J. Am. Chem. Soc. **1994**, *116*, 7433–7434 7433

1-Pyrrolylimido Complexes of Molybdenum and Tungsten: Synthesis of Pyrrole from Molecular Dinitrogen and Unusual β-Regioselective Substitution Reactions of the Pyrrole Ring on a Metal Complex[1]

Hidetake Seino, Youichi Ishii, and Masanobu Hidai*

Department of Chemistry and Biotechnology
Faculty of Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

Received May 10, 1994

Direct synthesis of organonitrogen compounds from molecular dinitrogen has been of extensive interest. An approach based on the chemical transformation of coordinated dinitrogen provides one of the most promising methods for that purpose.[2] Dinitrogen coordinated to molybdenum and tungsten is known to be converted into various organonitrogen ligands such as organohydrazido, organodiazenido, and diazoalkane ligands, which can be released from the metal as organonitrogen compounds such as alkylamines and azines under appropriate conditions. One of the most attractive targets from a standpoint of synthetic organic chemistry is to develop a method for preparation of nitrogen heteroaromatics from molecular dinitrogen. We have so far established the formation of diazoalkane complexes[3] by way of the condensation of carbonyl compounds with hydrazido(2–) complexes $[\mathrm{MX}(\mathrm{NNH}_2)(\mathrm{L})_4]^+$ or $[\mathrm{MX}_2(\mathrm{NNH}_2)(\mathrm{L})_3]$ (M = Mo, W; L = phosphine),[3a,4] which in turn are readily obtained from the protonation of dinitrogen complexes of the type $[\mathrm{M}(\mathrm{N}_2)_2(\mathrm{L})_4]$. The unique reactivities of the diazoalkane complexes have also been investigated in this laboratory.[5] We have now tried to use a succinaldehyde equivalent in the above condensation reaction in order to form the pyrrole ring.

The reaction of hydrazido(2–) complexes $[\mathrm{MF}(\mathrm{NNH}_2)(\mathrm{dpe})_2][\mathrm{BF}_4]$ (**1a**, M = Mo; **1b**, M = W, dpe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) with 2,5-dimethoxytetrahydrofuran in the presence of $\mathrm{HBF_4}$ gave 1-pyrrolylimido complexes $[\mathrm{MF}(\mathrm{N}\overline{\mathrm{NCH{=}CHCH{=}C}}\mathrm{H})(\mathrm{dpe})_2][\mathrm{BF}_4]$ (**2a**, M = Mo; **2b**, M = W) in good yields (eq 1).[6] The ^{13}C NMR spectrum of the tungsten complex **2b** in $\mathrm{CD_2Cl_2}$ showed signals due to α- and β-carbons of the pyrrole ring at δ 119.4 and 106.1, respectively, which were comparable to those of pyrrole (δ 118.0 (α-C), 107.7 (β-C)). In contrast, two triplets at δ 4.88 and 5.41 ($\mathrm{CD_2Cl_2}$, J = 2.3 Hz) in the ^{1}H NMR spectrum of **2b** were assigned to the α- and β-protons of the pyrrole ring, respectively, which exhibited considerable higher field shifts in comparison with those of pyrrole (δ 6.62 (α-H), 6.05 (β-H)) because of the shielding effect of the phenyl groups of the dpe ligands. The molecular structure of **2b** was further confirmed by the X-ray diffraction method.[7] As shown in Figure 1, the terminal nitrogen atom of the hydrazido ligand in **1b** (N(2)) is incorporated in the pyrrole ring to form the pyrrolylimido ligand. The structure of the pyrrolyl ring is essentially similar to that of pyrrole. The W–N(1)–N(2) bond is nearly linear, and the W and N(1) atoms lie almost in the plane of the pyrrole ring. The N(1)–N(2) bond (1.41(1) Å) is longer than those reported for similar hydrazido complexes (1.25–1.38 Å).[8]

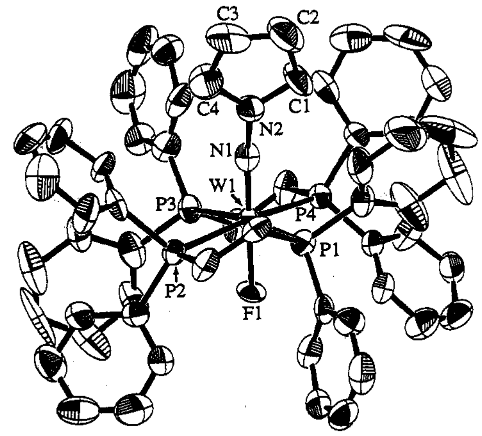
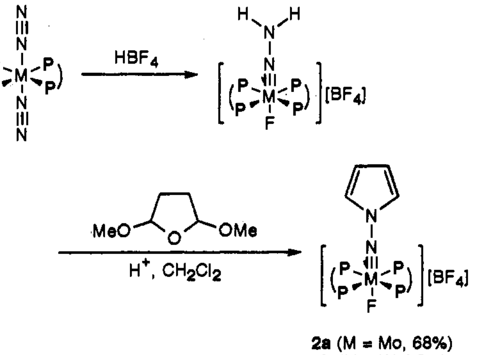


Figure 1. ORTEP drawing for the cationic part of **2b** (hydrogen atoms are omitted). Selected bond lengths (Å) and angles (deg): W–N(1), 1.74(1); N(1)–N(2), 1.41(1); N(2)–C(1), 1.39(1); N(2)–C(4), 1.39(1); C(1)–C(2), 1.35(2); C(2)–C(3), 1.42(2); C(3)–C(4), 1.32(2); W–N(1)–N(2), 173.8(8); N(1)–N(2)–C(1), 124.1(10); N(1)–N(2)–C(4), 124.8(10); C(1)–N(2)–C(4), 111.0(9); N(2)–C(1)–C(2), 107(1); C(1)–C(2)–C(3), 104(1); C(2)–C(3)–C(4), 113(1); N(2)–C(4)–C(3), 103(1).



(1)

2a (M = Mo, 68%)
2b (M = W, 75%)

Reduction with $\mathrm{LiAlH_4}$ was found to be effective for the purpose of liberating pyrrole from the pyrrolylimido complexes. Thus, when tungsten complex **2b** was treated with an excess amount of $\mathrm{LiAlH_4}$ at room temperature in THF for 2 h, pyrrole was obtained in 85–87% GC yield after workup with MeOH. A small quantity of *N*-aminopyrrole (*ca.* 10–14%) was also formed (eq 2).[9] It should be pointed out that the liberation of pyrrole from the metal occurred smoothly under milder conditions than those for

---

[1] Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 45. Part 44: Harada, Y.; Aoshima, T.; Mizobe, Y.; Oshita, H.; Hidai, M. *Chem. Lett.* **1994**, 797.

[2] (a) Hidai, M.; Mizobe, Y. In *Molybdenum Enzymes, Cofactors and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993; Chapter 22. (b) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2, p 53. (c) George, T. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; Chapter 13. (d) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, Chapter 60.

[3] (a) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740. (b) Bevan, P. C.; Chatt, J.; Hidai, M.; Leigh, G. J. *J. Organomet. Chem.* **1978**, *160*, 165. (c) Mizobe, Y.; Uchida, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1781.

[4] (a) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074. (b) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694. (c) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766.

[5] (a) Ishii, Y.; Miyagi, H.; Jitsukuni, S.; Seino, H.; Harkness, B. S.; Hidai, M. *J. Am. Chem. Soc.* **1992**, *114*, 9890. (b) Seino, H.; Ishii, Y.; Hidai, M. *Organometallics* **1994**, *13*, 364.

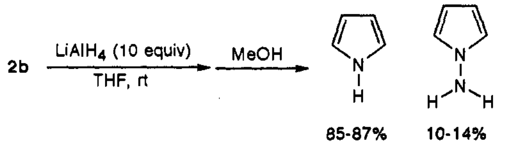
[6] The reaction of **1** with acetonylacetone under the same conditions did not afford the 2,5-dimethyl analogue of **2** but a diazoketone complex $[\mathrm{MF}(\mathrm{NN{=}CMe(CH_2)_2COMe})(\mathrm{dpe})_2][\mathrm{BF}_4]$.

[7] Crystal data: $\mathrm{C_{56}H_{52}N_2BF_5P_4W}$, M = 1166.59; monoclinic, space group Cc; a = 17.570(2) Å, b = 14.633(8) Å, c = 20.078(2) Å, β = 91.904(9)°; V = 5158(2) Å^3; Z = 4; D_{calcd} = 1.502 g/cm^3, D_{obsd} = 1.496 g/cm^3; μ(Mo Kα) = 24.64 cm^{-1}; R = 0.043, R_{w} = 0.025 for 4452 reflections with $I > 3\sigma(I)$.

[8] (a) Oshita, H.; Mizobe, Y.; Hidai, M. *Organometallics* **1992**, *11*, 4116. (b) Aoshima, T.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1992**, *423*, 39. (c) Barclay, J. E.; Hills, A.; Hughes, D. L.; Leigh, G. J.; Macdonald, C. J.; Bakar, M. A.; Mohd.-Ali, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2503 and references are cited therein.

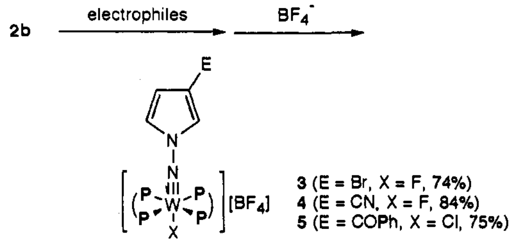
[9] Pyrrole and *N*-aminopyrrole were identified by comparing their GC-MS spectra with those of the authentic samples.

0002-7863/94/1516-7433$04.50/0



(2)

the corresponding reductions of alkylhydrazido or alkyldiazenido complexes with dpe ligands.[10] The facile cleavage of the N–N bond is considered to reflect the relatively long N–N bond distance in complex **2b**, *i.e.*, the reduced bond multiplicity of the N–N bond, compared with those in usual alkylhydrazido complexes. This is accounted for by the participation of the lone pair electrons on the N(2) atom in forming the 6π aromatic system; these electrons otherwise delocalize over the W–N–N moiety.



(3)

The pyrrole ring newly formed on the tungsten complex was found to undergo β-selective electrophilic substitution reactions. When **2b** was treated with *N*-bromosuccinimide (NBS) in THF at -10 °C, the β-bromo derivative **3** was obtained in 74% yield, and no α-brominated complex was detected in the ^{1}H NMR spectrum of the crude product (eq 3). The β-bromopyrrole structure of **3** was confirmed by ^{1}H and ^{13}C NMR[11] and fully characterized by X-ray analysis.[12] Further, exclusive β-cyanation and β-benzoylation of **2b** were also achieved by reaction with chlorosulfonyl isocyanate/DMF (0 °C)[13] and benzoyl chloride/$AlCl_3$ (0 °C), respectively,[11] although the latter reaction was accompanied by the halogen exchange on the tungsten atom.[14]

Since electrophilic substitutions of usual pyrrole derivatives are known to occur mostly at the α-position, it is of interest that the regioselectivity was completely changed in the reaction of **2b**. This fact may be explained by the steric effect of dpe ligands surrounding the pyrrole ring. The phenyl groups of dpe ligands effectively protect the α-position of the pyrrole ring, and therefore the electrophiles selectively attack the β-position. In order to realize the β-functionalization of pyrrole, reactivities of several *N*-substituted pyrroles have been investigated.[15] However, the β-selectivity of cyanation was not able to be controlled even by introducing the triisopropylsilyl group (TIPS),[15b] one of the most effective *N*-substituents to favor the β-selective substitution reactions of pyrrole. Therefore, essentially complete β-regiocontrol achieved by using **2b** is outstanding.

In conclusion, the chemistry of the 1-pyrrolylimido complex was found to be interesting not only in that it realized the mild, high-yield conversion of molecular dinitrogen into pyrrole in a fully defined manner but also in that the complex exhibited unusual regioselectivity in pyrrole substitution reactions. These findings provide a new possibility for the transformation of coordinated dinitrogen into organonitrogen compounds which are not prepared by conventional methods. Further reactivities of the 1-pyrrolylimido complexes as well as novel construction of various nitrogen heterocycles on metal complexes starting from molecular dinitrogen are now under investigation.

Acknowledgment. We are grateful for financial support from a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture of Japan.

Supplementary Material Available: Experimental procedures for the preparation of compounds **2a,b** and **3–5** and reduction of **2b**; crystallographic data for **2b**; tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **2b** (12 pages); tables of observed and calculated structure factors for **2b** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(10) Reaction temperatures of 75–150 °C and reaction times of 16–65 h were necessary. (a) Bevan, P. C.; Chatt, J.; Leigh, G. J.; Leelamani, E. G. *J. Organomet. Chem.* **1977**, *139*, C59. (b) Bossard, G. E.; Busby, D. C.; Chang, M.; George, T. A.; Allen Iske, S. D., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 1001.

(11) Selected spectroscopic data for **3–5** are as follows. **3**: ^{1}H NMR (CD_2Cl_2) δ 4.34 (br t, *J* = 2.0 Hz), 4.73 (br t, *J* = 2.8 Hz), 5.43 (dd, *J* = 3.2, 1.7 Hz); ^{13}C NMR (CD_2Cl_2) δ 93.9, 108.7, 118.9, 119.6. **4**: ^{1}H NMR (CD_2Cl_2) δ 4.61 (br t, *J* = 2.0 Hz), 4.89 (dd, *J* = 3.2, 2.2 Hz), 5.71 (dd, *J* = 3.2, 1.7 Hz); ^{13}C (CD_2Cl_2) δ 90.6, 108.7, 114.6, 120.1, 126.0; IR (KBr) 2228 cm^{-1} (ν(C$\equiv$N)). **5**: ^{1}H NMR (CD_2Cl_2) δ 4.81 (br t, *J* = 2.0 Hz), 4.89 (dd, *J* = 3.2, 2.2 Hz), 6.02 (dd, *J* = 3.2, 1.7 Hz); ^{13}C NMR (CD_2Cl_2) δ 107.9, 120.7, 121.1, 125.9, 188.7; IR (KBr) 1642 cm^{-1} (ν(C=O)).

(12) The details will be reported elsewhere.

(13) Lohaus, G. *Ber. Dtsch. Chem. Ges.* **1967**, *100*, 2719.

(14) Replacement of the F atom by a Cl atom was revealed from disappearance of the P–F coupling in ^{31}P NMR spectrum (J_{PF} = 44 Hz for **2b**) as well as the elemental analysis of **5**.

(15) (a) Anderson, H. J.; Loader, C. E.; Xu, R. X.; Lê, N.; Gogan, N. J.; McDonald, R.; Edwards, L. G. *Can. J. Chem.* **1985**, *63*, 896. (b) Bray, B. L.; Mathies, P. H.; Naef, R.; Solas, D. R.; Tidwell, T. T.; Artis, D. R.; Muchowski, J. M. *J. Org. Chem.* **1990**, *55*, 6317.