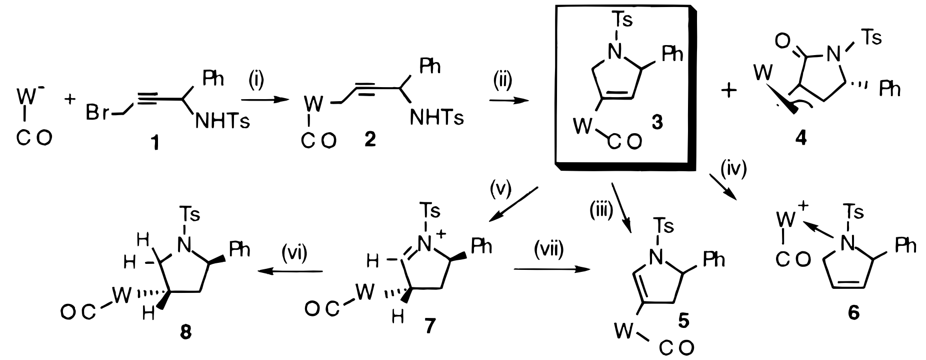
(3) (a) Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530. (b) Wang, S.-H.; Shiu, L.-H.; Shu, H.-G.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1994**, *116*, 5967.

(4) Chen, C.-C.; Fan, J.-S.; Shieh, S.-J.; Lee, G.-H.; Peng, S.-M.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 9279.

(5) Compound **5** crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.1136(13)$ Å, $b = 10.999(2)$ Å, $c = 12.543(5)$ Å, $\alpha = 67.33(3)°$, $\beta = 71.770(21)°$, $\gamma = 72.78(3)°$, $V = 1198.1(7)$ Å^3, and $Z = 2$. Final $R = 0.0240$ and $R_w = 0.026$ for 3569 reflections $>2.0\sigma(I)$, out of 4192 unique reflections.

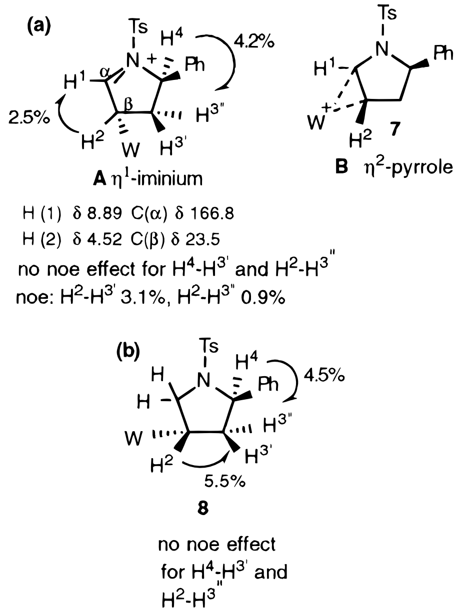
S0276-7333(97)00563-3 CCC: $14.00

Scheme 1[a]

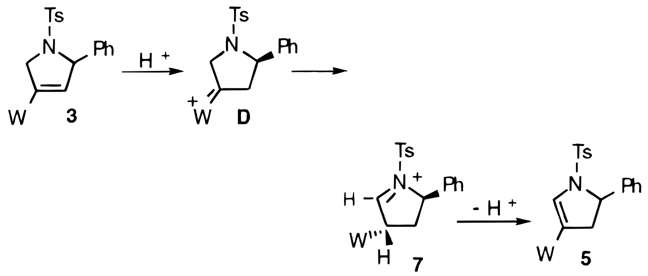


[a] Legend: W = CpW(CO)$_2$; (i) THF, 0 °C, 4 h, (ii) 40 °C, 8 h; (iii) CF_3CO_2H (1.0 equiv), 23 °C, 96 h; (iv) CF_3SO_3H (1.0 equiv), −40 °C, 2 h; (v) Ph_3CBF_4 (1.5 equiv) H_2O (1.0 equiv), (vi) $LiAlH_4$ (2.0 equiv); (vii) 23 °C.

Chart 1



Scheme 2[a]



[a] W = CpW(CO)$_3$.

lost one proton to generate **5** at a 42% conversion level. Assignment of the ^1H and ^{13}C NMR signals of **7** were made on the basis of proton NOE effects and $^1H-^{13}C$ NMR correlation spectra. Key NMR data for **7** are depicted in Chart 1. Spectral data for **7** suggest that the structure is more consistent with the η^1-iminium salt **A** rather than the η^2-pyrrole species[6a] **B**. Diagnostic for the structure are the large ^1H and ^{13}C NMR chemical shifts of $C_\alpha H^1$ (C_α, δ 166.8; H^1, δ 8.89) characteristic of an iminium group. The C_β carbon has a small chemical shift at δ 23.5 ppm characteristic of a sp^3-hybridized carbon. Moreover, the proton coupling constant J_{12} = 0−1 Hz shows a large dihedral angle (75−90°) between the C−H^1 and C−H^2 bonds. The proposed structure is also supported by proton NOE effects; irradiation of the H^2 signal gave a 3.1% intensity increase in the $H^{3'}$ signal, whereas the intensity of the $H^{3''}$ signal is only increased by 0.9%. One discrepancy here is the absence of the υ(C=N) vibration in the 1600−1750 cm^{-1} region; we envisage that this η^1-bonding mode is probably mixed with some signals of the η^2-bonding **B** with a weak W−C_α interaction. In this manner, the structure of **7** can be best described as an intermediate between η^1-iminium **A** and η^2-pyrrole **B**.

The $C_\beta H$ proton of the cation **7** was readily deprotonated by Et_3N (2.0 equiv) in CH_2Cl_2 to afford **5** in quantitative yield, as shown in Scheme 1. Reduction of **7** with $LiAlH_4$ in CH_2Cl_2 yielded the η^1-tetrahydropyrrolyl species **8** as a single diastereomer in 68% yield in addition to **5** (21%). The stereochemistry of **8** was determined by proton NOE difference spectra; the NOE map in part b of Chart 1 concludes that the CpW(CO)$_3$ and phenyl groups are on opposite sides relative to the pyrrolyl plane.

Clearly, the cation **7** is the intermediate in the isomerization of η^1-2,5-dihydropyrrole **3** to η^1-2,3-dihydropyrrole **5**. Scheme 2 depicts a plausible mechanism for this isomerization. The action of Ph_3CBF_4 with water is expected to release one proton. The isomerization is initiated by addition of this proton at the =C_γ carbon[7] of **3** to yield the tungsten−η^1-3-pyrrolylidenium species **D**, which subsequently undergoes a 1,2-hydrogen shift[8] to yield the η^1-pyrrolium cation **7**. The CpW(CO)$_3$ fragment of **7** preferably coordinates to the C_β carbon opposite the phenyl group to avoid steric interactions; this stereochemistry is inferred from the structure of its related derivative **8**. Further loss of the C_β proton[9] of **7** yields the η^1-2,3-dihydropyrrole species **5**. The role of Ph_3CBF_4 is to generate a proton with suitable acidity to effect the formation of the η^1-iminium intermediate **7**. If CF_3CO_2H was employed, the formation rate of **7**

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[6] (a) Hodges, L. M.; Moody, M. W.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 7931. (b) Myers, W. H.; Koontz, J. L.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684. (c) Ofial, A.; Mazyr, H., *J. Org. Chem.* **1996**, *61*, 5823.

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[8] (a) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (b) Casey, C. P.; Miles, W. H.; Kukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

[9] For formation of a metal−η^1-vinyl complex via deprotonation of a metal-η^2-olefin cation, see the representative example: Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729.

would be too slow compared to the loss of the $C_\beta H$ proton of **7**; a stronger Brønsted acids such as CF_3SO_3H and $HBF_4 \cdot Et_2O$ cleaved the σ W−C bond to yield the $\eta^1(N)$-pyrrole cation **6** instead.

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Supporting Information Available: Text giving spectral data for the new compounds **2**−**8** and tables of crystal data, atomic coordinates, and bond distances and angles for compound **5** (12 pages). Ordering information is given on any current masthead page.

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