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Bimetallic Arylation of Molecular Nitrogen[1]

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The anionic dinitrogen complex $[NBu_4][W(NCS)(N_2)(dppe)_2]$ (**6**, dppe = $Ph_2PCH_2CH_2PPh_2$) smoothly reacted with η^6-fluoroarene complexes such as $[Cr(\eta^6\text{-}p\text{-}FC_6H_4R)(CO)_3]$ (**3a**, R = COOMe) and $[RuCp(\eta^6\text{-}FC_6H_4R)][PF_6]$ (**5**, Cp = η^5-C_5H_5, R = H, Me, OMe, COOMe) in THF under mild conditions (0 °C to room temperature) to give novel μ-aryldiazenido complexes $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dppe)_2]$ (**7**) and $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4R)RuCp]\}(dppe)_2][PF_6]$ (**10**), respectively. μ-Aryldiazenido complexes **7** and $[WF\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4R)Cr(CO)_3]\}(dppe)_2]$ (**8a**, R = COOMe) were also obtained by irradiation of a THF solution of $[W(N_2)_2(dppe)_2]$ and **3a** in the presence of NBu_4X(X = SCN or F). The structures of these complexes were fully characterized by spectroscopic and X-ray diffraction analysis. The long N=N bond lengths (1.314(5) Å for **7**, 1.33(1) Å for **8a**, 1.28(1) Å for **10a** (R = H)) and the short N–C bond lengths (1.366(6) Å for **7**, 1.30(2) Å for **8a**, and 1.40(2) Å for **10a**) indicate delocalization of the N=N π-electrons over the aromatic ring. The reaction was suggested to proceed by the direct nucleophilic aromatic substitution mechanism, rather than the radical mechanism so far reported for alkylation reactions of coordinated dinitrogen. Furthermore, reactions of the diazenido complex $[WF(NNH)(dppe)_2]$ (**12**) with fluoroarene complexes **3** (R = COOMe, H) and $[FeCp(\eta^6\text{-}FC_6H_4R)][PF_6]$ (**4**; R = H, Me) also provide a route to μ-aryldiazenido complexes such as **8** and $[WF\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4R)FeCp]\}(dppe)_2][PF_6]$ (**13**), respectively. Crystallographic data for **7**·CH_2Cl_2: formula $C_{65}H_{57}N_3O_5SP_4Cl_2CrW$, space group $P2_1/n$ (monoclinic); a = 24.135(3) Å, b = 20.967(5) Å, c = 12.273(5) Å, β = 90.06(4)°, V = 6210(5) Å^3, Z = 4, R = 0.034, R_w = 0.029. **8a**·2THF: formula $C_{71}H_{71}N_2O_7FP_4CrW$, space group $P2_1/a$ (monoclinic); a = 23.110(5) Å, b = 23.402(7) Å, c = 12.046(3) Å, β = 93.89(2)°, V = 6500(3) Å^3, Z = 4, R = 0.056, R_w = 0.066. **10a**·CH_2Cl_2: formula $C_{65}H_{60}N_3F_6SP_5Cl_2RuW$, space group $P\bar{1}$ (triclinic); a = 12.630(2) Å, b = 23.648(3) Å, c = 11.507(3) Å, α = 103.11(1)°, β = 102.77(1)°, γ = 83.44(1)°, V = 3257.1(9) Å^3, Z = 2, R = 0.062, R_w = 0.054. **13b**·Me_2CO (R = Me): formula $C_{67}H_{66}N_2OF_7P_5FeW$, space group $C2/c$ (monoclinic); a = 38.090(9) Å, b = 18.507(4) Å, c = 18.359(3) Å, β = 91.25(2)°, V = 12939(5) Å^3, Z = 8, R = 0.061, R_w = 0.071.

Introduction

Chemical transformation of molecular dinitrogen has been among the central subjects of widespread and continuing interest in organometallic chemistry, and extensive studies have been done concerning the syntheses and reactivities of transition metal dinitrogen complexes.[2] Protonation, alkylation, acylation, and silylation of coordinated dinitrogen have so far been achieved by the reactions of mononuclear dinitrogen complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo or W, L = phosphine) with simple inorganic or organic reagents. Aiming at the development of new and efficient chemical transformation of dinitrogen which might be difficult at monometallic centers, we have focused our attention to bimetallic transformation of dinitrogen. At first we studied the reaction of dinitrogen complexes of the type $[M(N_2)_2(L)_4]$ with transition metal hydrides such as $[Cp_2ZrHCl]$ or $[H_2Fe(CO)_4]$, which resulted in the formation of ammonia after hydrolysis.[3] Saito et al. also investigated the reaction of dinitrogen complexes with hydridometal carbonyls from a similar point of view.[4] We extended this approach to the reactions of coordinated dinitrogen with silylcobalt complexes toward development of the catalytic hydrosilylation of dinitrogen to silylamines,[5] which led to isolation of W–Co and Mo–Co bimetallic silyldiazenido complexes.

Arylation of dinitrogen is one of the more intriguing reactions in the chemistry of dinitrogen complexes. However, such a reaction has rarely been achieved on a single metal center by either direct or indirect methods. Prior to this study, the only example of the direct arylation of coordinated dinitrogen was found in the reaction of a molybdenum dinitrogen complex with a tetrathia macrocycle ligand, $[Mo(N_2)_2(Me_8[16]aneS_4)]$, with iodo- or bromoarenes to give aryldiazenido complexes.[6] In contrast, it has been claimed that more readily available dinitrogen complexes of the type

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[1] Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 47. Part 46: Mizobe, Y.; Yokobayashi, Y.; Oshita, H.; Takahashi, T.; Hidai, M. *Organometallics* **1994**, *13*, 3764.

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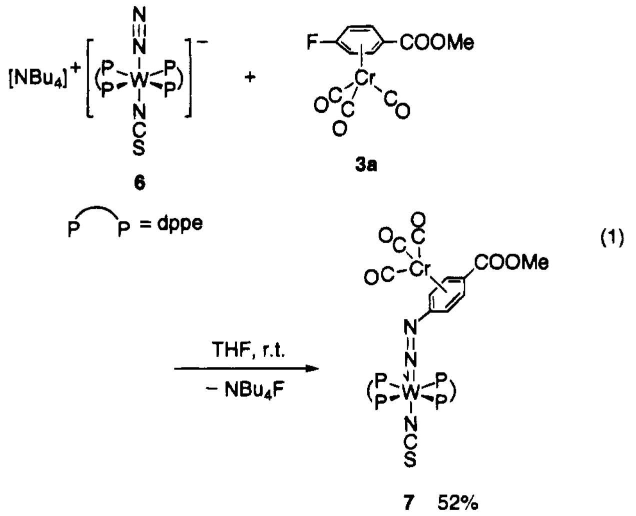
$[M(N_2)_2(L)_4]$ (M = Mo or W, L = phosphine) do not undergo direct arylation.[7]

On the other hand, an indirect arylation of coordinated dinitrogen has been investigated by using hydrazido complexes derived from dinitrogen complexes. Thus, hydrazido complexes $[WX(NNH_2)(dppe)_2]^+$ (X = Br, F, or CF_3COO), which can be obtained by the protonation of dinitrogen complex $[W(N_2)_2(dppe)_2]$ (**1**), react with 2,4-$(NO_2)_2C_6H_3F$ in the presence of K_2CO_3 to give (2,4-dinitrophenyl)diazenido complexes.[8] However, no other aryl group has been known to be introduced onto the N_2 unit, and therefore this indirect method seems to have a limitation.

On the basis of these backgrounds, we embarked on designing bimetallic reaction systems which enable the direct arylation of dinitrogen. We centered our guiding principle of seeking for such bimetallic reaction systems on the following points: (i) efficient activation of dinitrogen by coordination to a highly electron rich metal center in end-on fashion to enhance the nucleophilicity of the dinitrogen molecule, (ii) use of haloarenes activated by transition metal complexes as arylating agents, and (iii) appropriate combination of dinitrogen and haloarene complexes which results in the C−N bond formation under very mild conditions. Here we wish to describe the synthesis of a series of μ-aryldiazenido complexes by bimetallic arylation of dinitrogen as well as their detailed characterization.[9] Arylation of a diazenido complex derived from dinitrogen complex **1**, which corresponds to the indirect arylation of dinitrogen, is also described.

Results and Discussion

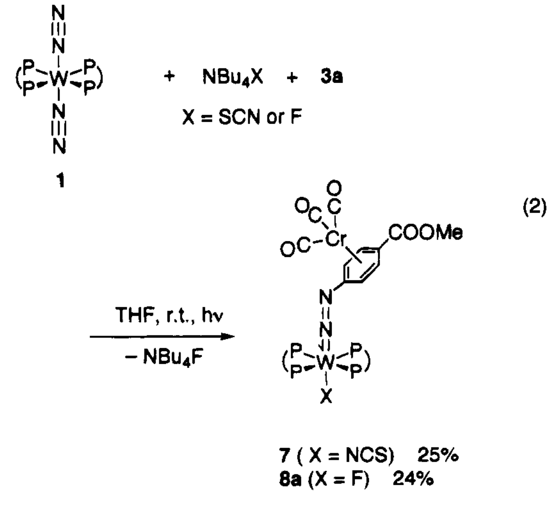
Arylation of Molecular Nitrogen at Bimetallic Centers. We at first examined reactions of **1** and $[W(N_2)_2(PMe_2Ph)_4]$ (**2**) with several haloarene complexes such as $[Cr(\eta^6\text{-}p\text{-}FC_6H_4COOMe)(CO)_3]$ (**3a**), $[FeCp(\eta^6\text{-}C_6H_5F)][PF_6]$ (**4a**), and $[RuCp(\eta^6\text{-}C_6H_5F)][PF_6]$ (**5a**), but in all cases no distinct reaction was observed at room temperature. We turned our attention to an anionic dinitrogen complex, $[NBu_4][W(NCS)(N_2)(dppe)_2]$ (**6**), which is readily prepared by irradiation of **1** in the presence of NBu_4SCN with a tungsten-filament lamp.[10] Since **6** shows lower ν_{NN} (1860 cm^{-1}) than **1** (2010, 1925 cm^{-1}) and **2** (1991, 1913 cm^{-1}), we presumed that the ligating dinitrogen in **6** is endowed the higher nucleophilicity than that in **1** and **2** since stronger back-donation is expected from the anionic tungsten center. In fact, **6** reacted with **3a** in very dry THF at room temperature to give a dark red new complex, $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dppe)_2]$ (**7**), in 52% yield after purification by column chromatography and recrystallization (eq 1). It is obvious that the activation of the fluoroarene is also essential for the reaction, since free $p\text{-}FC_6H_4COOMe$ did not react with **3a**.



(1)

The IR spectrum of complex **7** with lower ν_{CO} (1948, 1867, 1857 cm^{-1}) than those of **3a** (1991, 1902 cm^{-1}) indicated the F atom of **3a** was substituted by an electron donating N atom. In the ^{1}H NMR spectrum, the signals due to the aromatic hydrogens of the C_6H_4COOMe group appeared at higher fields (δ 5.73 (d, J = 7.3 Hz) and 4.11 (d, J = 7.3 Hz)) in comparison with those of related complexes such as $[Cr(Me_2NC_6H_4COOMe)(CO)_3]$ (δ 6.37 and 5.21).[11] This suggests that the C_6H_4COOMe group is surrounded by phenyl groups of the dppe ligand. These spectral data are in good agreement with the μ-aryldiazenido structure of the complex **7**, which was further confirmed by an X-ray diffraction study as described below.

Since the anionic dinitrogen complex **6** is obtained by irradiation of complex **1** in the presence of SCN$^-$,[10] it is expected that the reaction of **1**, **3a**, and NBu_4SCN under irradiation gives **7** by way of the in situ formation of **6**. In fact, irradiation of a THF solution of **1**, **3a**, and NBu_4SCN by means of a tungsten filament lamp at room temperature afforded **7** in 25% yield (eq 2), while a similar reaction in the dark failed to give **7**. It is also interesting to note that use of NBu_4F instead of NBu_4SCN yielded the corresponding μ-aryldiazenido complex $[WF\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dppe)_2]$ (**8a**) in 24% yield, whose molecular structure closely related to



(2)

complex **7** was confirmed crystallographically (vide infra). Although the formation of $[NBu_4][WF(N_2)$-

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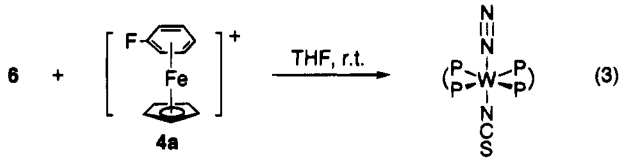
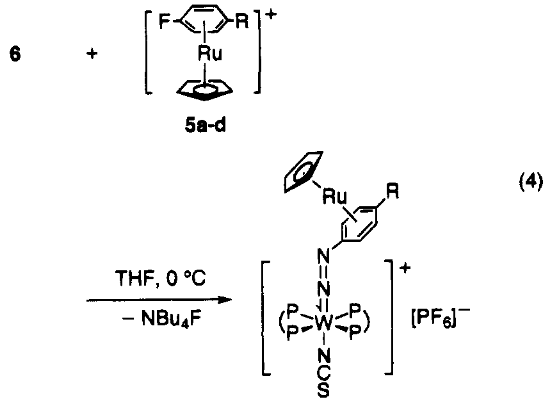
(dppe)$_2$] (**9**) could not be verified by IR in a reaction of **1** and NBu$_4$F under irradiation, in situ generated **9** is presumed to react further with **3a**.

In order to reveal the applicability of this bimetallic approach toward the arylation of dinitrogen, similar reactions of **6** with [Cr(η^6-C$_6$H$_5$F)(CO)$_3$] (**3b**) and **4a** were attempted, but neither of them yielded products with N-aryl bonds. Especially the latter reaction gave [W(NCS)(N$_2$)(dppe)$_2$][10] as the only identified product (IR ν_{NCS} 2040, ν_{NN} 1918 cm^{-1}), which is considered to be formed by the one-electron redox reaction between **6** and **4a** (eq 3).



4a

In contrast, a series of ruthenium fluoroarene complexes [RuCp(η^6-*p*-FC$_6$H$_4$R)][PF$_6$] (**5a**; R = H; **5b**, R = Me; **5c**, R = OMe; **5d**, R = COOMe) smoothly reacted with **6** in very dry THF at 0 °C to room temperature to give dark red solutions, from which a series of μ-aryldiazenido complexes [W(NCS){N=N[(η^6-*p*-C$_6$H$_4$R)RuCp]}(dppe)$_2$][PF$_6$] (**10a–d**) were isolated in 21–55% yields (eq 4). Interestingly, the ^{1}H NMR signals of the η^6-aryl protons (δ 4.7–5.7) and Cp protons (δ 4.61–4.67) appeared in higher-field regions than the reported values for [RuCp(arene)]$^+$ (aryl protons, δ 6.1–7.0; Cp protons, 5.1–5.8) due to the shielding effect of the dppe phenyls.[12] It should be noted that the use of RuCp$^+$ as the activating group for the fluoroarenes enabled the introduction of various aryl groups onto the coordinated dinitrogen. In this respect, RuCp$^+$ is the more efficient activating group for fluoroarenes than Cr(CO)$_3$. However, an attempted reaction of **6** with [RuCp(η^6-ClC$_6$H$_5$)] (**5e**) failed to give **10a**.



10a (R = H) 55%
10b (R = Me) 51%
10c (R = OMe) 38%
10d (R = COOMe) 22%

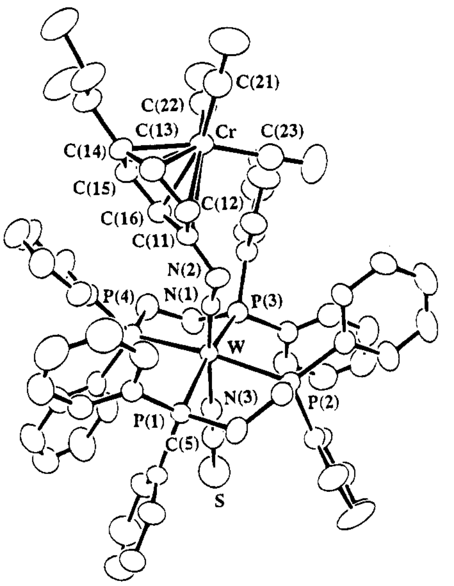


Figure 1. ORTEP drawing for complex [W(NCS){N=N-[(η^6-*p*-C$_6$H$_4$COOMe)Cr(CO)$_3$]}(dppe)$_2$]·CH$_2$Cl$_2$ (**7**·CH$_2$Cl$_2$). Hydrogen atoms and solvated dichloromethane are omitted.

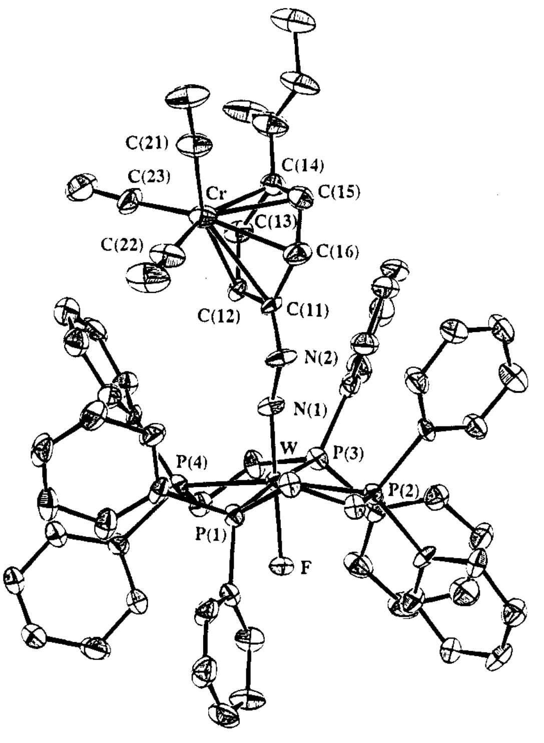


Figure 2. ORTEP drawing for complex [WF{N=N[(η^6-*p*-C$_6$H$_4$COOMe)Cr(CO)$_3$]}(dppe)$_2$]·2THF (**8a**·2THF). Hydrogen atoms and solvated THF are omitted.

The X-ray Structures of Bimetallic μ-Aryldiazenido Complexes. The detailed molecular structures of the bimetallic complexes **7**·CH$_2$Cl$_2$, **8a**·2THF, and **10a**·CH$_2$Cl$_2$ were unambiguously determined by X-ray diffraction studies. The ORTEP views are shown in Figures 1–3. The bond angles for the W–N–N (**7**, 164.9(3)°; **8a**, 161(1)°; **10a**, 166 (1)°) and N–N–C (**7**, 120.0(4)°; **8a**, 117(1)°; **10a**, 122 (1)°) linkages correspond to those of singly bent diazenido complexes. However, the N=N bond distances (**7**, 1.314(5) Å; **8a**, 1.33(1) Å; **10a**, 1.28(1) Å) belong to the longest class among those reported for similar singly bent diazenido complexes (1.16–1.29 Å)[5,6,13] and lie in the range of the N–N bond

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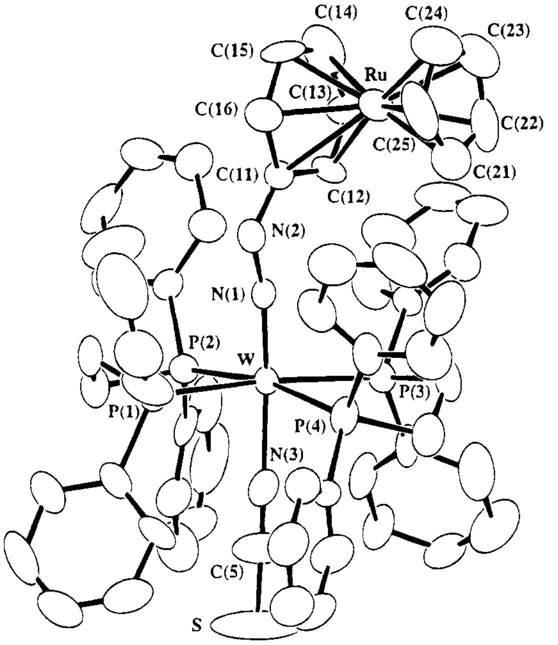


Figure 3. ORTEP drawing for the cationic part of complex $[W(NCS)\{N{=}N[(\eta^6\text{-}C_6H_5)RuCp]\}(dppe)_2][PF_6]\cdot CH_2Cl_2$ ($\mathbf{10}\cdot CH_2Cl_2$). Hydrogen atoms are omitted.

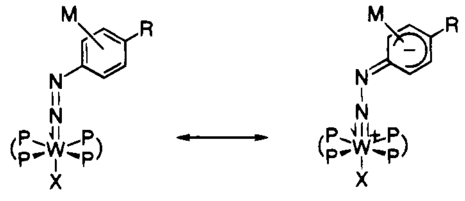
distances observed in hydrazido[4,5,8d,14] and diazoalkane[13b,15] complexes (1.25–1.38 Å). This indicates that the N=N bond multiplicity in **7**, **8a**, and **10a** is considerably reduced. Concomitantly the N(2)–C(11) bonds in these complexes are relatively short (**7**, 1.366(6) Å; **8a**, 1.30(2) Å; **10a**, 1.40(2) Å). On the other hand, notable change in the η^6-coordination mode of the aryl groups was observed. Thus, the Cr–C(11) bonds in **7** (2.431(5) Å) and **8a** (2.50(1) Å) and the Ru–C(11) bond in **10a** (2.39(2) Å) are much longer than the other Cr–arene (average 2.22 Å) and Ru–arene (average 2.17 Å) carbon bonds, respectively. These bond distances indicate that the Cr and Ru atoms are displaced away from the N(2) atoms in **7**, **8a**, and **10a**. All the structural characteristics described above strongly suggest that the μ-aryldiazenido complexes receive a large contribution of the unique zwitterionic resonance structure **11** (eq 5). Obviously the existence of both the electron rich W(II) center and the electron withdrawing $Cr(CO)_3$ or $RuCp^+$ group in **7** and **8a** or **10a**, respectively, might stabilize the charge-separated resonance structure of the μ-aryldiazenido ligands.

Table 1. Selected Bond Distances and Angles of $7\cdot CH_2Cl_2$ (Estimated Standard Deviations Cited in Parentheses)

Bond Distances (Å)			
W–P(1)	2.516(2)	W–P(2)	2.496(2)
W–P(3)	2.493(2)	W–P(4)	2.517(2)
W–N(1)	1.784(4)	W–N(3)	2.140(4)
Cr–C(11)	2.431(5)	Cr–C(12)	2.259(5)
Cr–C(13)	2.193(5)	Cr–C(14)	2.174(5)
Cr–C(15)	2.194(5)	Cr–C(16)	2.301(5)
Cr–C(21)	1.819(6)	Cr–C(22)	1.836(6)
Cr–C(23)	1.826(6)	N(1)–N(2)	1.314(5)
N(2)–C(11)	1.366(6)		
Bond Angles (deg)			
P(1)–W–P(2)	79.34(5)	P(1)–W–P(3)	169.09(5)
P(1)–W–P(4)	100.48(5)	P(1)–W–N(1)	87.7(1)
P(1)–W–N(3)	90.5(1)	P(2)–W–P(3)	98.43(5)
P(2)–W–P(4)	171.54(5)	P(2)–W–N(1)	87.9(1)
P(2)–W–N(3)	88.2(1)	P(3)–W–P(4)	80.14(5)
P(3)–W–N(1)	102.9(1)	P(3)–W–N(3)	78.7(1)
P(4)–W–N(1)	100.5(1)	P(4)–W–N(3)	83.3(1)
N(1)–W–N(3)	176.0(2)	W–N(1)–N(2)	164.9(3)
N(1)–N(2)–C(11)	120.0(4)		

Table 2. Selected Bond Distances and Angles of $8a\cdot 2THF$ (Estimated Standard Deviations Cited in Parentheses)

Bond Distances (Å)			
W–P(1)	2.476(4)	W–P(2)	2.504(4)
W–P(3)	2.507(4)	W–P(4)	2.489(4)
W–F	2.037(7)	W–N(1)	1.80(1)
Cr–C(11)	2.50(1)	Cr–C(12)	2.33(1)
Cr–C(13)	2.21(1)	Cr–C(14)	2.17(1)
Cr–C(15)	2.15(2)	Cr–C(16)	2.25(2)
Cr–C(21)	1.82(2)	Cr–C(22)	1.81(2)
Cr–C(23)	1.75(2)	N(1)–N(2)	1.33(1)
N(2)–C(11)	1.30(2)		
Bond Angles (deg)			
P(1)–W–P(2)	79.7(1)	P(1)–W–P(3)	173.3(1)
P(1)–W–P(4)	99.1(1)	P(1)–W–F	93.2(2)
P(1)–W–N(1)	86.5(4)	P(2)–W–P(3)	100.1(1)
P(2)–W–P(4)	170.9(1)	P(2)–W–F	90.5(2)
P(2)–W–N(1)	88.1(4)	P(3)–W–P(4)	80.0(1)
P(3)–W–F	80.1(2)	P(3)–W–N(1)	100.2(4)
P(4)–W–F	80.5(2)	P–W–N(1)	100.9(4)
F–W–N(1)	178.5(4)	W–N(1)–N(2)	161(1)
N(1)–N(2)–C(11)	117(1)		



(5)

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The Mechanism of the Bimetallic Arylation of Dinitrogen. The mechanism of alkylation of coordinated dinitrogen in molybdenum or tungsten complexes such as **1** and $[Mo(N_2)_2(Me_8[16]aneS_4)]$ with alkyl halides (RX) has been postulated to include the attack of the alkyl radical R• generated from the alkyl halide on coordinated dinitrogen.[6,7] Also in the alkylation of the molybdenum analogue of **6**, $[NBu_4][Mo(NCS)(N_2)(dppe)_2]$, with BuI, it has been assumed that the reaction mechanism should include an electron transfer process between the complex and the halide to give a Mo(I) dinitrogen complex $[Mo(NCS)(N_2)(dppe)_2]$, butyl radical,

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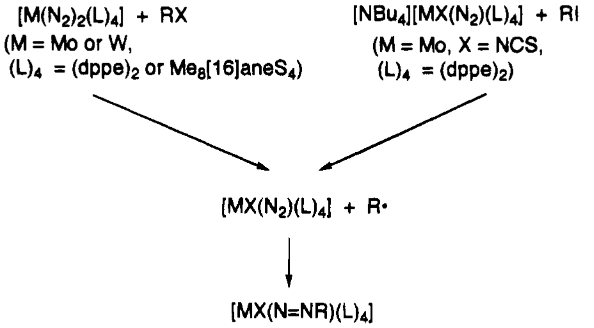
Table 3. Selected Bond Distances and Angles of 10a·CH_2Cl_2 (Estimated Standard Deviations Cited in Parentheses)

	Bond Distances (Å)		
W−P(1)	2.513(5)	W−P(2)	2.532(4)
W−P(3)	2.538(4)	W−P(4)	2.513(4)
W−N(1)	1.75(1)	W−N(3)	2.14(1)
Ru−C(11)	2.39(2)	Ru−C(12)	2.23(2)
Ru−C(13)	2.15(2)	Ru−C(14)	2.14(2)
Ru−C(15)	2.13(2)	Ru−C(16)	2.19(2)
Ru−C(21)	2.14(2)	Ru−C(22)	2.14(2)
Ru−C(23)	2.19(2)	Ru−C(24)	2.13(2)
Ru−C(25)	2.11(2)	N(1)−N(2)	1.28(1)
N(2)−C(11)	1.40(2)		
	Bond Angles (deg)		
P(1)−W−P(2)	78.7(2)	P(1)−W−P(3)	175.0(2)
P(1)−W−P(4)	99.1(2)	P(1)−W−N(1)	87.2(4)
P(1)−W−N(3)	87.5(4)	P(2)−W−P(3)	102.0(1)
P(2)−W−P(4)	169.2(2)	P(2)−W−N(1)	96.2(4)
P(2)−W−N(3)	85.7(3)	P(3)−W−P(4)	79.2(1)
P(3)−W−N(1)	97.6(4)	P(3)−W−N(3)	87.7(4)
P(4)−W−N(1)	94.3(4)	P(4)−W−N(3)	83.7(3)
N(1)−W−N(31)	173.9(5)	W−N(1)−N(2)	166(1)
N(1)−N(2)−C(11)	122(1)		

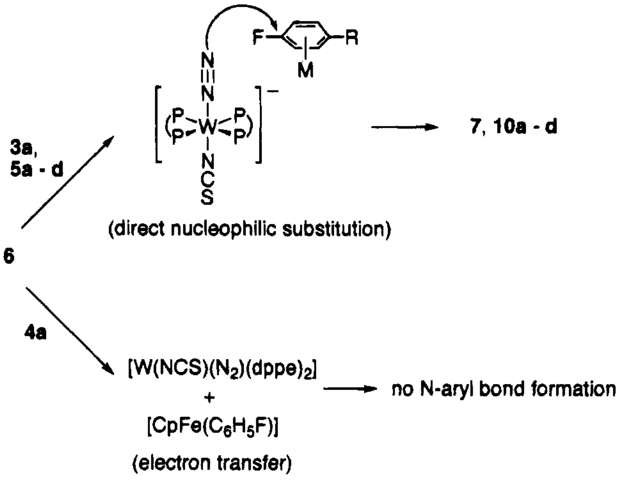
Scheme 1



and I−, the former two species coupling to each other to give a diazenido complex (Scheme 1). The radical mechanism has been strongly supported by the findings that alkylation reactions of the dinitrogen complexes in THF or toluene resulted in the formation of complexes with the N-tetrahydrofuranyl[7] or N-benzyl[6] group. The formation of such products can be accounted for by the incorporation of the tetrahydrofuranyl or benzyl radical generated by the hydrogen atom transfer between the solvent molecule and the alkyl radical initially formed. However, incorporation of the tetrahydrofuranyl radical was not observed in the present arylation reactions, and actually use of a THF−toluene (2:1) mixture as a solvent for the reaction of **6** with **3a** caused neither a decrease in the yield of **7** (62%) nor formation of *N*-benzyl complexes.

In order to obtain more direct information about the mechanism, a comparison between the oxidation potential of **6** and reduction potentials of **3a**, **4a**, and **5a** were made. In the cyclic voltammogram, the anionic dinitrogen complex **6** showed an oxidation wave at −1.15 V (reversible, $E_{1/2}$ vs SCE, in MeCN−0.1 M NBu_4BF_4). On the other hand, $[CpFe(arene)]^+$ cations are known to undergo chemical and electrochemical reduction to give 19e species,[16] and actually **4a** exhibited a reduction wave at −1.22 V. This is in accord with the observation that the reaction of **6** and **4a** ended in the precipitation of $[W(NCS)(N_2)(dppe)_2]$ (vide supra), and the arylation of dinitrogen did not occur. In contrast, $[RuCp(arene)]^+$ cations have been claimed to resist reduction,[17] and in fact no reduction wave was observed in the cyclic voltammogram of **5a** up to −1.6 V vs SCE. The reported value of the reduction potential of **3a** ($E_{1/2}$ − 1.65 V vs SCE, in DMF)[18] is also much more negative than the reduction potential of **4a**. Therefore in the reaction of **6** with **3a** or **5a**, where the arylation of dinitrogen was observed, involvement of the electron transfer process between the two complexes can be ruled out. These results clearly indicate that the arylation includes the direct nucleophilic substitution at the η^6-fluoroarene by the terminal nitrogen atom in **6** rather than the radical mechanism proposed for the alkylation (Scheme 2). The higher reactivity of a η^6-C_6H_5F complex **5a** than the η^6-C_6H_5Cl analogue **5e** also agrees with the general reactivity order of haloarene complexes in nucleophilic substitutions.[19]

Scheme 2



Indirect Method for Arylating Dinitrogen. Arylation of a hydrazido or diazenido complex provides an indirect method for arylating dinitrogen, since such a complex is readily derived from a dinitrogen complex by protonation. We examined the arylation by employing η^6-fluoroarene complexes as the arylating reagents. $[WF(NNH)(dppe)_2]$ (**12**) cleanly reacted with **3a**, **4a**, and $[FeCp(\eta^6\text{-}p\text{-}FC_6H_4Me)][PF_6]$ (**4b**) in THF at room temperature and with $[Cr(\eta^6\text{-}C_6H_5F)(CO)_3]$ (**3b**) under THF reflux (eq 6). The products isolated in good yields were confirmed to be the expected μ-aryldiazenido complexes **8a**, $[WF\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4R)FeCp]\}(dppe)_2][PF_6]$ (**13a**, R = H; **13b**, R = Me), and $[WF\{N{=}N[(\eta^6\text{-}C_6H_5)Cr(CO)_3]\}(dppe)_2]$ (**8b**), respectively, by spectroscopic analyses and X-ray diffraction study of **13b**·Me_2CO. The molecular structure of **13b**·Me_2CO (Figure 4) had features similar to those of the W−Ru complex **10a**. It would be interesting to point out that the $FeCp^+$ group also worked as an effective activating group of fluoroarenes in the reaction with **12**, although it was not suitable for the direct arylation of **6**. Obviously the lack of the

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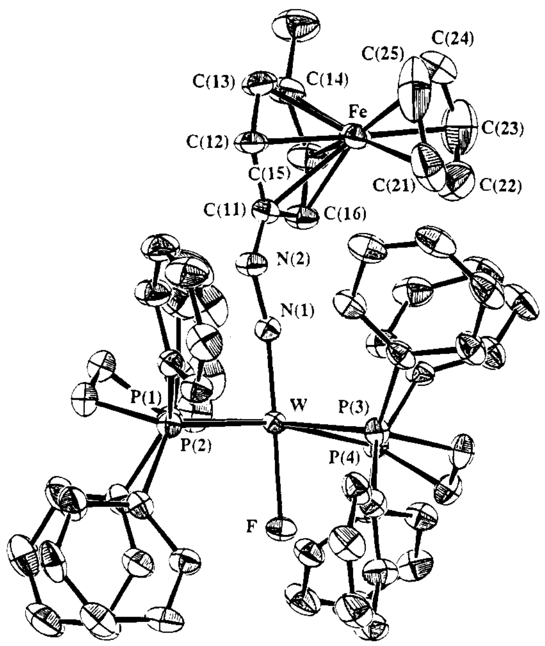
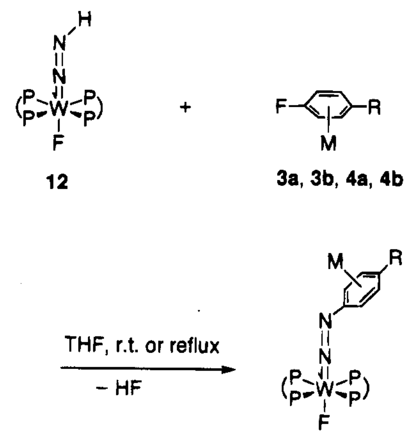


Figure 4. ORTEP drawing for the cationic part of complex $[WF\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4Me)FeCp]\}(dppe)_2][PF_6]\cdot Me_2CO$ (**13b·Me₂CO**). Hydrogen atoms are omitted.

redox process between complexes **4** and **12** made the C−N bond formation possible.[20]



12 **3a, 3b, 4a, 4b**

(6)

8a 63%
8b (M = $Cr(CO)_3$, R = H) 59%
13a (M = $[CpFe]^+[PF_6]^-$, R = H) 84%
13b (M = $[CpFe]^+[PF_6]^-$, R = Me) 75%

In contrast to the reaction of **12** with **3b**, no μ-aryldiazenido complex was prepared by the direct arylation of **6** with **3b** even under THF reflux conditions (vide supra). Fluorobenzene in **3b** has a sufficient reactivity for the reaction with **12** but not with **6**. This result supports that the arylation of **6** described above proceeds through a straightforward nucleophilic attack of coordinated dinitrogen rather than through a diazenido complex, $[W(NCS)(NNH)(dppe)_2]$, formed from **6** by an action of trace amounts of water.

Conclusions

This study has successfully illustrated the effectiveness of the bimetallic approach in the direct and indirect arylation of dinitrogen to give novel heterobimetallic μ-aryldiazenido complexes. The following three points have been found to be essential for the bimetallic direct arylation of dinitrogen: (1) activation of dinitrogen by coordination to an electron rich anionic tungsten complex, (2) activation of fluoroarenes by the η^6-coordination to an electron deficient metal center, and (3) a proper combination of the dinitrogen and fluoroarene complexes which can avoid undesirable redox reactions. A reaction mechanism has been proposed which involves the direct nucleophilic aromatic substitution, in sharp contrast to the alkylation reactions of dinitrogen complexes where a radical mechanism has been postulated to be operative. We believe the findings in this study provide helpful information in designing new bimetallic reaction systems toward unique chemical transformations. Studies aiming at developing further effective bimetallic reactions of dinitrogen and related molecules are in progress.

Table 4. Selected Bond Distances and Angles of 13b·Me₂CO (Estimated Standard Deviations Cited in Parentheses)

	Bond Distances (Å)		
W−P(1)	2.482(3)	W−P(2)	2.516(3)
W−P(3)	2.498(3)	W−P(4)	2.516(3)
W−F	2.025(6)	W−N(1)	1.778(8)
Fe−C(11)	2.24(1)	Fe−C(12)	2.09(1)
Fe−C(13)	2.03(1)	Fe−C(14)	2.04(1)
Fe−C(15)	2.04(1)	Fe−C(16)	2.09(1)
Fe−C(21)	2.02(2)	Fe−C(22)	2.05(2)
Fe−C(23)	2.00(2)	Fe−C(24)	2.01(2)
Fe−C(25)	1.98(2)	N(1)−N(2)	1.32(1)
N(2)−C(11)	1.35(1)		
	Bond Angles (deg)		
P(1)−W−P(2)	78.03(9)	P(1)−W−P(3)	176.75(9)
P(1)−W−P(4)	101.14(9)	P(1)−W−F	94.7(2)
P(1)−W−N(1)	88.0(3)	P(2)−W−P(3)	100.17(9)
P(2)−W−P(4)	168.78(8)	P(2)−W−F	90.3(2)
P(2)−W−N(1)	87.0(3)	P(3)−W−P(4)	80.09(9)
P(3)−W−F	82.6(2)	P(3)−W−N(1)	94.6(3)
P(4)−W−F	78.6(2)	P(4)−W−N(1)	104.2(3)
F−W−N(1)	175.8(3)	W−N(1)−N(2)	164.0(7)
N(1)−N(2)−C(11)	120.6(8)		

Experimental Section

General Comments. ^1H NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer. IR spectra were recorded with a Shimadzu FTIR-8100M spectrometer by the KBr method. Electrochemical measurements were made with Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) by using a glassy carbon working electrode; potentials were measured vs a pseudoreference electrode of a silver wire immersed in THF. Elemental analyses were performed at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

All the reactions were carried out under a nitrogen atmosphere. Solvents were dried and distilled under nitrogen before use. Complexes **1**,[21] **2**,[21], **3**,[22] **4**,[23] **5**,[12c] **6**[10] were prepared according to the published methods. Complex **12** was prepared from a reaction of $[WF(NNH_2)(dppe)_2][BF_4]$ with NaOMe in methanol.[24] Other organic reagents were commercial products and used without further purification.

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Table 5. Crystallographic Data for Complexes 7·CH_2Cl_2, 8a·2THF, 10a·CH_2Cl_2, and 13b·Me_2CO

	7·CH_2Cl_2	8a·2THF	10a·CH_2Cl_2	13b·Me_2CO
formula	$C_{65}H_{57}N_3O_5SP_4Cl_2CrW$	$C_{71}H_{71}N_2O_7FP_4CrW$	$C_{65}H_{60}N_3F_6P_5SCl_2RuW$	$C_{67}H_{66}N_2OF_7P_5FeW$
mol wt	1422.89	1443.09	1539.95	1442.83
cryst size, mm	0.53 × 0.46 × 0.38	0.40 × 0.25 × 0.15	0.30 × 0.40 × 0.15	0.65 × 0.45 × 0.15
cryst system	monoclinic	monoclinic	triclinic	monoclinic
space group	*P*2$P2_1/n$	$P2_1/a$	$P\bar{1}$	$C2/c$
a, Å	24.135(3)	23.110(5)	12.630(2)	38.090(9)
b, Å	20.967(5)	23.402(7)	23.648(3)	18.507(4)
c, Å	12.273(5)	12.046(3)	11.507(3)	18.359(3)
α, deg			103.11(1)	
β, deg	90.06(4)	93.89(2)	102.77(1)	91.25(2)
γ, deg			83.44(1)	
V, Å^3	6210(5)	6500(3)	3257.1(9)	12939(5)
Z	4	4	2	8
d(calcd), g cm^{-3}	1.522	1.475	1.570	1.481
d(obsd), g cm^{-3}	1.52	1.47	1.58	1.49
λ, Å	0.71069	0.71069	0.71069	0.71069
μ, cm^{-1}	23.31	21.22	22.94	22.22
temp, K	296	293	293	293
scan type	$\omega-2\theta$	ω ($2\theta < 30$) $\omega-2\theta$ ($2\theta \geq 30$)	$\omega-2\theta$	$\omega-2\theta$
2θ range, deg	3−50	4−50	5−55	5−60
no. of data collected	11795	9476	15655	20149
no. of unique data	11325	7975	14972	19484
no. of data used	7578 ($\lvert I\rvert > 3\sigma(I)$)	5396 ($\lvert F_o\rvert > 5\sigma(F_o)$)	7714 ($\lvert I\rvert > 3\sigma(I)$)	10134 ($\lvert F_o\rvert > 5\sigma(F_o)$)
R	0.034	0.056	0.062	0.061
R_w	0.029	0.066	0.054	0.071

Table 6. Atomic Coordinates for 7·CH_2Cl_2

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
W	0.57117(1)	0.21755(1)	0.33114(2)	C(125)	0.7530(4)	0.1496(4)	0.0933(7)
Cr	0.49101(4)	0.40793(4)	0.67322(7)	C(126)	0.7112(3)	0.1762(3)	0.1568(5)
S	0.6090(1)	0.01999(9)	0.1291(2)	C(211)	0.5183(2)	0.2120(3)	0.0451(4)
P(1)	0.64508(6)	0.27804(8)	0.2302(1)	C(212)	0.5301(3)	0.2397(3)	−0.0547(5)
P(2)	0.51708(6)	0.25767(6)	0.1718(1)	C(213)	0.5238(3)	0.2053(3)	−0.1500(5)
P(3)	0.50128(6)	0.14147(7)	0.4049(1)	C(214)	0.5060(3)	0.1437(3)	−0.1461(5)
P(4)	0.62880(6)	0.16297(7)	0.4746(1)	C(215)	0.4941(3)	0.1149(3)	−0.0487(5)
O(11)	0.5869(2)	0.4205(2)	0.9272(3)	C(216)	0.5001(2)	0.1496(3)	0.0462(4)
O(12)	0.5809(2)	0.5161(2)	0.8485(3)	C(221)	0.4438(2)	0.2799(3)	0.1822(4)
O(21)	0.4343(2)	0.5172(2)	0.7785(4)	C(222)	0.4038(3)	0.2581(3)	0.1102(5)
O(22)	0.4283(2)	0.3385(2)	0.8453(4)	C(223)	0.3497(3)	0.2753(4)	0.1213(6)
O(23)	0.3959(2)	0.4035(2)	0.5180(4)	C(224)	0.3336(3)	0.3153(4)	0.2033(6)
N(1)	0.5547(2)	0.2902(2)	0.3995(3)	C(225)	0.3724(3)	0.3389(3)	0.2738(5)
N(2)	0.5437(2)	0.3499(2)	0.4238(3)	C(226)	0.4276(2)	0.3206(3)	0.2650(5)
N(3)	0.5892(2)	0.1336(2)	0.2387(4)	C(311)	0.4549(2)	0.1626(3)	0.5163(4)
C(1)	0.6108(2)	0.3292(3)	0.1257(4)	C(312)	0.4441(2)	0.2252(3)	0.5420(5)
C(2)	0.5487(2)	0.3350(2)	0.1424(4)	C(313)	0.4062(3)	0.2399(3)	0.6228(6)
C(3)	0.5854(3)	0.1010(3)	0.5406(5)	C(314)	0.3803(3)	0.1928(4)	0.6800(6)
C(4)	0.5417(2)	0.0754(3)	0.4632(5)	C(315)	0.3906(3)	0.1300(3)	0.6560(6)
C(5)	0.5973(3)	0.0861(3)	0.1916(5)	C(316)	0.4270(3)	0.1151(3)	0.5738(5)
C(11)	0.5515(2)	0.3714(2)	0.5277(4)	C(321)	0.4521(2)	0.1006(3)	0.3141(4)
C(12)	0.5517(2)	0.4387(2)	0.5434(4)	C(322)	0.4627(3)	0.0423(3)	0.2654(5)
C(13)	0.5651(2)	0.4659(2)	0.6441(4)	C(323)	0.4246(3)	0.0163(3)	0.1937(6)
C(14)	0.5736(2)	0.4267(2)	0.7363(4)	C(324)	0.3762(3)	0.0472(4)	0.1702(6)
C(15)	0.5679(2)	0.3604(3)	0.7236(4)	C(325)	0.3656(3)	0.1053(4)	0.2168(6)
C(16)	0.5556(2)	0.3328(2)	0.6232(4)	C(326)	0.4032(3)	0.1317(3)	0.2903(5)
C(17)	0.5812(3)	0.4528(3)	0.8484(5)	C(411)	0.6904(3)	0.1190(3)	0.4325(5)
C(18)	0.5831(3)	0.5467(3)	0.9533(5)	C(412)	0.7420(3)	0.1484(3)	0.4337(5)
C(21)	0.4575(3)	0.4765(3)	0.7356(5)	C(413)	0.7885(3)	0.1171(4)	0.3951(6)
C(22)	0.4527(3)	0.3631(3)	0.7773(5)	C(414)	0.7842(3)	0.0568(5)	0.3523(6)
C(23)	0.4328(3)	0.4032(3)	0.5785(5)	C(415)	0.7341(4)	0.0272(4)	0.3496(7)
C(111)	0.6861(2)	0.3360(3)	0.3076(4)	C(416)	0.6873(3)	0.0575(3)	0.3889(6)
C(112)	0.6634(3)	0.3931(3)	0.3412(5)	C(421)	0.6549(2)	0.2088(3)	0.5906(4)
C(113)	0.6942(3)	0.4368(3)	0.4015(6)	C(422)	0.6724(2)	0.2706(3)	0.5757(4)
C(114)	0.7479(4)	0.4233(4)	0.4291(6)	C(423)	0.6946(3)	0.3057(3)	0.6615(6)
C(115)	0.7712(3)	0.3675(4)	0.3962(6)	C(424)	0.6981(3)	0.2790(4)	0.7625(6)
C(116)	0.7411(3)	0.3226(3)	0.3368(5)	C(425)	0.6800(3)	0.2181(4)	0.7801(5)
C(121)	0.6986(2)	0.2400(3)	0.1478(5)	C(426)	0.6591(3)	0.1827(3)	0.6948(5)
C(122)	0.7293(3)	0.2776(4)	0.0754(5)	Cl(1′)	0.7667(2)	0.0221(3)	0.7943(4)
C(123)	0.7706(3)	0.2492(5)	0.0132(6)	Cl(2′)	0.7600(3)	−0.0579(2)	0.6143(5)
C(124)	0.7819(4)	0.1860(6)	0.0222(7)	C(1′)	0.7577(7)	0.0121(7)	0.660(1)

Reaction of [NBu_4][W(NCS)(N_2)(dppe)$_2$] with [Cr(*p*-FC_6H_4COOMe)(CO)$_3$]. A mixture of [NBu_4][W(NCS)(N_2)(dppe)$_2$] (**6**, 123 mg, 0.094 mmol) and [Cr(*p*-FC_6H_4COOMe)(CO)$_3$] (**3a**, 33 mg, 0.114 mmol) in THF (5 mL) was stirred overnight at room temperature under N_2. The solution turned dark red from brown. The solvent was removed in vacuo, and the residue was purified by column chromatography (alumina; eluent CH_2Cl_2−hexane (1/1), then CH_2Cl_2). Unreacted **3a** was recovered first; then the dark red fraction of [W(NCS){N=N-[(η^6-*p*-C_6H_4COOMe)Cr(CO)$_3$]}(dppe)$_2$] (**7**) eluted. Recrystallization from CH_2Cl_2−hexane gave dark red crystals of **7** as mono CH_2Cl_2 solvate (70 mg, 52%). ^1H NMR (C_6D_6) δ 2.51

Table 7. Atomic Coordinates for 8a·2THF

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
W	0.25784(2)	0.20807(2)	0.15590(5)	C(214)	0.3202(8)	0.1017(8)	−0.304(2)
Cr	0.05673(9)	0.2046(1)	0.4738(2)	C(215)	0.2600(7)	0.0940(7)	−0.313(1)
P(1)	0.2151(1)	0.2913(2)	0.0535(4)	C(216)	0.2292(7)	0.1103(6)	−0.223(1)
P(2)	0.2146(1)	0.1596(1)	−0.0155(4)	C(221)	0.1663(6)	0.0988(5)	0.005(1)
P(3)	0.3116(2)	0.1259(2)	0.2479(4)	C(222)	0.1084(6)	0.1078(7)	0.030(2)
P(4)	0.3142(2)	0.2596(2)	0.3084(4)	C(223)	0.0753(8)	0.0614(8)	0.055(2)
F	0.3352(3)	0.2157(3)	0.0855(7)	C(224)	0.098(1)	0.0068(8)	0.053(2)
O(11)	0.0827(5)	0.0814(6)	0.694(1)	C(225)	0.1533(8)	−0.0028(7)	0.024(2)
O(12)	−0.0001(5)	0.0662(5)	0.589(1)	C(226)	0.1871(7)	0.0431(6)	0.002(1)
O(21)	−0.0593(5)	0.2041(7)	0.567(1)	C(311)	0.3583(6)	0.0846(6)	0.161(1)
O(22)	0.0271(6)	0.3104(6)	0.347(1)	C(312)	0.3381(6)	0.0362(7)	0.108(1)
O(23)	0.0870(5)	0.2684(6)	0.679(1)	C(313)	0.3694(7)	0.0070(8)	0.034(2)
N(1)	0.1888(4)	0.2005(5)	0.2149(10)	C(314)	0.4238(7)	0.0260(8)	0.012(2)
N(2)	0.1322(4)	0.1925(6)	0.2234(10)	C(315)	0.4456(7)	0.0736(8)	0.065(2)
C(1)	0.1501(5)	0.2611(6)	−0.022(1)	C(316)	0.4142(6)	0.1036(7)	0.141(2)
C(2)	0.1674(5)	0.2121(6)	−0.096(1)	C(321)	0.2740(6)	0.0701(6)	0.319(1)
C(3)	0.3627(6)	0.1527(6)	0.362(1)	C(322)	0.3042(8)	0.0331(6)	0.391(2)
C(4)	0.3783(6)	0.2158(7)	0.346(1)	C(323)	0.2747(10)	−0.0082(7)	0.450(2)
C(11)	0.1163(5)	0.1738(6)	0.319(1)	C(324)	0.2155(10)	−0.0118(8)	0.436(2)
C(12)	0.1470(5)	0.1733(5)	0.424(1)	C(325)	0.1864(9)	0.0248(8)	0.366(2)
C(13)	0.1277(6)	0.1438(6)	0.516(1)	C(326)	0.2128(7)	0.0654(7)	0.304(2)
C(14)	0.0726(6)	0.1148(6)	0.507(1)	C(411)	0.3488(6)	0.3295(6)	0.285(1)
C(15)	0.0386(6)	0.1210(7)	0.406(1)	C(412)	0.3744(7)	0.3370(7)	0.186(2)
C(16)	0.0574(6)	0.1510(7)	0.319(1)	C(413)	0.4002(7)	0.3888(8)	0.160(2)
C(17)	0.0547(7)	0.0865(8)	0.608(2)	C(414)	0.3991(7)	0.4324(7)	0.234(2)
C(18)	−0.0247(9)	0.0434(10)	0.688(2)	C(415)	0.3746(8)	0.4260(7)	0.332(2)
C(21)	−0.0159(7)	0.2056(8)	0.524(2)	C(416)	0.3499(7)	0.3736(7)	0.359(2)
C(22)	0.0415(7)	0.2701(8)	0.398(2)	C(421)	0.2771(6)	0.2707(6)	0.434(1)
C(23)	0.0759(7)	0.2443(8)	0.594(1)	C(422)	0.2948(6)	0.2462(7)	0.536(1)
C(111)	0.1891(6)	0.3521(6)	0.131(1)	C(423)	0.2639(9)	0.2519(7)	0.629(2)
C(112)	0.1334(7)	0.3521(7)	0.170(2)	C(424)	0.2168(8)	0.2899(8)	0.621(2)
C(113)	0.1157(8)	0.3978(8)	0.233(2)	C(425)	0.1983(7)	0.3139(7)	0.522(2)
C(114)	0.1521(9)	0.4434(7)	0.257(2)	C(426)	0.2275(6)	0.3060(6)	0.425(1)
C(115)	0.2073(8)	0.4431(7)	0.220(2)	O(11′)	0.4889(7)	0.3065(7)	−0.011(2)
C(116)	0.2258(8)	0.3978(7)	0.158(2)	C(11′)	0.4910(9)	0.295(1)	−0.132(2)
C(121)	0.2503(6)	0.3279(5)	−0.057(1)	C(12′)	0.468(1)	0.2420(10)	−0.153(3)
C(122)	0.3049(7)	0.3094(7)	−0.087(1)	C(13′)	0.484(1)	0.207(1)	−0.052(3)
C(123)	0.3312(7)	0.3369(8)	−0.172(2)	C(14′)	0.488(1)	0.254(1)	0.043(2)
C(124)	0.3043(8)	0.3827(8)	−0.225(2)	O(21′)	0.4615(8)	0.0632(10)	0.612(2)
C(125)	0.2504(8)	0.4010(7)	−0.197(2)	C(21′)	0.493(2)	0.039(2)	0.702(4)
C(126)	0.2240(7)	0.3745(7)	−0.113(1)	C(22′)	0.551(2)	0.058(2)	0.705(3)
C(211)	0.2572(6)	0.1342(6)	−0.127(1)	C(23′)	0.554(1)	0.081(2)	0.591(3)
C(212)	0.3167(6)	0.1384(6)	−0.120(1)	C(24′)	0.491(1)	0.101(2)	0.578(4)
C(213)	0.3467(7)	0.1227(7)	−0.211(1)				

(br, 8 H), 3.43 (s, 3 H), 4.11 (d, $J = 7.3$ Hz, 2 H), 5.73 (d, $J = 7.3$ Hz, 2 H), 6.9−7.5 (m, 40 H); IR (Kbr) 2070, 1948, 1867, 1857, 1715, 1532, 1490, 1465, 1440, 1412, 1367, 1345, 1285, 1240 cm^{-1}. Anal. Calcd for $C_{65}H_{57}N_3O_5P_4SCl_2CrW$: C, 54.87; H, 4.04; N, 2.95. Found: C, 54.58; H, 4.08; N, 2.95.

Reaction of [W(N_2)$_2$(dppe)$_2$] with [Cr(*p*-FC_6H_4COOMe)(CO)$_3$] in the Presence of NBu_4X (X = F, SCN). A mixture of [W(N_2)$_2$(dppe)$_2$] (**1**, 153 mg, 0.148 mmol), NBu_4SCN (46 mg, 0.153 mmol), and **3a** (43 mg, 0.148 mmol) in THF (7 mL) was irradiated overnight with a tungsten filament lamp at room temperature under N_2. The orange solution turned dark brown. Purification of the product by column chromatography (alumina; eluent CH_2Cl_2−hexane (1/1), then CH_2Cl_2) and recrystallization from CH_2Cl_2−hexane gave red crystals of **7**·CH_2Cl_2 (51 mg, 25%).

A similar reaction of **1**, NBu_4F, and **3a** in THF and purification of the product by column chromatography (alumina; eluent CH_2Cl_2−hexane (1/1), then CH_2Cl_2−AcOEt (1/1)) and recrystallization from THF−hexane gave orange-red crystals of [WF{N=N[(η^6-*p*-C_6H_4COOMe)Cr(CO)$_3$]}(dppe)$_2$]·2THF (**8a**·2THF) in 24%. ^{1}H NMR (C_6D_6) δ 2.39 (br, 4 H), 2.66 (br, 4 H), 3.48 (s, 3 H), 4.01 (d, $J = 6.4$ Hz, 2 H), 5.79 (d, $J = 6.4$ Hz, 2 H), 6.8−7.4 (m, 40 H); IR (KBr) 1942, 1850, 1714, 1530, 1490, 1471, 1437, 1410, 1357, 1329, 1278 cm^{-1}. Anal. Calcd for $C_{71}H_{71}O_7N_2FP_4CrW$: C, 59.09; H, 4.96; N, 1.94. Found: C, 59.14; H, 5.16; N, 1.98.

Reaction of [NBu_4][W(NCS)(N_2)(dppe)$_2$] with [RuCp(C_6H_5F)][PF_6]. Complexes **6** (96 mg, 0.073 mmol) and [RuCp(C_6H_5F)][PF_6] (**5a**, 40.5 mg, 0.099 mmol) were dissolved in THF (5 ml) at 0 °C and stirred for 2 h at this temperature under N_2. The resulting dark red solution was dried up under reduced pressure, and the residue was dissolved in CH_2Cl_2 (1 mL) containing an excess amount of [NBu_4][PF_6] (56.8 mg) and NEt_3 (1 drop). Addition of ether to the CH_2Cl_2 solution gave crude crystals of [W(NCS){N=N[(η^6-C_6H_5)RuCp]}(dppe)$_2$][PF_6] (**10a**), which was collected and washed with MeOH and then with ether. The crude product was further recrystallized from CH_2Cl_2−MeOH−hexane to give a pure sample of **10a**·CH_2Cl_2 as dark red blocks (62.4 mg, 55%). ^{1}H NMR ($CDCl_3$) δ 2.55 (br, 4 H), 2.82 (br, 4 H), 4.66 (s, 5 H), 4.72 (d, $J = 6.3$ Hz, 2 H), 5.04 (pseudo t, $J = 6.1$ Hz, 2 H), 5.27 (t, $J = 5.4$ Hz, 1 H), 6.8−7.5 (m, 40 H); IR (KBr) 2051, 1512, 1485, 1447, 1435, 1389, 1360, 1343, 1233 cm^{-1}. Anal. Calcd for $C_{65}H_{60}N_3F_6P_5SCl_2RuW$: C, 54.70; H, 3.93; N, 2.73. Found: C, 54.40; H, 3.88; N, 2.81.

Similar reactions of **6** with **5b**, **5c**, and **5d** yielded **10b**, **10c**, and **10d**, respectively.

[W(NCS){N=N[(η^6-*p*-C_6H_4Me)RuCp]}(dppe)$_2$][PF_6]·Et_2O (10b·Et_2O): isolated in 51% yield as brown needles after recrystallization from CH_2Cl_2−ether. ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 3 H), 2.53 (br, 4 H), 2.82 (br, 4 H), 4.61 (s, 5 H), 4.68 (d, $J = 6.4$ Hz, 2 H), 5.03 (d, $J = 6.4$ Hz, 2 H), 6.8−7.7 (m, 40 H); IR (KBr) 2047, 1532, 1485, 1466, 1435, 1399, 1366, 1233 cm^{-1}. Anal. Calcd for $C_{69}H_{70}N_3OF_6P_5SRuW$: C, 53.70; H, 4.57; N, 2.72. Found: C, 53.51; H, 4.59; N, 2.78.

[W(NCS){N=N[(η^6-*p*-C_6H_4OMe)RuCp]}(dppe)$_2$][PF_6] (10c): isolated in 38% yield as dark red blocks after recrystallization from CH_2Cl_2−MeOH−hexane. ^{1}H NMR ($CDCl_3$) δ

Table 8. Atomic Coordinates for 10a·CH_2Cl_2

atom	*x/a*	*y/b*	*z/c*
W	0.22284(6)	−0.19485(3)	0.08694(7)
Ru	0.1571(1)	−0.42336(6)	−0.2470(1)
S	0.2947(5)	−0.0463(4)	0.4618(6)
P(1)	0.3102(4)	−0.1320(2)	−0.0091(4)
P(2)	0.0630(3)	−0.1264(2)	0.0204(4)
P(3)	0.1414(3)	−0.2530(2)	0.2018(4)
P(4)	0.3912(4)	−0.2471(2)	0.1862(4)
N(1)	0.2093(9)	−0.2452(5)	−0.052(1)
N(2)	0.2159(9)	−0.2752(6)	−0.158(1)
N(3)	0.2543(9)	−0.1305(6)	0.252(1)
C(1)	0.198(1)	−0.1003(7)	−0.110(1)
C(2)	0.115(1)	−0.0702(7)	−0.041(1)
C(3)	0.251(1)	−0.3087(7)	0.245(2)
C(4)	0.355(1)	−0.2790(7)	0.299(1)
C(5)	0.274(1)	−0.0945(9)	0.344(2)
C(11)	0.147(1)	−0.3196(7)	−0.219(1)
C(12)	0.071(1)	−0.3406(7)	−0.169(1)
C(13)	0.000(1)	−0.3791(9)	−0.238(2)
C(14)	0.004(1)	−0.4018(9)	−0.357(2)
C(15)	0.088(2)	−0.3898(9)	−0.406(1)
C(16)	0.160(1)	−0.3507(8)	−0.334(2)
C(21)	0.283(2)	−0.4544(9)	−0.113(2)
C(22)	0.191(2)	−0.481(1)	−0.122(2)
C(23)	0.159(2)	−0.5145(10)	−0.234(3)
C(24)	0.230(2)	−0.5083(10)	−0.300(2)
C(25)	0.310(2)	−0.4708(10)	−0.225(3)
C(111)	0.376(1)	−0.0662(7)	0.083(2)
C(112)	0.363(1)	−0.0162(9)	0.043(2)
C(113)	0.419(2)	0.0318(9)	0.115(2)
C(114)	0.484(2)	0.0302(9)	0.221(2)
C(115)	0.496(1)	−0.020(1)	0.260(2)
C(116)	0.444(1)	−0.0691(7)	0.193(2)
C(121)	0.409(2)	−0.1661(7)	−0.105(2)
C(122)	0.516(1)	−0.1678(8)	−0.065(2)
C(123)	0.586(2)	−0.1942(10)	−0.138(2)
C(124)	0.549(2)	−0.221(1)	−0.255(3)
C(125)	0.440(2)	−0.222(1)	−0.305(2)
C(126)	0.367(2)	−0.1924(10)	−0.230(2)
C(211)	−0.013(1)	−0.0790(7)	0.129(1)
C(212)	0.039(2)	−0.0355(8)	0.223(2)
C(213)	−0.005(2)	0.001(1)	0.314(3)
C(214)	−0.103(3)	−0.008(1)	0.311(3)
C(215)	−0.167(2)	−0.047(1)	0.231(2)
C(216)	−0.118(2)	−0.0876(8)	0.129(2)
C(221)	−0.045(1)	−0.1515(7)	−0.109(1)
C(222)	−0.120(1)	−0.1104(7)	−0.159(2)
C(223)	−0.200(1)	−0.1345(10)	−0.266(2)
C(224)	−0.199(1)	−0.1940(9)	−0.318(2)
C(225)	−0.126(1)	−0.2322(8)	−0.271(2)
C(226)	−0.053(1)	−0.2113(8)	−0.167(2)
C(311)	0.102(1)	−0.2183(7)	0.343(1)
C(312)	0.051(1)	−0.1646(8)	0.361(2)
C(313)	0.015(2)	−0.1355(8)	0.464(2)
C(314)	0.032(1)	−0.1628(9)	0.560(1)
C(315)	0.083(2)	−0.216(1)	0.555(2)
C(316)	0.117(2)	−0.2453(8)	0.445(2)
C(321)	0.022(1)	−0.2960(7)	0.125(1)
C(322)	−0.072(1)	−0.2677(8)	0.087(2)
C(323)	−0.164(1)	−0.296(1)	0.035(2)
C(324)	−0.156(2)	−0.354(1)	0.020(2)
C(325)	−0.064(2)	−0.3829(10)	0.061(2)
C(326)	0.024(1)	−0.3531(9)	0.112(2)
C(411)	0.451(1)	−0.3093(7)	0.097(2)
C(412)	0.455(1)	−0.3069(7)	−0.019(2)
C(413)	0.512(1)	−0.3541(10)	−0.089(2)
C(414)	0.559(1)	−0.4018(9)	−0.036(2)
C(415)	0.552(2)	−0.400(1)	0.076(2)
C(416)	0.503(2)	−0.3535(9)	0.145(2)
C(421)	0.510(1)	−0.2069(7)	0.274(1)
C(422)	0.505(1)	−0.1710(9)	0.378(2)
C(423)	0.591(2)	−0.1381(9)	0.440(2)
C(424)	0.689(2)	−0.1443(10)	0.393(2)
C(425)	0.690(2)	−0.1812(10)	0.288(2)
C(426)	0.602(1)	−0.2123(8)	0.223(1)
P(1′)	0.7680(8)	0.4865(4)	0.7082(8)
F(1′)	0.790(1)	0.4231(9)	0.650(2)
F(2′)	0.888(1)	0.4861(8)	0.806(2)
F(3′)	0.829(1)	0.5068(8)	0.621(2)
F(4′)	0.663(1)	0.4886(8)	0.629(2)
F(5′)	0.737(1)	0.4613(8)	0.808(2)
F(6′)	0.761(1)	0.5490(9)	0.773(2)
Cl(1′)	0.3115(8)	0.3356(5)	0.5238(9)
Cl(2′)	0.1179(8)	0.3122(5)	0.6065(9)
C(1′)	0.248(3)	0.330(1)	0.643(3)

2.55 (br, 4 H), 2.83 (br, 4 H), 3.50 (s, 3 H), 4.67 (s, 5 H), 4.68 (d, overlapped by the Cp signal, 2 H), 5.14 (d, *J* = 6.3 Hz, 2 H), 6.8−7.6 (m, 40 H); IR (KBr) 2054, 1534, 1472, 1435, 1397, 1362, 1341, 1235 cm^{-1}. Anal. Calcd for $C_{65}H_{60}N_3OF_6P_5SRuW$: C, 52.57; H, 4.07; N, 2.83. Found: C, 52.53; H, 4.07; N, 2.96.

[W(NCS){N=N[(η^6-*p*-C_6H_4COOMe)RuCp]}(dppe)$_2$]·[PF$_6$]·0.5(Et$_2$O) (10d·0.5(Et$_2$O)): isolated in 22% yield as red needles after recrystallization from CH_2Cl_2−ether. ^{1}H NMR ($CDCl_3$) δ 2.59 (br, 4 H), 2.85 (br, 4 H), 3.82 (s, 3 H), 4.65 (s, 5 H), 4.83 (d, *J* = 6.8 Hz, 2 H), 5.65 (d, *J* = 6.8 Hz, 2 H), 6.8−7.5 (m, 40 H); IR (KBr) 2049, 1732, 1524, 1483, 1466, 1435, 1404, 1362, 1337, 1287 cm^{-1}. Anal. Calcd for $C_{68}H_{65}N_3O_{2.5}F_6P_5SRuW$: C, 52.69; H, 4.23; N, 2.71. Found: C, 52.21; H, 4.13; N, 2.68.

Reaction of [WF(NNH)(dppe)$_2$] with [Cr(*p*-FC$_6$H$_4$COOMe)(CO)$_3$]. [WF(NNH)(dppe)$_2$] (**12**, 470 mg, 0.46 mmol) and **3a** (200 mg, 0.69 mmol) were dissolved in THF (7.5 mL) and stirred at room temperature overnight. The solvent was removed in vacuo, and the residue was purified by column chromatography (alumina; eluent CH_2Cl_2−hexane (1/1), then CH_2Cl_2−AcOEt (1/1)) and recrystallization (THF/hexane) to give **8a**·2THF (0.419 g, 63%).

Similar reactions of **12** with **4a** or **4b** at room temperature (overnight) or with **3b** under THF reflux (6 h) afforded **13a**, **13b**, or **8b**, respectively.

[WF{N=N[(η^6-C_6H_5)FeCp]}(dppe)$_2$][PF$_6$]·$C_6H_5CH_3$ (13a·$C_6H_5CH_3$): isolated in 84% yield as purple-red crystals after column chromatography (alumina; eluent CH_2Cl_2−acetone (1/1)) and recrystallization from CH_2Cl_2(one drop of NEt$_3$ was added)−toluene−hexane. ^{1}H NMR (CD_2Cl_2) δ 2.32 (s, 3 H), 2.59 (br, 4 H), 2.83 (br, 4 H), 3.96 (s, 5 H), 4.02 (br, 2 H), 4.80 (br, 2 H), 5.18 (t, *J* = 5.5 Hz, 1 H), 6.9−7.4 (m, 40 H); IR (KBr) 1513, 1490, 1460, 1439, 1420, 1394, 1340 cm^{-1}. Anal. Calcd for $C_{70}H_{66}N_2F_7P_5FeW$: C, 57.47; H, 4.55; N, 1.91. Found: C, 57.17; H, 4.59; N, 2.09.

[WF{N=N[(η^6-*p*-C_6H_4Me)FeCp]}(dppe)$_2$][PF$_6$]·Me$_2$CO (13b·Me$_2$CO): isolated in 75% yield as purple-red crystals after column chromatography (alumina; eluent CH_2Cl_2−acetone (1/1)) and recrystallization from acetone (one drop of NEt$_3$ was added)−hexane. ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3 H), 2.58 (br, 4 H), 2.85 (br, 4 H), 3.90 (s, 5 H), 3.98 (d, *J* = 6.3 Hz, 2 H), 4.81 (d, *J* = 6.3 Hz, 2 H), 7.0−7.3 (m, 40 H); IR (KBr) 1542, 1490, 1481, 1440, 1420, 1405, 1361, 1338 cm^{-1}. Anal. Calcd for $C_{67}H_{66}N_2OF_7P_5FeW$: C, 55.78; H, 4.61; N, 1.94. Found: C, 55.95; H, 4.74; N, 2.04.

[WF{N=N[(η^6-C_6H_5)Cr(CO)$_3$]}(dppe)$_2$]·C_6H_6 (8b·C_6H_6): isolated in 59% yield as orange crystals after column chromatography (alumina; eluent CH_2Cl_2) and recrystallization from C_6H_6−hexane. ^{1}H NMR ($CDCl_3$) δ 2.44 (br, 4 H), 2.67 (br, 4 H), 3.98 (t, *J* = 6.5 Hz, 1 H), 4.11 (d, *J* = 6.5 Hz, 2 H), 4.66 (t, *J* = 6.5 Hz, 2 H), 6.9−7.4 (m, 40 H); IR (KBr) 1938, 1843, 1520, 1489, 1457, 1438, 1378, 1344 cm^{-1}. Anal. Calcd for $C_{67}H_{59}N_2O_3FP_4CrW$: C, 61.01; H, 4.51; N, 2.12. Found: C, 61.18; H, 4.90; N, 2.16.

Collection of Diffraction Data and Structure Refinements. Diffraction data were collected on Rigaku AFC5S (for **7**·CH_2Cl_2 and **13b**·Me$_2$CO), AFC6A (for **8a**·2THF), and AFC7R (for **10a**·CH_2Cl_2) four-cycle automated diffractometers with Mo Kα (λ = 0.7107 Å) radiation and a graphite monochromator. In each case, a crystal sealed in a glass capillary under argon was used, and data were collected at room temperature.

Table 9. Atomic Coordinates for 13b·Me_2CO

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
W	0.36844(1)	0.16575(2)	0.34272(2)	C(216)	0.3950(3)	−0.0467(6)	0.3323(6)
Fe	0.33430(5)	0.41803(10)	0.17309(9)	C(221)	0.3997(3)	0.0821(6)	0.1714(5)
P(1)	0.42726(7)	0.2064(2)	0.3869(2)	C(222)	0.3803(3)	0.0223(6)	0.1448(6)
P(2)	0.40866(7)	0.0878(1)	0.2694(1)	C(223)	0.3703(4)	0.0189(8)	0.0714(6)
P(3)	0.31019(7)	0.1177(2)	0.3004(1)	C(224)	0.3795(4)	0.0729(8)	0.0252(7)
P(4)	0.32941(7)	0.2244(1)	0.4344(1)	C(225)	0.3992(4)	0.1306(8)	0.0493(7)
F(1)	0.3643(2)	0.0863(3)	0.4179(3)	C(226)	0.4091(4)	0.1361(7)	0.1231(6)
N(1)	0.3713(2)	0.2307(4)	0.2718(4)	C(311)	0.3045(3)	0.0193(6)	0.3038(6)
N(2)	0.3769(3)	0.2633(5)	0.2093(5)	C(312)	0.3043(3)	−0.0212(6)	0.2407(7)
C(1)	0.4545(3)	0.2020(6)	0.3049(6)	C(313)	0.3031(4)	−0.0964(7)	0.2440(8)
C(2)	0.4543(3)	0.1258(7)	0.2750(6)	C(314)	0.3019(4)	−0.1299(7)	0.3099(9)
C(3)	0.2748(3)	0.1509(6)	0.3600(6)	C(315)	0.3015(4)	−0.0923(7)	0.3731(8)
C(4)	0.2893(3)	0.1690(7)	0.4372(6)	C(316)	0.3030(3)	−0.0163(7)	0.3710(7)
C(11)	0.3753(3)	0.3358(7)	0.2042(5)	C(321)	0.2926(3)	0.1414(6)	0.2093(6)
C(12)	0.3792(3)	0.3669(6)	0.1343(6)	C(322)	0.2563(3)	0.1402(7)	0.1948(7)
C(13)	0.3803(4)	0.4420(7)	0.1251(7)	C(323)	0.2439(3)	0.1566(8)	0.1247(8)
C(14)	0.3753(4)	0.4886(7)	0.1835(7)	C(324)	0.2667(4)	0.1724(8)	0.0706(7)
C(15)	0.3673(4)	0.4597(7)	0.2510(7)	C(325)	0.3018(4)	0.1729(8)	0.0842(6)
C(16)	0.3654(3)	0.3828(6)	0.2612(6)	C(326)	0.3150(3)	0.1576(7)	0.1540(6)
C(17)	0.3762(5)	0.5712(8)	0.1744(10)	C(411)	0.3138(3)	0.3181(5)	0.4223(5)
C(21)	0.2912(4)	0.3571(9)	0.152(1)	C(412)	0.2791(3)	0.3368(7)	0.4079(6)
C(22)	0.2853(4)	0.3932(10)	0.2098(9)	C(413)	0.2690(4)	0.4081(8)	0.4052(7)
C(23)	0.2876(5)	0.459(1)	0.199(1)	C(414)	0.2934(4)	0.4604(7)	0.4178(7)
C(24)	0.2949(5)	0.4774(10)	0.131(1)	C(415)	0.3281(4)	0.4440(7)	0.4330(7)
C(25)	0.2981(4)	0.411(2)	0.0942(8)	C(416)	0.3383(3)	0.3725(6)	0.4369(6)
C(111)	0.4531(3)	0.1550(6)	0.4538(6)	C(421)	0.3411(3)	0.2255(6)	0.5319(5)
C(112)	0.4860(3)	0.1810(8)	0.4767(8)	C(422)	0.3692(3)	0.1861(6)	0.5578(6)
C(113)	0.5056(4)	0.1415(9)	0.5289(9)	C(423)	0.3783(4)	0.1886(8)	0.6313(6)
C(114)	0.4922(4)	0.0785(9)	0.5572(8)	C(424)	0.3595(4)	0.2272(7)	0.6789(6)
C(115)	0.4597(4)	0.0526(8)	0.5336(8)	C(425)	0.3305(4)	0.2653(7)	0.6548(6)
C(116)	0.4411(3)	0.0912(7)	0.4818(6)	C(426)	0.3214(3)	0.2645(6)	0.5806(6)
C(121)	0.4326(3)	0.3008(6)	0.4171(6)	P(1′)	0.36871(10)	0.6595(2)	0.4002(2)
C(122)	0.4334(4)	0.3554(7)	0.3672(8)	F(1′)	0.3433(3)	0.6127(7)	0.3497(7)
C(123)	0.4346(5)	0.4269(8)	0.3916(10)	F(2′)	0.3924(4)	0.7056(7)	0.4498(7)
C(124)	0.4339(5)	0.4422(9)	0.4611(10)	F(3′)	0.3417(3)	0.6447(9)	0.4574(6)
C(125)	0.4336(4)	0.3899(9)	0.5122(10)	F(4′)	0.3929(4)	0.6799(9)	0.3406(7)
C(126)	0.4319(4)	0.3178(8)	0.4890(8)	F(5′)	0.3482(4)	0.7235(7)	0.3702(10)
C(211)	0.4173(3)	−0.0073(5)	0.2903(5)	F(6′)	0.3878(4)	0.5958(7)	0.427(1)
C(212)	0.4452(3)	−0.0411(7)	0.2559(8)	O(1′)	0.4670(6)	0.297(1)	0.147(1)
C(213)	0.4503(3)	−0.1148(7)	0.2667(8)	C(1′)	0.4698(7)	0.363(1)	0.121(2)
C(214)	0.4279(4)	−0.1534(7)	0.3102(7)	C(2′)	0.4656(7)	0.365(2)	0.035(1)
C(215)	0.4001(4)	−0.1206(7)	0.3424(6)	C(3′)	0.4735(8)	0.427(2)	0.171(2)

Empirical absorption and Lorentz-polarization corrections were made. Selected crystallographic data are summarized in Table 5.

All data reduction, absorption, least-squares, and Fourier calculations were carried out using the TEXSAN package of programs[25] (for **7**·CH_2Cl_2 and **10a**·CH_2Cl_2) or the UNIX-III package of programs[26] (for **8a**·2THF and **13b**·Me_2CO). The scattering factors were taken from International Tables for X-ray Crystallography.[27] The structures were solved by direct methods (MITHRIL for **7**·CH_2Cl_2 and SHELXS86 for **8a**·2THF and **13b**·Me_2CO) or by heavy-atom Patterson methods (PATTY for **10a**·CH_2Cl_2) and expanded using Fourier techniques. The structures of **7**·CH_2Cl_2 and **10a**·CH_2Cl_2 were refined by full-matrix least-squares, while those of **8a**·2THF and **13b**·Me_2CO were refined by block-diagonal least-squares. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms except for those of THF molecules in **8a**·2THF were placed at the calculated positions and included with isotropic thermal parameters in the final stage of refinement. The hydrogen atoms of THF molecules in **8a**·2THF were not included in the structure refinement. The most intense residual peaks in the final difference Fourier maps are as follows: **7**·CH_2Cl_2, 0.89 e/Å^3; **8a**·2THF, 2.07 e/Å^3; **10a**·CH_2Cl_2 1.99 e/Å^3; **13b**·Me_2CO, 2.02 e/Å^3. Final non-H atomic parameters are summarized in Tables 6−9.

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Supplementary Material Available: Tables of positional parameters, anisotropic displacement parameters, and bond lengths and angles for **8a**·2THF, **10a**·CH_2Cl_2, and **13b**·Me_2CO (32 pages). Ordering information is given on any current masthead page.

OM940720C

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