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Selective N–N and W–N Bond Cleavage of Tungsten Pyrrolylimido Complexes Derived from Tungsten Dinitrogen Complex[1)]

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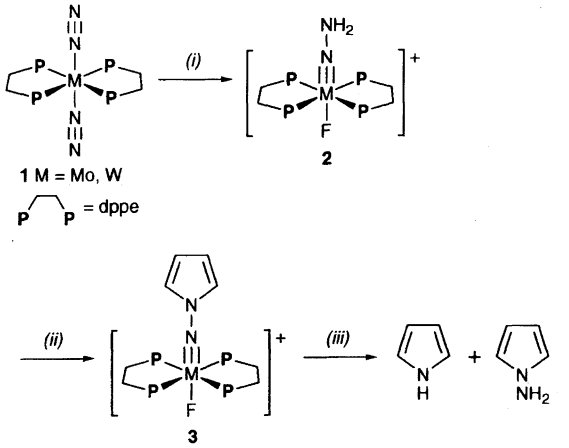
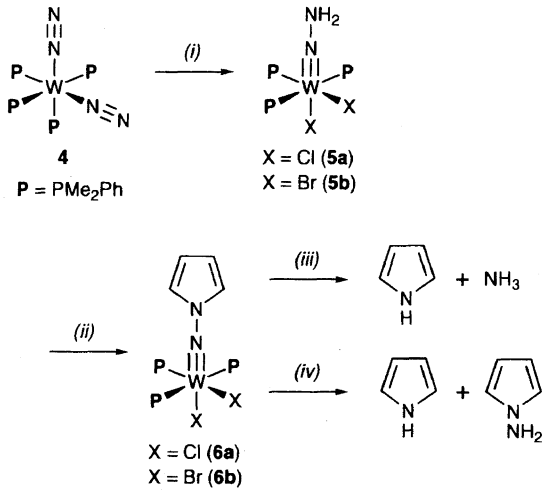
Treatment of the pyrrolylimido complexes *cis,trans*-[WX_2(NNCH=CHCH=CH)(L)(PMe_2Ph)$_2$] (X = Cl, Br, I; L = PMe_2Ph (**6**), $CNBu^t$, CO, PhC≡CH, PhCHO, Br) with $LiAlH_4$ or KOH produced pyrrole, 1-aminopyrrole, and ammonia, where both the reaction conditions and the nature of the ligand L showed significant effects on the pyrrole/1-aminopyrrole selectivity. Thus, reduction of *cis,trans*-[WBr_2(NNCH=CHCH=CH)($CNBu^t$)(PMe_2Ph)$_2$] with $LiAlH_4$ followed by methanolysis gave pyrrole and ammonia in almost quantitative yields. On the other hand, 1-aminopyrrole was quantitatively produced from the complexes by the reaction of KOH in alcohol when L = CO, PhC≡CH, or PhCHO. While analogous treatment of **6** with KOH in ethanol afforded both pyrrole and 1-aminopyrrole with low selectivity under N_2 atmosphere, 1-aminopyrrole was produced from **6** in excellent yield under 1 atm of CO. On the contrary, pyrrole and ammonia were selectively formed from the reaction of **6b** (X = Br) with KOH/18-crown-6 ether in THF. Replacement of one of the PMe_2Ph ligands in the diazoalkane complex *cis,mer*-[WBr_2(NN=CMeCH$_2$CH$_2$COMe)(PMe_2Ph)$_3$] (**12**) by CO or $CNBu^t$ facilitated the cyclization of the diazoalkane ligand to provide the (2,5-dimethylpyrrolyl)imido complexes *cis,trans*-[WBr_2(NNCMe=CHCH=CMe)(L)(PMe_2Ph)$_2$] (L = CO **14**; L = $CNBu^t$ **15**), although complex **12** failed to undergo the ring closure by aqueous HBr. 2,5-Dimethylpyrrole and 1-amino-2,5-dimethylpyrrole were selectively obtained by $LiAlH_4$ reduction of **15** and by treatment of **14** with KOH in EtOH, respectively.

In our continued study on chemical nitrogen fixation[2,3)] to synthesize organonitrogen compounds directly from dinitrogen under mild conditions,[4)] we have previously reported that pyrrolylimido complexes of the type *trans*-[MF(NNCH=CHCH=CH)(dppe)$_2$]$^+$ (**3**; M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$) are prepared by condensation of 2,5-dimethoxytetrahydrofuran with hydrazido(2−) complexes *trans*-[$MF(NNH_2)(dppe)_2$]$^+$ (**2**) readily derived from molybdenum and tungsten dinitrogen complexes *trans*-[$M(N_2)_2(dppe)_2$] (**1**) (Scheme 1).[4c)] The resulting organonitrogen ligand can be released from the metal as pyrrole and 1-aminopyrrole (mainly pyrrole) by treatment with $LiAlH_4$ followed by methanolysis. In a similar way, the tungsten dinitrogen complex with PMe_2Ph ligands *cis*-[$W(N_2)_2(PMe_2Ph)_4$] (**4**) gives rise to the formation of the analogous pyrrolylimido complexes *cis,mer*-[WX_2(NNCH=CHCH=CH)(PMe_2Ph)$_3$] (X = Cl (**6a**), Br (**6b**)), which liberate pyrrole by treatment with $LiAlH_4$ and produce a mixture of pyrrole and 1-aminopyrrole by reaction with KOH in alcohols. The ratio of pyrrole and 1-aminopyrrole in the latter reaction depends sharply on the nature of the alcohol solvent and the halogen ligand (Scheme 2). Here we wish to report the cleavage of the pyrrolylimido ligand in a new series of complexes derived from **6** by replacement of one of three PMe_2Ph ligands with π-acceptor ligands, together with W(V) pyrrolylimido complexes. The factors



(i) Aqueous HBF_4, THF; *(ii)* 2,5-dimethoxytetrahydrofuran, aqueous HBF_4, CH_2Cl_2; *(iii)* $LiAlH_4$, THF, then MeOH

Scheme 1.



(i) Aqueous HX, MeOH; *(ii)* 2,5-dimethoxytetrahydrofuran, aqueous HX, THF; *(iii)* $LiAlH_4$, THF, then MeOH; *(iv)* KOH, alcohol

Scheme 2.

which govern the selective N–N and W–N bond cleavage of the pyrrolylimido ligand in those complexes have now been elucidated in detail.

Experimental

All reactions were carried out under a dry nitrogen atmosphere unless otherwise specified. Solvents were dried by usual methods and distilled before use. Reagents were commercially obtained and used as received. NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^{1}H 270 MHz, ^{13}C 67.9 MHz, ^{31}P 109 MHz) and IR spectra were recorded on a Shimadzu FTIR-8100M spectrophotometer. Elemental analyses were performed on a Perkin–Elmer 2400 series II CHN analyzer (C, H, N). Electrochemical measurements were made by Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) using a glassy carbon working electrode; potentials were measured vs a saturated calomel electrode as reference.

Preparations of Pyrrolylimido Complexes. The iodo analogue *cis,mer*-[WI_2(NNCH=CHCH=CH)(PMe_2Ph)$_3$] (**6c**) was prepared from *cis,mer*-[$WI_2(NNH_2)(PMe_2Ph)_3$] (**5c**) by a procedure similar to that described for **6a** and **6b**.[4c] By modification of the literature method described for diazoalkane complexes, the pyrrolylimido complexes with π-acceptor ligands *cis,trans*-[WX_2(NNCH=CHCH=CH)(L)(PMe_2Ph)$_2$] were obtained by the reactions of **6** with L (**7**: Bu^{t}NC (1 equiv), **8**: CO (1 atm), **9**: PhC≡CH (3 equiv), **10**: PhCHO (3 equiv)) at 70 °C for 24 h, and *trans*-[WBr_3(NNCH=CHCH=CH)(PMe_2Ph)$_2$] (**11**) was synthesized by treatment of **6b** with CH_2Br_2 (7 equiv) at 80 °C for 5.5 h. Spectroscopic and analytical data for all new compounds were deposited as Document No. 72007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

***cis,trans*-[WBr_2(NNCMe=CHCH=CMe)(CO)(PMe_2Ph)$_2$] (14). Method I.** The diazoalkane complex *cis,mer*-[WBr_2(NN=CMeCH$_2$CH$_2$COMe)(PMe_2Ph)$_3$] **12**[4a] (30 mg, 0.034 mmol) was dissolved in THF (3 ml) and heated at 55 °C for 36 h under 1 atm of CO. The ^{1}H NMR spectrum of the resulting crude mixture showed that the starting complex **12** was almost consumed and the diazoalkane–CO complex *cis,trans*-[WBr_2(NN=CMeCH$_2$CH$_2$COMe)-(CO)(PMe_2Ph)$_2$] **13** was formed. Concentrated hydrobromic acid (1 drop) was then added to the mixture at room temperature. After the mixture was stirred for 3 h, the solvent was removed under reduced pressure. The resultant pale green sticky oil was extracted with diethyl ether, and the extract was evaporated to dryness. Recrystallization from benzene/hexane afforded yellowish green crystals of **14**, which were filtered, washed with hexane, and dried in vacuo (7.0 mg, 27%). Found: C, 36.09; H, 4.00; N, 3.58%. Calcd for $C_{23}H_{30}Br_2N_2OP_2W$: C, 36.54; H, 4.00; N, 3.71%. ^{1}H NMR (C_6D_6, 24 °C) δ = 1.73 (s, 6 H, α-Me), 1.88, 1.93 (t, 6 H each, J = 4.1 Hz, PMe), 5.22 (s, 2 H, β-H), 6.8—7.4 (m, 10 H, PPh); ^{31}P{^{1}H} NMR (C_6D_6, 24 °C) δ = −18.8 (s with ^{183}W satellites, J_{PW} = 278 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 24 °C) δ = 12.4 ($^1J_{CH}$ = 128 Hz, α-Me), 104.0 ($^1J_{CH}$ = 172 Hz, β-H), 247.1 (t, J_{CP} = 5 Hz, CO). IR (KBr) 1941 cm^{-1} (C≡O). Selected spectroscopic data for **13**: ^{1}H NMR (C_6D_6, 24 °C) δ = 0.94 (s, 3 H, NN=CMe), 1.42 (t, 2 H, J = 6.3 Hz, NN=CCH$_2$), 1.68 (s, 3 H, COMe), 1.86 (t, 2 H, J = 6.3 Hz, CH$_2$CO), 1.98, 1.99 (t, 6 H each, J = 4.0 Hz, PMe). IR (KBr) 1935 (C≡O), 1717 (C=O), 1577 cm^{-1} (N=C).

Method II. A suspension of hydrazido(2−) complex **5b** (500 mg, 0.634 mmol) and 2,5-hexanedione (223 μl, 1.90 mmol) in THF (20 ml) was stirred at 50 °C for 14 h under a CO atmosphere (1 atm). The resulting solution containing **13** and **14** (ca. 3 : 1) was treated with concentrated hydrobromic acid (ca. 400 mg), and the workup described above afforded **14** (155 mg, 32%).

***cis,trans*-[WBr_2(NNCMe=CHCH=CMe)(CNBu^t)(PMe_2Ph)$_2$] (15).** A toluene solution (10 ml) of **12** (200 mg, 0.226 mmol) and Bu^{t}NC (26 μl, 0.23 mmol) was heated at 70 °C for 12 h. To the resultant mixture was added further Bu^{t}NC (26 μl, 0.23 mmol) since the reaction was not finished completely, and this solution was stirred at 70 °C for a further 16 h. After cooling to room temperature, the reaction mixture was filtered in order to remove a small amount of yellow oily material. The brownish purple filtrate was evaporated to dryness, and the residue was washed with diethyl ether. Recrystallization of the residual solid from ClCH$_2$CH$_2$Cl/hexane afforded violet crystals of **15** (100 mg, 55%). Found: C, 40.41; H, 5.00; N, 5.50%. Calcd for $C_{27}H_{39}Br_2N_3P_2W$: C, 39.98; H, 4.85; N, 5.18%. ^{1}H NMR (C_6D_6, 24 °C) δ = 0.97 (s, 9 H, Bu^t), 1.94 (t, 6 H, J = 4.0 Hz, PMe), 1.98 (br s, 6 H, α-Me), 2.08 (t, 6 H, J = 4.0 Hz, PMe), 5.43 (br s, 2 H, β-H), 6.9—7.5 (m, 10 H, PPh); ^{31}P{^{1}H} NMR (C_6D_6, 24 °C) δ = −19.5 (s with ^{183}W satellites, J_{PW} = 288 Hz). IR (KBr) 2105, 2091 cm^{-1} (C≡N).

Reduction with $LiAlH_4$. A pyrrolylimido complex (0.07—0.09 mmol) and $LiAlH_4$ (10 equiv) in THF (3 ml) were stirred at 25—50 °C for 3—48 h, and the reaction mixture was quenched with methanol (1 ml) at room temperature. Organic products were identified by GC–MS and quantitatively determined by GLC. The reaction mixture was then evaporated under reduced pressure (ca. 15 mmHg, 20—25 °C, 1 mmHg = 133.322 Pa), and the distillate was trapped in aqueous H_2SO_4, which was used for the determination of ammonia (indophenol method[5]). Reaction conditions and yields of the products are summarized in Table 1 (vide infra). The tungsten hexahydride complex [$WH_6(PMe_2Ph)_3$][6] was isolated in 31% yield from the reduction products of **6b** by evaporation of the solvent, hexane extraction of the residual material, and recrystallization from hexane.

Reaction with KOH in EtOH. To a suspension of a pyrrolylimido complex (0.07—0.09 mmol) in EtOH (3 ml) was added KOH

(10 equiv), and the mixture was vigorously stirred under N_2 or CO atmosphere (1 atm). The yields of pyrrole and 1-aminopyrrole were periodically monitored by GLC analyses, and stirring was continued until their yields reached constant values. Ammonia was determined by a similar procedure to that described for the reduction with $LiAlH_4$. Reaction conditions and yields of ammonia and the organic products are summarized in Table 2 (vide infra).

Reaction with KOH/18-Crown-6 Ether in THF. A mixture of a pyrrolylimido complex (0.07—0.09 mmol), 18-crown-6 ether (1 equiv), KOH (10 equiv), and THF (3 ml) was stirred at 25—50 °C to give a colorless to pale yellow solution with a white precipitate after 24—50 h. The yields of pyrrole, 1-aminopyrrole, and ammonia were determined as described above, they are shown in Table 2 (vide infra).

Preparation of *cis,trans*-[WCl_2(NNCH$_2$C$_6$H$_4$CO)(η^2-PhC≡CH)(PMe_2Ph)$_2$] (17). The (phthalimidin-2-yl)imido complex *cis,mer*-[WCl_2(NNCH$_2$C$_6$H$_4$CO)(PMe_2Ph)$_3$]·0.5(C_6H_6) **16**·0.5(C_6H_6)[4e] (280 mg, 0.33 mmol) and PhC≡CH (108 μl, 0.98 mmol) were dissolved in THF (6 ml) and stirred at 50 °C for 12 h. The resulting mixture was filtered, and the pale brown filtrate was evaporated to dryness. The greenish brown oil obtained was triturated with diethyl ether (10 ml) and washed successively with the same solvent (3×5 ml). The pale brown residue was extracted with benzene, and the benzene solution was concentrated to 2 ml under reduced pressure. Addition of hexane (10 ml) gave brown crystals of **17**·0.25(C_6H_6) (97 mg, 37%). Found: C, 50.51; H, 4.59; N, 3.53%. Calcd for $C_{33.5}H_{35.5}Cl_2N_2OP_2W$: C, 50.37; H, 4.48; N, 3.51%. ^{1}H NMR ($CDCl_3$, 24 °C) δ = 1.48 (d, 3 H, J = 9.4 Hz, PMe), 2.05 (d, 3 H, J = 9.6 Hz, PMe), 2.20 (br d, 6 H, J = 9.7 Hz, PMe), 3.45—3.55 (m, 2 H, CH_2), 6.9—7.8 (m, 20.5 H, aromatic and 0.25(C_6H_6)), 10.05 (dd, 1 H, J = 18.2, 5.6 Hz, C≡CH); ^{31}P{^{1}H} ($CDCl_3$, 24 °C) δ = −9.81 (d with ^{183}W satellites, $J_{PP'}$ = 156 Hz, J_{PW} = 214 Hz), −5.29 (d with ^{183}W satellites, $J_{PP'}$ = 156 Hz, J_{PW} = 204 Hz); ^{1}H NMR (C_6D_6, 20 °C, 400 MHz, recorded on a JEOL JNM-LA-400 spectrometer) δ = 3.54, 3.62 (d, 1 H each, J = 17.3 Hz, CH_2). IR (KBr) 1716 cm^{-1} (C=O, C≡C).

Reaction of (Phthalimidin-2-yl)imido Complex with KOH in MeOH. The following procedure for the reaction of *cis,trans*-[WCl_2(NNCH$_2$C$_6$H$_4$CO)(CO)(PMe_2Ph)$_2$] (**18**)[4e] is representative. A mixture of **18** (53.4 mg, 0.757 mmol) and KOH (41.7 mg) in MeOH (2 ml) was stirred at room temperature for 6 h. The turbid orange brown solution was neutralized with acetic acid (51 μl) and dried up under reduced pressure. The residue was extracted with ether (20 ml), and phthalimidine and 2-aminophthalimidine in the extract were determined by NMR.

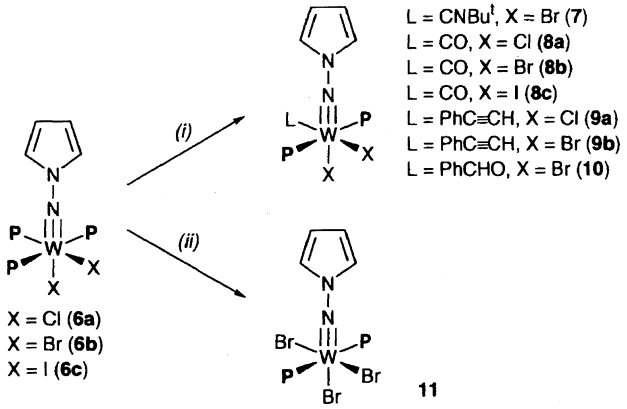
Results and Discussion

Preparation of Pyrrolylimido Complexes with Various Sets of Ancillary Ligands. We have previously found that tungsten(IV) hydrazido(2−) complexes *cis,mer*-[WX_2(NNR^{1}R^2)(PMe_2Ph)$_3$] (R^1, R^2 = H, alkyl, acyl, silyl) and diazoalkane complexes *cis,mer*-[WX_2(NN=CR^{1}R^2)(PMe_2Ph)$_3$] (R^1, R^2 = H, alkyl, aryl) accessible from dinitrogen complex **4** undergo ligand exchange reactions with various π-acceptor ligands.[4e,7] Similarly, pyrrolylimido complexes **6** showed reactivities toward various organic π-acceptor ligands such as Bu^{t}NC, CO, PhC≡CH, and PhCHO in toluene at 70 °C. Thus, the PMe_2Ph trans to the halogen ligand was exclusively substituted by these molecules to give *cis,trans*-[WX_2(NNCH=CHCH=CH)(L)(PMe_2Ph)$_2$] (**7**—**10**) (Scheme 3). A higher temperature (70 °C) was necessary for the reactions of **6** than for those of the hydrazido(2−) complex *cis,mer*-[WCl_2(NNH_2)(PMe_2Ph)$_3$] (50 °C), the diazoalkane complex *cis,mer*-[WCl_2(NN=CR^{1}R^2)(PMe_2Ph)$_3$] (50—55 °C) and the disilylhydrazido(2−) complex *cis,mer*-[WI_2(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)(PMe_2Ph)$_3$] (room temperature): The conversion of **6b** to **8b** was only 10% after 7 h under 1 atm of CO at 50 °C.

Analogously to W(IV) hydrazido(2−) or diazoalkane complexes,[7b,8] **6b** underwent formal one-electron oxidation of the tungsten center by treatment with an excess amount of CH_2Br_2 at 80 °C in toluene to give the W(V) pyrrolylimido complex *trans*-[WBr_3(NNCH=CHCH=CH)(PMe_2Ph)$_2$] (**11**) (Scheme 3). The molecular structure with two mutually trans PMe_2Ph ligands and three bromide ligands in mer configuration was confirmed by X-ray analysis (see Supplementary material).

The cyclic voltammogram of **6** showed a reversible oxidation/reduction wave due to W(IV/V) couple at $E_{1/2}$ = 0.16—0.27 V vs. SCE. The corresponding reversible redox couples of Bu^{t}NC complex **7** were also observed at $E_{1/2}$ = 0.37 V. In contrast, the oxidations of CO, PhC≡CH, and PhCHO complexes **8**, **9**, and **10** occurred at much more positive potentials and were observed as irreversible processes (E_{ox} = 1.11—1.24, 1.60—1.63, and 1.72 V, respectively).

Preparation of 2,5-Dimethylpyrrolylimido Complexes. We have previously reported that condensation of the hydrazido(2−) complex **5b** with 2,5-hexanedione leads to the diazoalkane complex **12** rather than to the corresponding pyrrolylimido complex under conditions similar to those used for the preparation of **6b** (Scheme 4).[4a] The cyclization at the remote nitrogen of **12** to form a 2,5-dimethylpyrrole



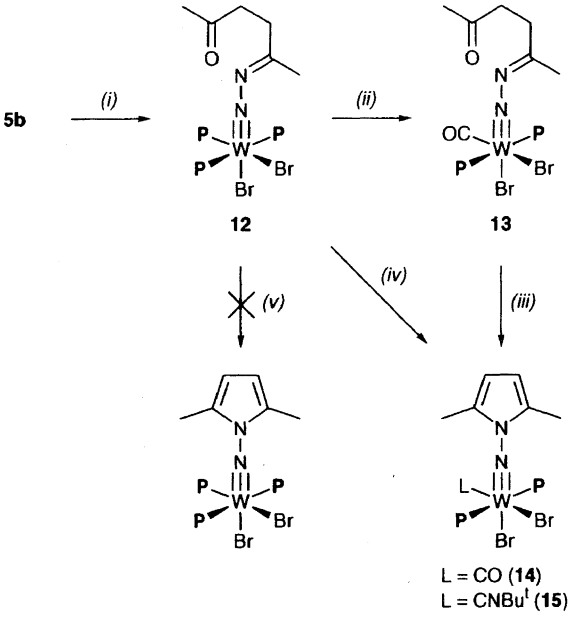
(i) L, toluene, 70 °C (L = CNBu^t, CO, PhC≡CH, PhCHO); *(ii)* CH_2Br_2, toluene, 80 °C (X = Br)

Scheme 3.

ring could not be accomplished even by heating with hydrobromic acid at 68 °C, probably due to the large steric congestion between the diazoalkane and the phosphine ligands. Our previous findings that benzophenone hardly condenses with **5a** but smoothly does with *cis,trans*-[$WCl_2(NNH_2)$-$(CO)(PMe_2Ph)_2$][7] to give the corresponding diphenyldiazomethane complex led us to expect that such steric hindrance could be reduced by substituting one of the PMe_2Ph ligands with less bulky ligands such as CO. In fact, the diazoalkane–CO complex **13**, prepared by the ligand exchange of one of the PMe_2Ph ligands with CO, readily underwent the ring closure reaction by hydrobromic acid at room temperature to afford the (2,5-dimethylpyrrol-1-yl)imido complex **14** (Scheme 4). Complex **14** was more conveniently prepared from the reaction of **5b** and 2,5-hexanedione under CO atmosphere (1 atm) at 50 °C, followed by treatment with hydrobromic acid at room temperature. Furthermore, treatment of **12** with Bu^tNC at 70 °C under neutral conditions directly provided the (2,5-dimethylpyrrol-1-yl)imido complex **15** through replacement of one of the PMe_2Ph ligands by Bu^tNC and the following cyclization of the 5-diazohexan-2-one ligand. In the course of the latter reaction, the intermediary diazoalkane–isocyanide complex was not detected by NMR.

Steric interactions between the dimethylpyrrolylimido and PMe_2Ph ligands in **14** and **15** were confirmed by their variable-temperature NMR measurements. In the ^1H NMR spectrum of **14** at room temperature, methyl protons of the (2,5-dimethylpyrrol-1-yl)imido ligand were observed as one 6 H singlet, indicating the free rotation around the W–N–N axis. On cooling, however, this signal broadened and began to split into two 3 H singlets below 200 K (Fig. 1). At the same time, the β-proton signal of this ligand split into two broad signals below 210 K. These observations indicate that the pyrrole-ring plane of complex **14** takes the conformation parallel to the Br–W–CO axis, and the rotation around the W–N–N axis is slow at lower temperatures than 200 K, so that each of the two methyl groups and the two β-hydrogens of the (2,5-dimethylpyrrol-1-yl)imido ligand become inequivalent. Complex **15** also exhibited similar signal splitting at higher temperature than that for **14**. The pyrrolyl methyl ^1H resonance of **15** was observed as a broad signal even at 300 K (δ = 1.81 in THF-d_8) and as two separate singlets below 240 K (δ = 1.68, 1.90). The β-proton signal of **15** split below 230 K into two doublets (δ = 5.21, 5.28, ^3J = 2.6 Hz at 200 K). This type of temperature dependency of the ^1H NMR spectrum was not observed in the case of the unsubstituted pyrrolylimido complexes **7** and **8b** even at 160 K, while the (2,4,6-trimethylpyridinio)imido complex *cis,trans*-[WCl_2(NN=CMeCH=CMeCH=CMe)-$(CO)(PMe_2Ph)_2]^+$ (**19**) was found to exhibit analogous signal splitting on cooling.[4d]

Reduction of Pyrrolylimido Complexes with $LiAlH_4$. In a previous paper we have described that the $LiAlH_4$ reduction of the pyrrolylimido complexes **3** (M = W, X = F) and **6b** produced pyrrole with moderate selectivity.[4c] In this study, we have further examined the $LiAlH_4$ reduction of the



(i) 2,5-Hexanedione, aqueous HBr, CH_2Cl_2, rt; *(ii)* CO, THF, 55 °C; *(iii)* aqueous HBr, THF, rt (L = CO); *(iv)* Bu^tNC, toluene, 70 °C (L = $CNBu^t$); *(v)* aqueous HBr, THF, 68 °C

Scheme 4.

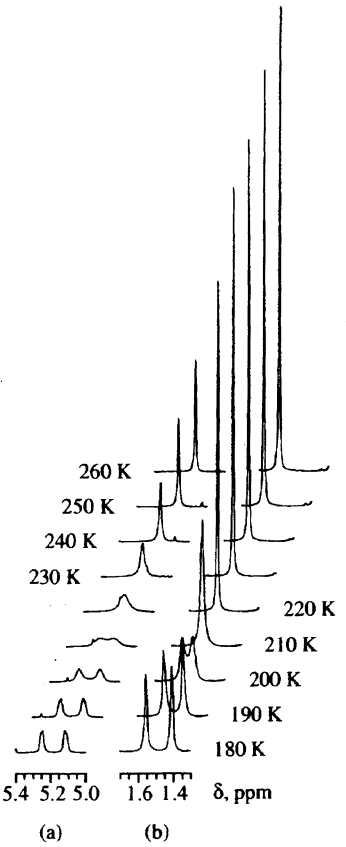


Fig. 1. Variable-temperature ^1H NMR spectra of **14**. (a) Pyrrolyl β-ring and (b) α-methyl protons.

pyrrolylimido complexes with various π-acceptor ligands. The reaction was typically carried out with 10 equiv of $LiAlH_4$ in THF at 50 °C and quenched with excess MeOH at room temperature. The yields of nitrogenous products are summarized in Table 1.

In all cases, pyrrole was formed as the major or exclusive product. This indicates that the N–N bond in the pyrrolylimido complexes *cis,mer*-[WBr_2(NNCH=CHCH=CH)(L)(PMe_2Ph)$_2$] is more readily cleaved by the action of $LiAlH_4$ than the W–N bond, although the selectivity is affected by the nature of L. In particular, complex **7** with Bu^{t}NC ligand gave pyrrole in a quantitative yield, while complex **8b** with CO ligand exhibited the lowest selectivity. The W(V) complex **11** showed much higher reactivity toward $LiAlH_4$ than the W(IV) complexes, but the ratio of pyrrole to 1-aminopyrrole was about 8 : 1. Concurrent formation of ammonia in comparable yields to those of pyrrole was revealed in several reactions, which confirmed the fate of the nitrogen atom directly bound to the tungsten after the N–N bond cleavage. The $LiAlH_4$ reduction of the 2,5-dimethylpyrrolylimido–Bu^{t}NC complex **15** was slower and less selective than the reaction of the parent complex **7**: It took 48 h at 50 °C to allow the reaction to be completed, and 2,5-dimethylpyrrole and 1-amino-2,5-dimethylpyrrole were formed in 85 and 12% yields, respectively.

Decomposition of Pyrrolylimido Complexes with KOH. Previously, pyrrolylimido complexes **6a** and **6b** were shown to undergo the N–N or W–N bond cleavage at room temperature by the action of excess amounts of KOH in alcohols to liberate pyrrole and 1-aminopyrrole, respectively.[4c] The yields of pyrrole (6—56%) and 1-aminopyrrole (15—89%) were significantly affected by the halogen co-ligand of **6** as well as by the alcohol used. The highest selectivity was observed in the reaction of **6b** with KOH in EtOH, where 1-aminopyrrole was formed in 89% yield. With a new series of the pyrrolylimido complexes described above in hand, we have investigated their reactions with KOH in alcohols for the purpose of gaining detailed information about the factors which control the N–N and W–N bond fission in the pyrrolylimido complexes. Typical results are summarized in Table 2, and extensive data are shown in Supplementary material.

Table 1. Reduction of the Pyrrolylimido Complexes with $LiAlH_4$

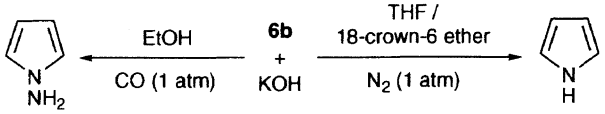
Complex	Temp	Time	Yield/%		
	°C	h	Pyrrole	1-Aminopyrrole	NH_3[a]
6b[b]	50	24	75	Trace	74
7	50	24	100	0	80
8b	50	24	50	24	ND
9b[c]	50	24	83	5	ND
10	50	24	89	0	ND
11	25	3	89	11	68
15	50	48	85[d]	12[e]	ND

a) ND = not determined. b) Ref. 4c. Tungsten hydride complex [WH_6(PMe_2Ph)$_3$] was recovered in 31% yield. c) Ethylbenzene (57% yield) and a trace of styrene was obtained. d) Yield of 2,5-dimethylpyrrole. e) Yield of 1-amino-2,5-dimethylpyrrole.

The reaction of Bu^{t}NC complex **7** required a higher temperature (50 °C) than those of the other pyrrolylimido complexes examined and produced 1-aminopyrrole and pyrrole with only moderate selectivity. Complexes **8**—**10** afforded 1-aminopyrrole in excellent yields. In sharp contrast to the reactions of the tris(phosphine) complexes **6**, the selectivity in the reactions of **8** (X = Cl, Br, I) and **9** (X = Cl, Br) did not essentially depend on the halogen ligand nor on the alcohol used (MeOH, EtOH, and Pr^{i}OH). The reactions of **9** and **10** were accompanied by the formation of styrene and benzyl alcohol in considerable yields. Analogously, the 2,5-dimethylpyrrolylimido–CO complex **14** liberated 1-amino-2,5-dimethylpyrrole in 93% yield and a trace amount of 2,5-dimethylpyrrole (3%) by treatment with KOH in EtOH at room temperature. Interestingly, treatment of **6a** and **6b** with KOH in EtOH under a CO atmosphere at room temperature also led to the formation of 1-aminopyrrole with a higher selectivity (89—92% yields) than under N_2. Since the ligand exchange reaction of **6** with CO requires heating at 70 °C (vide supra), CO is considered to be involved in some subsequent steps after the initial reaction of **6** with KOH, which results in the selective W–N bond fission.

The tungsten(V) complex **11** rapidly reacted with KOH in alcohols at room temperature, where the selectivity of the pyrrole compounds was not good under N_2 and could not be improved by changing the alcohol. However, the reaction under 1 atm of CO improved the yield of 1-aminopyrrole up to 92%.

Interestingly, use of THF as the solvent dramatically changed the product distribution in some cases. Thus, KOH-treatment of **6b** in THF in the presence of 18-crown-6 ether under N_2 liberated pyrrole in 82% yield, while 1-aminopyrrole was formed in only 5% yield. In addition, formation of ammonia in 85% yield was also confirmed. Addition of crown ether was necessary for dissolving KOH in THF. It should be pointed out that pyrrole and 1-aminopyrrole can be selectively and complementarily liberated from **6b** only by changing the reaction media (Eq. 1). In the cases of complexes **8**—**10**, however, no remarkable change in the ratio of pyrrole and 1-aminopyrrole was observed.



(1)

The structure of the tungsten species after liberation of the pyrrole compounds could not be characterized: the major signals observed by the NMR analysis of the reaction mixtures were only those attributable to the free PMe_2Ph.[9]

The detailed investigation of the reactions of various pyrrolylimido complexes with KOH indicates that the substitution of one of the PMe_2Ph ligands in **6** with a π-acceptor ligand substantially suppresses the N–N bond fission and that N–N bond cleavage is more favored in THF than in alcoholic solvents. On the basis of these findings, the reaction mech-

Table 2. Reaction of the Pyrrolylimido Complexes with KOH

Complex	Solvent	Atmosphere	Temp	Time	Yield/%		
			°C	h	Pyrrole	1-Aminopyrrole	
6a	EtOH	N_2	25	24	56[a]	37[a]	b)
6b	EtOH	N_2	25	2	11[a]	89[a]	
6c	EtOH	N_2	25	15	6	41	
7	EtOH	N_2	50	20	19	58	
8a	EtOH	N_2	25	4	<5	91	
8b	EtOH	N_2	25	7	<5	95	
8c	EtOH	N_2	25	3	Trace	91	
9a	EtOH	N_2	25	1	2	98	c)
9b	EtOH	N_2	25	2	<4	95	d)
10	EtOH	N_2	25	5	0	>99	e)
11	EtOH	N_2	25	2	32	55	
14	EtOH	N_2	25	24	3[f]	93[g]	
6a	EtOH	CO	25	5	5	89	
6b	EtOH	CO	25	16	2	92	
11	EtOH	CO	25	3	6	92	
6b	THF[h]	N_2	25	24	82	5	i)
8b	THF[h]	N_2	50	48	45	55	
9b	THF[h]	N_2	50	50	7	93	j)
10	THF[h]	N_2	50	44	12	88[k]	l)

a) Ref. 4c. b) 68% yield of NH_3 was detected. c) $PhCH{=}CH_2$ was formed in 71% yield. d) $PhCH{=}CH_2$ was formed in 54% yield. e) $PhCH_2OH$ was formed in 32% yield. f) Yield of 2,5-dimethylpyrrole. g) Yiled of 1-amino-2,5-dimethylprrole. h) One equiv of 18-crown-6 ether was added. i) 85% yield of NH_3 was detected. j) $PhCH{=}CH_2$ was formed in 54% yield. k) Sum of the yields of 1-aminopyrrole (66%) and 1-benzylideneaminopyrrole (22%). l) $PhCH_2OH$ was formed in 58% yield.

anism for the N–N and N–W bond fission in pyrrolylimido complexes by treatment with KOH is proposed as follows. First, the halide ligand(s) around the metal are substituted with a hydroxide anion having a stronger π-donating character. π-Donation to the W–N antibonding MOs (LUMO and second LUMO) from the ligating oxygen is expected to weaken the W–N multiple bond through the orbital interactions (Fig. 2, A—C). Thus, the nitrogen atom directly bound to the tungsten becomes more nucleophilic, leading to successive protonation by solvent and/or the coordinated OH anion to form 1-aminopyrrole (path A). Alternatively, the interaction between the filled tungsten d (HOMO) and the oxygen p orbitals (Fig. 2, D) is expected to raise the energy level of the HOMO. This may cause the fission of the N–N bond followed by protonation of the resulting pyrrolide anion by the coordinated OH anion to give pyrrole and a W(VI) nitrido complex, the latter of which liberates ammonia finally (path B).[10] We presume that in the course of the KOH decomposition of **6**, both paths A and B compete in alcohols to give 1-aminopyrrole and pyrrole, respectively, while path B is favored over path A in THF to form pyrrole predominantly.

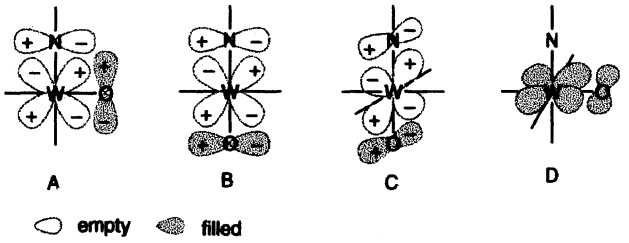
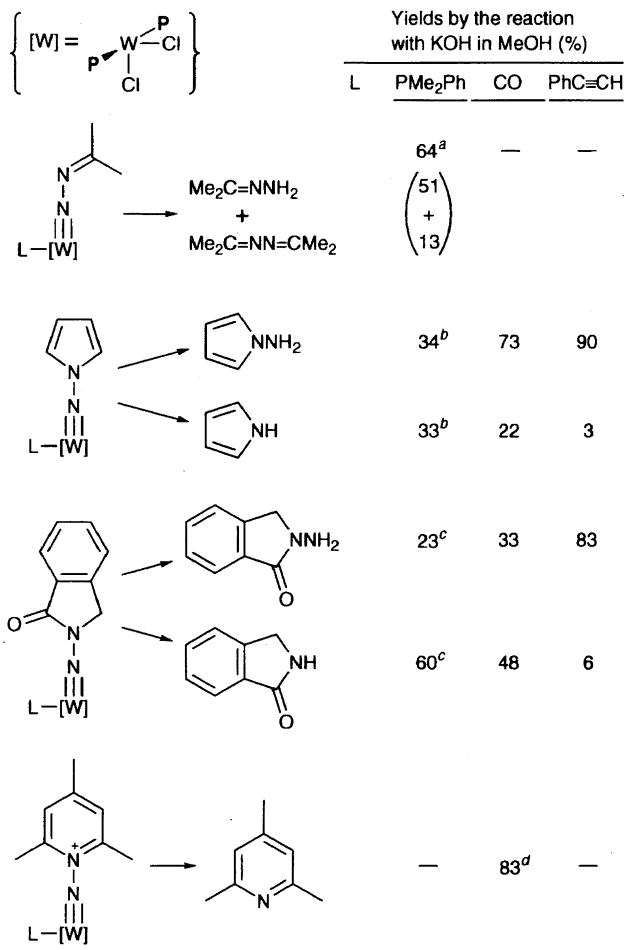


Fig. 2. Possible orbital interactions between oxygen ligand and frontier MOs in tungsten pyrrolylimido complex.

When the HOMO is stabilized by a strong π-acceptor ligand and its level is too low to induce the N–N bond cleavage, the pyrrole formation through path B would be suppressed. The oxidation potentials of the W(IV) pyrrolylimido complexes are regarded to reflect the relative differences in their HOMO levels. It is of great interest to note that the nearly quantitative formation of 1-aminopyrrole in EtOH is achieved with the complexes whose W(IV/V) couples are comparable with or more positive than those of CO–complexes **8** (> +1.1 V vs. SCE). In addition, the d^2 electrons of the tungsten atom in **9** and **10** are not used for the cleavage of the N–N bond but for the reduction of the PhC≡CH or the PhCHO ligand, respectively.[11] Furthermore, those complexes predominantly liberate 1-aminopyrrole even in THF.

Although the W(V) complex **11** does not have enough d-electrons to reduce the N–N bond, it was found to afford appreciable amounts of pyrrole (1-aminopyrrole/pyrrole = 1.5—2). We suspect that intermolecular electron transfer between the two W(V) species might generate the W(IV) pyrrolylimido complex responsible for the formation of pyrrole. This was supported by the experimental fact that the W(IV) complex **6b** was recovered from the reaction of **11** with KOH in 2-methyl-2-butanol.[12]

Comparison of the Reactivities of Organohydrazido(2−) Type Ligands toward KOH. Scheme 5 summarizes the N–N and N–W bond cleavage reactions of various organohydrazido(2−) type complexes derived from the dinitrogen complex **4** with KOH in MeOH.[4c,4d,4e,13] The N–N bond cleavage takes place more easily in the following order, 2-diazopropane ≪ pyrrolylimido < (phthalimidin-2-yl)imido ≪ (1-pyridinio)imido ligand. The 2-diazopropane complex *cis,mer*-[$WCl_2(NN{=}CMe_2)(PMe_2Ph)_3$] gave acetone azine and hydrazone with complete retention of the N–N bond, while the pyridinioimido complex *cis,trans*-[$WCl_2(NN{=}CMeCH{=}CMeCH{=}CMe)(CO)(PMe_2Ph)_2]^+$ (**19**) readily released 2,4,6-collidine in high yield. The N–N and W–N bond cleavage reactions competed in the case of the pyrrolylimido and (phthalimidine-2-yl)imido complexes. However, the N–N bond cleavage of the latter complex could be suppressed effectively only when the PhC≡CH ligand was introduced. On the other hand, the N–N bond cleavage of *cis,mer*-[$WCl_2(NNCH_2C_6H_4CO)(PMe_2Ph)_3$] (**16**) occurred selectively to give phthalimidine in a THF solution of KOH/18-crown-6 ether.[4e]



Conditions: N_2 atmosphere, at room temperature except where indicated; [a] reference 13; conducted at 50 °C; [b] reference 4c; [c] reference 4e; [d] reference 4d

Scheme 5.

Spectroscopic and analytical data for **6**—**11**, details of the X-ray crystallographic study of **11**, and extensive data of the reactions of pyrrolylimido complexes with KOH were deposited as Document No. 72007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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9) In the reactions of the CO–complexes **8** under N_2 or complexes **6** and **11** under CO atmosphere, the reaction mixtures showed ^{31}P NMR signals with ^{183}W satellites (J_{PW} = 212—275 Hz) assigned to coordinated phosphines, and strong IR absorptions due to ν(CO) in the region of 1750—2050 cm^{-1}.

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11) Reactions of **9** and **10** with KOH in 2-methyl-2-butanol also formed styrene and benzyl alcohol in 60 and 58% yields, respectively. This indicates that the PhC≡CH and the PhCHO ligands are not reduced via the hydrogen transfer from alcohol.

12) Complex **6b** was inert toward KOH in 2-methyl-2-butanol at room temperature.

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