# Synthesis and Structure Determinations of Complexes Containing a Five-Membered Lactam Structure Based on Organohydrazido(2−) Ligands[1]

**Hidetake Seino, Youichi Ishii, and Masanobu Hidai***

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

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Acid-catalyzed reactions of the hydrazido(2−) complexes *cis,mer*-$[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl, Br) with phthalaldehyde gave the (phthalimidin-2-yl)imido complexes *cis,mer*-$[WX_2(NN\overline{CH_2C_6H_4CO})(PMe_2Ph)_3]$, via the condensation of the terminal $NH_2$ group with one of the formyl groups and the following cyclization to form a phthalimidine ring. Crystal structure of the chloro complex **3a** was unambiguously determined by X-ray analysis. Reaction of **3a** with HBr liberated the (phthalimidin-2-yl)imido ligand as 2-aminophthalimidine in moderate yield, while treatment of **3a** with KOH in THF selectively cleaved the N−N bond to give phthalimidine. A similar condensation of the hydrazido(2−) complex *trans*-$[WF(NNH_2)(dppe)_2]^+$ (**8a**$^+$; dppe = $Ph_2PCH_2CH_2PPh_2$) with phthalaldehyde resulted in the formation of the diazoalkane complex *trans*-$[WF(NN{=}CHC_6H_4CHO)(dppe)_2]^+$. However, further treatment of the latter complex with $AlCl_3$ afforded the corresponding (phthalimidin-2-yl)imido complex *trans*-$[WF(NN\overline{CH_2C_6H_4CO})(dppe)_2]^+$. When **8a**$^+$ and its molybdenum analogue were reacted with 2,5-dimethoxy-2,5-dihydrofuran in the presence of a catalytic amount of acid, *trans*-$[MF(NN\overline{CH{=}CHCH_2CO})(dppe)_2]^+$ (**11**$^+$; M = Mo, W) was formed as the kinetic product, which gradually isomerized to the thermodynamically more stable compound *trans*-$[MF(NN\overline{CH_2CH{=}CHCO})(dppe)_2]^+$ (**12**$^+$). Both **11**$^+$ and **12**$^+$ (M = W) were crystallographically characterized, and the mechanism for the isomerization of **11**$^+$ to **12**$^+$ was proposed based on the results of the $^1$H NMR measurements.

## Introduction

Much effort has been involved in the development of the chemical transformations of dinitrogen by using transition metal complexes under mild conditions.[2,3,4] Direct synthesis of organonitrogen compounds from dinitrogen is one of the ultimate goals in this field. Toward this goal, reactivities of dinitrogen complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo, W; L = phosphine)[5] have been widely investigated, and a series of organonitrogen ligands have been synthesized from the coordinated dinitrogen via several routes.[6,7,8]

One way for the C−N bond formation at the coordinated dinitrogen is the direct alkylation, acylation, or arylation by reaction with alkyl halides, acyl halides, or $\eta^6$-fluorobenzene complexes, respectively.[6] Another more versatile method is based upon the utilization of the nucleophilic reactivity of hydrazido(2−) complexes,[7,8] which can be readily obtained by the protonation of the dinitrogen complexes of molybdenum and tungsten.[8a,9] This has led to discovery of the condensation reaction of molybdenum or tungsten hydrazido(2−) complexes with aldehydes or ketones to afford diazoalkane complexes.[7] This reaction is applicable to a wide variety of carbonyl compounds, and reactivities of the diazoalkane ligands thus obtained have been extensively investigated.[10] In this context, the coordinated dinitrogen has recently been transformed into

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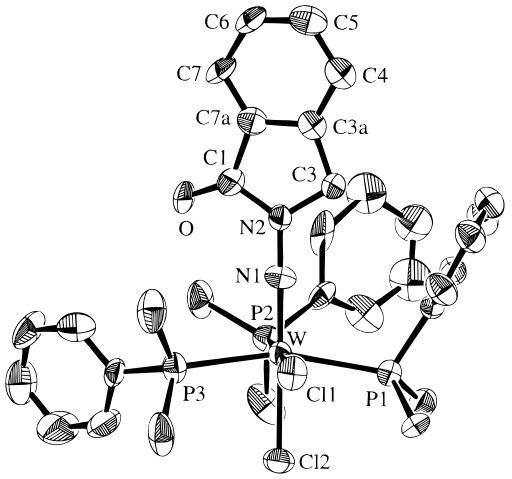
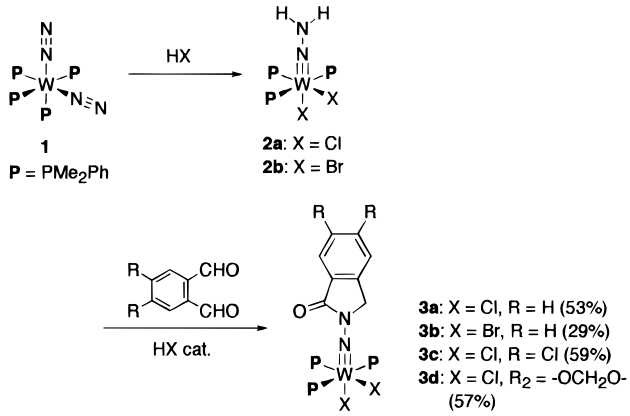



**Figure 1.** ORTEP drawing for *cis,mer*-[$WCl_2$(NNCH$_2$C$_6$H$_4$CO)($PMe_2$Ph)$_3$] (**3a**). Hydrogen atoms are omitted for clarity.

**Scheme 1**




a pyrrolylimido ligand[11] by using this condensation reaction, where 2,5-dimethoxytetrahydrofuran, a succinaldehyde equivalent, was employed as the reactant. Further, the pyrrolylimido ligand has been released from the metal as pyrrole or *N*-aminopyrrole in good yield. To extend this type of reaction, we have now investigated the reactions of the hydrazido(2−) complexes with other dialdehydes and their equivalents. Details of syntheses and reactivities of novel organohydrazido complexes having nitrogen heterocycles will be described here.

## Results and Discussion

**Synthesis and Characterization of the (Phthalimidin-2-yl)imido Complexes.** Tungsten hydrazido(2−) complexes *cis,mer*-[$WX_2$($NNH_2$)($PMe_2$Ph)$_3$] (**2a**, X = Cl; **2b**, X = Br), readily derived from the dinitrogen complex *cis*-[W($N_2$)$_2$($PMe_2$Ph)$_4$] (**1**) by protonation with HCl or HBr,[9b] reacted with phthalaldehyde in the presence of a catalytic amount of aqueous HCl or HBr to form novel organohydrazido complexes **3a** or **3b**, which have a phthalimidine ring involving the terminal nitrogen atom (Scheme 1). The reaction proceeded smoothly at room temperature, and the organohydrazido complexes **3** with substituted (phthalimidin-2-yl)imido ligands were similarly obtained from the corresponding phthalaldehydes in moderate yields.

The representative complex **3a** was fully characterized by X-ray crystallographic analysis (Figure 1, Table 1), confirming the presence of a phthalimidine ring including the terminal nitrogen atom. The W−N−N bond is essentially linear and almost coplanar to the phthalimidine ring. The coordination geometry around the tungsten in the hydrazido(2−) complex **2a** is completely retained in **3a**, and the W−N and N−N bond lengths and W−N−N angle are essentially similar to the previously reported hydrazido(2−) type complexes, indicating that the (phthalimidin-2-yl)imido ligand behaves as a six-electron donor.

**Table 1.** Selected Bond Lengths and Angles in **3a**·0.5($C_6H_6$)

| Bond Lengths (Å) | | | |
|---|---|---|---|
| W−P(1) | 2.515(3) | O−C(1) | 1.21(1) |
| W−P(2) | 2.451(3) | C(1)−C(7a) | 1.50(2) |
| W−P(3) | 2.522(3) | C(3)−C(3a) | 1.48(1) |
| W−Cl(1) | 2.530(3) | C(3a)−C(4) | 1.40(2) |
| W−Cl(2) | 2.464(3) | C(4)−C(5) | 1.40(2) |
| W−N(1) | 1.734(9) | C(5)−C(6) | 1.34(2) |
| N(1)−N(2) | 1.35(1) | C(6)−C(7) | 1.39(2) |
| N(2)−C(1) | 1.40(1) | C(7)−C(7a) | 1.35(2) |
| N(2)−C(3) | 1.45(1) | C(3a)−C(7a) | 1.41(2) |
| **Bond Angles (deg)** | | | |
| P(1)−W−P(2) | 95.2(1) | W−N(1)−N(2) | 179.0(8) |
| P(1)−W−P(3) | 158.5(1) | O−C(1)−N(2) | 124(1) |
| P(1)−W−Cl(1) | 84.9(1) | O−C(1)−C(7a) | 129(1) |
| P(1)−W−Cl(2) | 80.1(1) | N(2)−C(1)−C(7a) | 105(1) |
| P(1)−W−N(1) | 99.8(3) | N(1)−N(2)−C(3) | 121.1(9) |
| P(2)−W−P(3) | 99.6(1) | N(1)−N(2)−C(1) | 125(1) |
| P(2)−W−Cl(1) | 177.7(1) | C(1)−N(2)−C(3) | 113(1) |
| P(2)−W−Cl(2) | 88.1(1) | N(2)−C(3)−C(3a) | 102.8(9) |
| P(2)−W−N(1) | 87.9(3) | C(3)−C(3a)−C(4) | 132(1) |
| P(3)−W−Cl(1) | 79.7(1) | C(3)−C(3a)−C(7a) | 110(1) |
| P(3)−W−Cl(2) | 84.9(1) | C(4)−C(3a)−C(7a) | 117(1) |
| P(3)−W−N(1) | 96.2(3) | C(1)−C(7a)−C(3a) | 107(1) |
| Cl(1)−W−Cl(2) | 89.7(1) | C(1)−C(7a)−C(7) | 128(1) |
| Cl(1)−W−N(1) | 94.4(3) | C(3a)−C(7a)−C(7) | 124(1) |
| Cl(2)−W−N(1) | 175.9(3) | | |

Spectroscopic data for complexes **3a**−**d** are consistent with the solid-state structure of **3a**. The IR carbonyl stretching frequencies are in the region of 1690−1710 $cm^{-1}$, comparable to that of free phthalimidine (1686 $cm^{-1}$). The $^1$H NMR resonances due to the methylene protons of the phthalimidine rings of **3a**−**d** appear at $\delta$ 3.5−3.9 as singlets, which are slightly higher field shifted than that of phthalimidine ($\delta$ 4.48 in $CDCl_3$). The $^{13}$C NMR spectra of **3a** showed signals of methylene and carbonyl carbons at $\delta$ 45.8 and 161.3, respectively, the latter being shifted by 11 ppm to a higher field than that of phthalimidine ($\delta$ 45.8 ($CH_2$, $^1J_{CH}$ = 143 Hz) and 172.4 (CO) in $CDCl_3$). Measurements of the $^1$H (**3a**−**d**) and $^{31}$P{$^1$H} (**3a**) NMR spectra indicated that a pair of $PMe_2$Ph ligands coordinated to the metal in the trans position to each other are equivalent in solution even at −80 °C. In the crystal structure of **3a**, the orientation of the phthalimidine ring nearly parallel to the P(1)−W−P(3) axis makes the P(1) and P(3) atoms inequivalent, but the rotation of the phthalimidin-2-yl group around the W−N−N axis is quite facile in solution.

According to our previous study on preparation of diazoalkane complexes from hydrazido(2−) complexes, the condensation with ketones required a HX catalyst, but aldehydes readily reacted even without any additives.[7] In the case of phthalaldehyde, the reaction with **2a** provided **3a** in a moderate yield by the catalytic action of HCl, but no more than a low yield of diazoalkane complex **4a** was obtained in the absence of an acid. Use of acetic acid as the catalyst instead of HCl resulted in the formation of complex **4a** (Scheme 2). As confirmed by these experimental facts, the diazoalkane complex **4a** is stable under neutral or weakly acidic conditions, but rapid isomerization of **4a** to **3a** occurs at room temperature by addition of a strong acid. $^1$H NMR measurements revealed that the methylene protons of **3a** formed by the ring closure of **4a** with $DCl/D_2O$

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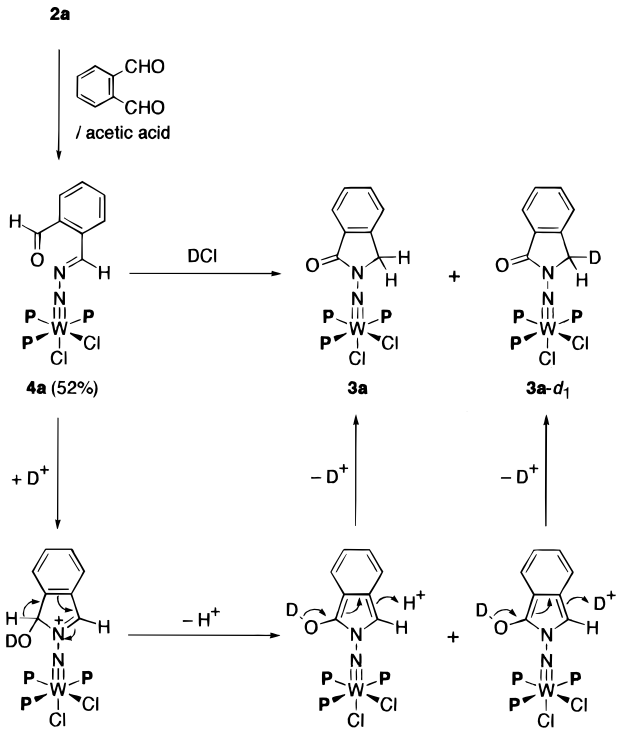
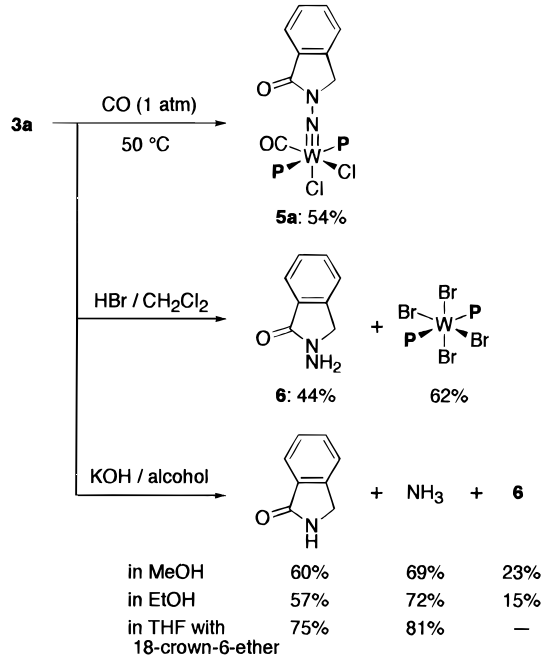
**Scheme 2**




were partially deuterated (∼0.5 H), although **3a** scarcely underwent H−D exchange even after 40 h under the same conditions.

On the basis of these observations, the mechanism for the phthalimidine ring formation is proposed as shown in Scheme 2. At first, the diazoalkane complex **4a** is formed by the monocondensation of **2a** with phthalaldehyde with the aid of an acid catalyst. Intramolecular nucleophilic attack of the terminal nitrogen atom on the remaining formyl group is promoted by a strong acid to form an intermediate (1-hydroxyisoindolin-2-yl)imido complex, which is further converted to **3a** by the prototropic isomerization. When $D^+$ is present in the reaction system, a deuterium is introduced to the methylene group in the last proton shift step. This mechanism is similar to that proposed for the reaction of phthalaldehyde with primary amine to give 2-alkylphthalimidine.[12] On the other hand, the reactions of hydrazine and monoarylhydrazines with phthalaldehyde are known to give mostly six-membered-ring products such as phthalazine[13] and 2-aryl-1,2-dihydro-1-hydroxyphthalazines.[12a,14] Although complex **2a** may be regarded as a metallahydrazine, only the terminal nitrogen exhibits nucleophilicity, because the nitrogen atom directly bound to the tungsten acts as a six-electron donor and the lone pair on the nitrogen is donated to the metal. Therefore, only the phthalimidine-ring formation was observed in the reaction of **2a** with phthalaldehyde.

**Scheme 3**




**Reactivities of the (Phthalimidin-2-yl)imido Complex.** Tungsten imido or oxo complexes of the type $[WX_2(E)(L)_3]$ (X = halogen; E = NR, O; L = phosphine) are known to undergo ligand exchange reactions with various $\pi$-acceptor ligands (L′) to give complexes of the type $[WX_2(E)(L)_2(L')]$, in which efficient back-donation from the $d^2$-metal center to L′ has been claimed.[15] The diazoalkane and hydrazido complexes, which have the isoelectronic structures to the imido and oxo complexes, have recently been found to show similar reactivities toward $\pi$-acceptor ligands.[16] As expected, the (phthalimidin-2-yl)imido complex **3a** underwent ligand exchange by gentle warming (50 °C) under 1 atm of CO to afford the CO-substituted (phthalimidin-2-yl)imido complex **5a** (Scheme 3). However, the reaction was slower than those of diazoalkane or disilylhydrazido complexes (100% conversion after 12 h at 50 °C or at room temperature, respectively[16]); conversion of the starting complex **3a** was not high (90% after 48 h). In addition, the CO stretching frequency of **5a** (1991 $cm^{-1}$) was much higher than those of CO−diazoalkane or −disilylhydrazido complexes (1940−1950 or 1931 $cm^{-1}$, respectively). These facts imply a weaker $\pi$-electron-donating ability of the (phthalimidin-2-yl)-imido ligand with an electron-withdrawing amide−carbonyl group.

From a view point of direct synthesis of organonitrogen compounds from molecular nitrogen, it is important to cleave the metal−nitrogen or nitrogen−nitrogen bond of the organonitrogen ligands derived from coordinated dinitrogen. A previous study showed that treatment of the diazoalkane complex $[WBr_2(NN{=}CMe_2)(PMe_2Ph)_3]$ with HBr gives a mixture of acetone azine and hydrazine through the disproportionation of acetone hydrazone initially formed from the tungsten−nitrogen bond scission.[7b] Similarly, the reaction of **3a** with excess HBr gave rise to the cleavage of the W−N bond, and 2-aminophthalimidine **6** was isolated in a moderate yield

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(Scheme 3). Metal species was recovered as *trans*-[$WBr_4(PMe_2Ph)_2$].[17] It is of great interest to note that the direct reaction between phthalaldehyde and hydrazine does not lead to the formation of **6** (vide supra).

When **3a** was reacted with KOH in methanol or ethanol, the nitrogen−nitrogen bond cleavage proceeded to give phthalimidine in 57−60% yield. The other nitrogen fragment was liberated as ammonia (69−72%) in yields comparable to those of the phthalimidine. Competitive cleavage of the W−N bond also occurred in this reaction to generate **6** as a byproduct in 15−23% yield. The reaction was completed faster in methanol (1.5 h) than in ethanol (3 h), but the selectivities of the organic products were essentially identical. Recently we reported that the pyrrolylimido complex [$WCl_2(NNCH{=}CHCH{=}CH)(PMe_2Ph)_3$] also reacts with KOH under the same conditions to liberate pyrrole and *N*-aminopyrrole (56% pyrrole and 37% *N*-aminopyrrole after 24 h in ethanol).[11] The reactivity of **3a** toward KOH as well as its selectivity for the N−N bond cleavage is evidently higher than that of the pyrrolylimido complex.

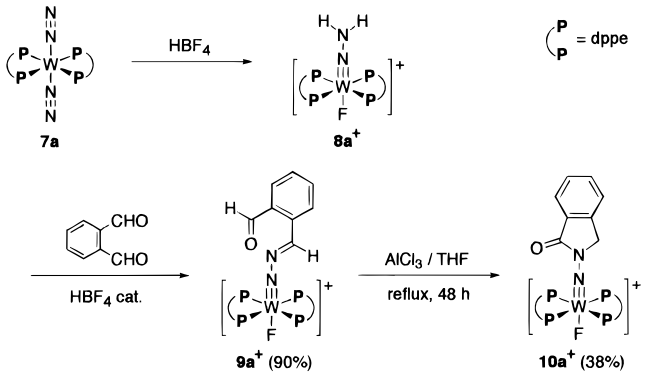
When **3a** was treated with excess KOH and an equivalent amount of 18-crown-6 ether in THF at room temperature, the yields of phthalimidine and ammonia were improved to 75 and 81%, respectively. However, the reaction was slower than in alcoholic solvents and required more than 4 h for completion (vide supra). It is probably because of the low solubility of KOH in THF, and the reaction scarcely occurred without the crown ether. It is worth mentioning that no 2-aminophthalimidine was formed under these conditions.

The reductive N−N bond cleavage promoted by KOH to release phthalimidine from the complex is considered to be accompanied by the oxidation of the W(IV) center to W(VI). Although we must await further study to elucidate the N−N bond cleavage mechanism, we consider that exchange of the chloro ligands in **3a** with hydroxide ligands promotes such a process. Another nitrogen fragment remaining on the W(VI) center is liberated as ammonia by further reaction with hydroxide anions; however, no characterizable metal complexes were obtained after the reactions in both alcohols and THF.

Phthalimidine was also obtained in 30−60% yield from complex **3a** by treatment with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in THF, but the yield was sensitive to the reaction time and temperature. In conclusion, the preferential W−N or N−N bond cleavage of **3a** to liberate 2-aminophthalimidine or phthalimidine, respectively, was achieved by choosing appropriate reaction conditions.

**Reaction of Hydrazido(2−) dppe Complex with Phthalaldehyde.** Synthesis of the corresponding (phthalimidin-2-yl)imido derivative from a cationic hydrazido(2−) complex *trans*-$[WF(NNH_2)(dppe)_2]BF_4$ (**8a**$^+BF_4^-$, dppe = $Ph_2PCH_2CH_2PPh_2$) was also investigated, the latter of which is readily obtained by protonation of the dinitrogen complex *trans*-$[W(N_2)_2(dppe)_2]$ (**7a**) with aqueous $HBF_4$.[7a] In contrast to neutral hydrazido(2−) complexes **2**, the reaction of **8a**$^+$ with phthalaldehyde in the presence of $HBF_4$ gave no complex containing a phthalimidine ring, but the diazoalkane complex **9a**$^+$ in a high yield (Scheme 4). Complex **9a**$^+$ was rather inert toward protic acids and did not show any appreciable change after treatment with $CF_3SO_3H$ or $HBF_4{\cdot}OEt_2$ even at 68 °C. However, Lewis acids such as aluminum chloride slowly isomerized **9a**$^+$ to the (phthalimidin-2-yl)imido complex **10a**$^+$ in refluxing THF. The fluorine atom on the tungsten remained intact during the reaction, although the halogen exchange was observed in the Friedel−Crafts reactions of the pyrrolylimido complex [MF-

**Scheme 4**




$(NNCH{=}CHCH{=}CH)(dppe)_2]^+$ (M = Mo, W) promoted by aluminum chloride.[11]

Complex **10a**$^+$ showed spectroscopic properties similar to those of **3a**, except that the NMR signal of the phthalimidine methylene protons appeared at $\delta$ 2.29, which may be due to the shielding effect of the phenyl groups of the dppe ligands. Similar high-field shifts have also been reported in related diazoalkane,[7a] aryldiazenido,[6h] and pyrrolylimido[11] complexes having dppe ligands.

Two reasons may be considered for the much severer conditions required for the isomerization of the diazoalkane complex **9a**$^+$ to **10a**$^+$ compared with that of **4a**. One is the weaker nucleophilicity of the terminal nitrogen atom in **9a**$^+$ due to the electron-withdrawing effect of the cationic metal center. The other reason lies in the steric hindrance of the dppe ligands, which makes it difficult to take adequate conformation for the cyclization.

**Reaction of Hydrazido(2−) dppe Complexes with Malealdehyde Equivalent.** 2,5-Dimethoxy-2,5-dihydrofuran is a cyclic acetal of malealdehyde *cis*-OHCCH=CHCHO, and can be used as its synthetic equivalent. The hydrazido(2−) complex **8a**$^+$ and its molybdenum analogue **8b**$^+$ [9a] readily reacted with 2,5-dimethoxy-2,5-dihydrofuran under acidic conditions to provide two kinds of ligands having isomeric $\gamma$-lactam structures (Scheme 5). When the reactions were stopped within short reaction times (1 h for **8a**$^+$ and 3 h for **8b**$^+$ at room temperature), complexes **11**$^+$ with the (2-oxo-1,3-dihydro-2*H*-pyrrol-1-yl)imido ligand were selectively obtained. On standing under acidic conditions or by treatment with a base, complexes **11**$^+$ slowly but completely isomerized to complexes **12**$^+$ with the (2-oxo-1,5-dihydro-2*H*-pyrrol-1-yl)imido ligand, where the C−C double bond is conjugated with the amide carbonyl group.

The tungsten complexes **11a**$^+$ and **12a**$^+$ were unambiguously characterized by the X-ray crystallographic analysis (Figures 2 and 3, Tables 2 and 3). Crystals obtained for the two salts **11a**$^+BF_4^-$ and **12a**$^+BF_4^-$ were isomorphic and showed closely related structures and packing, but the C−C double bond in each isomeric ligand was clearly distinguished. In the lactam ring of **11a**$^+$, the C(3)−C(4) and C(4)−C(5) bonds are recognized as a single (1.52(1) Å) and a double (1.33(1) Å) bond, respectively, indicating that **11a**$^+$ has the 1,3-dihydro-2*H*-pyrrol-2-one structure. Conversely, the bond lengths in **12a**$^+$ (C(3)−C(4), 1.333(9) Å; C(4)−C(5), 1.470(8) Å) correspond to the 1,5-dihydro-2*H*-pyrrol-2-one structure. The lactam rings of both ligands are essentially planar as expected for the ene lactams.

(17) Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 595.

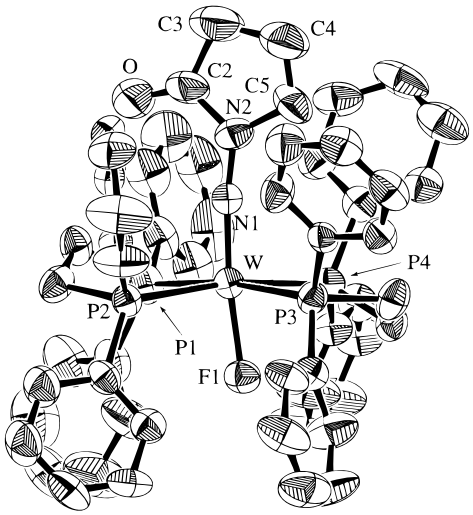



**Figure 2.** ORTEP drawing for $[WF(NNCH{=}CHCH_2CO)(dppe)_2]^+$ (**11a**$^+$). Hydrogen atoms are omitted for clarity.

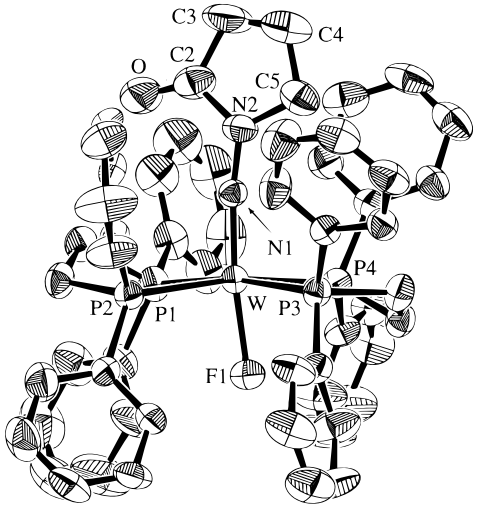
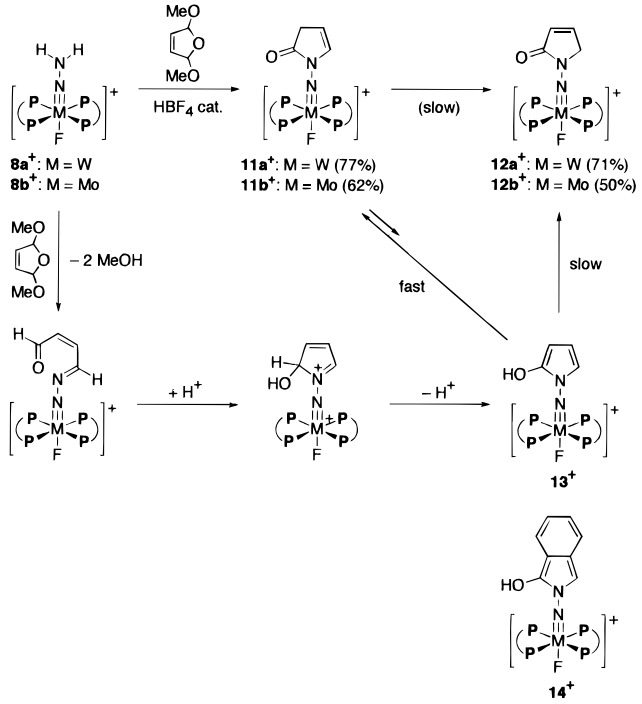



**Figure 3.** ORTEP drawing for $[WF(NNCH_2CH{=}CHCO)(dppe)_2]^+$ (**12a**$^+$). Hydrogen atoms are omitted for clarity.

**Scheme 5**




The NMR data of **11a**$^+$ and **12a**$^+$ were compared with those of free 1,3- and 1,5-dihydro-2*H*-pyrrol-2-ones[18a,b] (Tables 4 and 5). The $^{13}C$ NMR chemical shifts and $^{13}C-^1H$ coupling constants of the lactam parts in **11a**$^+$ and **12a**$^+$ are in good accord with the organic counterparts, except that the chemical shifts for the carbonyl carbons of **11a**$^+$ and **12a**$^+$ appeared by ∼10 ppm in a higher field than the reference compounds. It is noteworthy that the long-range coupling constants of 1,3-dihydro-2*H*-pyrrol-2-one were first estimated by using **11a**$^+$ (Table 5), because the low stability of free 1,3-dihydro-2*H*-pyrrol-2-one prevented detailed measurements (vide infra).

The $^1H$ signals of the lactam parts of **11**$^+$ and **12**$^+$ were observed in a higher field region than the reference organic counterparts, because of the shielding effect of the dppe ligands (vide supra). The protons at the 5-position, which are located closest to the phosphines, exhibited the largest high-field shift (−2.4 to −2.8 ppm), and the protons at the 4-position showed a larger shift (−0.9 to −1.2 ppm) than those at the 3-position (−0.2 to −0.4 ppm). The greater shielding effect toward the 4-protons than the 3-protons might be interpreted in terms of the solid-state structures of these complexes. As in Figures 2 and 3, the W−N−N bonds of **11a**$^+$ and **12a**$^+$ are slightly bent (172−173°) toward one dppe ligand so as to reduce the congestion between the other dppe ligand and the carbonyl oxygen atom. As a result, the 3-position of the ring goes away from the basal plane while the 4-position approaches the phenyl groups of one dppe ligand.

Finally, IR spectra, which has been reported only for a mixture of 1,3- and 1,5-dihydro-2*H*-pyrrol-2-ones,[18a,c] were measured for both **11**$^+$ and **12**$^+$. Carbonyl absorption frequencies of **12**$^+$ were ∼20 cm$^{-1}$ lower than those of **11**$^+$, which is due to the conjugation of the carbonyl group with the C−C double bond in **12**$^+$.

Reaction of the neutral hydrazido(2−) complex **2a** and 2,5-dimethoxy-2,5-dihydrofuran was also attempted under acidic or nonacidic conditions, but no characterizable compound was obtained from the mixture.

**Table 2.** Selected Bond Lengths and Angles in **11a**$^+BF_4^-$

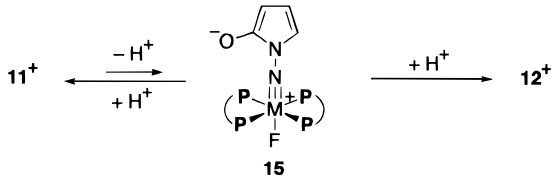
| | | | |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| W−P(1) | 2.523(2) | N(2)−C(2) | 1.41(1) |
| W−P(2) | 2.524(2) | N(2)−C(5) | 1.43(1) |
| W−P(3) | 2.539(2) | O−C(2) | 1.22(1) |
| W−P(4) | 2.493(2) | C(2)−C(3) | 1.51(1) |
| W−F(1) | 1.964(4) | C(3)−C(4) | 1.52(1) |
| W−N(1) | 1.746(6) | C(4)−C(5) | 1.33(1) |
| N(1)−N(2) | 1.356(8) | | |
| Bond Angles (deg) | | | |
| P(1)−W−P(2) | 78.36(7) | P(4)−W−N(1) | 94.2(2) |
| P(1)−W−P(3) | 172.47(8) | F(1)−W−N(1) | 173.4(2) |
| P(1)−W−P(4) | 99.07(8) | W−N(1)−N(2) | 172.2(6) |
| P(1)−W−F(1) | 92.2(1) | N(1)−N(2)−C(2) | 125.4(8) |
| P(1)−W−N(1) | 93.0(2) | N(1)−N(2)−C(5) | 123.5(8) |
| P(2)−W−P(3) | 101.07(7) | C(2)−N(2)−C(5) | 111.0(8) |
| P(2)−W−P(4) | 171.04(7) | O−C(2)−N(2) | 126(1) |
| P(2)−W−F(1) | 90.6(1) | O−C(2)−C(3) | 128(1) |
| P(2)−W−N(1) | 94.5(2) | N(2)−C(2)−C(3) | 105.9(9) |
| P(3)−W−P(4) | 80.34(7) | C(2)−C(3)−C(4) | 103.5(9) |
| P(3)−W−F(1) | 80.3(1) | C(3)−C(4)−C(5) | 110(1) |
| P(3)−W−N(1) | 94.5(2) | N(2)−C(5)−C(4) | 109(1) |
| P(4)−W−F(1) | 80.8(1) | | |

(18) (a) Bocchi, V.; Chierici, L.; Gardini, G. P.; Mondelli, R. *Tetrahedron* **1970**, *26*, 4073. (b) Fronza, G.; Mondelli, R.; Randall, E. W.; Gardini, G. P. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1746. (c) Baker, J. T.; Sifniades, S. *J. Org. Chem.* **1979**, *44*, 2798.

**Table 3.** Selected Bond Lengths and Angles in $\mathbf{12a}^+BF_4^-$

| Bond Lengths (Å) | | | |
|---|---|---|---|
| W−P(1) | 2.525(2) | N(2)−C(2) | 1.400(7) |
| W−P(2) | 2.528(2) | N(2)−C(5) | 1.456(7) |
| W−P(3) | 2.538(2) | O−C(2) | 1.214(7) |
| W−P(4) | 2.502(2) | C(2)−C(3) | 1.483(9) |
| W−F(1) | 1.984(3) | C(3)−C(4) | 1.333(9) |
| W−N(1) | 1.769(4) | C(4)−C(5) | 1.470(8) |
| N(1)−N(2) | 1.346(5) | | |
| **Bond Angles (deg)** | | | |
| P(1)−W−P(2) | 77.97(5) | P(4)−W−N(1) | 94.5(1) |
| P(1)−W−P(3) | 172.02(5) | F(1)−W−N(1) | 173.4(2) |
| P(1)−W−P(4) | 98.54(5) | W−N(1)−N(2) | 172.4(4) |
| P(1)−W−F(1) | 91.67(9) | N(1)−N(2)−C(2) | 124.6(5) |
| P(1)−W−N(1) | 93.6(1) | N(1)−N(2)−C(5) | 122.9(5) |
| P(2)−W−P(3) | 101.85(5) | C(2)−N(2)−C(5) | 112.3(5) |
| P(2)−W−P(4) | 170.37(5) | O−C(2)−N(2) | 125.4(7) |
| P(2)−W−F(1) | 90.29(9) | O−C(2)−C(3) | 130.8(7) |
| P(2)−W−N(1) | 94.6(1) | N(2)−C(2)−C(3) | 103.7(6) |
| P(3)−W−P(4) | 80.34(5) | C(2)−C(3)−C(4) | 110.6(7) |
| P(3)−W−F(1) | 80.35(9) | C(3)−C(4)−C(5) | 110.5(7) |
| P(3)−W−N(1) | 94.4(1) | N(2)−C(5)−C(4) | 102.9(6) |
| P(4)−W−F(1) | 80.79(9) | | |

**Scheme 6**




15

**Mechanism for the Formation of the Two Isomeric (2-Oxodihydro-2*H*-pyrrol-1-yl)imido Ligands.** The formation of $\mathbf{11}^+$ and $\mathbf{12}^+$ from $\mathbf{8}^+$ is rationalized as in Scheme 5. At first, the condensation reaction of the hydrazido(2−) ligand with 2,5-dimethoxy-2,5-dihydrofuran gives the (*Z*)-4-diazobut-2-enal ligand. Similar to the formation of the (phthalimidin-2-yl)imido ligand in **3** (vide supra), this ligand is then converted to the (2-hydroxypyrrol-1-yl)imido ligand $\mathbf{13}^+$ through the ring closure followed by deprotonation. The ring closure proceeds under milder conditions (at room temperature in the presence of an acid catalyst) than that for $\mathbf{9a}^+$. This is probably because the intermediate complex $\mathbf{14}^+$ for the cyclization of $\mathbf{9a}^+$ has the isoindoline type structure, which is considered to be less stable than the intermediate complex $\mathbf{13}^+$ with the pyrrole structure. The tautomerization of $\mathbf{13}^+$ gives rise to complex $\mathbf{11}^+$ or $\mathbf{12}^+$, but the protonation of the (2-hydroxypyrrol-1-yl)imido ligand is supposed to proceed much faster at the 3-position than at the 5-position and hence $\mathbf{11}^+$ is initially formed. This kinetic product $\mathbf{11}^+$ slowly isomerizes to the thermodynamically more stable product $\mathbf{12}^+$ via complex $\mathbf{13}^+$ by the action of an acid catalyst (Scheme 5) or via complex **15** by a base catalyst (Scheme 6).

In order to confirm this mechanism, the isomerization of $\mathbf{11a}^+$ to $\mathbf{12a}^+$ was followed by means of $^1$H NMR. Complex $\mathbf{11a}^+BF_4^-$ was stable under neutral conditions at room temperature in $CDCl_3/CD_3OD$ (4:1), but when $DCl/D_2O$ or $PhCH_2NMe_2$ was added to the solution, rapid and complete deuteration at the 3-position of $\mathbf{11a}^+$ was first observed. Along with the deuteration, the signals of $\mathbf{11a}^+$ started to decrease slowly, and signals due to the 4- and 5-protons of $\mathbf{12a}^+$ emerged. Each process was confirmed to be a pseudo-first-order reaction, and under both acidic and basic conditions, the isomerization was much slower than the deuteration: the half-life periods of the deuteration of $\mathbf{11a}^+$ and the isomerization to $\mathbf{12a}^+$ under the acidic conditions (17 $\mu$mol of $\mathbf{11a}^+$ in 0.6 mL of solvent and 0.1 mL of 20% $DCl/D_2O$) were 1.2 and 58 h, respectively. On the basis of this measurement, the protonation rate at the 3-position of the (2-hydroxypyrrol-1-yl)imido ligand in $\mathbf{13}^+$ was estimated to be ∼100 times faster than at the 5-position. The half-life period of the isomerization of $\mathbf{11a}^+$ under basic conditions (17 $\mu$mol of $\mathbf{11a}^+$ and $PhCH_2NMe_2$ in 0.6 mL of solvent) was ∼3 days in $CDCl_3$ and 36 days in $CDCl_3/CD_3OD$ (4:1). Although the isomerization in the latter solvent was much slower than that under acidic conditions, the deuteration of the 3-position was completed within 30 min. It is noteworthy that only monodeuteration occurred at the 5-position of $\mathbf{12a}^+$. This finding shows that the reverse reaction of $\mathbf{12a}^+$ forming $\mathbf{13a}^+$ or **15a** did not proceed under these acidic or basic conditions.

The 2*H*-pyrrol-2-one structures are often observed in naturally occurring compounds and have attracted great interest especially as a model for the terminal ring of linear tetrapyrrolic pigments.[19] Although compounds of this class having substituents on the ring carbons have been investigated widely, studies on the chemical properties of the C-unsubstituted dihydro-2*H*-pyrrol-2-one rings are limited.[18] The first reliable synthesis of 1,3- and 1,5-dihydro-2*H*-pyrrol-2-ones was reported by Bocchi et al. in 1970,[18a] and their 1-substituted derivatives were prepared by Baker and Sifniades in 1979.[18c] They showed that dihydro-2*H*-pyrrol-2-ones and their 1-methyl derivatives readily give equilibrium mixtures of 1,5- and 1,3-dihydro isomers in ∼9:1 ratio, while the 1-trifluoroacetyl derivative only exists as the 1,5-dihydro form. Pure 1,3-dihydro isomers can hardly be isolated.

In sharp contrast, complex $\mathbf{11}^+$ containing the 1,3-dihydro-2*H*-pyrrol-2-one moiety can be isolated in a pure form, stored under ambient conditions for a long period both as crystals and as a neutral solution, and fully characterized spectroscopically and crystallographically in spite of its thermodynamic instability. Obviously the stabilization of the 1,3-dihydro-2*H*-pyrrol-2-one structure in $\mathbf{11a}^+$ is brought about by its conjugation with the W−N moiety and the steric effect caused by the dppe ligands.

**Reactivities of the (2-Oxodihydro-2*H*-pyrrol-1-yl)imido Ligands.** Reactivities of free 1,3- and 1,5-dihydro-2*H*-pyrrol-2-ones have been little investigated in spite of the considerable attention to their thermodynamic and spectroscopic properties. A few examples of conjugate additions, Diels−Alder reactions, and 1,3-dipolar cycloadditions of some C-substituted 1,5-dihydro-2*H*-pyrrol-2-ones have appeared in literature,[20] while reactivities of 1,3-dihydro-2*H*-pyrrol-2-ones have been rarely reported. Therefore we have investigated the reactivities of the dihydro-2*H*-pyrrol-2-one rings in complexes $\mathbf{11}^+$ and $\mathbf{12}^+$. Although conjugate additions of $\mathbf{12}^+$ have failed to proceed under any condition we examined, complex $\mathbf{11}^+$ showed an interesting reactivity toward NBS.

When $\mathbf{11}^+$ was allowed to react with 2 equiv of NBS in the presence of $Et_3N$ and further treated with aqueous $Na_2S_2O_3$ or methanol, the (3-bromo-5-thiosulfato-2-oxo-1,5-dihydro-2*H*-pyrrol-1-yl)imido complex (**17**) or the (3-bromo-5-methoxy-2-oxo-1,5-dihydro-2*H*-pyrrol-1-yl)imido complex ($\mathbf{18}^+$) was isolated, respectively, in good to moderate yields (Scheme 7). The structures of **17** and $\mathbf{18}^+$ were determined by $^1$H and $^{13}$C NMR spectroscopy. Further, the structure of complex $\mathbf{18}^+BF_4^-$ was unambiguously confirmed by single-crystal X-ray analysis

(19) (a) Krafft, G. A; Garcia, E. A.; Guram, A.; O'Shaughnessy, B.; Xu, X. *Tetrahedron Lett.* **1986**, *27*, 2691. (b) Claret, J.; Farrera, J. A.; Ribó, J. M. *Tetrahedron* **1990**, *46*, 1039.

(20) (a) Jiménez, M. D.; Ortega, R.; Tito, A.; Fariña, F. *Heterocycles* **1988**, *27*, 173. (b) Koot, W.-J.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron Asymmetry* **1993**, *4*, 1941. (c) Koot, W.-J.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1992**, *57*, 1059. (d) Fariña, F.; Martín, M. V.; Paredes, M. C.; Tito, A. *J. Heterocycl. Chem.* **1987**, *24*, 1269. (e) Cooper, D. M.; Grigg, R.; Hargreaves, S.; Kennewell, P.; Redpath, J. *Tetrahedron* **1995**, *51*, 7791 and references therein.

**Table 4.** Comparison of the NMR Data for Complexes **11a**$^+$ and **12a**$^+$ with the Reference Organic Compounds

| | $^1$H ($\delta$, $J$ in Hz) | | | $^{13}$C ($\delta$, $J$ in Hz) | | | |
|---|---|---|---|---|---|---|---|
| | 3-H | 4-H | 5-H | 2-C | 3-C | 4-C | 5-C |
| **11a**$^+$ [a] | 2.62 | 4.21 | 3.83 | 170.1 | 34.5 | 102.3 | 130.0[b] |
| | $J_{34} = 2.4$ | $J_{35} = 2.0$ | $J_{45} = 5.1$ | | $^1J_{CH} = 134$ | $^1J_{CH} = 182$ | |
| 1,3-dihydro-2*H*-pyrrol-2-one[c] | 2.91 | 5.19 | 6.59 | 180.8 | 37.1 | 105.1 | 130.9 |
| | $J_{34} = 2.44$ | $J_{35} = 2.23$ | $J_{45} = 4.93$ | | $^1J_{CH} = 133.0$ | $^1J_{CH} = 179.5$ | $^1J_{CH} = 185.0$ |
| **12a**$^+$ [a] | 5.73 | 6.13 | 1.62 | 165.0 | 124.0 | 142.6 | 52.7 |
| | $J_{34} = 6.6$ | $J_{35} = 2.0$ | $J_{45} = 1.7$ | | $^1J_{CH} = 179$ | $^1J_{CH} = 178$ | $^1J_{CH} = 146$ |
| 1,5-dihydro-2*H*-pyrrol-2-one[c] | 6.10 | 7.30 | 4.07 | 175.5 | 127.6 | 147.6 | 49.5 |
| | $J_{34} = 5.75$ | $J_{35} = 1.95$ | $J_{45} = 1.75$ | | $^1J_{CH} = 175.4$ | $^1J_{CH} = 174.2$ | $^1J_{CH} = 142.2$ |

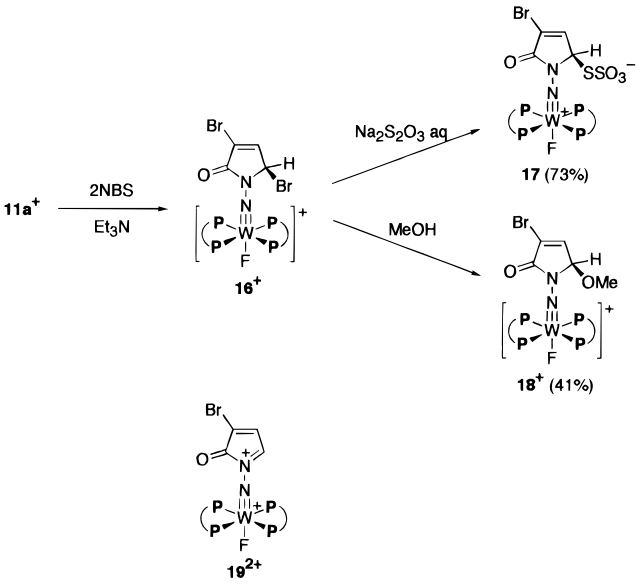
[a] Tetrafluoroborate in $CD_2Cl_2$ solution. [b] Overlapping with the signals of dppe ligands. The chemical shift was determined from the HC COSY spectrum. [c] In acetone-$d_6$ ($^1$H, ref 18a; $^{13}$C, ref 18b).

**Table 5.** Long-Range C−H Coupling Constants (Hz) for Complexes **11a**$^+$ and **12a**$^+$

| | $^2J$[2-C,3-H] | $^2J$[3-C,4-H] | $^2J$[4-C,3-H] | $^2J$[4-C,5-H] | $^2J$[5-C,4-H] | $^3J$[2-C,4-H] | $^3J$[2-C,5-H] | $^3J$[3-C,5-H] | $^3J$[5-C,3-H] |
|---|---|---|---|---|---|---|---|---|---|
| **11a**$^+$ [a] | 6 | 5 | 6 | 6 | *b* | 6 | 6 | 5 | *b* |
| **12a**$^+$ [a] | 8 | *c* | 3 | 6 | 9 | 11 | 11 | *c* | 9 |
| 1,5-dihydro-2*H*-pyrrol-2-one[d] | 8.0 | 3.0 | 4.0 | 5.0 | 9.0 | 11.0 | *e* | 3.0 | 9.0 |

[a] Tetrafluoroborate in $CD_2Cl_2$ solution. [b] Could not be determined by the overlapping of the signals. [c] Broad signal. [d] In acetone-$d_6$.[18b] [e] Not assigned.

**Scheme 7**




(Figure 4, Table 6). It has been revealed that an endocyclic double bond exists at the C(3)−C(4) position (C(3)−C(4), 1.28(1) Å; C(4)−C(5), 1.51(1) Å) and the C(3) and C(5) atoms exhibit the sp$^2$ and sp$^3$ characters, respectively. The 5-methoxy group and the carbonyl oxygen atom are subject to steric interaction with the dppe ligands. The bulky former group determines the orientation of the lactam ring, and the ring becomes nearly parallel to the P(1)−W−P(3) axis. The carbonyl group pushes the P(1) atom away from the basal plane defined by the other phosphorus atoms. This effect accounts for the large P(1)−W−N(1) angle (98.2(2)°) and the small P(1)−W−F(1) angle (81.2(1)°) in comparison with the other P−W−N(1) (89.2−93.0(2)°) and P−W−F(1) angles (87.5−90.2(1)°). It should be noted that investigations of halogenated 1,3- or 1,5-dihydro-2*H*-pyrrol-2-ones have been very limited, and the above bromination of **11a**$^+$ provides the first route to the brominated 1,5-dihydro-2*H*-pyrrol-2-one derivatives via the bromination of the 1,3-dihydro-2*H*-pyrrol-2-one ring.[21]

(21) Previously, 3-bromo-1,5-dihydro-5-methoxy-2*H*-pyrrol-2-one was prepared from 3-bromo-1,5-dihydro-5-methoxy-2*H*-furan-2-one: Fariña, F.; Martín, M. V.; Paredes, M. C. *Synthesis* **1973**, 167.

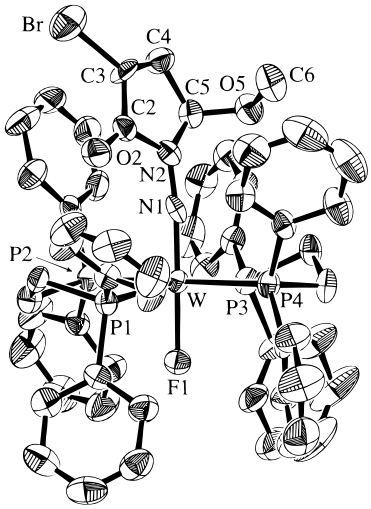



**Figure 4.** ORTEP drawing for [WF{NNCH(OCH$_3$)CH═CBrCO}(dppe)$_2$]$^+$ (**18**$^+$). Hydrogen atoms are omitted for clarity. Intramolecular contact of the lactam ring and one of the phenyl rings (left-beneath) of a dppe ligand can be viewed: the dihedral angle and the closest distance between the two rings are 6.4° and 3.3 Å.

It is of much interest that the methoxy and thiosulfato groups are bound to the hindered 5-position of the 1,5-dihydro-2*H*-pyrrol-2-one ring. A possible mechanism for the formation of **17** and **18**$^+$ is as follows. First, complex **15a** is formed by the deprotonation of **11a**$^+$ with $Et_3N$ and then dibrominated at the 3- and 5-positions by NBS to give the (3,5-dibromo-2-oxo-1,5-dihydro-2*H*-pyrrol-1-yl)imido complex **16**$^+$ (Scheme 7), although the latter complex has not been fully characterized so far. The bromination of **11a**$^+$ was not observed in the absence of $Et_3N$, suggesting that the reaction proceeds via **15a**. Moreover, **12a**$^+$ did not undergo bromination even in the presence of $Et_3N$ due to the difficulty of the deprotonation (vide supra). The substitution for the 5-bromine atom of **16**$^+$ is considered to be facile at room temperature, even though that the 5-position of the lactam ligand is sterically hindered. Thus, complex **16**$^+$ liberates a bromide anion quite readily to generate a reactive dicationic intermediate **19**$^{2+}$, which reacts with $S_2O_3^{2-}$ or methanol to give **17** or **18**$^+$, respectively. Attempts to obtain monobrominated product(s) from the equimolar reaction of **11a**$^+$ and NBS failed, because the second bromination was rather fast

**Table 6.** Selected Bond Lengths and Angles in $\mathbf{18}^{+}BF_4^{-}\cdot 0.5CH_2Cl_2$

| Bond Lengths (Å) | | | |
|---|---|---|---|
| W−P(1) | 2.561(2) | N(2)−C(5) | 1.453(9) |
| W−P(2) | 2.522(2) | O(2)−C(2) | 1.196(9) |
| W−P(3) | 2.555(2) | C(2)−C(3) | 1.45(1) |
| W−P(4) | 2.533(2) | Br−C(3) | 1.874(7) |
| W−F(1) | 1.947(4) | C(3)−C(4) | 1.28(1) |
| W−N(1) | 1.728(6) | C(4)−C(5) | 1.51(1) |
| N(1)−N(2) | 1.360(7) | O(5)−C(5) | 1.405(8) |
| N(2)−C(2) | 1.438(9) | O(5)−C(6) | 1.428(9) |
| **Bond Angles (deg)** | | | |
| P(1)−W−P(2) | 78.97(6) | W(1)−N(1)−N(2) | 173.6(5) |
| P(1)−W−P(3) | 168.63(7) | N(1)−N(2)−C(2) | 123.3(6) |
| P(1)−W−P(4) | 102.72(6) | N(1)−N(2)−C(5) | 122.7(6) |
| P(1)−W−F(1) | 81.2(1) | C(2)−N(2)−C(5) | 110.5(7) |
| P(1)−W−N(1) | 98.2(2) | O(2)−C(2)−N(2) | 123.8(8) |
| P(2)−W−P(3) | 99.42(7) | O(2)−C(2)−C(3) | 133.1(9) |
| P(2)−W−P(4) | 178.24(7) | N(2)−C(2)−C(3) | 103.0(7) |
| P(2)−W−F(1) | 89.5(1) | C(2)−C(3)−C(4) | 114.7(8) |
| P(2)−W−N(1) | 89.2(2) | Br−C(3)−C(2) | 118.7(7) |
| P(3)−W−P(4) | 78.82(6) | Br−C(3)−C(4) | 126.3(7) |
| P(3)−W−F(1) | 87.5(1) | C(3)−C(4)−C(5) | 108.8(7) |
| P(3)−W−N(1) | 93.0(2) | O(5)−C(5)−N(2) | 113.4(6) |
| P(4)−W−F(1) | 90.2(1) | O(5)−C(5)−C(4) | 114.9(7) |
| P(4)−W−N(1) | 91.0(2) | N(2)−C(5)−C(4) | 102.8(6) |
| F(1)−W−N(1) | 178.7(2) | C(5)−O(5)−C(6) | 115.4(6) |

even at −40 °C. Thus, major products after treatment with $Na_2S_2O_3$ were $\mathbf{12a}^{+}$ and **17**, from which **17** was isolated in 10%.

## Conclusion

Hydrazido(2−) complexes, readily available from dinitrogen complexes **1** and **7** by protonation, react with phthalaldehyde and 2,5-dimethoxy-2,5-dihydrofuran (malealdehyde equivalent) to form the novel organohydrazido complexes containing a five-membered lactam ring. The condensation with phthalaldehyde to give the (phthalimidin-2-yl)imido ligand and the subsequent reaction with HBr or KOH lead to the preparation of 2-aminophthalimidine or phthalimidine starting from coordinated dinitrogen. This reaction exemplifies direct and fully characterized synthesis of a lactam from molecular nitrogen. Similar reactions using 2,5-dimethoxy-2,5-dihydrofuran and dinitrogen complexes **7** give the organohydrazido complexes with the 1,3- and 1,5-dihydro-2*H*-pyrrol-2-one structures. The former organohydrazido complex is a kinetic product and slowly isomerized to the latter compound.

## Experimental Section

**General Information.** All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. 4,5-Dichloro- and 4,5-methylenedioxyphthalaldehydes were prepared by the oxidation of the corresponding phthalyl alcohols using NBS[22] and $MnO_2$,[13c] respectively. Other reagents were commercially obtained and used as received. Dinitrogen complexes **1**, **7a**,**b**[23] and hydrazido(2−) complexes **2a**,**b**[9b] and **8a**,**b**$^{+}$ [7a,9a] were prepared according to the literature methods. 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. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by $^1$H NMR spectroscopy. Direct bonding and long-range $^{13}$C−$^1$H coupling constants were measured using $^1$H-gated decoupling method and assigned according to the HC COSY and the selective $^1$H-decoupled spectra. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer (C, H, N) or at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo (S, Cl, Br).

**Preparation of *cis,mer*-[$WCl_2$(NNC$H_2C_6H_4$CO)($PMe_2Ph$)$_3$]·0.5$C_6H_6$ (3a·0.5$C_6H_6$).** To a stirred suspension of hydrazido(2−) complex **2a** (150 mg, 0.215 mmol) in THF (10 mL) were added phthalaldehyde (34.6 mg, 0.258 mmol) and one drop of concentrated hydrochloric acid. After stirring for 1 h at room temperature, the solvent was removed under reduced pressure and the resultant green oil was dissolved in benzene (3 mL). The solution was diluted with hexane (3 mL) with stirring and filtered rapidly, and hexane (15 mL) was added to the filtrate. Green crystals deposited were collected, washed with hexane, and dried in vacuo (96.9 mg, 53%): $^1$H NMR ($CDCl_3$) $\delta$ 1.51 (t, 6 H, $J$ = 3.9 Hz, PMe), 1.81 (d, 6 H, $J$ = 8.7 Hz, PMe), 1.89 (t, 6 H, $J$ = 3.9 Hz, PMe), 3.84 (s, 2 H, $CH_2$), 7.0−7.8 (m, 19 H, aromatic); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.6, 15.1 (PMe, t, $J_{CP}$ = 14 Hz), 21.5 (PMe, d, $J_{CP}$ = 31 Hz), 48.5 ($CH_2$, $^1J_{CH}$ = 148 Hz), 122−139 (aromatic), 140.4 (*ipso*-C of PPh, t, $J_{CP}$ = 18 Hz), 149.3 (*ipso*-C of PPh, d, $J_{CP}$ = 38 Hz), 161.3 (CO); $^{31}$P{$^1$H} NMR ($CDCl_3$) $\delta$ −17.3 (P(trans), s with $^{183}$W satellites, $J_{PW}$ = 294 Hz), −14.0 (P(unique), s with $^{183}$W satellites, $J_{PW}$ = 389 Hz); IR (KBr) 1712 (sh), 1694 ($\nu$(C═O)) cm$^{-1}$. Anal. Calcd for $C_{35}H_{42}N_2OP_3Cl_2W$: C, 49.20; H, 4.95; N, 3.28; Cl, 8.30. Found: C, 49.38; H, 5.27; N, 3.27; Cl, 8.71.

**Preparation of *cis,mer*-[$WBr_2$(NNC$H_2C_6H_4$CO)($PMe_2Ph$)$_3$] (3b).** A mixture of hydrazido(2−) complex **2b** (150 mg, 0.190 mmol), phthalaldehyde (38.2 mg, 0.285 mmol), and one drop of 48% hydrobromic acid in THF (10 mL) was stirred at room temperature for 80 min. The solution was dried, and diethyl ether (2 mL) was added to the resulting green oil. The green crystals deposited were filtered, washed with diethyl ether (3 mL), and extracted with benzene (10 mL). Recrystallization of the benzene extract from THF/hexane gave the title complex (49.7 mg, 29%): $^1$H NMR ($CDCl_3$) $\delta$ 1.61 (t, 6 H, $J$ = 3.8 Hz, PMe), 1.86 (d, 6 H, $J$ = 8.9 Hz, PMe), 2.05 (t, 6 H, $J$ = 3.8 Hz, PMe), 3.86 (s, 2 H, $CH_2$), 7.0−7.8 (m, 19 H, aromatic); IR (KBr) 1715 (sh), 1698 ($\nu$(C═O)) cm$^{-1}$. Anal. Calcd for $C_{32}H_{39}N_2OP_3Br_2W$: C, 42.50; H, 4.35; N, 3.10. Found: C, 42.29; H, 4.46; N, 3.43.

**Preparation of *cis,mer*-[$WCl_2$(NNC$H_2C_6H_2Cl_2$CO)($PMe_2Ph$)$_3$]·0.5$CH_2Cl_2$ (3c·0.5$CH_2Cl_2$).** A mixture of hydrazido(2−) complex **2a** (150 mg, 0.215 mmol), 4,5-dichlorophthalaldehyde (52.4 mg, 0.285 mmol), and one drop of concentrated hydrochloric acid in THF (10 mL) was stirred at room temperature for 90 min and evaporated to dryness. The residual green powder was washed with a small amount of benzene and recrystallized from $CH_2Cl_2$/hexane to give hygroscopic green plates (117 mg, 59%): $^1$H NMR ($CDCl_3$) $\delta$ 1.48 (t, 6 H, $J$ = 3.9 Hz, PMe), 1.85 (d, 6 H, $J$ = 8.8 Hz, PMe), 1.91 (t, 6 H, $J$ = 3.9 Hz, PMe), 3.59 (s, 2 H, $CH_2$), 7.0−7.9 (m, 17 H, aromatic); IR (KBr) 1709 ($\nu$(C═O)) cm$^{-1}$. Anal. Calcd for $C_{32.5}H_{38}N_2OP_3Cl_5W$: C, 42.12; H, 4.13; N, 3.02. Found: C, 42.40; H, 4.17; N, 3.20.

**Preparation of *cis,mer*-[$WCl_2${NNC$H_2C_6H_2$($O_2CH_2$)CO}($PMe_2Ph$)$_3$] (3d).** A mixture of hydrazido(2−) complex **2a** (150 mg, 0.215 mmol), 4,5-methylenedioxyphthalaldehyde (57.5 mg, 0.323 mmol), and one drop of concentrated hydrochloric acid in THF (10 mL) was stirred at room temperature for 1 h and evaporated to dryness. The pale green residue was washed with diethyl ether and extracted with benzene (30 mL). The extract was concentrated to ∼0.5 mL, and the brown solution was discarded. The residual green powdery solid was recrystallized from $CH_2Cl_2$/hexane to give **3d** as green crystals (106 mg, 57%): $^1$H NMR ($CDCl_3$) $\delta$ 1.49 (t, 6 H, $J$ = 3.8 Hz, PMe), 1.80 (d, 6 H, $J$ = 8.7 Hz, PMe), 1.88 (t, 6 H, $J$ = 3.8 Hz, PMe), 3.68 (s, 2 H, $NCH_2$), 6.07 (s, 2 H, $OCH_2O$), 6.51 (s, 1 H, aromatic), 7.0−7.6 (m, 16 H, aromatic); IR (KBr) 1690 ($\nu$(C═O)) cm$^{-1}$. Anal. Calcd for $C_{33}H_{39}N_2O_3P_3Cl_2W$: C, 46.12; H, 4.57; N, 3.26. Found: C, 46.28; H, 4.76; N, 3.22.

**Reaction of 2a and Phthalaldehyde Catalyzed by Acetic Acid.** Phthalaldehyde (72.8 mg, 0.543 mmol) and acetic acid (12 $\mu$L, 0.21 mmol) were added to a suspension of hydrazido(2−) complex **2a** (152 mg, 0.217 mmol) in THF (10 mL). The mixture was stirred at room temperature for 21 h, and the homogeneous brown solution was dried. Addition of diethyl ether (20 mL) to the resulting oil gave a yellow-brown powder and a brown solution, and the latter was concentrated to half of its original volume. The liquid phase containing the excess

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phthalaldehyde was discarded. The residual powder was extracted with diethyl ether (30 mL), and the extract was evaporated to dryness. Recrystallization from $C_6H_6$/hexane gave brown crystals of **4a** (92 mg, 52%): $^1$H NMR ($CDCl_3$) $\delta$ 1.45 (d, 6 H, $J$ = 8.4 Hz, PMe), 1.71, 1.95 (t, 6 H each, $J$ = 3.9 Hz, PMe), 7.0−7.8 (m, 19 H, aromatic), 8.44 (s, 1 H, NN=CH), 9.95 (s, 1 H, CHO); IR (KBr) 1688 ($\nu$(C=O)), 1530 ($\nu$(N=C)) cm$^{-1}$. Anal. Calcd for $C_{32}H_{39}N_2OP_3Cl_2W$: C, 47.14; H, 4.82; N, 3.44. Found: C, 47.40; H, 4.91; N, 3.36.

**Reaction of 4a with DCl.** To a $CDCl_3$ (0.6 mL) solution of **4a** (10 mg) was added 20% DCl /$D_2O$ (1 drop), and the mixture was shaken for 1 min. During this period, the color of the solution changed from brown to green. $^1$H NMR measurement confirmed the quantitative formation of **3a**, while the integrated intensity of the signal due to the phthalimidine $CH_2$ protons was estimated as 1.5 H.

**Reaction of 3a with CO.** A THF solution (15 mL) of **3a**·0.5$C_6H_6$ (610 mg, 0.714 mmol) was stirred under 1 atm of CO at 50 °C for 48 h. The $^1$H NMR spectrum of the crude mixture indicated that it contained **3a** and the carbonyl complex *cis*,*trans*-[$WCl_2$(NNC$H_2$-$C_6H_4$CO)($PMe_2Ph$)$_2$(CO)] (**5a**) in ∼1:9 ratio. A small amount of a green precipitate was filtered off, and the filtrate was evaporated to dryness. Addition of diethyl ether to the resultant brown oil formed a brownish purple crystalline solid, which was collected by filtration and washed with diethyl ether. The solid was extracted with benzene (10 mL), and the extract was concentrated to ∼3 mL. Addition of hexane (15 mL) deposited brown crystals of **5a** (273 mg, 54%): $^1$H NMR ($CDCl_3$) $\delta$ 1.98, 2.12 (t, 6 H each, $J$ = 4.1 Hz, PMe), 3.45 (s, 2 H, $CH_2$), 7.0−7.7 (m, 14 H, aromatic); IR (KBr) 1991 ($\nu$(C≡O)), 1711 ($\nu$(C=O)) cm$^{-1}$; $^{31}$P{$^1$H} NMR ($CDCl_3$) $\delta$ −11.3 (s with $^{183}$W satellites, $J_{PW}$ = 286 Hz). Anal. Calcd for $C_{25}H_{28}N_2O_2P_2Cl_2W$: C, 42.58; H, 4.00; N, 3.97. Found: C, 42.61; H, 4.15; N, 4.06.

**Reaction of 3a with HBr.** Hydrogen bromide gas was bubbled through a solution of **3a**·0.5$C_6H_6$ (200 mg, 0.234 mmol) in $CH_2Cl_2$ (15 mL) at 0 °C for 5 min. The red solution formed was stirred at 0 °C for 16 h and then at room temperature for 8 h. The solvent was removed under reduced pressure, and methanol (5 mL) was added to the residue. Red crystals of [$WBr_4$($PMe_2Ph$)$_2$] were filtered, washed with methanol (6 mL), and dried in vacuo (113 mg, 62%). The combined methanol solution was evaporated to dryness, and the green oily residue was extracted with water (10 mL) and 1% hydrobromic acid (2 × 10 mL). The extracts were combined, alkalified with KOH (∼200 mg), and extracted with $CH_2Cl_2$ (3 × 10 mL). After being dried over $MgSO_4$, the solution was evaporated to dryness under reduced pressure, and the resultant yellow solid was extracted with hot hexane (3 × 10 mL). Recrystallization of the hexane extract from benzene−hexane gave colorless crystals of 2-aminophthalimidine **6** (15.1 mg, 44%): $^1$H NMR ($CDCl_3$) $\delta$ 4.36 (br s, 2 H, $NH_2$), 4.52 (s, 2 H, $CH_2$), 7.4−7.9 (m, 4 H, aromatic); $^{13}$C NMR ($CDCl_3$) $\delta$ 53.0 ($CH_2$), 122.7, 123.5, 128.1, 131.4, 131.5, 139.5 (aromatic), 167.7 (CO); IR (KBr) 3293, 3270 ($\nu$(N−H)), 1705 ($\nu$(C=O)) cm$^{-1}$; mp 89−90 °C (lit.[24] mp 96 °C). Selected data for [$WBr_4$($PMe_2Ph$)$_2$]: $^1$H NMR ($CDCl_3$) $\delta$ −27.56 (br s, 12 H, PMe), 8.16 (t, 2 H, $J$ = 7 Hz, *p*-H), 9.02 (t, 4 H, $J$ = 7 Hz, *m*-H), 12.11 (d, 4 H, $J$ = 7 Hz, *o*-H). Anal. Calcd for $C_{16}H_{22}P_2Br_4W$: C, 24.65; H, 2.84; Br, 40.99. Found: C, 24.97; H, 2.81; Br, 40.16.

**Reaction of 3a with KOH. 1. In alcoholic solvents.** A mixture of **3a**·0.5$C_6H_6$ (100 mg, 0.117 mmol) and KOH (∼50 mg, 0.89 mmol) in methanol or ethanol (3 mL) was stirred at room temperature. The reaction mixture in methanol changed to slightly turbid orange after 1.5 h, while the ethanol solution became pale yellow and deposited a white solid after 3 h. Phthalimidine thus formed was identified by GC−MS and determined by GLC after neutralization of the reaction mixture with acetic acid (60 $\mu$L, 1.05 mmol). The solvent was removed under reduced pressure, and the $CDCl_3$ extract of the residue was analyzed by NMR. Phthalimidine, **6**, and $PMe_2Ph$ were confirmed, and the amount of **6** was estimated based on the GLC yield of phthalimidine and the integration values of the NMR signals. On the other hand, volatile components of the reaction mixture before neutralization were trapped in aqueous $H_2SO_4$ under reduce pressure, and the resulting solution was used for the determination of ammonia (indophenol method).[25]

**2. In THF.** To a solution of **3a**·0.5$C_6H_6$ (100 mg, 0.117 mmol) in THF (3 mL) was added KOH (∼50 mg, 0.89 mmol) and 18-crown-6 ether (∼31 mg, 0.12 mmol), and the mixture was stirred at room temperature for 6 h. The brownish yellow solution and white solid formed were analyzed by the methods described above.

**Preparation of *trans*-[WF(NN=CH$C_6H_4$CHO)(dppe)$_2$][$BF_4$]·0.5$CH_2Cl_2$ (9a$^+BF_4^-$·0.5$CH_2Cl_2$).** To a $CH_2Cl_2$ (10 mL) suspension of hydrazido(2−) complex **8a**$^+BF_4^-$·$CH_2Cl_2$ (1.00 g, 0.832 mmol) and phthalaldehyde (1.12 g, 8.32 mmol) was added 42% aqueous $HBF_4$ (2 drops). After the mixture was stirred for 19 h, the light green solution was dried over $MgSO_4$ and filtered through Celite. The solvent was removed by a rotary evaporator, and the resultant sticky oil was washed repeatedly with diethyl ether. The green oil was recrystallized twice from $CH_2Cl_2$/diethyl ether to give green crystals (951 mg, 90%): $^1$H NMR ($CDCl_3$) $\delta$ 2.6−3.1 (m, 8 H, $CH_2$ of dppe), 6.9−7.4 (m, 41 H, Ph of dppe and NN=CH at $\delta$ 7.14 (confirmed by HC COSY)), 7.5−7.8 (m, 4 H, $C_6H_4$), 9.55 (s, 1 H, CHO); $^{13}$C{$^1$H} NMR ($CDCl_3$) $\delta$ 31.7 ($CH_2$ of dppe, quint, $J_{CP}$ = 10 Hz), 126−135 (aromatic), 162.0 (NN=CH), 191.7 (CHO); $^{31}$P{$^1$H} NMR ($CDCl_3$) $\delta$ 31.3 (d with $^{183}$W satellites, $J_{PF}$ = 40, $J_{PW}$ = 286 Hz); IR (KBr) 1690 ($\nu$(C=O)), 1532 ($\nu$(C=N)) cm$^{-1}$. Anal. Calcd for $C_{60.5}H_{55}N_2OBF_5P_4ClW$: C, 56.99; H, 4.35; N, 2.20. Found: C, 57.03; H, 4.38; N, 2.21.

**Preparation of *trans*-[WF(NNC$H_2C_6H_4$CO)(dppe)$_2$][$BF_4$] (10a$^+BF_4^-$).** A solution of **9a**$^+BF_4^-$·0.5$CH_2Cl_2$ (1.00 g, 0.785 mmol) and $AlCl_3$ (104.5 mg, 0.785 mmol) in THF (40 mL) was refluxed for 48 h. The brown opaque mixture was diluted with $CH_2Cl_2$ (50 mL), washed successively with 5% aqueous $NH_4BF_4$ (4 × 100 mL), and dried over $MgSO_4$. The solvent was evaporated, and the resultant orange-brown oil was recrystallized from $CH_2Cl_2$−methanol/diethyl ether to give orange-brown crystals (370 mg, 38%). An analytical sample was obtained by further recrystallization from $CH_2Cl_2$/hexane: $^1$H NMR ($CDCl_3$) $\delta$ 2.29 (s, 2 H, $CH_2$), 2.6−2.8, 3.3−3.5 (m, 4 H each, $CH_2$ of dppe), 6.8−7.6 (m, 44 H, aromatic); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 32.9 ($CH_2$ of dppe, quint, $J_{CP}$ = 9 Hz), 50.3 ($NCH_2$, $^1J_{CH}$ = 147 Hz), 122−139 (aromatic), 162.9 (CO); $^{31}$P{$^1$H} NMR ($CDCl_3$) $\delta$ 30.8 (d with $^{183}$W satellites, $J_{PF}$ = 43, $J_{PW}$ = 286 Hz); IR (KBr) 1701 ($\nu$(C=O)) cm$^{-1}$. Anal. Calcd for $C_{60}H_{54}N_2OBF_5P_4W$: C, 58.46; H, 4.42; N, 2.27. Found: C, 57.77; H, 4.44; N, 2.32.

**Preparation of *trans*-[WF(NNCH=C$HCH_2$CO)(dppe)$_2$][$BF_4$] (11a$^+BF_4^-$).** To a solution of hydrazido(2−) complex **8a**$^+BF_4^-$·$CH_2Cl_2$ (200 mg, 0.166 mmol) in $CH_2Cl_2$ (10 mL) were added 2,5-dimethoxy-2,5-dihydrofuran (24 $\mu$L, 0.20 mmol) and 42% aqueous $HBF_4$ (1 drop). After stirring for 1 h, the reddish brown solution was dried over $MgSO_4$, filtered through Celite, and evaporated. The resulting dark-brown oil was fractionated by gel chromatography (Sephadex LH-20; eluent, methanol/$CH_2Cl_2$ (4:1)). The orange band was collected and recrystallized from $CH_2Cl_2$−methanol/diethyl ether. The title complex was crystallized in two different crystal forms: an orange-red columnar crystal (61.7 mg, 31%), and the other dark-red prismatic and efflorescent (92.8 mg, 46%; contained 0.5 molecule of diethyl ether after vacuum drying). The former crystals were used for X-ray and elemental analyses: $^1$H NMR ($CDCl_3$) $\delta$ 2.53 (br t, 2 H, $J$ = 2.2 Hz, $COCH_2$), 2.6−2.8, 3.1−3.3 (m, 4 H each, $CH_2$ of dppe), 4.06 (dt, 1 H, $J$ = 5.0, 2.2 Hz, NCH), 4.30 (dt, 1 H, $J$ = 5.0, 2.5 Hz, NCH=C*H*), 6.9−7.4 (m, 40 H, Ph of dppe); $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 32.8 ($CH_2$ of dppe, quint, $J_{CP}$ = 10 Hz), 34.5 ($COCH_2$), 102.3 (NCH=*C*H), 128−134 (Ph of dppe and NCH ($\delta$ 130.0)), 170.1 (CO); $^{31}$P{$^1$H} NMR ($CDCl_3$) $\delta$ 30.9 (d with $^{183}$W satellites, $J_{PF}$ = 43, $J_{PW}$ = 285 Hz); IR (KBr) 1705 ($\nu$(C=O)), 1609 ($\nu$(C=C)) cm$^{-1}$. Anal. Calcd for $C_{56}H_{52}N_2OBF_5P_4W$: C, 56.88; H, 4.43; N, 2.37. Found: C, 56.25; H, 4.37; N, 2.44.

Its molybdenum analogue *trans*-[MoF(NNCH=C$HCH_2$CO)(dppe)$_2$][$BF_4$] (**11b**$^+BF_4^-$) was prepared similarly from **8b**$^+BF_4^-$ in 63% yield, but the reaction required a longer time (3 h). Reddish purple crystals from $CH_2Cl_2$/hexane: $^1$H NMR ($CDCl_3$) $\delta$ 2.50 (br s, 2 H, $COCH_2$), 2.6−2.8, 3.1−3.3 (m, 4 H each, $CH_2$ of dppe), 4.35−4.45

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**Table 7.** Crystallographic Data for **3a**·0.5$C_6H_6$, **11a**$^+BF_4^-$, **12a**$^+BF_4^-$, and **18**$^+BF_4^-$·0.5$CH_2Cl_2$

| | **3a**·0.5$C_6H_6$ | **11a**$^+BF_4^-$ | **12a**$^+BF_4^-$ | **18**$^+BF_4^-$·0.5$CH_2Cl_2$ |
|---|---|---|---|---|
| formula | $C_{35}H_{42}N_2OP_3Cl_2W$ | $C_{56}H_{52}N_2OBF_5P_4W$ | $C_{56}H_{52}N_2OBF_5P_4W$ | $C_{57.5}H_{54}N_2O_2BF_5P_4ClBrW$ |
| formula weight | 854.41 | 1182.59 | 1182.59 | 1333.98 |
| space group | *C*2/*c* (No.15) | $P2_1/n$ (No.14) | $P2_1/n$ (No.14) | $P2_1/n$ (No.14) |
| *a* (Å) | 37.952(4) | 17.712(4) | 17.710(2) | 12.798(2) |
| *b* (Å) | 18.382(3) | 17.933(5) | 17.885(2) | 27.619(2) |
| *c* (Å) | 10.368(2) | 17.715(3) | 17.785(2) | 17.002(2) |
| $\beta$ (deg) | 93.97(2) | 110.16(2) | 110.278(8) | 109.79(1) |
| *V* (Å$^3$) | 7215(1) | 5282(2) | 5283.9(9) | 5655(1) |
| *Z* | 8 | 4 | 4 | 4 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.573 | 1.487 | 1.486 | 1.567 |
| $\rho_{obsd}$ (g cm$^{-3}$) | 1.548 (17 °C) | 1.488 (24 °C) | 1.487 (25 °C) | 1.589 (17 °C) |
| $\mu_{calc}$ (cm$^{-1}$) | 35.16 | 24.08 | 24.08 | 29.74 |
| transmn factor | 0.6396−0.9985 | 0.7131−0.9996 | 0.9283−0.9986 | 0.6613−1.0000 |
| $R^a$ | 0.054 | 0.048 | 0.039 | 0.049 |
| $R_w{}^b$ | 0.046 | 0.026 | 0.022 | 0.033 |

$^a$ $R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(m, 2 H, CH=CH), 6.9−7.4 (m, 40 H, Ph of dppe); IR (KBr) 1713 ($\nu$(C=O)), 1609 ($\nu$(C=C)) cm$^{-1}$. Anal. Calcd for $C_{56}H_{52}N_2OBF_5P_4Mo$: C, 61.44; H, 4.79; N, 2.56. Found: C, 61.25; H, 4.84; N, 2.69.

**Preparation of *trans*-[WF(NNCH$_2$CH=CHCO)(dppe)$_2$][BF$_4$] (12a$^+$BF$_4^-$).** A $CH_2Cl_2$ (5 mL) solution of **11a**$^+BF_4^-$ (200 mg, 0.169 mmol) and $Et_3N$ (24 $\mu$L, 0.17 mmol) was stirred for 1 week at room temperature. Purification by gel chromatography (Sephadex LH-20; eluent, methanol/$CH_2Cl_2$ (4:1)) and recrystallization from $CH_2Cl_2$−methanol/diethyl ether afforded orange-red crystals and small amounts of [$Et_3NH$]$BF_4$. The crystals were washed with water to remove the ammonium salt and recrystallized from $CH_2Cl_2$−methanol/diethyl ether to give pure crystals of **12a**$^+BF_4^-$ (141 mg, 71%): $^1$H NMR ($CDCl_3$) $\delta$ 1.91 (br s, 2 H, $NCH_2$), 2.6−2.8, 3.15−3.35 (m, 4 H each, $CH_2$ of dppe), 5.59 (br d, 1 H, $J$ = 6.5 Hz, COCH), 6.29 (br d, 1 H, $J$ = 6.5 Hz, $NCH_2CH$), 6.9−7.4 (m, 40 H, Ph of dppe); $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 32.8 ($CH_2$ of dppe, quint, $J_{CP}$ = 9 Hz), 52.7 ($NCH_2$), 124.0 (COCH), 128−135 (Ph of dppe), 142.6 ($NCH_2CH$), 165.0 (CO); $^{31}$P-{$^1$H} NMR ($CDCl_3$) $\delta$ 30.8 (d with $^{183}$W satellites, $J_{PF}$ = 43, $J_{PW}$ = 286 Hz); IR (KBr) 1686 ($\nu$(C=O)) cm$^{-1}$. Anal. Calcd for $C_{56}H_{52}N_2OBF_5P_4W$: C, 56.88; H, 4.43; N, 2.37. Found: C, 56.59; H, 4.54; N, 2.29.

Its molybdenum analogue *trans*-[MoF(NNCH$_2$CH=CHCO)(dppe)$_2$][BF$_4$] (**12b**$^+BF_4^-$) was prepared similarly from **11b**$^+BF_4^-$ in 50% yield. Purple crystals from $CH_2Cl_2$/hexane: $^1$H NMR ($CDCl_3$) $\delta$ 2.19 (br s, 2 H, $NCH_2$), 2.55−2.75, 3.1−3.3 (m, 4 H each, $CH_2$ of dppe), 5.50 (br d, 1 H, $J$ = 6.4 Hz, COCH), 6.36 (br d, 1 H, $J$ = 6.4 Hz, $CH_2CH$), 7.0−7.4 (m, 40 H, Ph of dppe); IR (KBr) 1694 ($\nu$(C=O)) cm$^{-1}$. Anal. Calcd for $C_{56}H_{52}N_2OBF_5P_4Mo$: C, 61.44; H, 4.79; N, 2.56. Found: C, 61.31; H, 4.91; N, 2.67.

**Isomerization of 11a$^+$ to 12a$^+$. 1. Acidic Conditions.** To a solution of **11a**$^+BF_4^-$ (20 mg, 17 $\mu$mol) in $CDCl_3$/$CD_3OD$ (4:1, 0.6 mL) was added DCl/$D_2O$ (20%, 0.1 mL). The mixture was shaken for a few minutes and analyzed by $^1$H NMR. The deuteration at the 3-position and the isomerization to **12a**$^+$ were monitored periodically over two weeks. The products ratio was estimated on the basis of the integrated intensities of the heterocyclic ring protons. The pseudo-first-order rate constant for the deuteration and isomerization were estimated to be $5.7 \times 10^{-1}$ h$^{-1}$ (half-life period 1.2 h) at 23 ± 2 °C and $1.2 \times 10^{-2}$ h$^{-1}$ (half-life period 58 h) at 23 ± 2 °C, respectively.

**2. Basic Conditions.** To a solution of **11a**$^+BF_4^-$ (20 mg, 17 $\mu$mol) in $CDCl_3$/$CD_3OD$ (4:1, 0.6 mL) or $CDCl_3$ (0.6 mL) was added $PhCH_2NMe_2$ (2.5 $\mu$L, 17 $\mu$mol), and the reaction was followed by $^1$H NMR in a manner similar to that described above. The deuteration at the 3-position of **11a**$^+$ in $CDCl_3$/$CD_3OD$ (4:1) completed within 30 min, and the rate constant for the isomerization to **12a**$^+$ was $8.3 \times 10^{-4}$ h$^{-1}$ (half-life period 36 days, at 23 ± 2 °C). In contrast, the rate constant for the isomerization in $CDCl_3$ was much larger ($9.4 \times 10^{-3}$ h$^{-1}$, half-life period 74 h at 23 ± 2 °C).

**Preparation of *trans*-[WF{NNCH(SO$_3$)CH=CBrCO}(dppe)$_2$]·0.5(diethyl ether) (17·0.5(diethyl ether)).** To a THF (5 mL) suspension of **11a**$^+BF_4^-$ (100 mg, 0.0846 mmol) were added NBS (30.1 mg, 0.169 mmol) and $Et_3N$ (12 $\mu$L, 0.086 mmol) at −40 °C. After stirring at the same temperature for 4 h, the resulting orange solution was slowly warmed to room temperature and quenched with 5% aqueous $Na_2S_2O_3$ (5 mL). The mixture was immediately diluted with $CH_2Cl_2$ (20 mL) and washed successively with 5% aqueous $Na_2S_2O_3$ (2 × 50 mL) and 5% aqueous $NH_4BF_4$ (4 × 50 mL). The organic layer was dried over $MgSO_4$ and evaporated to leave an orange-red oil, which was crystallized from $CH_2Cl_2$−methanol/diethyl ether to give **17**·0.5(diethyl ether) as red crystals (81.6 mg, 73%): $^1$H NMR ($CDCl_3$) $\delta$ 2.6−2.8, 3.3−3.5 (m, 4 H each, $CH_2$ of dppe), 5.50 (d, 1 H, $J$ = 2.2 Hz, NCH), 7.0−7.4 (m, 41 H, Ph of dppe and NCH(SO$_3$)C*H* at $\delta$ 7.21 (confirmed by HH COSY)); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 31−32.5 ($CH_2$ of dppe), 66.5 (5-C, $^1J_{CH}$ = 167, $^2J_{CH}$ = 7 Hz), 113.0 (3-C, $^2J_{CH}$ < 2, $^3J_{CH}$ = 5 Hz), 128−136 (Ph of dppe), 143.5 (4-C, $^1J_{CH}$ = 190, $^2J_{CH}$ = 4 Hz), 159.4 (2-C, $^3J_{CH}$ = 10 (4-H), < 2 (5-H) Hz); $^{31}$P{$^1$H} NMR ($CDCl_3$) $\delta$ 29−34 (m); IR (KBr) 1732 ($\nu$(C=O)), 1252, 1028 ($\nu$(S=O)) cm$^{-1}$. Anal. Calcd for $C_{58}H_{55}N_2O_{4.5}FP_4S_2BrW$: C, 52.66; H, 4.19; N, 2.12; S, 4.85; Br, 6.04. Found: C, 52.46; H, 4.19; N, 2.09; S, 4.61; Br, 6.19.

**Preparation of *trans*-[WF{NNCH(OMe)CH=CBrCO}(dppe)$_2$][BF$_4$]·$CH_2Cl_2$ (18$^+BF_4^-$·$CH_2Cl_2$).** A reaction of **11a**$^+BF_4^-$ (80 mg, 0.0677 mmol) with NBS (24.1 mg, 0.135 mmol) and $Et_3N$ (10 $\mu$L, 0.072 mmol) in THF (5 mL) was conducted similarly to the preparation of **17**. The resulting solution was diluted with $CH_2Cl_2$ (20 mL) and washed with 5% aqueous $NH_4BF_4$ (2 × 50 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The $^1$H NMR spectrum of the residual oil exhibited a pair of doublets at $\delta$ 5.21 and 6.92 ($J$ = 2.2 Hz) which are tentatively assigned as the ring protons of **16**$^+$. Orange crystals obtained after purification by gel chromatography (Sephadex LH-20; eluent, methanol/$CH_2Cl_2$ (4:1)) and crystallization from $CH_2Cl_2$−methanol/diethyl ether consisted of **16**$^+$ and **18**$^+$ in ∼1:1 ratio. They were dissolved in methanol (5 mL) and heated at 50 °C for 12 h to complete the conversion to **18**$^+$. The solution was diluted with $CH_2Cl_2$ (20 mL) and washed with 5% aqueous $NH_4BF_4$ (2 × 50 mL), and further recrystallization from $CH_2Cl_2$−methanol/diethyl ether gave orange crystals of **18**$^+BF_4^-$ containing 0.5$CH_2Cl_2$ (37.1 mg, ∼41%). A single crystal for X-ray diffraction measurement was selected from them. Analytical sample formulated as **18**$^+BF_4^-$·$CH_2Cl_2$ was obtained by further recrystallization from $CH_2Cl_2$/diethyl ether: $^1$H NMR ($CDCl_3$) $\delta$ 2.3−2.5 (m, 2 H, $CH_2$ of dppe), 2.60 (s, 3 H, $OCH_3$), 2.9−3.3 (m, 6 H, $CH_2$ of dppe), 4.60 (d, 1 H, $J$ = 1.9 Hz, NCH), 6.86 (d, 1 H, $J$ = 1.9 Hz, NCH(OMe)C*H*), 7.0−7.4 (m, 40 H, Ph of dppe); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 30−31 ($CH_2$ of dppe), 51.8 ($OCH_3$, $^1J_{CH}$ = 144, $^3J_{CH}$ = 7 Hz), 87.6 (5-C, $^1J_{CH}$ = 167, $^2J_{CH}$ = 5, $^3J_{CH}$ < 5 Hz), 119.2 (3-C, $^2J_{CH}$ < 2, $^3J_{CH}$ = 4 Hz), 128−137 (Ph of dppe), 138.8 (4-C, $^1J_{CH}$ = 184, $^2J_{CH}$ = 3 Hz), 159.1 (2-C, $^3J_{CH}$ = 9 (4-H), < 2 (5-H) Hz); $^{31}$P-{$^1$H} NMR ($CDCl_3$) $\delta$ 29.5 (br d with $^{183}$W satellites, $J_{PF}$ = 43, $J_{PW}$ = 289 Hz); IR (KBr) 1728 ($\nu$(C=O)), 1605 ($\nu$(C=C)) cm$^{-1}$. Anal. Calcd for $C_{58}H_{55}N_2O_2BF_5P_4Cl_2BrW$: C, 50.61; H, 4.03; N, 2.04. Found: C, 50.63; H, 3.97; N, 1.95.

**Crystallography.** Crystals suitable for X-ray analysis were sealed in Pyrex glass capillaries under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-

circle automated diffractometer with Mo Kα ($\lambda = 0.710\ 69$ Å) radiation and a graphite monochromator at $20 \pm 1$ °C. Accurate cell dimensions of each crystal were determined by least-squares refinement of 25 machine-centered reflections. Empirical absorption correction based on $\psi$ scan and Lorentz−polarization corrections were applied. Details of the X-ray diffraction study are summarized in Table 7.

The structure solution and refinement were performed by using the TEXSAN (Molecular Structure Corp.) program package. The structures were solved by a combination of heavy-atom Patterson methods and Fourier techniques. All non-hydrogen atoms were found from the difference Fourier maps and refined by full-matrix least-squares techniques with anisotropic thermal parameters, except for the carbon atom of the $CH_2Cl_2$ molecule in **18**$^+BF_4^-$·$0.5CH_2Cl_2$, where isotropic parameters were used. All hydrogen atoms were placed at calculated positions and were included in the final stage of refinements with fixed isotropic parameters. The atomic scattering factors were taken from ref 26, and anomalous dispersion effects were included; the values for $\Delta f'$ and $\Delta f''$ were taken from ref 27.

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**Supporting Information Available:** X-ray crystallographic files in CIF format are available for **3a**·$0.5C_6H_6$, **11a**$^+BF_4^-$, **12a**$^+BF_4^-$, and **18**$^+BF_4^-$·$0.5CH_2Cl_2$ on the Internet only. Access information is given on any current masthead page.

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