Synthesis and Reactivities of Pyrrolylimido Complexes of Molybdenum and Tungsten: Formation of Pyrrole and *N*-Aminopyrrole from Molecular Nitrogen[1]

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Abstract: Hydrazido(2−) complexes *trans*-$[MX(NNH_2)(dppe)_2]^+$ (M = Mo, W; X = F, Cl; dppe = $Ph_2PCH_2CH_2PPh_2$) and *cis,mer*-$[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl, Br), which are readily derived from *trans*-$[M(N_2)_2(dppe)_2]$ (**1**) and *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ by protonation, condensed with 2,5-dimethoxytetrahydrofuran to afford pyrrolylimido complexes of the type *trans*-$[MX(NNCH{=}CHCH{=}CH)(dppe)_2]^+$ (**3**$^+$) and *cis,mer*-$[WX_2(NNCH{=}CHCH{=}CH)(PMe_2Ph)_3]$ (**6**), respectively. Their structures were characterized spectroscopically and further confirmed by X-ray diffraction study. Electrophilic substitution reactions at the pyrrole ring in complexes **3**$^+$ occurred selectively at the β-position to give the corresponding β-substituted pyrrolylimido complexes *trans*-$[MX(NNCH{=}C(E)CH{=}CH)(dppe)_2]^+$ (E = Br, CN, SO_3^-, COR), although only chlorination of **3**$^+$ with *N*-chlorosuccinimide in THF took place predominantly at the α-position. This β-regioselectivity is in sharp contrast to the α-regioselectivity of free pyrrole and is probably caused by the steric effect of the dppe ligands. Complexes **3**$^+$ were readily reduced under ambient conditions with $LiAlH_4$ to liberate pyrrole and *N*-aminopyrrole in high yields. Further, the tetrahydrido complexes $[MH_4(dppe)_2]$, which can be converted back into the original dinitrogen complexes **1**, were recovered in moderate yields after the reduction. This accomplishes the synthetic cycle for pyrrole and *N*-aminopyrrole starting from the dinitrogen complexes **1**. β-Heptylpyrrole was also prepared by starting from **3c**$^+$ (M = W, X = Cl) by the β-selective heptanoylation followed by the reduction with $LiAlH_4$. On the other hand, reduction of **6b** (X = Br) with $LiAlH_4$ predominantly produced pyrrole, whereas treatment of **6b** with KOH/EtOH liberated *N*-aminopyrrole in a high yield.

Introduction

Nitrogen in most of artificial organonitrogen compounds is fundamentally supplied from ammonia, which is industrially synthesized from dinitrogen and dihydrogen under drastic conditions (Haber process). Development of the synthetic methods for organonitrogen compounds directly from dinitrogen as the nitrogen source under mild conditions has been receiving much interest but has met with only limited success.[2,3] One of the most promising approaches for this purpose lies on development of the chemical transformation of coordinated dinitrogen, and extensive studies have been done so far by using various dinitrogen complexes of transition metals.[2] We and some other groups have long been investigating the reactivities of dinitrogen complexes of the type $[M(N_2)_2(phosphine)_4]$ (M = Mo, W), and revealed that the dinitrogen complexes are converted into various organonitrogen complexes such as organohydrazido,[4] organodiazenido,[4a−f,5] and diazoalkane complexes[6] under mild conditions. In some cases, these nitrogen-containing ligands can be released from the metal as organonitrogen compounds, but those obtained by this method were limited to simple ones such as alkylamines[6b,7] and azines.[6b,8]

In order to extend the range of organonitrogen compounds derived from dinitrogen, we have recently embarked on the synthesis of other nitrogen-heterocyclic ligands from coordinated dinitrogen in *trans*-$[M(N_2)_2(dppe)_2]$ (**1a**, M = Mo; **1b**, M = W; dppe = $Ph_2PCH_2CH_2PPh_2$) and *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**4**). Liberation of the heterocyclic ligands from the resultant complexes would accomplish the direct synthesis of

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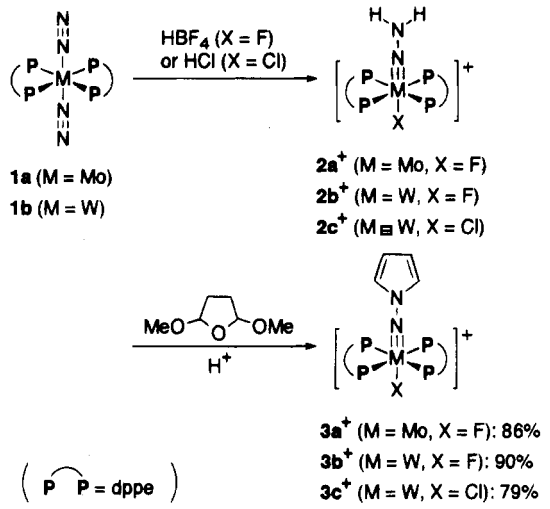
nitrogen heterocycles, one of the most attractive targets in the field of the synthetic chemistry, from molecular nitrogen. This type of transformation has been partially achieved by Chatt *et al.* They prepared pyrrolidine or piperidine by the reduction of hydrazido(2−) complexes $[MBr\{NN(CH_2)_nCH_2\}(dppe)_2]^+$ (M = Mo, W; n = 3, 4), which in turn were prepared by the reaction of **1** with 1,4-dibromobutane or 1,5-dibromopentane. However, such an approach has never been applied to the synthesis of more valuable target molecules than simple alkylamines.[7] An important feature of this approach is that it enables not only effective transformation of dinitrogen under very mild conditions but also full characterization of the chemical transformation process of coordinated dinitrogen owing to the moderate stability of intermediate complexes. Further, we expected unique chemical reactivities of the heterocyclic ligands by taking advantage of the electronic and steric effects of phosphine ligands. In this paper, we wish to report the synthesis, characterization, and reactivities of pyrrolylimido complexes of molybdenum and tungsten and their use in the synthesis of pyrrole and *N*-aminopyrrole from dinitrogen. A preliminary communication has already been reported.[9]

Results and Discussion

1. Synthesis and Properties of Pyrrolylimido Complexes. Molybdenum and tungsten hydrazido(2−) complexes *trans*-$[MX(NNH_2)(dppe)_2]^+$ (**2**$^+$) and *cis,mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ (**5**) (M = Mo, W; X = halogen), which are formed by protonation at the terminal nitrogen atom of the dinitrogen complexes *trans*-$[M(N_2)_2(dppe)_2]$ (**1**) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**4**), respectively, have a nucleophilic feature arising from the lone pair on the NH_2 group.[6a,10] Consequently, these complexes exhibit reactivities similar to those of hydrazine and amines and are convenient intermediates for the introduction of organic substituents onto dinitrogen. From **2**$^+$ and **5** have been prepared various organonitrogen ligands such as diazoalkane[6a−d] and substituted hydrazido(2−)[4d,f,h,10b] ligands. Especially, the condensation reactions of **2**$^+$ and **5** with ketones or aldehydes to form diazoalkane complexes developed in this laboratory are very useful for the C−N bond formation at coordinated dinitrogen. We have now applied this reaction to the synthesis of nitrogen heterocycles.

Thus, 2,5-dimethoxytetrahydrofuran, a cyclic acetal of succinaldehyde, reacted with cationic dppe hydrazido(2−) complexes **2**$^+$ to form a series of air-stable (*N*-pyrrolyl)imido complexes $[MX(NNCH{=}CHCH{=}CH)(dppe)_2]^+$ (**3a**$^+$, M = Mo, X = F; **3b**$^+$, M = W, X = F; **3c**$^+$, M = W, X = Cl) obtained as BF_4^- (**3a**$^+$, **3b**$^+$) or Cl^- salts (**3c**$^+$) in high yields, with a pyrrole ring containing the terminal nitrogen atom (Scheme 1). The reactions proceeded at room temperature by acid catalysis (HBF_4 for **3a**$^+$ and **3b**$^+$, HCl for **3c**$^+$). The pyrrole ring of **3**$^+$ is considered to be formed via stepwise condensations at the terminal nitrogen: the first step is the formation of 4-diazobutanal complexes $[MX(NN{=}CHCH_2CH_2CHO)(dppe)_2]^+$, and the second is the ring closure. In fact, one of such 4-diazobutanal complexes, $[WF(NN{=}CHCH_2CH_2CHO)(dppe)_2][BF_4]$, and its dimethyl acetal complex were obtained from a reaction of **2b**$^+$ in the absence of the acid.[11] Small amounts of the 4-diazobutanal complexes were also detected by ^{1}H NMR in the acid-catalyzed reaction products. This indicates that the first

Scheme 1



condensation is fast under acidic conditions and proceeds even in the absence of an acid, but the second step is relatively slow and requires an acid catalyst. This type of pyrrole ring formation is known as modified Paal−Knorr synthesis.[12] When **2b**$^+$ was treated with acetonylacetone, which is often used in Paal−Knorr synthesis,[13] only the monocondensation occurred even in the presence of HBF_4 catalyst at elevated temperature (in refluxing $ClCH_2CH_2Cl$) to give the 5-diazohexan-2-one complex $[WF(NN{=}C(CH_3)CH_2CH_2COCH_3)(dppe)_2]^+$.[14]

The molecular structure of the pyrrolylimido complex **3b**$^+PF_6^-$ was confirmed by X-ray analysis.[15] The structure is shown in Figure 1, and bond lengths and angles are summarized in Table 1. The geometry around the tungsten is a distorted octahedral with the pyrrolylimido ligand and the fluorine atom in trans positions. The terminal nitrogen atom N(2) is incorporated in the pyrrole ring to form the (*N*-pyrrolyl)imido ligand. The bond lengths in the pyrrole ring are similar to those of free pyrrole, although the distances between the α- and β-carbons (C(1)−C(2) and C(3)−C(4)) are somewhat shorter than 1.382 Å for free pyrrole (by microwave determination).[16] The pyrrolyl nitrogen exhibits the planar geometry as expected, which is reflected on the sum of the bond angles around the N(2) (360-(2)°). The W−N(1)−N(2) linkage is nearly linear, and the W and N(1) atoms lie almost in the same plane of the pyrrole ring. The N(1)−N(2) distance (1.362(7) Å) belongs to the longest

(9) Seino, H.; Ishii, Y.; Hidai, M. *J. Am. Chem. Soc.* **1994**, *116*, 7433.

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

(11) Selected data for $[WF(NN{=}CHCH_2CH_2CHO)(dppe)_2][BF_4]$: ^{1}H NMR ($CDCl_3$) δ 1.5−1.6 (m, 2 H, N=CHC*H*$_2$), 2.50 (br t, 2 H, J = 5.9 Hz, C*H*$_2$CHO), 2.6−2.8, 2.8−3.0 (m, 4 H each, CH_2 of dppe), 5.44 (t, 1 H, J = 3.1 Hz, N=CH), 6.8−7.4 (m, 40 H, Ph of dppe), 9.71 (s, 1 H, CHO); IR (KBr, cm^{-1}) 1718 (C=O), 1586 (N=C). Anal. Calcd for $C_{56}H_{54}N_2OBF_5P_4W$: C, 56.78; H, 4.59; N, 2.36. Found: C, 56.14; H, 4.60; N, 2.22. Its dimethyl acetal complex $[WF\{NN{=}CHCH_2CH_2CH(OMe)_2\}(dppe)_2][BF_4]$ was characterized by ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 1.2−1.5 (m, 4 H, $(CH_2)_2$), 3.33 (s, 6 H, OCH_3), 4.22 (t, 1 H, J = 4.9 Hz, C*H*$(OCH_3)_2$), 5.51 (br t, 1 H, $J \cong$ 4 Hz, N=CH).

(12) (a) Clauson-Kaas, N.; Tyle, Z. *Acta Chem. Scand.* **1952**, *6*, 667. (b) *Ibid.* **1952**, *6*, 867.

(13) Young, D. M.; Allen, C. F. H. *Organic Synthesis*; Wiley: New York, 1943; Collect. Vol. No. II, p 219.

(14) Selected data for $[WF(NN{=}C(CH_3)CH_2CH_2COCH_3)(dppe)_2][BF_4]$: ^{1}H NMR ($CDCl_3$) δ −0.69 (s, 3 H, N=C*H*$_3$), 1.71 (t, 2 H, J = 6.4 Hz, N=C(CH$_3$)C*H*$_2$), 2.36 (s, 3 H, $COCH_3$), 2.70 (t, 2 H, J = 6.4 Hz, CH_2CO), 2.7−2.9, 2.9−3.1 (m, 4 H each, CH_2 of dppe) 6.8−7.4 (m, 40 H, Ph of dppe); IR (KBr, cm^{-1}) 1711 (C=O), 1586 (N=C). Anal. Calcd for $C_{58}H_{58}N_2OBF_5P_4W$: C, 57.45; H, 4.82; N, 2.31. Found: C, 56.94; H, 4.88; N, 2.29.

(15) In the X-ray analysis of **3b**$^+BF_4^-$,[9] the BF_4^- anion showed considerable disorder. So the molecular structure of **3b**$^+$ was re-examined by using a single crystal of its PF_6^- salt.

(16) Nygaard, L.; Nielsen, J. T.; Kirchheiner, J.; Maltesen, G.; Rastrup-Andersen, J.; Sorensen, G. O. *J. Mol. Struct.* **1969**, *3*, 491.

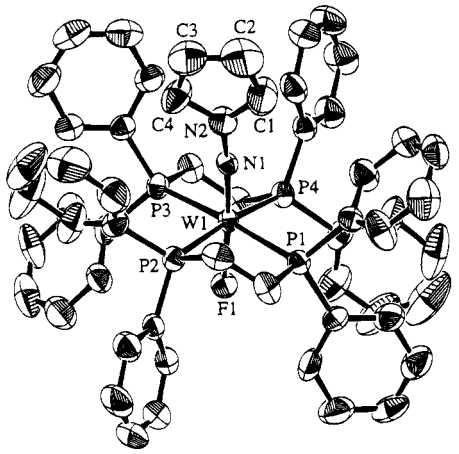
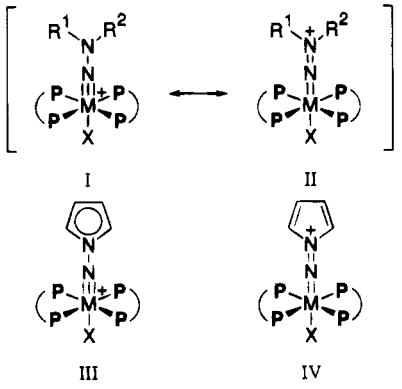


Figure 1. ORTEP drawing for $[WF(NNCH{=}CHCH{=}CH)(dppe)_2]^+$ (**3b**$^+$). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths and Angles in **3b**$^+PF_6^-$

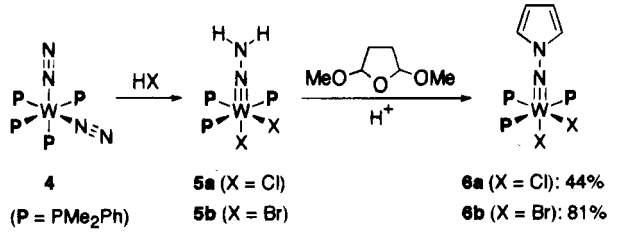
	Bond Lengths (Å)		
W−P(1)	2.512(2)	N(1)−N(2)	1.362(7)
W−P(2)	2.526(2)	N(2)−C(1)	1.363(9)
W−P(3)	2.588(2)	N(2)−C(4)	1.373(8)
W−P(4)	2.514(2)	C(1)−C(2)	1.32(1)
W−F(1)	1.953(3)	C(2)−C(3)	1.40(1)
W−N(1)	1.761(5)	C(3)−C(4)	1.34(1)
	Bond Angles (deg)		
P(1)−W−P(2)	79.32(6)	W−N(1)−N(2)	174.4(5)
P(1)−W−P(3)	173.24(6)	N(1)−N(2)−C(1)	127.1(6)
P(1)−W−P(4)	99.30(6)	N(1)−N(2)−C(4)	125.7(6)
P(1)−W−F(1)	88.8(1)	C(1)−N(2)−C(4)	107.1(6)
P(1)−W−N(1)	93.1(2)	N(2)−C(1)−C(2)	109.1(8)
P(2)−W−P(3)	102.62(6)	C(1)−C(2)−C(3)	108.2(8)
P(2)−W−P(4)	172.22(7)	C(2)−C(3)−C(4)	106.7(8)
P(2)−W−F(1)	92.4(1)	N(2)−C(4)−C(3)	108.8(8)
P(2)−W−N(1)	84.1(2)		
P(3)−W−P(4)	77.88(6)		
P(3)−W−F(1)	84.7(1)		
P(3)−W−N(1)	93.5(2)		
P(4)−W−F(1)	79.9(1)		
P(4)−W−N(1)	103.6(2)		
F(1)−W−N(1)	175.7(2)		

Scheme 2



class among those reported for similar hydrazido(2−) complexes (1.25−1.38 Å). In most hydrazido(2−) complexes so far reported, it has been assumed that the lone pair on the terminal nitrogen atom is considerably delocalized over the N−N−M moiety to relieve the positive charge on the metal center (structure II in Scheme 2), and consequently, the N−N bond has substantial multiple bond character.[4b,d,6a,10a,17] On the contrary, the lone pair of the pyrrole nitrogen atom of the pyrrolylimido complex **3b**$^+$ is majorly delocalized over the pyrrole ring to form the 6π aromatic system (structure III), and

Scheme 3



hence, the multiplicity of the N−N bond is smaller in comparison with those of other hydrazido(2−) complexes. This accounts for the long N−N bond in **3b**$^+$.[18]

The ^{1}H and ^{13}C NMR spectra of complexes **3a**−**c**$^+$ were investigated in detail. The ^{13}C NMR spectra of **3**$^+$ showed two signals due to the pyrrole ring at about δ 120 and 106 assignable to the α- and β-carbons, respectively. $^1J_{CH}$ values in **3b**$^+$ were 192 and 174 Hz at the α- and β-positions, respectively. These chemical shifts and coupling constants are closely comparable to those of free pyrrole.[19] In contrast, the ^{1}H NMR spectra of **3**$^+$ showed considerable high-field shifts in comparison with those of pyrrole. Signals for the α- and β-protons of the pyrrole ring appeared as two broad triplets at about δ 4.8 and 5.4, respectively. These high-field shifts are due to the shielding effect of the phenyl groups of the dppe ligands, and therefore, the α-protons, which are closer to the dppe ligands, showed the larger shift (−1.9 ppm) than the β-protons (−0.8 ppm).[19,20] The ^{31}P NMR spectra for **3a**−**c**$^+$ were similar to those of **2a**−**c**$^+$, respectively.[10b,21]

Similarly to the synthesis of complexes **3**$^+$, tungsten hydrazido(2−) complexes having PMe_2Ph ligands **5** were converted to the corresponding pyrrolylimido complexes *cis,mer*-$[WX_2(NNCH{=}CHCH{=}CH)(PMe_2Ph)_3]$ (**6a**, X = Cl; **6b**, X = Br) through a reaction with 2,5-dimethoxytetrahydrofuran in the presence of a catalytic amount of HX (Scheme 3). In contrast to **3**$^+$, monophosphine complexes **6** showed ^{1}H NMR signals due to the pyrrole moiety (α-H, δ 6.3; β-H, δ 5.8) at comparable chemical shifts to those of free pyrrole.[19] Obviously this is because the three PMe_2Ph ligands cis to the pyrrolylimido ligand do not constitute a cavity surrounded by Ph groups which is observed in **3**$^+$. The condensation reaction of **5b** with acetonylacetone ended in the formation of the 5-diazohexane-2-one complex;[6b] the corresponding (2,5-dimethylpyrrolyl)imido complex could not be obtained even by a reaction at 67 °C in the presence of HBr.

The molecular structure of **6** was also unambiguously determined by X-ray diffraction analysis. The ORTEP view is shown in Figure 2, and selected bond lengths and angles are summarized in Table 2. The tungsten−pyrrolylimido moiety

(17) (a) Heath, G. A.; Mason, R.; Thomas, K. M. *J. Am. Chem. Soc.* **1974**, *96*, 259. (b) Hidai, M.; Komori, K.; Kodama, T.; Jin, D.-M.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. *J. Organomet. Chem.* **1984**, *272*, 155.

(18) (a) This N−N bond length is much shorter than that of hydrazine (1.47 Å); the latter distance is considered to be exceptionally large due to strong repulsive interaction between the lone-pair electrons on nitrogen atoms.[18b] The N−N bond length of hydrazinium ion ($N_2H_6^{2+}$, 1.40 Å) is comparable to that of **3**$^+$, and this fact indicates that the N−N bond of the pyrrolylimido ligand has only a small contribution of multiple-bond character. (b) Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill: Singapore, 1985; p 54.

(19) (a) NMR data for pyrrole: ^{1}H ($CDCl_3$) δ 6.22 (β-H), 6.68 (α-H); ^{13}C (acetone-d_6) δ 108.1 (β-C, $^1J_{CH}$ = 168.8 Hz), 118.1 (α-C, $^1J_{CH}$ = 183.3 Hz).[19b] (b) Bundgaard, T.; Jakobsen, H. J.; Rahkamaa, E. J. *J. Magn. Reson.* **1975**, *19*, 345.

(20) Similar high-field shifts have also been reported in related diazoalkane and aryldiazenido complexes.[5c,6a]

(21) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1520.

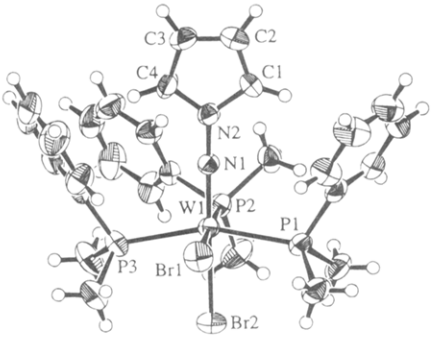


Figure 2. ORTEP drawing for [WBr_2(NNCH=CHCH=CH)(PMe_2-$Ph)_3$] (**6b**).

Table 2. Selected Bond Lengths and Angles in **6b**

Bond Lengths (Å)			
W−P(1)	2.514(1)	N(1)−N(2)	1.365(4)
W−P(2)	2.451(1)	N(2)−C(1)	1.384(5)
W−P(3)	2.523(1)	N(2)−C(4)	1.379(5)
W−Br(1)	2.6786(6)	C(1)−C(2)	1.353(6)
W−Br(2)	2.6527(6)	C(2)−C(3)	1.392(6)
W−N(1)	1.743(4)	C(3)−C(4)	1.340(6)
Bond Angles (deg)			
P(1)−W−P(2)	93.18(4)	W−N(1)−N(2)	177.9(3)
P(1)−W−P(3)	159.64(4)	N(1)−N(2)−C(1)	125.4(4)
P(1)−W−Br(1)	85.37(3)	N(1)−N(2)−C(4)	125.3(4)
P(1)−W−Br(2)	80.84(3)	C(1)−N(2)−C(4)	109.0(4)
P(1)−W−N(1)	98.7(1)	N(2)−C(1)−C(2)	106.3(4)
P(2)−W−P(3)	95.41(4)	C(1)−C(2)−C(3)	109.0(4)
P(2)−W−Br(1)	177.04(4)	C(2)−C(3)−C(4)	108.1(4)
P(2)−W−Br(2)	88.26(3)	N(2)−C(4)−C(3)	107.6(4)
P(2)−W−N(1)	88.0(1)		
P(3)−W−Br(1)	85.15(3)		
P(3)−W−Br(2)	81.01(3)		
P(3)−W−N(1)	100.1(1)		
Br(1)−W−Br(2)	88.96(2)		
Br(1)−W−N(1)	94.8(1)		
Br(2)−W−N(1)	176.2(1)		

is essentially planar, and two of the phosphine phosphorous atoms, P(1) and P(3), lie on the plane. This conformation is different from that of complex **3b**$^+$, in which the pyrrolylimido plane bisects the P(1)−W−P(4) and P(2)−W−P(3) angles. The N(1)−N(2) bond distance is close to that of **3b**$^+$.

2. Reaction at the Pyrrole Ring of Pyrrolylimido Complexes. Pyrrole is a highly electron rich heteroaromatic compound and readily undergoes substitution reactions on the ring with a variety of electrophiles.[22] As is well-known, electrophilic substitutions exclusively take place at the α-position due to the stability of the transient pyrrolium ions.[23] In contrast to free pyrrole, a pyrrole ring ligating to a metal complex has a potential to react in different manners; electronic and steric effects caused by adjunct ligands around the metal are supposed to alter the reactive site of the pyrrole ring. Although many types of pyrrole or pyrrolyl complexes of transition metals have been synthesized,[24] only recently have appeared studies which highlighted the reactivities of the ligating pyrroles such as in η^1-*N*-pyrrolyl-Re(III),[24a] η^2-pyrrole-Os(II),[24e] η^5-pyrrolyl-Re(III),[24g] or η^5-pyrrolyl-Ru(II) and -Os(II)[24i] complexes.

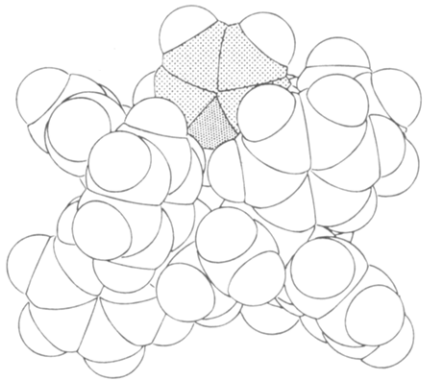


Figure 3. Van der Waals sphere of complex **3b**$^+$.

In contrast, the pyrrole ring of the dppe complexes **3**$^+$ is separated from the metal center by one nitrogen atom. As is supported by the above X-ray analysis and NMR studies, the electronic interaction between the metal and the pyrrole ring is considered to be weaker than those of the directly-bound complexes. Therefore, the pyrrole ring of **3**$^+$ is expected to undergo electrophilic substitution reactions. Conversely, the space-filling view of **3b**$^+$ (Figure 3) indicates that the large steric effect of the dppe ligands controls the reaction site of the pyrrole ring. The α-position of the pyrrole ring is completely covered by the phenyl groups of the dppe ligands, while the β-position sticks out of the hindered region. This fact suggests that the attack of electrophiles toward the α-position of the pyrrolylimido ligand in **3**$^+$ will be strongly obstructed by the steric hindrance and the electrophilic substitutions would undergo at the β-position, in a sharp contrast to those of free pyrrole. The predicted unique reactivity of the pyrrolylimido ligand in **3**$^+$ was confirmed with various electrophiles.[25]

Halogenation. Tungsten pyrrolylimido complex **3b**$^+$ underwent bromination on the pyrrole ring by treatment with an equimolar amount of *N*-bromosuccinimide (NBS) in THF (Scheme 4). The reaction proceeded even at −78 °C. Bromination predominantly occurred at the β-position, but when the reaction was conducted at 0 °C, in addition to the β-monobromo product **7b**$^+$, small amounts of the α-monobromo- and dibromo products were observed (Table 3, runs 1 and 2). The selectivity of the β-monobromination was improved at lower temperatures; the α-bromination was completely inhibited below −10 °C (run 2), and the dibromination was suppressed below −50 °C despite that an excess amount of NBS was used (run 5). Molybdenum complex **3a**$^+$ also gave the corresponding β-monobrominated complex **7a**$^+$ in 69% yield on treatment with 1 equiv of NBS at 0 °C, while the reaction was slower and required a higher

(22) Reviews: (a) *Comprehensive Heterocyclic Chemistry*; Clive, W. B., Gordon, W. H., Cheeseman, W. H., Eds.; Pergamon Press: Oxford, U.K., 1984; Vol. 4, Part 3, pp 1−376. (b) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Academic Press: London, 1977.

(23) (a) Theoretical calculations have assigned a larger electron density to the β- than to the α-position.[23b] In practice, pyrrole and *N*-alkylpyrroles undergo exceptionally predominant β-substitution reactions by hard electrophiles such as trimethylsilyl trifluoromethanesulfonate,[23c] dimethylfluoronium,[23d] and *tert*-butyl cation.[23e] Further, β-protonation of pyrrole occurs at a rate faster than that of α-protonation.[23f] (b) Catalán, J.; Yáñez, M. *J. Am. Chem. Soc.* **1984**, *106*, 421 and references cited therein. (c) Majchrzak, M. W.; Simchen, G. *Tetrahedron* **1986**, *42*, 1299. (d) Angelini, G.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 7084. (e) Margonelli, A.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1491. (f) Chiang, Y.; Whipple, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2763.

(24) For examples: (a) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728 and references therein. (b) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147 and references therein. (c) Bynum, R. V.; Zhang, H.-M.; Hunter, W. E.; Atwood, J. L. *Can. J. Chem.* **1986**, *64*, 1304. (d) Clark, G. R.; Ng, M. M. P.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1995**, *491*, 219. (e) Hodges, L. M.; Moody, M. W.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 7931. (f) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719. (g) Zakrzewski, J. *Heterocycles* **1990**, *31*, 383. (h) Kuhn, N.; Henkel, G.; Kreutzberg, J.; Stubenrauch, S. *J. Organomet. Chem.* **1993**, *456*, 97 and references therein. (i) Kvietok, F.; Allured, V.; Carperos, V.; DuBois, M. R. *Organometallics* **1994**, *13*, 60 and references therein.

(25) Electrophilic substitution reactions of the pyrrolylimido complexes with PMe_2Ph ligands **6** were also attempted, but any characterizable products could not be obtained.

Scheme 4

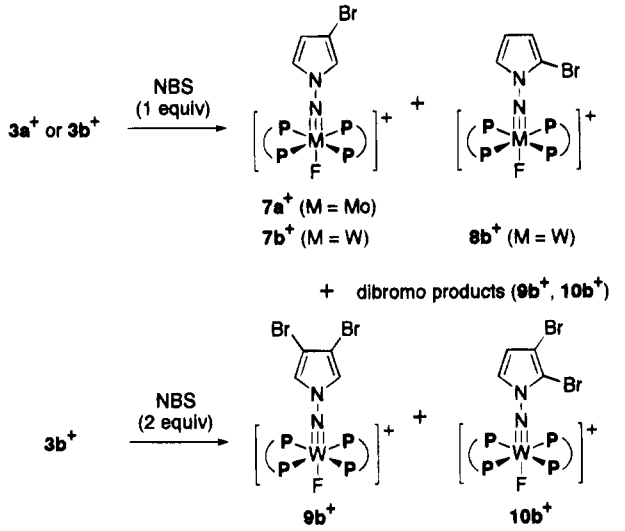


Table 3. Bromination of Pyrrolylimido Complex $\mathbf{3b}^{+}$ [a]

run	NBS (equiv)	temp (°C)	time (h)	ratio of products (%)[b] 7b+	8b+	9b+	10b+	3b+
1	1.0	0	2	81 (73[c])	3	5	6	5
2	1.0	−10	5	88 (74[c])	trace	4	5	3
3	2.0	−10	5	0	0	80[d]	20[d]	0
4	2.0	−25	5	11	0	72[e]	16[e]	0
5	2.0	−50	9	>99 (74[c])	0	trace	trace	trace
6	2.0	−78	26	43	0	0	0	57

[a] Conditions: $\mathbf{3b}^{+}BF_4^{-}$ (0.17 mmol), THF (10 mL), in the dark. [b] Determined by ^{1}H NMR. [c] Isolated yield. [d] Isolated yield of the mixture of $\mathbf{9b}^{+}$ and $\mathbf{10b}^{+}$ was ca. 80%. [e] Isolated yield of the mixture of $\mathbf{9b}^{+}$ and $\mathbf{10b}^{+}$ was ca. 74%.

temperature than $\mathbf{3b}^{+}$. Bromination at the phenyl groups of the dppe ligands was negligible. It is interesting to mention that $\mathbf{7a,b}^{+}$ were air stable and thermostable although most halogenated pyrroles are known to be very unstable.[26]

When $\mathbf{3b}^{+}$ was allowed to react with 2 equiv of NBS at −25 or −10 °C, two isomers of the dibrominated complexes were formed in good yields (runs 3 and 4). The major product was the 3,4-dibromo complex $\mathbf{9b}^{+}$ (β,β'-substitution), and the minor was identified as the 2,3-dibromo complex $\mathbf{10b}^{+}$ (α,β-substitution). Selectivity of $\mathbf{9b}^{+}$ to $\mathbf{10b}^{+}$ was slightly increased at −25 °C, but the second bromination did not proceed below −50 °C (vide supra). Evidently, the first bromination of $\mathbf{3b}^{+}$ exclusively occurs at the β-position, and the directing effect of the 3-bromo group[27] drives the second bromination to occur at the 2-position as well in spite of the strong steric hindrance.

Iodination of $\mathbf{3b}^{+}$ with *N*-iodosuccinimide in THF was also found to be β-selective but proceeded sluggishly. No more than 10% of $\mathbf{3b}^{+}$ was converted to the β-iodo product even after a reaction for 72 h at 25 °C.[28]

In contrast to the bromination, chlorination in THF was found to be α-selective (Scheme 5, Table 4). Treatment of $\mathbf{3b}^{+}$ with 1.05 equiv of *N*-chlorosuccinimide (NCS) in THF gave a mixture of the α-monochloro complex $\mathbf{12b}^{+}$ and the α,α′-dichloro complex $\mathbf{13b}^{+}$ with unreacted $\mathbf{3b}^{+}$ (run 1). The reaction was slower than the bromination and hardly proceeded below room temperature. A reaction with *N*-chlorophthalimide (NCP) in THF gave a similar mixture of the products (run 2).

(26) Gilow, H. M.; Burton, D. E. *J. Org. Chem.* **1981**, *46*, 2221.
(27) (a) Reference 22a, p 44. (b) Reference 22b, p 151.
(28) Selected ^{1}H NMR data for $[WF(NNCH{=}CICH{=}CH)(dppe)_2]^{+}$ ($CDCl_3$): δ 4.16 (br t, 1 H, J = 2.1 Hz, 2-H), 4.71 (br t, 1 H, J = 2.9 Hz, 5-H), 5.48 (dd, 1 H, J = 3.2, 1.7, 4-H).

Scheme 5

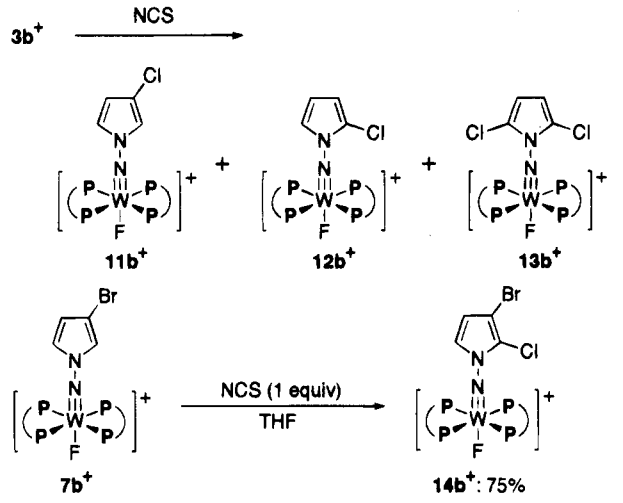


Table 4. Chlorination of Pyrrolylimido Complex $\mathbf{3b}^{+}$ [a]

run	reagent[b]	solvent	temp (time (h))	ratio of products (%)[c] 11b+	12b+	13b+	3b+
1	NCS (1.05)	THF	rt (72)	0	67	16	16
2	NCP (1.0)	THF	rt (130)	0	60	17	23
3	SO_2Cl_2 (1.0)	THF	−60 °C (2) → rt (15)	0	3	41	56
4	NCS (2.0)	THF	rt (24)	0	2	98[d]	0
5	NCS (1.05)	CH_2Cl_2	rt (20)	7	67	20	6
6	NCS (1.0)	DMF	rt (13)	47	21	0	32
7[e]	SO_2Cl_2 (1.0)	DMF	−20 °C (8)	28	5	0	59

[a] Conditions: $\mathbf{3b}^{+}BF_4^{-}$ (0.17 mmol), solvent (10 mL (THF, CH_2Cl_2) or 5 mL (DMF)), in the dark. [b] Ratios of the reagent to $\mathbf{3b}^{+}$ are given in parentheses. [c] Determined by ^{1}H NMR. [d] Isolated in 84% yield. [e] The β,β'-dichloro product was also formed (8%).

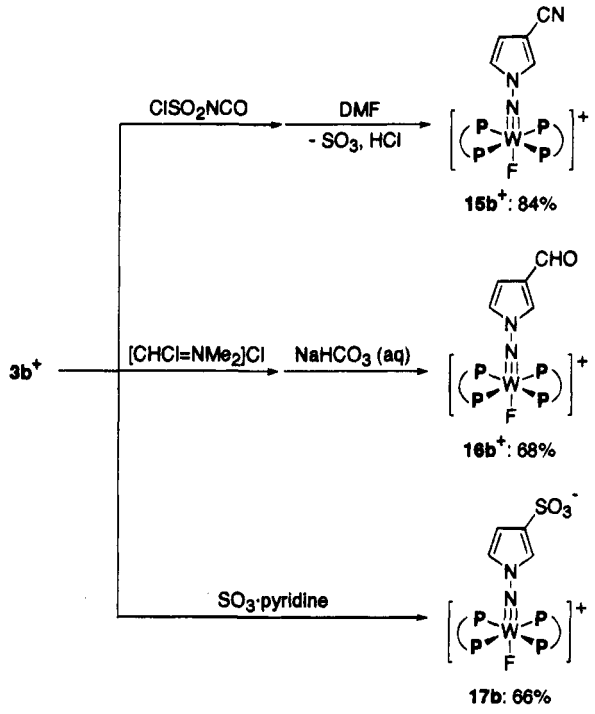
Sulfuryl chloride was more reactive and yielded mainly the dichloro product $\mathbf{13b}^{+}$ (run 3). The high reactivity of sulfuryl chloride and the low solubility of the salt $\mathbf{3b}^{+}BF_4^{-}$ in THF are considered to be the reasons for the predominant formation of $\mathbf{13b}^{+}$ over $\mathbf{12b}^{+}$. With 2 equiv of NCS in the same solvent, $\mathbf{13b}^{+}$ was exclusively isolated in 84% yield (run 4). Chlorination with NCS in CH_2Cl_2 showed a selectivity similar to that in THF, except that a small amount of β-chloro complex $\mathbf{11b}^{+}$ was observed (run 5). Interestingly, use of DMF as the solvent reversed the selectivity to give $\mathbf{11b}^{+}$ as the major product (runs 6 and 7), although satisfactory selectivity of the β-chlorination could not be achieved by controlling the reaction temperature.

Similarly, chlorination of (β-bromopyrrolyl)imido complex $\mathbf{7b}^{+}$ with NCS in THF provided (3-bromo-2-chloropyrrolyl)-imido complex $\mathbf{14b}^{+}$ in a fair yield (Scheme 5). In this case, the regioselectivity was rather high. According to the ^{1}H NMR analysis of the crude product, only the 2-position, the most electronically activated position,[27] was chlorinated but the 4- and 5-positions were not attacked. From these observations, it can be concluded that the reaction of the pyrrolylimido complexes with NCS in THF is strongly controlled by the electronic factor but not by the steric effect of dppe ligands.

Cyanation. Reaction of $\mathbf{3b}^{+}$ with a small excess of chlorosulfonyl isocyanate (CSI)[29] followed by treatment with DMF afforded the (β-cyanopyrrolyl)imido complex $\mathbf{15b}^{+}$, as the sole product in a high yield (Scheme 6). The α-cyanated complex was not found at all in the ^{1}H NMR spectrum of the crude product. While tungsten complex $\mathbf{3b}^{+}$ was effectively converted to $\mathbf{15b}^{+}$, the molybdenum analogue $\mathbf{3a}^{+}$ did not react with CSI

(29) (a) Lohaus, G. *Chem. Ber.* **1967**, *100*, 2719. (b) Loader, C. E.; Anderson, H. J. *Can. J. Chem.* **1981**, *59*, 2673.

Scheme 6



at room temperature. This fact might reflect the stronger back-bonding ability of tungsten than molybdenum.

Formylation. The exclusive β-formylation of $\mathbf{3b}^+$ was achieved by a reaction with $[CHCl{=}NMe_2]Cl$ followed by hydrolysis (Scheme 6). The reaction was slow at room temperature, and a small amount of $\mathbf{3b}^+$ (ca. 8%) was recovered after 72 h even when the reaction was conducted with 5 equiv of the reagent. Reactions of $\mathbf{3b}^+$ with other cationic carbon electrophiles such as $[Me_3O][BF_4]$ or $[CH_2{=}NMe_2]I$ failed to proceed.

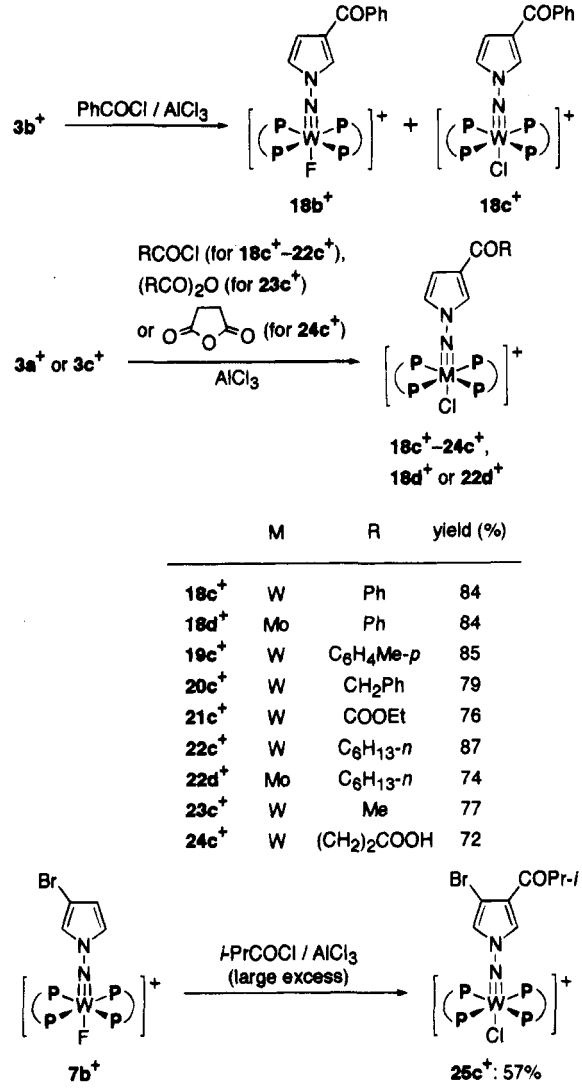
Sulfonation. SO_3–pyridine complex reacted with $\mathbf{3b}^+$ in refluxing $ClCH_2CH_2Cl$ (83 °C) to give the β-sulfonated complex **17b**. This complex was isolated as a zwitterionic form after basic aqueous workup (Scheme 6). It has been reported that the α-sulfonation of free pyrrole and alkylpyrroles by SO_3–pyridine proceeds at 100 °C in $ClCH_2CH_2Cl$, but the β-sulfonation of the pyrroles whose α-positions are both blocked appears to be more difficult.[30] In contrast, $\mathbf{3b}^+$ underwent the selective β-sulfonation under relatively mild conditions.

Acylation. Friedel–Crafts benzoylation of the pyrrolylimido complexes was studied under several conditions with benzoyl chloride/$AlCl_3$ (Scheme 7). As shown in Table 5, $\mathbf{3b}^+BF_4^-$ did not undergo benzoylation by using 1.5 equiv of the reagents (run 1), and only the halogen exchange between $\mathbf{3b}^+$ and $AlCl_3$ was observed. Excess amounts ($AlCl_3$, 2.4 equiv) of the reagents lead to the β-selective benzoylation accompanied by considerable halogen exchange to give a mixture of the fluoro complex $\mathbf{18b}^+$ and the chloro complex $\mathbf{18c}^+$ (run 2). The fluoro complex $\mathbf{18b}^+$ could not be obtained selectively. Use of a large excess ($AlCl_3$, 6 equiv) of the reagents lead to the clean formation of $\mathbf{18c}^+$ (run 3). As is expected, the (chloro)(pyrrolylimido) complex $\mathbf{3c}^+Cl^-$ smoothly reacted to give the (β-benzoylpyrrolyl)imido complex in a high yield (run 4).

A variety of acid chlorides or acid anhydrides were employed for further investigation into Friedel–Crafts acylation of $\mathbf{3c}^+$. Similarly to the benzoylation, $\mathbf{3c}^+Cl^-$ reacted with various acyl chlorides shown in Scheme 7 to afford the corresponding (β-acylpyrrolyl)imido complexes in good yields. Acid anhydrides

(30) Reference 22a, p 217.

Scheme 7



	M	R	yield (%)
$\mathbf{18c}^+$	W	Ph	84
$\mathbf{18d}^+$	Mo	Ph	84
$\mathbf{19c}^+$	W	C_6H_4Me-*p*	85
$\mathbf{20c}^+$	W	CH_2Ph	79
$\mathbf{21c}^+$	W	COOEt	76
$\mathbf{22c}^+$	W	C_6H_{13}-*n*	87
$\mathbf{22d}^+$	Mo	C_6H_{13}-*n*	74
$\mathbf{23c}^+$	W	Me	77
$\mathbf{24c}^+$	W	$(CH_2)_2COOH$	72

were also effective for the acylation of $\mathbf{3c}^+$. Treatment of molybdenum complex $\mathbf{3a}^+$ with excess acyl chloride/$AlCl_3$ also yielded the corresponding [(β-acylpyrrolyl)imido](chloro) complex. Further, acylation of (β-bromopyrrolyl)imido complex $\mathbf{7b}^+$ with excess isobutyryl chloride (7.5 equiv) and $AlCl_3$ (7 equiv) proceeded selectively at the β'-position, and the (4-bromo-3-isobutyrylpyrrolyl)imido complex $\mathbf{25c}^+$ was isolated as the PF_6^- salt in 57%. With respect to the acylation of the pyrrolylimido ligands, the β-regioselectivity is concluded to be very high.

Comparison with Substitution Reactions of Other Pyrrole Derivatives. As is described above, the pyrrole ring of the pyrrolylimido complexes undergoes electrophilic aromatic substitution reactions, where the regioselectivities are effectively controlled by the steric effect of the dppe ligands and the β-substituted complexes are exclusively formed in most reactions. This makes a remarkable contrast to the strongly α-directed substitution reactions of free pyrrole. β-Substituted pyrrole rings have been widely found in natural products and biologically active compounds as an important fundamental structure.[31] From this point of view, the β-selective substitution of the pyrrolylimido complexes may be used as a potential tool for the synthesis of β-substituted pyrroles.

(31) (a) Sessler, J. L.; Hemmi, G.; Mody, T. D.; Murai, T.; Burrell, A.; Young, S. W. *Acc. Chem. Res.* **1994**, *27*, 43. (b) Nichols, R.; Andrews, P. C.; Zhang, P.; Bergstrom, D. E. *Nature* **1994**, *369*, 492. (c) Garnier, F.; Youssoufi, H. K.; Srivastava, P.; Yassar, A. *J. Am. Chem. Soc.* **1994**, *116*, 8813.

Table 5. Benzoylation of Pyrrolylimido Complexes $\mathbf{3b}^+$ and $\mathbf{3c}^+$ [a]

run	complex	PhCOCl (equiv)	$AlCl_3$ (equiv)	temp (time (h))	ratio of products (%)[b]			
					$\mathbf{18b}^+$	$\mathbf{18c}^+$	$\mathbf{3b}^+$	$\mathbf{3c}^+$
1	$\mathbf{3b}^+$	1.5	1.5	rt (1)	trace	0	88	12
2	$\mathbf{3b}^+$	3.0	2.4	0 °C (1.5) → rt (1.5)	62 (25)	18	5	14
3	$\mathbf{3b}^+$	7.5	6.0	0 °C (1) → rt (1)	0	91 (75)	7	2
4	$\mathbf{3c}^+$	3.6	3.0	0 °C (1.5) → rt (1)		96 (84)		4

[a] Conditions: $\mathbf{3b}^+BF_4^-$ or $\mathbf{3c}^+Cl^-$ (0.16−0.17 mmol), CH_2Cl_2 (5 mL). [b] Determined by ^1H NMR. Isolated yields of the major products are given in parentheses.

So far, several *N*-substituted pyrroles have been investigated for the purpose of achieving the β-substitution of pyrrole.[32] Introduction of *N*-phenylsulfonyl group to pyrrole is reported to lower the electron density at the α-position, and their electrophilic reactions are consequently controlled to occur at the β-position.[32a] However, this group is only effective to reactions with hard electrophiles such as Friedel−Crafts acylation or nitration, but not to formylation or cyanation.[32a,b] *N*-Triisopropylsilyl (TIPS) group is also known effective to enhance the β-substitution of pyrrole.[32c] The directing effect of the TIPS group is considered to arise from its steric bulkiness. Nevertheless, its directing ability is not satisfactory in some cases. For example, the bromination of TIPS-pyrrole is moderately β-selective (α/β = 1/5.7 at −20 °C), and its cyanation occurred predominantly at the α-position (α/β = 6/1 at −78 °C). Therefore, steric protection of the α-position of the pyrrole ring by the dppe ligands in $\mathbf{3}^+$ is concluded to be more effective than that by the TIPS group. However, the pyrrolylimido complexes are less reactive toward electrophiles than most organic pyrrole derivatives. The lower reactivity of the pyrrolylimido complexes can be explained by considering the contribution of the resonance structure IV illustrated in Scheme 2.

Characterization of the Substituted Pyrrolylimido Complexes. The characterization of the complexes with the (substituted-pyrrolyl)imido ligands should be mentioned here. The chemical shifts of the pyrrole moiety in the ^1H NMR spectra were considerably affected by the shielding effect of the dppe phenyl groups and showed a large difference from those of organic pyrrole derivatives. Therefore, all the substituted pyrrolylimido complexes were fully characterized by using the coupling constants ($^{3,4}J_{HH}$ and $^1J_{CH}$) and the HC-COSY spectra.

Further, the molecular structures of three substituted pyrrolylimido complexes, β-bromo complex $\mathbf{7b}^+$, α,α′-dichloro complex $\mathbf{13b}^+$, and β-toluoyl complex $\mathbf{19c}^+$, were determined by X-ray diffraction methods. Because molecular structures of partially halogenated pyrroles have not been investigated due to their instability, the X-ray analyses of those complexes are of some interest. Views of those structures are shown in Figures 4 (for $\mathbf{7b}^+$), 5 (for $\mathbf{13b}^+$), and 6 (for $\mathbf{19c}^+$), which confirmed the positions of the substitution. Selected bond lengths and angles are listed in Tables 6 (for $\mathbf{7b}^+$), 7 (for $\mathbf{13b}^+$), and 8 (for $\mathbf{19c}^+$). Their coordination structures are very similar to that of the unsubstituted complex $\mathbf{3b}^+$, but small deformation was observed in the pyrrolylimido ligands. In complexes $\mathbf{7b}^+$ and $\mathbf{13b}^+$, the endocyclic angles at the halogenated carbon atoms (C(1)−C(2)−C(3) of $\mathbf{7b}^+$, 112(1)°; N(2)−C(1)−C(2) of $\mathbf{13b}^+$, 110.8(8)°; N(2)−C(4)−C(3) of $\mathbf{13b}^+$, 110.4(8)°) are larger than other endocyclic angles of the pyrrolylimido ligands (107° av). Similar effects of electronegative substituents on the endocyclic bond angles have been pointed out in monosubstituted benzenes.[33] In complex $\mathbf{19c}^+$, the toluoyl group and the pyrrole ring are twisted by 41° so as to reduce the steric congestion between the rings.

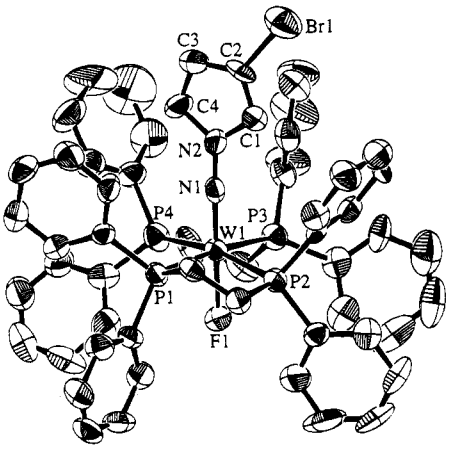


Figure 4. ORTEP drawing for $[WF(NNCH{=}CBrCH{=}CH)(dppe)_2]^+$ ($\mathbf{7b}^+$). Hydrogen atoms are omitted for clarity.

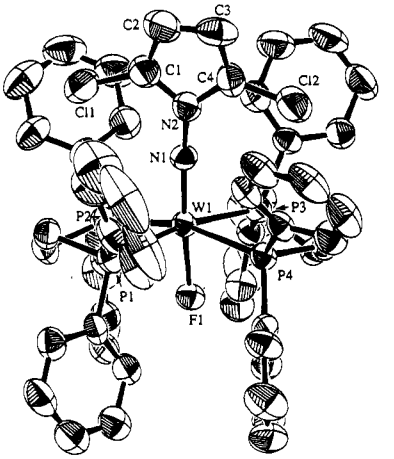


Figure 5. ORTEP drawing for $[WF(NNCCl{=}CHCH{=}CCl)(dppe)_2]^+$ ($\mathbf{13b}^+$). Hydrogen atoms are omitted for clarity.

3. Liberation of Pyrrole and *N*-Aminopyrrole from Pyrrolylimido Complexes. Liberation of pyrrole derivatives from the pyrrolylimido complexes has been investigated in detail. This accomplishes the synthetic process for pyrroles from molecular nitrogen. Our attention has been focused on achieving the selective production of pyrrole and *N*-aminopyrrole by the fission of the N−N and metal−N bonds of the pyrrolylimido complexes, respectively.

Reduction of $\mathbf{3a}^+$ and $\mathbf{3b}^+$ with $LiAlH_4$ in THF followed by workup with MeOH resulted in the formation of pyrrole and *N*-aminopyrrole. As shown in Scheme 8, the total yields of pyrrole and *N*-aminopyrrole after reactions for 20 h at room temperature were essentially quantitative. The major product

(32) (a) Rokach, J.; Hamel, P.; Kakushima, M. *Tetrahedron Lett.* **1981**, *22*, 4901. (b) Anderson, H. J.; Loader, C. E.; Xu, R. X.; Lê, N.; Gogan, N. J.; McDonald, R.; Edwards, L. G. *Can. J. Chem.* **1985**, *63*, 896. (c) Bray, B. L.; Mathies, P. H.; Naef, R.; Solas, D. R.; Tidwell, T. T.; Artis, D. R.; Muchowski, J. M. *J. Org. Chem.* **1990**, *55*, 6317 and references therein.

(33) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr.* **1975**, *B31*, 221.

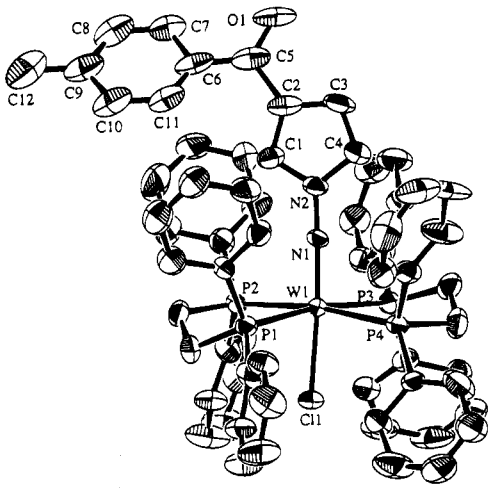


Figure 6. ORTEP drawing for [WCl{NNCH=C($COC_6H_4CH_3$-*p*)-CH=CH}$(dppe)_2$]$^+$ (**19c**$^+$). Hydrogen atoms are omitted for clarity.

Table 6. Bond Lengths and Angles of the (*β*-Bromopyrrolyl)imido Moiety in **7b**$^+BF_4^-$·$ClCH_2CH_2Cl$

bond lengths (Å)		bond angles (deg)	
W−N(1)	1.73(1)	W−N(1)−N(2)	178.2(7)
N(1)−N(2)	1.37(1)	N(1)−N(2)−C(1)	127(1)
N(2)−C(1)	1.39(1)	N(1)−N(2)−C(4)	125(1)
N(2)−C(4)	1.40(1)	C(1)−N(2)−C(4)	108(1)
C(1)−C(2)	1.33(1)	N(2)−C(1)−C(2)	106(1)
C(2)−C(3)	1.40(2)	Br(1)−C(2)−C(1)	123(1)
C(3)−C(4)	1.36(2)	Br(1)−C(2)−C(3)	125(1)
Br−C(2)	1.90(1)	C(1)−C(2)−C(3)	112(1)
		C(2)−C(3)−C(4)	105(1)
		N(2)−C(4)−C(3)	109(1)

Table 7. Bond Lengths and Angles of the (α,α′-Dichloropyrrolyl)imido Moiety in **13b**$^+PF_6^-$·2(toluene)

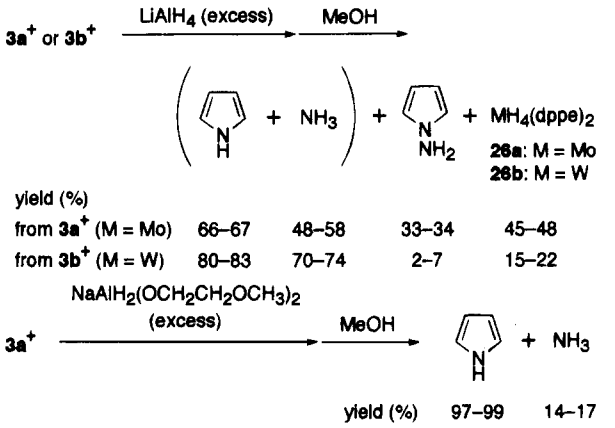
bond lengths (Å)		bond angles (deg)	
W−N(1)	1.764(6)	W−N(1)−N(2)	176.6(5)
N(1)−N(2)	1.366(8)	N(1)−N(2)−C(1)	126.7(7)
N(2)−C(1)	1.38(1)	N(1)−N(2)−C(4)	128.7(7)
N(2)−C(4)	1.389(9)	C(1)−N(2)−C(4)	104.4(7)
C(1)−C(2)	1.37(1)	Cl(1)−C(1)−N(2)	121.2(7)
C(2)−C(3)	1.39(1)	Cl(1)−C(1)−C(2)	127.9(9)
C(3)−C(4)	1.36(1)	N(2)−C(1)−C(2)	110.8(8)
Cl(1)−C(1)	1.693(9)	C(1)−C(2)−C(3)	106(1)
Cl(2)−C(4)	1.678(9)	C(2)−C(3)−C(4)	108.1(9)
		Cl(2)−C(4)−N(2)	121.8(8)
		Cl(2)−C(4)−C(3)	127.5(9)
		N(2)−C(4)−C(3)	110.4(8)

was pyrrole for both complexes, but the selectivity of pyrrole was much higher in the case of the tungsten complex **3b**$^+$ compared with the molybdenum analogue **3a**$^+$. It is of great interest to note that the hydride reduction of related alkylhydrazido(2−) complexes of molybdenum and tungsten required much more drastic conditions and longer reaction time (80 °C, 65 h).[7a] In contrast, the above reduction took place at room temperature, and furthermore, **3a**$^+$ reacted with $LiAlH_4$ even at −78 °C to give pyrrole and *N*-aminopyrrole in 49 and 28%, respectively, after 20 h. The remarkably high reactivity of **3**$^+$ can be accounted for by the lower multiplicity of the N−N bond in comparison with alkylhydrazido(2−) complexes (vide supra). In addition to the organonitrogen compounds, NH_3 was detected in almost comparable yields to those of pyrrole. This indicates that, in the case of the pyrrole formation via the N−N bond cleavage, the nitrogen atom directly bound to the metal center was released as NH_3. Further, the tetrahydrido complexes [MH_4-

Table 8. Selected Bond Lengths and Angles of the [*β*-(*p*-Toluoyl)pyrrolyl]imido Moiety in **19c**$^+BF_4^-$·2(benzene)

bond lengths (Å)		bond angles (deg)	
W−N(1)	1.778(5)	W−N(1)−N(2)	176.7(5)
N(1)−N(2)	1.352(6)	N(1)−N(2)−C(1)	124.0(6)
N(2)−C(1)	1.365(8)	N(1)−N(2)−C(4)	125.7(6)
N(2)−C(4)	1.367(7)	C(1)−N(2)−C(4)	110.1(5)
C(1)−C(2)	1.380(8)	N(2)−C(1)−C(2)	106.7(6)
C(2)−C(3)	1.41(1)	C(1)−C(2)−C(3)	107.2(6)
C(3)−C(4)	1.346(8)	C(1)−C(2)−C(5)	128.2(9)
C(2)−C(5)	1.51(1)	C(3)−C(2)−C(5)	124.4(8)
O−C(5)	1.23(1)	C(2)−C(3)−C(4)	108.2(6)
C(5)−C(6)	1.46(2)	N(2)−C(4)−C(3)	107.7(6)
		O−C(5)−C(2)	115(1)
		O−C(5)−C(6)	123(1)
		C(2)−C(5)−C(6)	121.0(9)

Scheme 8



$(dppe)_2$] (**26a**, M = Mo; **26b**, M = W) were recovered in moderate yields. Chatt et al. also mentioned the recovery of **26b** from $LiAlH_4$ reduction of a tungsten dialkylhydrazido(2−) complex at 80 °C, but in contrast to our results, they detected no NH_3 and the fate of the metal-bound nitrogen atom was not clarified.[7a] These tetrahydrido complexes **26** are known to be converted to the original dinitrogen complexes **1** by irradiation under a nitrogen atmosphere,[34] and in fact, we confirmed that the molybdenum hydrido complex **26a** recovered after the reduction of **3a**$^+$ was converted back to **1a** in 95% yield by irradiation with a tungsten lamp for 40 h under 1 atm of dinitrogen. Thus, a synthetic cycle for formation of pyrrole and *N*-aminopyrrole from dinitrogen has been accomplished by starting from dinitrogen complexes **1** (Scheme 9).

The reduction of **3a**$^+$ with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ produced pyrrole in an almost quantitative yield (Scheme 8), although the reaction was slower than that with $LiAlH_4$. In contrast to the reduction with $LiAlH_4$, the yield of NH_3 was low and a complex mixture of hydrides were recovered. Reduction of **3**$^+$ with $NaBH_4$ did not proceed even at 68 °C.

In order to show the potentiality of the newly developed synthesis of pyrroles from molecular nitrogen, we have also examined the liberation of *β*-substituted pyrroles, which are hardly obtained by conventional electrophilic substitution reactions of pyrrole, from the *β*-substituted pyrrolylimido complexes. The hydride reduction of (*β*-heptanoylpyrrolyl)imido complex **22c**$^+$ occurred with concomitant reduction of the carbonyl group to generate *β*-heptylpyrrole (Scheme 10). Thus, treatment of

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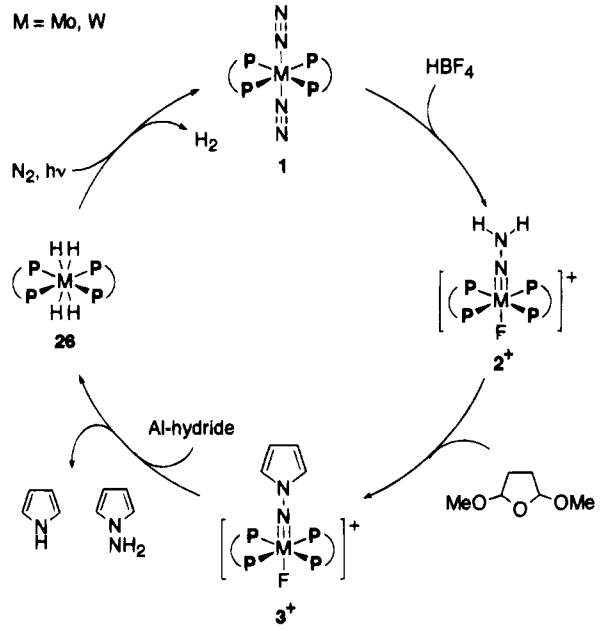
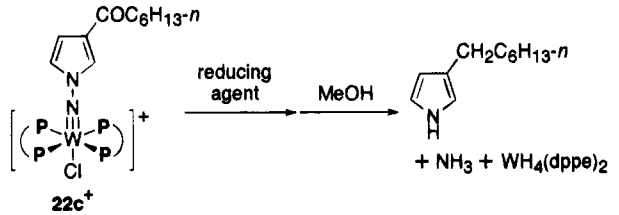
Scheme 9



Scheme 10

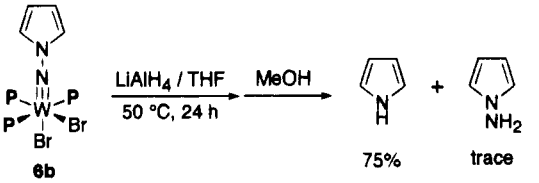


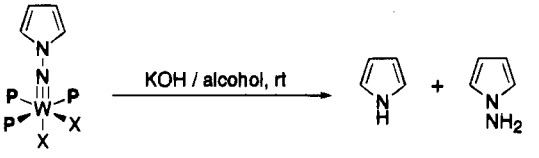
reducing agent	yield (%) β-heptylpyrrole	yield (%) NH_3
$LiAlH_4$	56–63	73–78
$NaAlH_2(OCH_2CH_2OCH_3)_2$	69–74	20–25

22c$^+$ with $LiAlH_4$ (10 equiv) or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (20 equiv) at room temperature for 20 h yielded β-heptylpyrrole in 56–63% or 69–74%, respectively. In these cases, *N*-amino-β-heptylpyrrole could not be detected by GC–MS. Carbonyl groups directly bound to electron-rich aromatics such as pyrrole are known to be easily reduced to methylene groups by hydride reductions.[35] In the $LiAlH_4$ reduction of **22c**$^+$, the tetrahydride **26b** was also obtained after workup with MeOH in 20% yield together with an unidentified tungsten hydrido complex (ca. 30%).

$LiAlH_4$ reduction of monophosphine complex **6b** at 50 °C for 24 h also gave pyrrole selectively (75%, Scheme 11).[36] On the other hand, treatment of **6** with KOH in alcoholic solvents at room temperature gave both pyrrole and *N*-aminopyrrole. Results obtained by using several alcohols as the solvents are summarized in Scheme 11. Interestingly, the ratio of products and the time to bring the reaction to completion were strongly dependent on the alcohol solvent and the halogen ligands of the complexes. The reaction of the bromo complex **6b**$^+$ in EtOH exhibited the highest selectivity of *N*-aminopyrrole (89%) produced through the fission of the W–N bond. It should be pointed out that both pyrrole and *N*-aminopyrrole were selectively obtained from molecular nitrogen in this study.

Scheme 11





	X	alcohol	time (h)	yield (%)	
6a	Cl	MeOH	1	33	34
		EtOH	24	56	37
		i-PrOH	48	40	15*
6b	Br	MeOH	0.5	27	73
		EtOH	2	11	**89**
		i-PrOH	48	52	15

* Not completed.

Conclusion

We have developed a synthetic cycle for pyrrole and *N*-aminopyrrole using molecular nitrogen as the nitrogen source based on the stepwise transformation of dinitrogen complexes of molybdenum and tungsten. Each step can be conducted under very mild conditions (mostly at room temperature or below) and has been fully characterized. It should also be emphasized that the introduction of various substituent groups to the β-position of the pyrrole ring is achieved during the process, which is hardly attained by conventional methods. Further studies aiming at developing novel synthetic routes to a series of nitrogen heterocycles from molecular nitrogen are now under way.

Experimental Section

General Procedure. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by usual methods and distilled before use. Reagents were commercially obtained and used as received except for NBS, which was recrystallized from water and dried under vacuum. Dinitrogen complexes **1a,b** and **4**,[37] hydrazido(2–) complexes **2a–c**$^+$ [6a,10a,b] and **5a,b**,[10c] and authentic samples of tetrahydrido complexes **23a,b**[38] 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. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. GC–MS analyses (70 eV) were carried out on a Shimadzu GC–MS QP-2000 spectrometer. 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 (Cl, Br, S).

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(36) (a) From the reaction mixture, only the hexahydride complex $[WH_6(PMe_2Ph)_3]$[36b] was identified by NMR. Its conversion to dinitrogen complex **4** and the characterization of other metal-containing products are still under investigation. (b) Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1984**, *23*, 2388.

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Preparation of the Pyrrolylimido Complexes of dppe Ligands (3a−c$^+$). The following procedure for the preparation of **3a**$^+$BF$_4^-$ is representative. Hydrazido(2−) complex **2a**$^+$BF$_4^-$·CH$_2$Cl$_2$ (1.00 g, 0.898 mmol) and 2,5-dimethoxytetrahydrofuran (175 μL, 1.36 mmol) were dissolved in CH$_2$Cl$_2$ (40 mL), and 42% aqueous HBF$_4$ (ca. 200 mg) was added to the solution. After the mixture was stirred for 48 h at room temperature, the resultant red solution was washed with water (2 × 100 mL) and 5% aqueous NH$_4$BF$_4$ (2 × 100 mL), dried over MgSO$_4$, and evaporated to give an orange-red oil. Crystallization from CH$_2$Cl$_2$−MeOH/ether afforded red crystals of **3a**$^+$BF$_4^-$, which were collected, washed with ether and hexane, and dried in vacuo (828 mg, 86%): ^{1}H NMR (CDCl$_3$) δ 2.6−2.9 (m, 8 H, CH$_2$ of dppe), 4.83 (br t, 2 H, J = 2.2 Hz, α-H), 5.34 (br t, 2 H, J = 2.2 Hz, β-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD$_2$Cl$_2$) δ 28.0 (quint, J_{CP} = 9 Hz, CH$_2$ of dppe), 106.6 (β-C), 120.6 (α-C), 128−134 (Ph of dppe); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 42.4 (d, J_{PF} = 36 Hz). Anal. Calcd for C$_{56}$H$_{52}$N$_2$BF$_5$P$_4$Mo: C, 62.36; H, 4.86; N, 2.60. Found: C, 62.21; H, 4.90; N, 2.41. Its tungsten analogues **3b**$^+$BF$_4^-$ and **3c**$^+$Cl$^-$ were prepared by similar procedures from **2b**$^+$BF$_4^-$ and **2c**$^+$Cl$^-$, respectively.

3b$^+$**BF$_4^-$.** Orange-red crystals from CH$_2$Cl$_2$−MeOH/ether (90%): ^{1}H NMR (CDCl$_3$) δ 2.6−2.8 (m, 8 H, CH$_2$ of dppe), 4.80 (br t, 2 H, J = 2.3 Hz, α-H), 5.37 (br t, 2 H, J = 2.3 Hz, β-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD$_2$Cl$_2$) δ 31.0 (quint, J_{CP} = 10 Hz, CH$_2$ of dppe), 106.1 (β-C, $^1J_{CH}$ = 174 Hz), 119.4 (α-C, $^1J_{CH}$ = 192 Hz), 128−134 (Ph of dppe); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 31.5 (d with ^{183}W satellites, J_{PF} = 44 Hz, J_{PW} = 286 Hz). Anal. Calcd for C$_{56}$H$_{52}$N$_2$BF$_5$P$_4$W: C, 57.66; H, 4.49; N, 2.40. Found: C, 57.41; H, 4.59; N, 2.42.

3c$^+$**Cl$^-$·1.5CH$_2$Cl$_2$.** Concentrated hydrochloric acid and 5% aqueous NaCl were used instead of aqueous HBF$_4$ and NH$_4$BF$_4$, respectively. Purple crystals from CH$_2$Cl$_2$/hexane (79%): ^{1}H NMR (CDCl$_3$) δ 2.7−3.1 (m, 8 H, CH$_2$ of dppe), 4.73 (br t, 2 H, J = 2.3 Hz, α-H), 5.40 (br t, 2 H, J = 2.3 Hz, β-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD$_2$Cl$_2$) δ 30.7 (quint, J_{CP} = 10 Hz, CH$_2$ of dppe), 106.7 (β-C), 119.6 (α-C), 128−134 (Ph of dppe); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 26.4 (s with ^{183}W satellites, J_{PW} = 275 Hz). Anal. Calcd for C$_{57.5}$H$_{55}$N$_2$P$_4$Cl$_5$W: C, 54.85; H, 4.40; N, 2.22. Found: C, 55.03; H, 4.58; N, 2.23.

Preparation of the Pyrrolylimido Complexes with Monophosphine Ligands (6a,b). The following procedure for the preparation of **6b** is representative. 2,5-Dimethoxytetrahydrofuran (252 mg, 1.91 mmol) and 48% hydrobromic acid (3 drops) were added to a light-brown suspension of **5b** (1.00 g, 1.27 mmol) in THF (40 mL). After stirring at room temperature for 20 h, the resulting dark-blue solution was evaporated to dryness. The residual oil was extracted with four 50 mL portions of ether, and the combined ether solution was dried up to give deep-violet powder. The powder was recrystallized from benzene−hexane to yield dark-blue crystals of **6b**, which were filtered, washed with hexane, and dried in vacuo (875 mg, 81%): ^{1}H NMR (C$_6$D$_6$) δ 1.47 (d, 6 H, J = 8.5 Hz, PMe), 1.99, 2.03 (t, 6 H each, J = 3.9 Hz, PMe), 5.80 (br t, 2 H, J = 2.3 Hz, β-H), 6.33 (br t, 2 H, J = 2.3 Hz, α-H), 6.7−7.3 (m, 15 H, PPh); ^{13}C NMR (C$_6$D$_6$) δ 15.0, 17.5 (t, J_{CP} = 15 Hz, PMe), 23.5 (d, J_{CP} = 31 Hz, PMe), 106.3 (β-C, $^1J_{CH}$ = 173 Hz), 119.6 (α-C, $^1J_{CH}$ = 192 Hz), 128−129 (m (overlapping with C$_6$D$_6$), *m*- and *p*-C of PPh), 130.1 (d, J_{CP} = 9 Hz, *o*-C of PPh), 130.4 (t, J_{CP} = 5 Hz, *o*-C of PPh), 142.9 (t, J_{CP} = 17 Hz, *ipso*-C of PPh), 144.9 (d, J_{CP} = 37 Hz, *ipso*-C of PPh); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −24.5 (d with ^{183}W satellites, J_{PP} = 2 Hz, J_{PW} = 287 Hz, P(trans)), −20.1 (t with ^{183}W satellites, J_{PP} = 2 Hz, J_{PW} = 378 Hz, P(unique)). Anal. Calcd for C$_{28}$H$_{37}$N$_2$P$_3$Br$_2$W: C, 40.12; H, 4.45; N, 3.34. Found: C, 40.34; H, 4.54; N, 3.26.

The chloro analogue **6a** was prepared from **5a** by a similar procedure except that 35% hydrochloric acid was used instead of hydrobromic acid. **6a.** Green crystals from ether at −78 °C (44%): ^{1}H NMR (C$_6$D$_6$) δ 1.47 (d, 6 H, J = 8.6 Hz, PMe), 1.85, 1.93 (t, 6 H each, J = 3.9 Hz, PMe), 5.84 (br t, 2 H, J = 2.3 Hz, β-H), 6.31 (br t, 2 H, J = 2.3 Hz, α-H), 6.7−7.3 (m, 15 H, PPh); ^{13}C NMR (C$_6$D$_6$) δ 12.7, 15.9 (each t, J_{CP} = 14 Hz, PMe), 23.0 (d, J_{CP} = 31 Hz, PMe), 106.2 (β-C, $^1J_{CH}$ = 173 Hz), 118.8 (α-C, $^1J_{CH}$ = 191 Hz), 128−129 (m (overlapping with C$_6$D$_6$), *m*- and *p*-C of PPh), 130.2 (d, J_{CP} = 9 Hz, *o*-C of PPh), 130.4 (t, J_{CP} = 5 Hz, *o*-C of PPh), 142.9 (t, J_{CP} = 17 Hz, *ipso*-C of PPh), 144.8 (d, J_{CP} = 37 Hz, *ipso*-C of PPh). Anal. Calcd for C$_{28}$H$_{37}$N$_2$P$_3$Cl$_2$W: C, 44.88; H, 4.98; N, 3.74; Cl, 9.46. Found: C, 44.65; H, 4.91; N, 3.69; Cl, 9.73.

Substitution of the Pyrrole Ring in Pyrrolylimido Complexes 3$^+$. a. Bromination. Monobromination of **3b**$^+$ is representative. To a suspension of **3b**$^+$BF$_4^-$ (200 mg, 0.171 mmol) in THF (10 mL) was added NBS (30.4 mg, 0.171 mmol) at −10 °C. After being stirred at the same temperature for 5 h, the resulting orange solution was quenched with 5% aqueous Na$_2$S$_2$O$_3$ (5 mL), diluted with CH$_2$Cl$_2$ (20 mL), and washed successively with 5% aqueous Na$_2$S$_2$O$_3$ (2 × 50 mL) and 5% aqueous NH$_4$BF$_4$ (4 × 50 mL). The organic layer was dried over MgSO$_4$ and evaporated to leave an orange-red oil, whose ^{1}H NMR spectrum was measured in order to determine the ratio of the products (**7b**$^+$−**10b**$^+$). The oil was purified by gel chromatography (Sephadex LH-20; eluent, MeOH−CH$_2$Cl$_2$) and crystallized from ClCH$_2$CH$_2$Cl/ether to give (β-bromopyrrolyl)imido complex **7b**$^+$BF$_4^-$·ClCH$_2$CH$_2$Cl as orange crystals (169 mg, 74%): ^{1}H NMR (CDCl$_3$) δ 2.6−2.8 (m, 8 H, CH$_2$ of dppe), 4.19 (br t, 1 H, J = 2.1 Hz, 2-H), 4.74 (br t, 1 H, J = 2.9 Hz, 5-H), 5.40 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD$_2$Cl$_2$) δ 93.9 (3-C), 108.7 (4-C, $^1J_{CH}$ = 180 Hz), 118.9 (2-C, $^1J_{CH}$ = 198 Hz), 119.6 (5-C, $^1J_{CH}$ = 195 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 31.0 (d with ^{183}W satellites, J_{PF} = 43 Hz, J_{PW} = 286 Hz). Anal. Calcd for C$_{58}$H$_{55}$N$_2$BF$_5$P$_4$Cl$_2$BrW: C, 51.82; H, 4.12; N, 2.08; Br, 5.94. Found: C, 51.88; H, 4.17; N, 2.27; Br, 5.54. α-Brominated pyrrolylimido complex **8b**$^+$BF$_4^-$ was detected and characterized by the ^{1}H NMR measurement of the crude reaction mixture: (CDCl$_3$) δ 5.15 (dd, 1 H, J = 3.4, 1.9 Hz, 5-H), 5.25 (br t, 1 H, J = 3.8 Hz, 4-H), 5.50 (dd, 1 H, J = 4.0, 1.9 Hz, 3-H).

7a$^+$**BF$_4^-$·0.5CH$_2$Cl$_2$.** Obtained by a similar procedure (at 0 °C for 3 h) as orange crystals from CH$_2$Cl$_2$/ether (69%): ^{1}H NMR (CDCl$_3$) δ 2.6−2.9 (m, 8 H, CH$_2$ of dppe), 4.19 (br t, 1 H, J = 2.0 Hz, 2-H), 4.83 (br t, 1 H, J = 2.8 Hz, 5-H), 5.40 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 42.0 (d, J_{PF} = 36 Hz). Anal. Calcd for C$_{56.5}$H$_{53}$N$_2$BF$_5$P$_4$ClBrMo: C, 56.50, H, 4.45; N, 2.33; Br, 6.65. Found: C, 55.95; H, 4.52; N, 2.41; Br, 6.96.

Dibromination reactions of **3b**$^+$ were also carried out in a similar way, and the products were characterized by NMR. **9b**$^+$BF$_4^-$: ^{1}H NMR (CD$_2$Cl$_2$) δ 4.30 (s, 2 H, α-H); ^{13}C NMR (CD$_2$Cl$_2$) δ 97.1 (β-C), 119.0 (α-C, $^1J_{CH}$ = 200 Hz). **10b**$^+$BF$_4^-$: ^{1}H NMR (CD$_2$Cl$_2$) δ 5.09 (d, 1 H, J = 3.7 Hz, 5-H), 5.39 (d, 1 H, J = 3.7 Hz, 4-H); ^{13}C NMR (CD$_2$Cl$_2$) δ 109.3 (4-C, $^1J_{CH}$ = 183 Hz), 124.0 (5-C, $^1J_{CH}$ = 197 Hz). Signals assignable to 2-C and 3-C could not be found because of the low yield of this complex.

b. Chlorination. The following procedure is representative. NCS (2 equiv, 45.7 mg, 0.342 mmol) was added to a suspension of **3b**$^+$BF$_4^-$ (200 mg, 0.171 mmol) in THF (10 mL). The mixture was stirred at 0 °C for 2 h and at room temperature for 22 h, and the resulting orange-red solution was worked up according to the method used for bromination. Recrystallization from CH$_2$Cl$_2$−MeOH/ether gave dark-red crystals of (α,α′-dichloropyrrolyl)imido complex **13b**$^+$BF$_4^-$·0.5CH$_2$Cl$_2$ (184 mg, 84%): ^{1}H NMR (CDCl$_3$) δ 2.6−2.8, 2.9−3.1 (m, 4 H each, CH$_2$ of dppe), 5.41 (s, 2 H, β-H), 6.8−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD$_2$Cl$_2$) δ 105.0 (β-C, $^1J_{CH}$ = 182 Hz), 114.6 (α-C); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 31.5 (d with ^{183}W satellites, J_{PF} = 51 Hz, J_{PW} = 288 Hz). Anal. Calcd for C$_{56.5}$H$_{51}$N$_2$BF$_5$P$_4$Cl$_3$W: C, 53.10; H, 4.02; N, 2.19; Cl, 8.32. Found: C, 52.88; H, 4.28; N, 2.26; Cl, 7.46.

Monochlorinated complexes **11b**$^+$ and **12b**$^+$ were obtained from the reaction with 1 equiv of chlorinating reagent and characterized by NMR.

11b$^+$**BF$_4^-$.** ^{1}H NMR (CDCl$_3$) δ 4.23 (br t, 1 H, J = 1.7 Hz, 2-H), 4.72 (br t, 1H, J = 2.8 Hz, 5-H), 5.33 (br t, 1 H, J = 2.9 Hz, 4-H).

12b$^+$**BF$_4^-$.** ^{1}H NMR (CDCl$_3$) δ 5.15 (dd, 1 H, J = 3.4, 1.9 Hz, 5-H), 5.29 (br t, 1 H, J = 3.8 Hz, 4-H), 5.36 (dd, 1 H, J = 4.0, 1.9 Hz, 3-H); ^{13}C NMR (CD$_2$Cl$_2$) δ 104.6 (3-C, $^1J_{CH}$ = 179 Hz), 105.8 (4-C, $^1J_{CH}$ = 178 Hz), 113.1 (2-C), 122.0 (5-C, $^1J_{CH}$ = 195 Hz).

c. Chlorination of (β-Bromopyrrolyl)imido Complex 7b$^+$. A suspension of **7b**$^+$BF$_4^-$·ClCH$_2$CH$_2$Cl (150 mg, 0.112 mmol) in THF (10 mL) and NCS (15.2 mg, 0.114 mmol) was stirred for 40 h at room temperature. The resulting reddish-orange solution was worked up as above and crystallized from CH$_2$Cl$_2$−MeOH/ether to afford (3-bromo-2-chloropyrrolyl)imido complex **14b**$^+$BF$_4^-$ as orange crystals (109.7 mg, 75%): ^{1}H NMR (CDCl$_3$) δ 2.6−3.1 (m, 8 H, CH$_2$ of dppe), 5.41, 5.48 (d, 1 H each, J = 3.7 Hz, 4- and 5-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD$_2$Cl$_2$) δ 93.5 (3-C), 108.3 (4-C, $^1J_{CH}$ = 184 Hz),

113.0 (2-C), 121.6 (5-C, $^1J_{CH}$ = 197 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.2 (d with ^{183}W satellites, J_{PF} = 46 Hz, J_{PW} = 286 Hz). Anal. Calcd for $C_{56}H_{50}N_2BF_5P_4ClBrW$: C, 52.55; H, 3.94; N, 2.19; Cl, 2.77; Br, 6.24. Found: C, 52.44; H, 3.95; N, 2.25; Cl, 2.71; Br, 6.12.

d. Cyanation. To an ice-cooled solution of **3b**$^+BF_4^-$ (200 mg, 0.171 mmol) in MeCN (5 mL) was added chlorosulfonyl isocyanate (18 μL, 0.21 mmol). After the mixture was stirred at 0 °C for 2 h and at room temperature for 12 h, DMF (1 mL) was added and the mixture was stirred for a further 1.5 h. The resulting red solution was diluted with CH_2Cl_2 (30 mL), washed with 5% aqueous NH_4BF_4 (4 × 50 mL), and dried over $MgSO_4$. The solvent was evaporated, and the residue was analyzed by ^1H NMR, which indicated that the β-cyanation of **3b**$^+$ proceeded quantitatively. Reddish-purple crystals of (β-cyanopyrrolyl)imido complex **15b**$^+BF_4^-\cdot 0.5CH_2Cl_2$ were obtained by crystallization from CH_2Cl_2–MeOH/ether (178 mg, 84%): ^1H NMR ($CDCl_3$) δ 2.6–3.0 (m, 8 H, CH_2 of dppe), 4.35 (br t, 1 H, J = 2.0 Hz, 2-H), 5.16 (dd, 1 H, J = 3.2, 2.2 Hz, 5-H), 5.72 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 6.9–7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD_2Cl_2) δ 90.6 (3-C), 108.7 (4-C, $^1J_{CH}$ = 181 Hz), 114.6 (CN), 120.1 (5-C, $^1J_{CH}$ = 197 Hz), 126.0 (2-C, $^1J_{CH}$ = 199 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.1 (d with ^{183}W satellites, J_{PF} = 44 Hz, J_{PW} = 284 Hz); IR (KBr, cm^{-1}) 2228 (C≡N). Anal. Calcd for $C_{57.5}H_{52}N_3BF_5P_4ClW$: C, 55.96; H, 4.25; N, 3.41. Found: C, 55.75; H, 4.46; N, 3.39.

e. Formylation. Pyrrolylimido complex **3b**$^+BF_4^-$ (200 mg, 0.171 mmol) and $[Me_2N{=}CHCl]Cl$ (127 mg, 0.992 mmol) were dissolved in CH_2Cl_2 (5 mL) and stirred at room temperature for 72 h. The solution was quenched with 5% aqueous $NaHCO_3$ (5 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was successively washed with 5% aqueous $NaHCO_3$ (2 × 50 mL) and then 5% aqueous NH_4BF_4 (4 × 50 mL), dried ($MgSO_4$), and evaporated to dryness. The residual orange oil was purified by gel chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2) and crystallized from CH_2Cl_2/ether to give (β-formylpyrrolyl)imido complex **16b**$^+BF_4^-$ as orange crystals (138 mg, 68%): ^1H NMR ($CDCl_3$) δ 2.6–3.0 (m, 8 H, CH_2 of dppe), 4.84 (br t, 1 H, J = 2.6 Hz, 5-H), 5.08 (br t, 1 H, J = 1.9 Hz, 2-H), 5.84 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0–7.4 (m, 40 H, Ph of dppe), 9.13 (s, 1 H, CHO); ^{13}C NMR (CD_2Cl_2) δ 104.6 (4-C), 121.7 (5-C), 122.7 (3-C), 127.0 (2-C), 184.1 (CHO); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.3 (d with ^{183}W satellites, J_{PF} = 43 Hz, J_{PW} = 285 Hz); IR (KBr, cm^{-1}) 1671 (CH=O). Anal. Calcd for $C_{57}H_{52}N_2OBF_5P_4W$: C, 57.31; H, 4.39; N, 2.35. Found: C, 56.89; H, 4.45; N, 2.23.

f. Sulfonation. A mixture of **3b**$^+BF_4^-$ (200 mg, 0.171 mmol) and SO_3–pyridine (95.0 mg, 0.597 mmol) in $ClCH_2CH_2Cl$ (5 mL) was refluxed for 24 h. The resulting solution was cooled and washed successively with 5% aqueous $NaHCO_3$ (2 × 50 mL) and 5% aqueous NH_4BF_4 (2 × 50 mL). The organic layer was dried over $MgSO_4$, filtered through a Celite plug, and evaporated to dryness. The oily orange residue was purified by gel chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2). Recrystallization from CH_2Cl_2/ether gave 142 mg of crystalline product which was formulated as **17b**$\cdot CH_2Cl_2$ (ca. 66%). The analytical sample was prepared by further recrystallization from C_6H_6–MeOH/ether to yield **17b**$\cdot$MeOH: ^1H NMR (CD_2Cl_2) δ 2.5–2.8 (m, 8 H, CH_2 of dppe), 4.44 (br t, 1 H, J = 2.7 Hz, 5-H), 5.47 (br t, 1 H, J = 2.0 Hz, 2-H), 5.56 (dd, 1 H, J = 3.1, 1.6 Hz, 4-H), 7.0–7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD_2Cl_2) δ 105.6 (4-C, $^1J_{CH}$ = 178 Hz), 118.0 (2-C, $^1J_{CH}$ = 197 Hz), 119.7 (5-C, $^1J_{CH}$ = 192 Hz). The signal of 3-C was obscured by overlapping with the dppe phenyl signals; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 31.6 (d with ^{183}W satellites, J_{PF} = 44 Hz, J_{PW} = 286 Hz); IR (KBr, cm^{-1}) 1229, 1190, 1038 (SO_3^-). Anal. Calcd for $C_{57}H_{55}N_2O_4FP_4SW$: C, 57.49; H, 4.66; N, 2.35; S, 2.69. Found: C, 56.94; H, 4.90; N, 2.51; S, 2.71.

g. Acylation. Method A (from Acid Chlorides). The following procedure for the acylation of **3c**$^+$ is representative. Acid chloride RCOCl (0.57 mmol) was added to a slurry of $AlCl_3$ (63 mg, 0.47 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After 10–30 min, to the resulting colorless or pale-yellow solution was added **3c**$^+BF_4^-\cdot 1.5CH_2Cl_2$ (200 mg, 0.159 mmol). The mixture was stirred at 0 °C for 1.5–2 h and at room temperature for 1–2 h. The green solution was quenched with 5% aqueous $NaHCO_3$ (5 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was washed with 5% aqueous $NaHCO_3$ (2 × 50 mL) and then 5% aqueous NH_4BF_4 (4 × 50 mL), dried ($MgSO_4$), and evaporated to dryness. Purification by gel chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2) and recrystallization afforded the corresponding (β-acylpyrrolyl)imido complexes.

18c$^+BF_4^-\cdot 0.5CH_2Cl_2$ **(R = Ph).** Purple crystals from CH_2Cl_2/ether, then CH_2Cl_2/hexane (84%): ^1H NMR ($CDCl_3$) δ 2.8–3.1 (m, 8 H, CH_2 of dppe), 4.81 (br t, 1 H, J = 1.8 Hz, 2-H), 4.91 (dd, 1 H, J = 3.2, 2.2 Hz, 5-H), 6.03 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0–7.35 (m, 42 H, Ph of dppe and *o*-H of COPh), 7.40 (t, 2 H, J = 7.7 Hz, *m*-H of COPh), 7.56 (br t, 1 H, J = 7.3 Hz, *p*-H of COPh); ^{13}C NMR (CD_2Cl_2) δ 107.9 (4-C, $^1J_{CH}$ = 179 Hz), 120.7 (5-C, $^1J_{CH}$ = 195 Hz), 121.1 (3-C), 125.9 (2-C, $^1J_{CH}$ = 197 Hz), 188.7 (CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 24.7 (s with ^{183}W satellites, J_{PW} = 273 Hz); IR (KBr, cm^{-1}) 1642 (C=O). Anal. Calcd for $C_{63.5}H_{57}N_2OBF_4P_4Cl_2W$: C, 57.36; H, 4.47; N, 2.11; Cl, 5.33. Found: C, 57.37; H, 4.65; N, 1.96; Cl, 5.92.

19c$^+BF_4^-$ **(R = *p*-Tol).** Purple crystals from CH_2Cl_2–acetone/ether, then CH_2Cl_2/hexane (85%): ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H, CH_3), 2.8–3.1 (m, 8 H, CH_2 of dppe), 4.84 (br t, 1 H, J = 1.7 Hz, 2-H), 4.88 (br t, 1 H, J = 2.7 Hz, 5-H), 6.01 (dd, 1 H, J = 3.1, 1.6 Hz, 4-H), 7.0–7.4 (m, 44 H, Ph of dppe and $C_6H_4CH_3$); IR (KBr, cm^{-1}) 1638 (C=O). Anal. Calcd for $C_{64}H_{58}N_2OBF_4P_4ClW$: C, 59.08; H, 4.49; N, 2.15. Found: C, 59.22; H, 4.82; N, 2.08.

20c$^+BF_4^-\cdot 1.5CH_2Cl_2$ **(R = CH_2Ph).** Purple crystals from CH_2Cl_2–acetone/ether, then CH_2Cl_2/hexane (79%): ^1H NMR ($CDCl_3$) δ 2.8–3.1 (m, 8 H, CH_2 of dppe), 3.49 (s, 2 H, CH_2Ph), 4.64 (dd, 1 H, J = 3.2, 2.0 Hz, 5-H), 5.24 (br t, 1 H, J = 2.0 Hz, 2-H), 5.89 (dd, 1 H, J = 3.2, 1.6 Hz, 4-H), 7.0–7.4 (m, 45 H, Ph of dppe and CH_2Ph); IR (KBr, cm^{-1}) 1663 (C=O). Anal. Calcd for $C_{65.5}H_{61}N_2OBF_4P_4Cl_4W$: C, 55.07; H, 4.30; N, 1.96. Found: C, 55.24; H, 4.41; N, 1.94.

21c$^+BF_4^-\cdot 0.5CH_2Cl_2$ **(R = COOEt).** Larger amounts of $AlCl_3$ (0.85 mmol) than in the representative procedure were required to complete the acylation. Purple crystals from CH_2Cl_2–MeOH/ether (76%): ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7.1 Hz, CH_3), 2.8–3.1 (m, 8 H, CH_2 of dppe), 4.26 (q, 2 H, J = 7.1 Hz, OCH_2), 4.78 (dd, 1 H, J = 3.2, 2.2 Hz, 5-H), 5.67 (br t, 1 H, J = 1.8 Hz, 2-H), 6.02 (dd, 1 H, J = 3.2, 1.6 Hz, 4-H), 7.0–7.4 (m, 40 H, Ph of dppe); IR (KBr, cm^{-1}) 1725, 1673 (C=O), 1235 (C–O). Anal. Calcd for $C_{60.5}H_{57}N_2O_3BF_4P_4Cl_2W$: C, 54.82; H, 4.33; N, 2.11. Found: C, 55.23; H, 4.36; N, 2.07.

22c$^+BF_4^-\cdot$**0.5(ether) (R = *n*-C_6H_{13}).** Purple crystals from CH_2Cl_2/ether (87%): ^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H, J = 6.8 Hz, CH_3), 1.2–1.4 (m, 6 H, $(CH_2)_3CH_3$), 1.48 (br quint, 2 H, J = 7.3 Hz, $COCH_2CH_2$), 2.11 (t, 2 H, J = 7.4 Hz, $COCH_2$), 2.8–3.1 (m, 8 H, CH_2 of dppe), 4.68 (dd, 1 H, J = 3.2, 2.1 Hz, 5-H), 5.04 (br t, 1 H, J = 1.9 Hz, 2-H), 5.85 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0–7.4 (m, 40 H, Ph of dppe); IR (KBr, cm^{-1}) 1663 (C=O). Anal. Calcd for $C_{65}H_{69}N_2O_{1.5}BF_4P_4ClW$: C, 58.60; H, 5.22; N, 2.10. Found: C, 58.33; H, 5.25; N, 2.14.

Method B (from Acid Anhydrides). To a solution prepared from $AlCl_3$ (0.994 mmol) and acetic anhydride (54 μL, 0.57 mmol) in CH_2Cl_2 (5 mL) was added **3c**$^+BF_4^-\cdot 1.5CH_2Cl_2$ (200 mg, 0.159 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 1.5 h and then at room temperature for 1 h. After workup similar to method A, recrystallization from CH_2Cl_2/ether, then CH_2Cl_2/hexane gave **23c**$^+BF_4^-\cdot CH_2Cl_2$ as purple crystals (160 mg, 77%): ^1H NMR ($CDCl_3$) δ 1.90 (s, 3 H, CH_3), 2.8–3.1 (m, 8 H, CH_2 of dppe), 4.68 (dd, 1 H, J = 3.2, 2.1 Hz, 5-H), 5.04 (br t, 1 H, J = 1.8 Hz, 2-H), 5.84 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0–7.5 (m, 40 H, Ph of dppe); IR (KBr, cm^{-1}) 1655 (C=O). Anal. Calcd for $C_{59}H_{56}N_2OBF_4P_4Cl_3W$: C, 54.09; H, 4.31; N, 2.14. Found: C, 53.72; H, 4.40; N, 2.12.

Complex **24c**$^+BF_4^-$ was prepared similarly from **3c**$^+BF_4^-$ and succinic anhydride in 72% yield and obtained as purple crystals from CH_2Cl_2–MeOH/ether. ^1H NMR signal for the –COOH group could not be found: ^1H NMR ($CDCl_3$) δ 2.45, 2.62 (br t, 2 H each, J = 6.5 Hz, $COCH_2CH_2$), 2.7–3.0 (m, 8 H, CH_2 of dppe), 4.65 (dd, 1 H, J = 3.2, 2.0 Hz, 5-H), 5.10 (br t, 1 H, J = 2.0 Hz, 2-H), 5.85 (dd, 1 H, J = 3.2, 1.7 Hz, 4-H), 7.0–7.5 (m, 40 H, Ph of dppe); IR (KBr, cm^{-1}) 3350 (OH), 1736, 1671 (C=O). Anal. Calcd for $C_{60}H_{56}N_2O_3BF_4P_4ClW$: C, 56.16; H, 4.40; N, 2.18. Found: C, 55.86; H, 4.51; N, 2.09.

Method C. Complex **3b**$^+BF_4^-$ (200 mg, 0.171 mmol) was treated with a solution prepared from benzoyl chloride (150 μL, 1.28 mmol) and $AlCl_3$ (144 mg, 1.08 mmol) in CH_2Cl_2 (5 mL) at 0 °C for 1 h and at room temperature for 1 h. Similar workup of the resulting solution as in method A and recrystallization gave purple crystals of

Table 9. Crystallographic Data for **3b**$^+PF_6^-$, **6b**, **7b**$^+BF_4^-\cdot ClCH_2CH_2Cl$, **13b**$^+PF_6^-\cdot$2(toluene), and **19c**$^+BF_4^-\cdot$2(benzene)

	3b$^+PF_6^-$	**6b**	**7b**$^+BF_4^-\cdot ClCH_2CH_2Cl$	**13b**$^+PF_6^-\cdot$2(toluene)	**19c**$^+BF_4^-\cdot$2(benzene)
formula	$C_{56}H_{52}N_2F_7P_5W$	$C_{28}H_{37}N_2P_3Br_2W$	$C_{58}H_{55}N_2BF_5P_4Cl_2BrW$	$C_{70}H_{66}N_2F_7P_5Cl_2W$	$C_{76}H_{70}N_2OBF_4P_4ClW$
formula weight	1224.75	838.19	1344.44	1477.92	1457.40
cryst size (mm^3)	0.5 × 0.3 × 0.25	0.6 × 0.3 × 0.3	0.6 × 0.3 × 0.3	0.8 × 0.4 × 0.1	0.6 × 0.3 × 0.05
cryst system	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	*Cc*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*P*1
cryst color	orange	dark green	orange	orange	purple
a (Å)	17.862(2)	10.574(2)	16.595(2)	13.963(1)	13.040(2)
b (Å)	14.709(2)	16.441(2)	14.578(2)	21.878(3)	13.154(3)
c (Å)	20.157(2)	9.837(1)	24.343(2)	11.390(1)	12.446(4)
α (deg)	90	96.78(1)	90	101.477(9)	114.74(2)
β (deg)	91.841(8)	107.13(1)	102.851(7)	98.847(8)	95.48(2)
γ (deg)	90	75.15(1)	90	74.612(8)	112.35(2)
V (Å^3)	5293.3(9)	1578.0(4)	5741(1)	3268.9(6)	1708(1)
Z	4	2	4	2	1
d_{calcd} (g cm^{-3})	1.537	1.764	1.555	1.501	1.416
d_{obsd} (g cm^{-3})	1.530 (20 °C)	1.762 (22 °C)	1.553 (27 °C)	1.491 (18 °C)	1.417 (19 °C)
F (000)	2456	816	2680	1492	740
μ_{calcd} (cm^{-1})	24.00	63.76	29.72	20.68	18.81
transmn factor	0.8605−0.9995	0.7210−1.0000	0.8050−0.9992	0.6378−1.0000	0.6727−1.0000
reflns measd	(+*h*, +*k*, ±*l*) (*h* + *k* = 2*n*)	(+*h*, ±*k*, ±*l*)	(+*h*, +*k*, ±*l*)	(+*h*, ±*k*, ±*l*)	(+*h*, ±*k*, ±*l*)
no. of unique data	6308	7235	13685	15048	7827
no. of data used ($I > 3\sigma(I)$)	5456	5988	5697	9091	7696
no. of params refined	638	325	648	722	808
R^a	0.028	0.029	0.058	0.050	0.032
$R_w{}^b$	0.021	0.023	0.038	0.040	0.024
goodness of fit indicater	1.90	2.45	2.18	2.29	1.51
maximum residuals (e Å^{-3})	0.77	0.70	1.31	1.10	1.26

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

18c$^+BF_4^-\cdot 0.5CH_2Cl_2$ (175 mg, 75%). Benzoylation and heptanoylation of molybdenum complex **3a**$^+$ were also conducted similarly to afford **18d**$^+BF_4^-$ and **22d**$^+BF_4^-$, respectively.

18d$^+BF_4^-\cdot 0.5CH_2Cl_2$. Violet crystals from CH_2Cl_2/ether (84%): ^{1}H NMR ($CDCl_3$) δ 2.8−3.1 (m, 8 H, CH_2 of dppe), 4.90 (br t, 1 H, *J* = 1.7 Hz, 2-H), 5.03 (dd, 1 H, *J* = 3.2, 2.0 Hz, 5-H), 6.01 (dd, 1 H, *J* = 3.2, 1.5 Hz, 4-H), 7.0−7.4 (m, 42 H, Ph of dppe and *o*-H of COPh), 7.41 (t, 2 H, *J* = 7.5 Hz, *m*-H of COPh), 7.57 (t, 1 H, *J* = 7.5 Hz, *p*-H of COPh); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 40.7 (s); IR (KBr, cm^{-1}) 1644 (C=O). Anal. Calcd for $C_{63.5}H_{57}N_2OBF_4P_4Cl_2Mo$: C, 61.42; H, 4.63; N, 2.26; Cl, 5.71. Found: C, 61.53; H, 5.13; N, 2.22; Cl, 5.51.

22d$^+BF_4^-\cdot$**0.5(ether).** Violet crystals from CH_2Cl_2/ether (74%): ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H, *J* = 6.8 Hz, CH_3), 1.2−1.4 (m, 6 H, $(CH_2)_3CH_3$), 1.4−1.6 (m, 2 H, $COCH_2CH_2$), 2.11 (t, 2 H, *J* = 7.4 Hz, $COCH_2$), 2.8−3.1 (m, 8 H, CH_2 of dppe), 4.77 (dd, 1 H, *J* = 3.2, 2.2 Hz, 5-H), 5.10 (br t, 1 H, *J* = 2.0 Hz, 2-H), 5.84 (dd, 1 H, *J* = 3.2, 1.5 Hz, 4-H), 7.0−7.4 (m, 40 H, Ph of dppe); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 41.0 (s); IR (KBr, cm^{-1}) 1663 (C=O). Anal. Calcd for $C_{65}H_{69}N_2O_{1.5}BF_4P_4ClMo$: C, 62.74; H, 5.59; N, 2.25. Found: C, 62.40; H, 5.63; N, 2.22.

When the reaction of **3b**$^+BF_4^-$ (200 mg, 0.171 mmol) was performed with smaller amounts of benzoyl chloride (61 μL, 0.52 mmol) and $AlCl_3$ (56.1 mg, 0.421 mmol), **18b**$^+BF_4^-$ was obtained as the major product and isolated in 25% (orange-red crystals from CH_2Cl_2/ether): ^{1}H NMR ($CDCl_3$) δ 2.6−2.9 (m, 8 H, CH_2 of dppe), 4.85 (br t, 1 H, *J* = 1.8 Hz, 2-H), 5.28 (dd, 1 H, *J* = 2.9, 2.2 Hz, 5-H), 6.05 (dd, 1 H, *J* = 2.9, 1.7 Hz, 4-H), 7.0−7.4 (m, 44 H, Ph of dppe and *o*, *m*-H of COPh), 7.52 (t, 1 H, *J* = 7.4 Hz, *p*-H of COPh); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 30.2 (d with ^{183}W satellites, J_{PF} = 44 Hz, J_{PW} = 285 Hz); IR (KBr, cm^{-1}) 1640 (C=O). Anal. Calcd for $C_{63}H_{56}N_2OBF_5P_4W$: C, 59.55; H, 4.44; N, 2.20. Found: C, 58.87; H, 4.40; N, 2.26.

h. Acylation of (β-Bromopyrrolyl)imido Complex 7b$^+$**.** Complex **7b**$^+$ was added to an ice-cooled solution of $AlCl_3$ (104.4 mg, 0.783 mmol) and isobutyryl chloride (88 μL, 0.83 mmol) in CH_2Cl_2 (5 mL). After being stirred for 2.5 h at 0 °C and for 1.5 h at ambient temperature, the solution was quenched with 5% aqueous $NaHCO_3$, diluted with CH_2Cl_2, and washed successively with 5% aqueous $NaHCO_3$ (50 mL × 2) then 5% aqueous NH_4PF_6 (50 mL × 4). Purification by gel chromatography (Sephadex LH-20; eluent, MeOH−CH_2Cl_2) and recrystallization from acetone/ether provided (4-bromo-3-isobutyrylpyrrolyl)imido complex **25c**$^+PF_6^-\cdot$1.5(acetone) as purple crystals (95.1 mg, 57%): ^{1}H NMR ($CDCl_3$) δ 0.94 (d, 6 H, *J* = 6.8 Hz, Me), 2.39 (sep, 1 H, *J* = 6.8 Hz, COCH), 2.8−3.1 (m, 8 H, CH_2 of dppe), 4.17 (d, 1 H, *J* = 2.5 Hz, 5-H), 5.09 (d, 1 H, *J* = 2.5 Hz, 2-H), 7.0−7.5 (m, 40 H, Ph of dppe); ^{13}C NMR (CD_2Cl_2) δ 19.1 (Me, $^1J_{CH}$ = 128 Hz), 37.4 (*C*OCH, $^1J_{CH}$ = 128 Hz), 94.8 (4-C), 118.4 (3-C), 121.5 (5-C, $^1J_{CH}$ = 201 Hz), 123.1 (2-C, $^1J_{CH}$ = 195 Hz), 197.5 (CO); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 24.9 (s with ^{183}W satellites, J_{PW} = 273 Hz, dppe), 179.8 (sep, J_{PF} = 713 Hz, PF_6^-); IR (KBr, cm^{-1}) 1671 (C=O), 1705 (C=O of acetone). Anal. Calcd for $C_{64.5}H_{66}N_2O_{2.5}F_6P_5ClBrW$: C, 52.44; H, 4.50; N, 1.90. Found: C, 52.92; H, 4.70; N, 2.01.

Reduction of the Pyrrolylimido Complexes 3$^+$ **and 22c**$^+$**.** To a suspension of pyrrolylimido complex (0.07−0.10 mmol) in 3 mL of THF was added $LiAlH_4$ (10 equiv) or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (70% solution in toluene, 20 equiv) at room temperature. After stirring for 16−20 h, the mixture was quenched with MeOH (1 mL). Organic products were identified by GC−MS and quantitatively determined by GLC. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in aqueous H_2SO_4, which was used for the determination of ammonia (indophenol method).[39] The residue was further purified by chromatography (alumina; eluent, benzene−THF) and recrystallized from THF−hexane to give tetrahydrido complexes **26**.

Reduction of the Pyrrolylimido Complex 6b. To a deep-blue solution of **6b** (72 mg, 0.085 mmol) in THF (3 mL) was added $LiAlH_4$ (38 mg, 0.85 mmol). The mixture was stirred at 50 °C for 24 h. The resulting yellow solution was treated with MeOH (1 mL), and the yields of pyrrole and *N*-aminopyrrole in this solution were determined by GLC analyses.

Reaction of the Pyrrolylimido Complex 6 with KOH in Alcohol. Typically, to a suspension of complex **6** (0.08−0.09 mmol) in alcohol (3 mL) was added KOH (10 equiv), and the mixture was stirred at room temperature. The formation of pyrrole and *N*-aminopyrrole was monitored periodically by GLC analyses until their yields reached constant values. The products were identified by GC−MS.

Crystallography. Anion metatheses of **3b**$^+BF_4^-$ and **13b**$^+BF_4^-$ to the corresponding PF_6^- salts were carried out by washing their CH_2Cl_2 solutions with 5% aqueous NH_4PF_6. Single crystals suitable for X-ray analysis were prepared by recrystallization from acetone−CH_2Cl_2/hexane (**3b**$^+PF_6^-$), C_6H_6−ether/hexane (**6b**), $ClCH_2CH_2Cl$/ether (**7b**$^+BF_4^-\cdot ClCH_2CH_2Cl$), acetone/toluene (**13b**$^+PF_6^-\cdot$2(toluene)), or

(39) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461.

CH_2Cl_2/benzene (**19c**$^+BF_4^-$·2(benzene)). Crystals 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 (λ = 0.710 69 Å) radiation and a graphite monochromator at 20 ± 1 °C using the $\omega-2\theta$ scan technique ($6 < 2\theta < 55°$ for **3b**$^+PF_6^-$; $5 < 2\theta < 55°$ for **6b**, **7b**$^+BF_4^-$·$ClCH_2CH_2Cl$, **13b**$^+PF_6^-$·2(toluene), and **19c**$^+BF_4^-$·2(benzene)). Accurate cell dimensions of each crystal were determined by least-squares refinement of 25 machine-centered reflections. Empirical absorption correction based on ψ scan and Lorentz–polarization corrections were applied. Details of the X-ray diffraction study are summarized in Table 9.

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 BF_4^- anion and carbon atoms of the $ClCH_2CH_2Cl$ molecule in **7b**$^+BF_4^-$·$ClCH_2CH_2Cl$ and the toluene molecules in **13b**$^+PF_6^-$·2(toluene), where isotropic parameters were used. Fluorine atoms of the BF_4^- anion in **7b**$^+BF_4^-$·$ClCH_2CH_2Cl$ and methyl carbons of toluene molecules in **13b**$^+PF_6^-$·2(toluene) were found in disordered form from the difference Fourier maps and refined with an atom multiplicity of 0.5. All hydrogen atoms except for those of the $ClCH_2CH_2Cl$ molecule in **7b**$^+BF_4^-$·$ClCH_2CH_2Cl$ and the toluene molecules in **13b**$^+PF_6^-$·2(toluene) were placed at calculated positions and were included in the final stage of refinements with fixed isotropic parameters. The absolute structures of **3b**$^+PF_6^-$ and **19c**$^+BF_4^-$·2(benzene) were determined by comparison of the R and R_w values and the goodness of fit factors of the enantiomorph. The atomic scattering factors were taken from ref 40, and anomalous dispersion effects were included; the values for $\Delta f'$ and $\Delta f''$ were taken from ref 41.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **3b**$^+PF_6^-$, **6b**, **7b**$^+BF_4^-$·$ClCH_2CH_2Cl$, **13b**$^+PF_6^-$·2(toluene), and **19c**$^+BF_4^-$·2(benzene) (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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