Alkenyldiazenido Complexes of Molybdenum and Tungsten Derived from Dinitrogen Complexes: Their Synthesis, Characterization, and Novel Reactivities[1]

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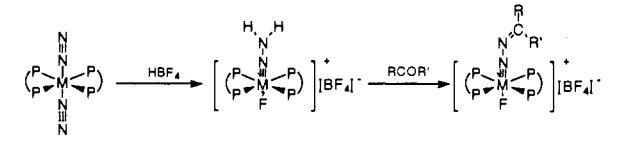
Abstract: α-Deprotonation of molybdenum or tungsten diazoalkane complexes *trans*-[MF(NN=CR^{1}CHR^{2}R^3)(dpe)$_2$][BF$_4$] (**1**, M = Mo or W, dpe = $Ph_2PCH_2CH_2PPh_2$) by LDA (lithium diisopropylamide) or NaN(SiMe$_3$)$_2$ provides a general route to alkenyldiazenido complexes *trans*-[MF(NNCR^1=CR^{2}R^3)(dpe)$_2$] (**2**). When 1-diazopropane complexes **1b** and **1i** were deprotonated, the *Z*-isomers of alkenyldiazenido complexes were predominantly obtained (*Z*/*E* = 6-12). The molecular structure of *trans*-[WF(NNCH=CMe$_2$)(dpe)$_2$]·C$_6$H$_6$ (**2f**·C$_6$H$_6$) was fully characterized by X-ray analysis: $C_{62}H_{61}N_2WP_4F$, space group $P\bar{1}$ (triclinic); a = 13.398 (8) Å, b = 19.051 (13) Å, c = 11.950 (8) Å, α = 98.30 (7)°, β = 114.54 (5)°, γ = 81.81 (6)°, Z = 2, R = 0.070, R_w = 0.082. Relatively long N=N and C=C bond distances (1.29 (3), 1.38 (4) Å) and short C-N bond distance (1.26 (3) Å) in complex **2f**·C$_6$H$_6$ as well as the IR data of complexes **2** indicated considerable contribution of a resonance structure where the terminal carbon of the C=C bond is negatively charged. This has been substantiated by the finding that complexes **2** reacted rapidly with alkyl halides or heterocumulenes such as isocyanates and diphenylketene to give the corresponding C-alkylated or acylated diazoalkane complexes in moderate to high yields, respectively. The deprotonation-alkylation reaction of diazoalkane complexes **1** proceeded regioselectively on the carbon atom cis to the lone pair on the nitrogen of the C=N bond, and the repeated deprotonation-alkylation reactions led to the selective α,α-dialkylation of the diazoalkane ligand. Acylation with excess aryl isocyanates gave the α,α-diacylated complexes, whose molecular structure was confirmed by X-ray analysis of *trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$] (**7a**): formula $C_{69}H_{64}O_2N_4WP_4F_5B$, space group $P2_12_12_1$ (orthorhombic); a = 13.764 (4) Å, b = 35.917 (7) Å, c = 12.986 (4) Å, Z = 4, R = 0.064, R_w = 0.069. Reactions of **2** with aldehydes yielded the Aldol-type condensation products. On the other hand, reactions with I_2 or $CuCl_2$ caused the oxidative coupling to give novel μ-bis(diazo)alkane complexes, and their dimeric structure was revealed by the X-ray diffraction study of *threo,trans,trans*-[(dpe)$_2$WF(NN=CHCHMeCHMeCH=NN)FW(dpe)$_2$][BF$_4$]$_2$·6(C$_6$H$_6$) (*threo*-**14b**·6(C$_6$H$_6$)): formula $C_{146}H_{142}N_4W_2P_8F_{10}B_2$, space group $C2/c$ (monoclinic); a = 32.899 (3) Å, b = 13.091 (1) Å, c = 32.866 (4) Å, β = 109.782 (7)°, Z = 4, R = 0.077, R_w = 0.078. Electrochemical study of **2** indicated that the oxidative coupling proceeded by the coupling of a cationic species generated by the one-electron oxidation of **2**.

Introduction

Much effort has recently been made for the chemical transformation of ligating dinitrogen in molybdenum and tungsten complexes into organo-nitrogen compounds under mild conditions. The C-N bond formation at the coordinated dinitrogen readily occurs to form a series of organo-diazenido, organo-hydrazido, and diazoalkane complexes.[2] Among them, diazoalkane complexes,[3-7] which are obtained by condensation of hydrazido complexes with carbonyl compounds (Scheme I),[3,6,7] are of particular interest because of the unique conjugated structure including the central metal atom. However, little has been known concerning the reactivities of the diazoalkane ligands.[5,6,8] Only a few reports concerning nucleophilic addition of alkyl lithium,[5] reduction with $LiAlH_4$,[5,6] reaction with HBr,[6] and reductive coupling[8] have appeared in literature. In our continuous study on the reactivities of the diazoalkane complexes, especially with the intention of utilizing the diazoalkane complexes for organic synthesis, we have now investigated their reaction with a strong base.

Scheme I



Previously we have reported that certain diazoalkane complexes *trans*-[MF(NN=CMeCH$_2$COMe)(dpe)$_2$][BF$_4$] (M = Mo, W), which are derived from dinitrogen complexes and acetylacetone, are deprotonated by NaOCH$_3$ to give alkenyldiazenido complexes *trans*-[MF(NNCMe=CHCOMe)(dpe)$_2$],[9] although *trans*-[WBr(NN=CMe$_2$)(dpe)$_2$]Br failed to react with NaOCH$_3$.[5] On the other hand, cyanoalkenyldiazenido complexes such as *trans*-[WBr{N=NCX=C(CN)$_2$}(dpe)$_2$] (X = H or Cl) were obtained by the reaction of a dichlorodiazomethane complex *trans*-[WBr(NN=CCl$_2$)(dpe)$_2$]$^+$ with CH(CN)$_2^-$[10] or reactions of a hydrazido complex *trans*-[WBr(NNH$_2$)(dpe)$_2$]$^+$ with cyanoalkenes.[11] However, alkenyldiazenido complexes so far obtained

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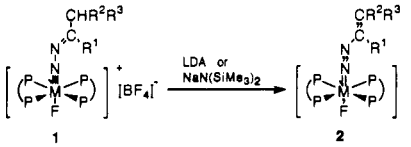
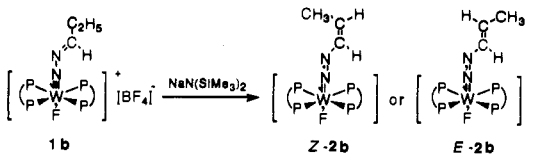
Scheme II



	M	R^1	R^2	R^3
1a,2a	W	Me	H	H
1b,2b	W	H	H	Me
1c,2c	W	H	H	H
1d,2d	W	H	H	Ph
1e,2e	W	-(CH$_2$)$_4$-		H
1f,2f	W	H	Me	Me
1g,2g	W	H	Ph	Ph
1h,2h	Mo	Me	H	H
1i,2i	Mo	H	H	Me

Scheme III



6 : 1 (at r.t. in C_6D_6)
12 : 1 (at 0 °C in $C_6D_5CD_3$)

are limited to those conjugated with strong electron-withdrawing functional group(s), and their reactivity has not been known except for simple protonation.[9] Obviously, the lack of more versatile preparation methods has prevented extensive studies on the reactivities of alkenyldiazenido complexes. The hydrazone-like structure of the diazoalkane complexes suggested that the use of stronger bases as the deprotonating agent leads to a more general route to alkenyldiazenido complexes. On the basis of these hypotheses, we have embarked on an investigation into the preparation and properties of the alkenyldiazenido complexes[12] and found that they show high nucleophilic reactivities and undergo unique oxidative coupling. Here we wish to describe the preparation of molybdenum and tungsten alkenyldiazenido complexes by this methodology, their characterization, and novel reactivities.

Results and Discussion

Preparation and Characterization of Alkenyldiazenido Complexes. Cationic diazoalkane complexes *trans*-[MF(NN=CR^{1}CHR^{2}R^3)(dpe)$_2$][BF$_4$] (**1**) are essentially insoluble in benzene, but addition of 1.5 equiv of NaN(SiMe$_3$)$_2$ or LDA to a benzene suspension of **1** led to the formation of an air- and moisture-sensitive orange-red solution. This is in accordance with the expected generation of nonelectrolyte alkenyldiazenido complexes *trans*-[WF(N=NCR^1=CR^{2}R^3)(dpe)$_2$] (**2**) by the α-deprotonation of **1**. Although **2** could not be isolated in pure forms except for sterically hindered **2f** and **2g** because of their instability, spectroscopic data clearly indicated the quantitative formation of **2** (Scheme II).[13]

The deprotonation product of 2-diazopropane complex **1a** in C_6D_6 showed two singlets at δ 3.36 and 3.40 in ^{1}H NMR assignable to the vinyl protons of isopropenyldiazenido ligand -N=NCMe=CH_2, confirming the formation of **2a**. Interestingly, the methyl signal of **2a** appeared at δ 1.46, while the corresponding *endo*-methyl[14] group of **1a**, which is known to be held in a sandwich position relative to two phenyl groups of a dpe ligand,[3,15] appears at δ -0.68 due to the shielding effect of the phenyls. The large difference in the chemical shifts suggests a substantial change in the conformation of the ligands around the tungsten atom, as was verified by the X-ray diffraction study (vide infra). ^{1}H NMR analysis of the deprotonation product of 1-diazopropane complex **1b** by NaN(SiMe$_3$)$_2$ at room temperature in C_6D_6 revealed that the reaction proceeded stereoselectively to give a 6:1 mixture of two stereoisomers *Z*- and *E*-**2b** (Scheme III). The major product which showed the coupling constant between the vinyl protons (7.0 Hz) smaller than the other (13.1 Hz) was identified as the *Z*-isomer.[16] Reaction at 0 °C in $C_6D_5CD_3$ increased the *Z*/*E* ratio to 12:1. The molybdenum analogue **1i** also exhibited similar stereoselectivity (*Z*/*E* = 10:1 at room temperature in C_6D_6), but the deprotonation of **1d** resulted in the formation of 1:1 mixture of the stereoisomers.

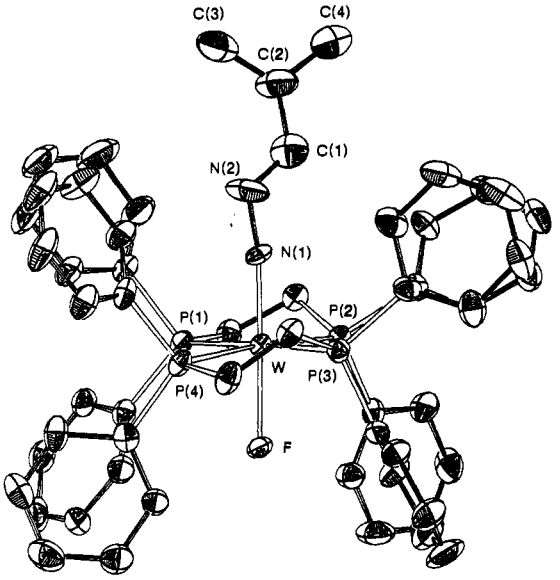


Figure 1. ORTEP drawing for complex *trans*-[WF(NNCH=CMe$_2$)(dpe)$_2$]·(C_6H_6) (**2f**·C_6H_6). Solvated benzene is omitted.

IR spectra of **2** showed absorptions at 1376–1448 cm^{-1} assignable to ν(N=N) and at 1567–1610 cm^{-1}, if any, assignable to ν(C=C). These IR features are quite different from those of known alkenyldiazenido complexes such as *trans*-[WF(NNCMe=CHCOMe)(dpe)$_2$][9] and *trans*-[WBr{N=NCCl=C(CN)$_2$}(dpe)$_2$],[10,11] which show one strong band at 1470–1510 cm^{-1} due to the alkenyldiazenido group coupled with the electron-withdrawing functional group(s). In addition, the ν(N=N) values of **2** are much lower than those reported for tungsten and molybdenum alkyldiazenido complexes (1475–1550 cm^{-1}).[17] In order to ascertain the assignment, $^{15}N_2$-labeled analogues of **2h** and **2i**, *trans*-[MoF(^{15}N=^{15}NCMe=CH$_2$)(dpe)$_2$] and *trans*-[MoF(^{15}N=^{15}NCH=CHMe)(dpe)$_2$], were prepared from **1h**-$^{15}N_2$ and **1i**-$^{15}N_2$, respectively.[3] These ^{15}N-derivatives showed IR bands at 1381 and 1400 cm^{-1}, respectively, while the ^{14}N-derivatives **2h** and **2i** showed the corresponding bands at 1407 and 1448 cm^{-1}, respectively. No other remarkable change in IR was observed. The shifts of IR bands at 1400–1450 cm^{-1} support the above assignment of ν(N=N). The low ν(N=N) and ν(C=C) values suggest that there is a considerable contribution of resonance

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(13) Tungsten diazoalkane complexes having PMe$_2$Ph ligands such as *mer*-[WI$_2$(NN=CMeEt)(PMe$_2$Ph)$_3$] also reacted with LDA, but the products were only stable at -78 °C and could not be characterized. However, addition of MeI to this solution at -78 °C gave *mer*-[WI$_2$(NN=CMe-*i*-Pr)(PMe$_2$Ph)$_3$] (66%, ^{1}H NMR (C_6D_6) δ 0.73 (d, J = 7.0 Hz, 6 H, CH*Me*$_2$), 1.34 (s, 3 H, NN=CMe), 1.56 (septet, J = 7.0 Hz, 1 H, C*H*Me$_2$), 1.76 (d, J = 8.6 Hz, 6 H, PMe), 1.88 (t, J = 3.7 Hz, 6 H, PMe), 2.40 (t, J = 4.0 Hz, 6 H, PMe), 6.9–7.7 (m, 15 H, Ph); IR 1582 cm^{-1} (C=N). Anal. Calcd for $C_{29}H_{43}N_2WI_2P_3$: C, 36.65; H, 4.56; N, 2.95; I, 27.34. Found: C, 36.48; H, 4.54; N, 2.85; I, 27.43). This suggests that reactions similar to those shown in Schemes II and V also occurred in the case of the PMe$_2$Ph complex.

(14) The position cis or trans to the lone pair of the nitrogen atom with regard to the C=N bond in complex **1** is referred to as exo or endo, respectively.[2c,10]

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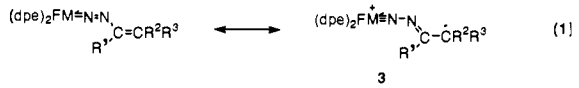
Table I. Selected Bond Lengths and Angles of **2f**·C_6H_6 (Estimated Standard Deviations Cited in Parentheses)

Bond Lengths (Å)			
W-P(1)	2.482 (4)	W-P(2)	2.467 (4)
W-P(3)	2.491 (4)	W-P(4)	2.511 (4)
W-F	2.029 (9)	W-N(1)	1.79 (1)
N(1)-N(2)	1.29 (3)	N(2)-C(1)	1.26 (3)
C(1)-C(2)	1.38 (4)	C(2)-C(3)	1.42 (3)
C(2)-C(4)	1.47 (4)		
Bond Angles (deg)			
P(1)-W-P(2)	79.6 (1)	P(1)-W-P(3)	178.4 (1)
P(1)-W-P(4)	100.7 (1)	P(1)-W-F	90.6 (2)
P(1)-W-N(1)	88.5 (4)	P(2)-W-P(3)	100.6 (1)
P(2)-W-P(4)	175.4 (1)	P(2)-W-F	93.6 (2)
P(2)-W-N(1)	87.2 (3)	P(3)-W-P(4)	79.1 (1)
P(3)-W-F	87.8 (2)	P(3)-W-N(1)	93.1 (4)
P(4)-W-F	81.8 (2)	P(4)-W-N(1)	97.4 (3)
F-W-N(1)	178.7 (4)	W-N(1)-N(2)	171.0 (10)
N(1)-N(2)-C(1)	119.6 (16)	N(2)-C(1)-C(2)	123.2 (18)
C(1)-C(2)-C(3)	129.4 (25)	C(1)-C(2)-C(4)	117.4 (19)

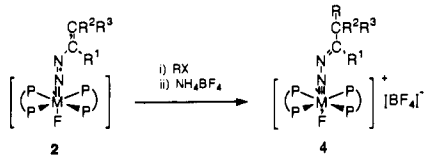
structure **3**, where the terminal carbon of the C=C bond is negatively charged (eq 1). Evidently the metal center accommodates the positive charge to stabilize the charge-separated resonance structure.



3 (1)

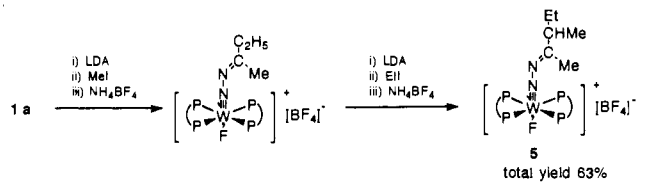
The molecular structure of an alkenyldiazenido complex *trans*-[WF(NNCH=CMe_2)(dpe)$_2$]·C_6H_6 (**2f**·C_6H_6) was unambiguously determined by the single-crystal X-ray diffraction method (Figure 1, Table I). The alkenyldiazenido ligand is of singly bent type (W-N(1)-N(2) 171.0 (10)°, N(1)-N(2)-C(1) 119.6 (16)°) and almost planar, and the ligand plane lies in the space between the two dpe chelates. Interestingly, this conformation differs from those of diazoalkane complexes in which the N=C bonds of the diazoalkane ligands are known to stretch toward one of the dpe chelates,[3,15] while such a difference in the conformation has not been reported in the case of *trans*-[WBr{N=NCCl=$C(CN)_2$}(dpe)$_2$].[10] It is clear that the α-deprotonation of a diazoalkane ligand causes the rotation of the ligand around the W-N-N axis, although factors which control the orientation of the alkenyldiazenido ligands are not known. As mentioned above, ^{1}H NMR chemical shifts of the corresponding methyl groups in **1a** and **2a** are quite different from each other, the former being high-field shifted due to a shielding effect of dpe phenyl groups. The deprotonation of **1a** probably induces rotation of the alkenyldiazenido ligand -N=NCMe=CH_2 as in **2f** to make the *endo*-methyl group come out of the sandwich position between two dpe phenyl groups, which accounts for the disappearance of the high-field shift. The N(1)=N(2) bond length of **2f** (1.29 (3) Å) is among the longest of those reported for similar singly bent diazenido complexes (1.16–1.30 Å).[8b,10,18,19] The C(1)–C(2) bond (1.38 (4) Å) is also long as an olefinic double bond. The N(2)–C(1) bond length (1.26 (3) Å) is shorter than reported values for alkenyl- or aryldiazenido complexes (1.30–1.51 Å)[10,18] but more falls into the range of N=C bond lengths of diazoalkane complexes (1.27–1.30 Å).[3,10,12b,15] These bond lengths also support considerable contribution of the resonance structure **3** in complex **2**, which has been assumed on the basis of the IR spectra (vide supra).

Scheme IV



2 4

Scheme V



5
total yield 63%

Alkylation and Arylation of Alkenyldiazenido Complexes. Alkenyldiazenido ligands have a partial structure which can be regarded as that of enamines. Spectroscopic and crystallographic data strongly indicate that the terminal carbon of the alkenyldiazenido group has a nucleophilicity due to the contribution of the resonance structure **3**. Thus, the reactions of alkyl halides with complexes **2** are expected to give new diazoalkane complexes as C-alkylation products, although N-alkylation has been reported in the case of alkyldiazenido complexes.[17b,20] In fact, addition of an excess amount of an alkyl halide RX to an in situ generated benzene solution of complex **2** at room temperature resulted in a rapid reaction (Scheme IV), and the corresponding C-alkylated cationic diazoalkane complex *trans*-[MF(NN=$CR^1CR^2R^3$R)(dpe)$_2$][BF_4] (**4**) was isolated in a high yield after anion-exchange with NH_4BF_4 and purification by gel-chromatography (Table II). In addition, a similar reaction of **2a** with a fluorobenzene or *p*-fluorotoluene coordinated by $Cr(CO)_3$, which is known to activate haloarenes toward nucleophilic reactions,[21] gave a novel μ-1-aryl-2-diazopropane complex **4d** or **4e** as a C-arylated product. Therefore the sequential deprotonation–alkylation or arylation of diazoalkane complexes provides a facile C-alkylation or arylation method of the diazoalkane ligands.

The alkylation of alkenyldiazenido complexes has several remarkable features in comparison with that of enamines and metallohydrazones. In the reactions of alkenyldiazenido complexes listed in Table II, the mono-C-alkylation products were obtained in high yields, while the alkylation of enamines is known to be often accompanied by polyalkylation and N-alkylation.[22] Furthermore, when complexes **1a**, **1e**, and **1h** were subjected to the deprotonation–alkylation, the alkyl groups were introduced exclusively at the *exo*-carbon to give the *E*-diazoalkane isomers with regard to the C=N bond as the single products. Probably the bulky dpe ligands effectively control the deprotonation–alkylation to proceed at the *exo*-carbon by protecting the *endo*-carbon from attack by a base and prevent the side reactions as well. The high regioselectivity makes it possible to attain selective α,α-dialkylation of **1a** by repeated deprotonation–alkylation reactions. Thus, sequential methylation and ethylation of **1a** gave **5** in 63% total yield (Scheme V). This point is quite distinct from the alkylation of enamines and metallohydrazones where α,α'-dialkylation usually occurs.[22]

It is also worth mentioning that the reactivity of the alkenyldiazenido group in the alkylation is higher than those of usual enamines. In order to compare their reactivities, 1-pyrrolidino-1-cyclohexene was allowed to react with MeI under reaction

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Table II. Alkylation and Arylation of Diazoalkane Complexes via Alkenyldiazenido Complexes[a]

diazoalkane complex	alkenyldiazenido complex	alkyl or aryl halide	product	yield[b] (%)
1a	**2a**	MeI	*trans*-[WF(NN=CMeEt)(dpe)$_2$][BF$_4$] (**4a**)	91
1a	**2a**	EtI	*trans*-[WF(NN=CMe-*n*-Pr)(dpe)$_2$][BF$_4$] (**4b**)	87
1a	**2a**	*p*-BrCH$_2$C$_6$H$_4$-*i*-Pr	*trans*-[WF{NN=CMeCH$_2$CH$_2$(*p*-C$_6$H$_4$-*i*-Pr)}(dpe)$_2$][BF$_4$] (**4c**)	84
1a	**2a**	(η^6-PhF)Cr(CO)$_3$	*trans*-[WF{NN=CMeCH$_2$[(η^6-Ph)Cr(CO)$_3$]}(dpe)$_2$][BF$_4$] (**4d**)	56
1a	**2a**	(η^6-*p*-TolF)Cr(CO)$_3$	*trans*-[WF{NN=CMeCH$_2$[(η^6-*p*-Tol)Cr(CO)$_3$]}(dpe)$_2$][BF$_4$] (**4e**)	54
1b	**2b**	MeI	*trans*-[WF(NN=CHCHMe$_2$)(dpe)$_2$][BF$_4$] (**1f**)	82
1e	**2e**	MeI	*trans*-[WF(NN=CCHMe(CH$_2$)$_3$CH$_2$)(dpe)$_2$][BF$_4$] (**4f**)	73
1h	**2h**	MeI	*trans*-[MoF(NN=CMeEt)(dpe)$_2$][BF$_4$] (**4g**)	53
1h	**2h**	PhCH$_2$Br	*trans*-[MoF(NN=CMeCH$_2$CH$_2$Ph)(dpe)$_2$][BF$_4$] (**4h**)	58

[a] For reaction conditions, see Experimental Section. [b] Yields are based on the starting diazoalkane complexes.

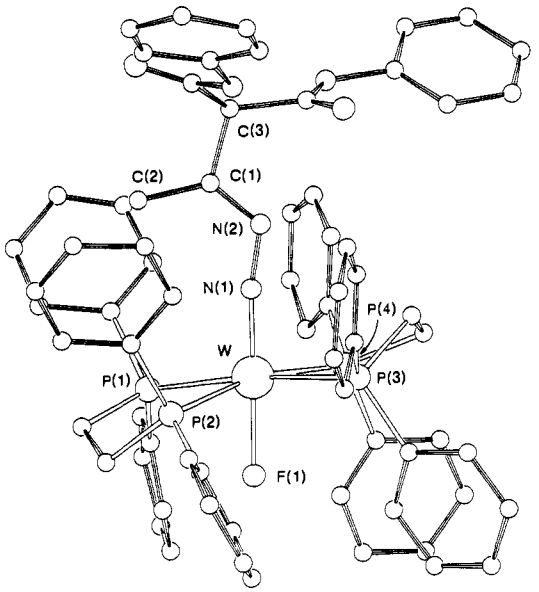
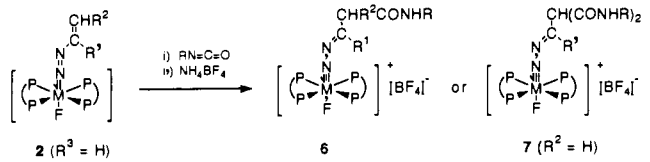


Figure 2. ORTEP drawing for the cationic part of complex *trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$] (**7a**).

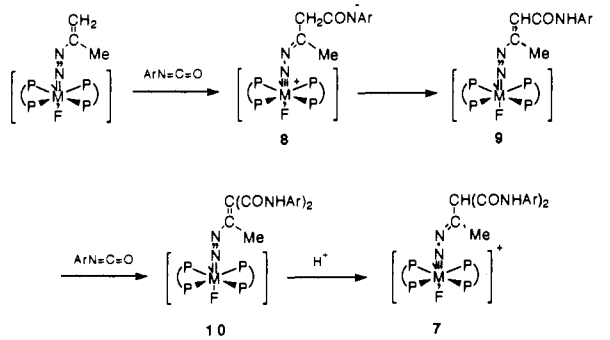
Scheme VI



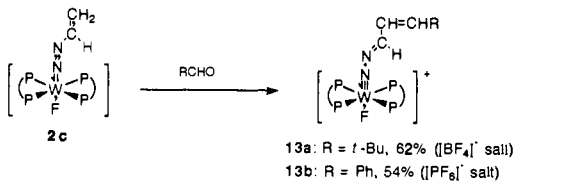
conditions similar to those for the methylation of **1e** via **2e** (reaction time, 3 h). In contrast to the smooth reaction of **2e** (Table II), the yield of 2-methylcyclohexanone after hydrolysis was only 2% and cyclohexanone was recovered in 76%. Apparently the high nucleophilicity of **2** can be ascribed to substantial contribution of the resonance structure **3**. It would be interesting to point out that the hydrolysis of the alkylated diazoalkane complexes completes a unique regioselective alkylation procedure of carbonyl compounds, since the starting diazoalkane complexes are readily derived from the corresponding carbonyl compounds and dinitrogen complexes (Scheme I). In fact, base-promoted hydrolysis of **4f** and **5** (aqueous KOH–THF reflux) gave 2-methylcyclohexanone and 3-methyl-2-pentanone, respectively, in ca. 40% yield. These results exemplify the potentiality of the diazoalkane complexes as novel reagents in organic synthesis.

Acylation of Alkenyldiazenido Complexes. Alkenyldiazenido complexes **2** also reacted rapidly with isocyanates to give C-acylated diazoalkane complexes **6** or **7** after aqueous workup (Scheme VI, Table III). Again high *exo*-regioselectivity was observed. In the reactions of **2a** and **2h**, the use of a controlled amount of PhNCO led to the formation of the mono-C-acylation product **6**, while the use of an excess amount of aryl isocyanate yielded the α,α-di-C-acylated product **7**. The α,α-diacylated structure of **7** was not only supported by their ^{1}H NMR spectra

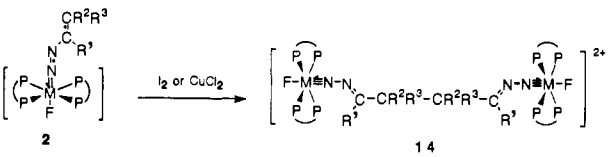
Scheme VII



Scheme VIII



Scheme IX



but also confirmed by the X-ray analysis of *trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$] (**7a**) as depicted in Figure 2. The structure around the tungsten atom is totally similar to those of known diazoalkane complexes;[3,15] the W–N(1)–N(2) linkages is almost linear (Table IV), and the methyl group (C(2)) is located in a sandwich position between two phenyl rings.

The diacylation is considered to proceed by the mechanism shown in Scheme VII. The first condensation of **2a** or **2h** with ArNCO forms a zwitterionic diazoalkane complex **8**, which undergoes intramolecular proton migration to give an acylated alkenyldiazenido complex **9**. Complex **9** is also nucleophilic enough to react with excess ArNCO, and a diacylated alkenyldiazenido complex **10** is formed after the second intramolecular proton migration. Complex **10** is protonated by aqueous workup to yield the diacylated diazoalkane complex **7**.

Similarly to the reaction with isocyanates, complexes **2** reacted regioselectively with phenyl isothiocyanate or diphenylketene to give **11** or **12**, respectively (Table III). However, no diacylated products were observed in these reactions.

Reaction of Alkenyldiazenido Complexes with Aldehydes and Ketones. Aldol-type condensation was observed in the reaction of **2c** and aldehydes without α-hydrogens such as pivalaldehyde or benzaldehyde (Scheme VIII). The isolated products were the dehydrated α,β-unsaturated diazoalkane complexes **13**. However, reaction of **2a** with acetone or propionaldehyde resulted in the recovery of **1a**. Enolizable ketones and aldehydes are considered

Table III. Acylation of Diazoalkane Complexes via Alkenyldiazenido Complexes[a]

diazoalkane complex	alkenyldiazenido complex	heterocumulene[b]	product	yield[c] (%)
1a	**2a**	PhNCO (1.1)	*trans*-[WF(NN=CMeCH$_2$CONHPh)(dpe)$_2$][BF$_4$] (**6a**)	35
1a	**2a**	PhNCO (5.0)	*trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$] (**7a**)	51
1a	**2a**	*p*-TolNCO (3.0)	*trans*-[WF{NN=CMeCH(CONH-*p*-Tol)$_2$}(dpe)$_2$][BF$_4$] (**7b**)	69[d]
1a	**2a**	1-NaphNCO (3.0)	*trans*-[WF{NN=CMeCH(CONH-1-Naph)$_2$}(dpe)$_2$][BF$_4$] (**7c**)	66[e]
1a	**2a**	*t*-BuNCO (3.0)	*trans*-[WF(NN=CMeCH$_2$CONH-*t*-Bu)(dpe)$_2$][BF$_4$] (**6b**)	59
1a	**2a**	PhNCS (1.1)	*trans*-[WF(NN=CMeCH$_2$CSNHPh)(dpe)$_2$][BF$_4$] (**11a**)	67
1a	**2a**	Ph$_2$CCO (2.2)	*trans*-[WF(NN=CMeCH$_2$COCHPh$_2$)(dpe)$_2$][BF$_4$] (**12**)	80
1b	**2b**	*p*-TolNCO (3.0)	*trans*-[WF(NN=CHCHMeCONH-*p*-Tol)(dpe)$_2$][BF$_4$] (**6c**)	50
1b	**2b**	*t*-BuNCO (3.0)	*trans*-[WF(NN=CHCHMeCONH-*t*-Bu)(dpe)$_2$][BF$_4$] (**6d**)	48
4a	*f*	*p*-TolNCO (3.0)	*trans*-[WF(NN=CMeCHMeCONH-*p*-tol)(dpe)$_2$][BF$_4$] (**6e**)	54
4a	*f*	*t*-BuNCO (3.0)	*trans*-[WF(NN=CMeCHMeCONH-*t*-Bu)(dpe)$_2$][BF$_4$] (**6f**)	76
1h	**2h**	PhNCO (1.1)	*trans*-[MoF(NN=CMeCH$_2$CONHPh)(dpe)$_2$][BF$_4$] (**6g**)	36
1h	**2h**	PhNCO (5.0)	*trans*-[MoF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$] (**7d**)	55
1h	**2h**	PhNCS (1.2)	*trans*-[MoF(NN=CMeCH$_2$CSNHPh)(dpe)$_2$][BF$_4$] (**11b**)	60
1i	**2i**	PhNCO (5.0)	*trans*-[MoF(NN=CHCHMeCONHPh)(dpe)$_2$][BF$_4$] (**6h**)	65

[a] For reaction conditions, see Experimental Section. [b] Ratios of heterocumulene/alkenyldiazenido complex are given in parentheses. [c] Yields are based on the starting diazoalkane complexes. [d] Reaction time, 1 h. [e] Reaction time, 3 h. [f] Not characterized.

Table IV. Selected Bond Lengths and Angles of **7a** (Estimated Standard Deviations Cited in Parentheses

	Bond Lengths (Å)		
W-P(1)	2.536 (5)	W-P(2)	2.500 (5)
W-P(3)	2.493 (5)	W-P(4)	2.521 (5)
W-F(1)	1.96 (1)	W-N(1)	1.77 (1)
N(1)-N(2)	1.33 (2)	N(2)-C(1)	1.30 (3)
C(1)-C(2)	1.48 (3)	C(1)-C(3)	1.54 (3)
	Bond Angles (deg)		
P(1)-W-P(2)	79.7 (2)	P(1)-W-P(3)	174.6 (2)
P(1)-W-P(4)	102.9 (2)	P(1)-W-F(1)	81.3 (3)
P(1)-W-N(1)	98.7 (4)	P(2)-W-P(3)	98.8 (2)
P(2)-W-P(4)	167.8 (2)	P(2)-W-F(1)	78.9 (3)
P(2)-W-N(1)	99.3 (4)	P(3)-W-P(4)	77.5 (2)
P(3)-W-F(1)	93.3 (3)	P(3)-W-N(1)	86.7 (4)
P(4)-W-F(1)	89.7 (3)	P(4)-W-N(1)	92.1 (4)
F(1)-W-N(1)	178.2 (5)	W-N(1)-N(2)	170.4 (12)
N(1)-N(2)-C(1)	122.2 (16)	N(2)-C(1)-C(2)	126.1 (19)
N(2)-C(1)-C(3)	115.8 (17)		

to be deprotonated by highly bulky and strongly basic **2a** to give rise to the regeneration of **1a**.

Oxidative Coupling of Alkenyldiazenido Complexes. In addition to the nucleophilic reactivities, alkenyldiazenido complexes were found to undergo a novel oxidative coupling by treatment with I_2 or $CuCl_2$ (Scheme IX, Table V). The products are dinuclear μ-bis(diazo)alkane complexes **14**, which were characterized by spectroscopic and elemental analyses. It should be mentioned that the oxidation of 1-propenyldiazenido complex **2b** yielded *trans,trans*-[(dpe)$_2$WF(NN=CHCHMeCHMeCH=NN)FW(dpe)$_2$][BF$_4$]$_2$ (**14b**) as a mixture of two stereoisomers in ratios 2.1:1–8.3:1, the ratio being higher in reactions at lower temperatures. The molybdenum analogue **2i** showed a similar stereoselectivity.

In order to clarify the structure of a μ-bis(diazo)alkane complex, the X-ray single-crystal diffraction analysis of the major isomer of **14b** was performed. The ORTEP views with and without dpe phenyl groups are given in Figure 3. Although the bond lengths and angles around the C(2) atom involve a few unusual values

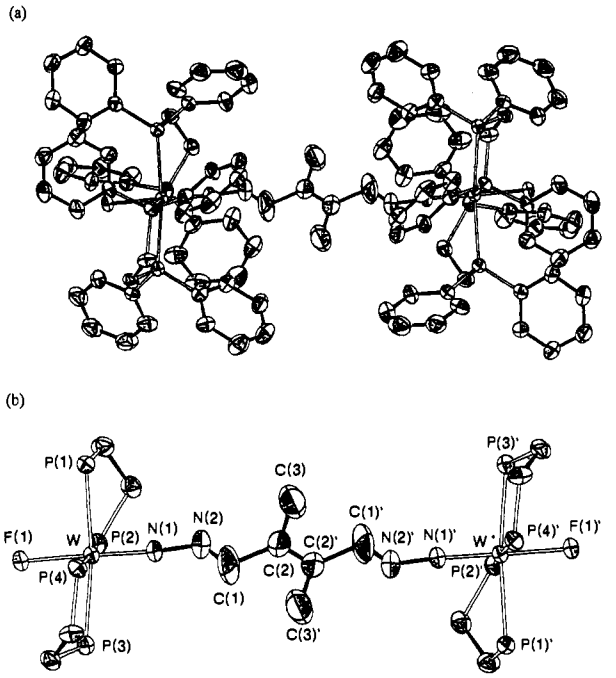


Figure 3. (a) ORTEP drawing for the cationic part of complex *threo,trans,trans*-[(dpe)$_2$WF(NN=CHCHMeCHMeCH=NN)WF(dpe)$_2$][BF$_4$]$_2$·6(C$_6$H$_6$) (*threo*-**14b**·6(C$_6$H$_6$)), viewed down the *C*2 symmetry axis. (b) The view without dpe phenyl groups.

probably because of the disorder of the carbon chain in the μ-bis(diazo)alkane ligand, it was unambiguously revealed that the complex contains a dinuclear structure bridged by μ-bis(diazo)alkane ligand with *C*2 symmetry, where the *C*2 axis is perpendicular to and goes across the C(2)–C(2)′ bond. On the basis of the X-ray analysis, the major isomer was determined to be threo. The W≡N—N=C moiety is almost similar to those of **7a** and other tungsten diazoalkane complexes (Table VI).[3,15] It should

Table V. Oxidative Coupling of Alkenyldiazenido Complexes[a]

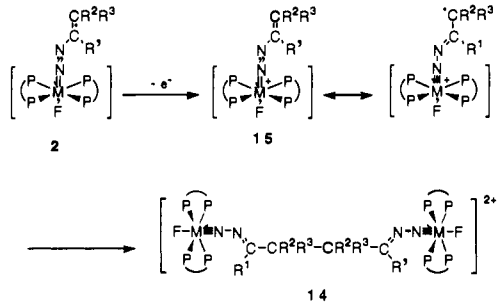
alkenyldiazenido complex	oxidant	reaction conditions[c]	product	yield[b] (%)
2a	I_2	C$_6$H$_6$, rt	*trans,trans*-[{(dpe)$_2$WF(NN=CMeCH$_2$)}$_2$]I$_2$ (**14a**)	45
2a	$CuCl_2$	C$_6$H$_6$, rt	*trans,trans*-[{(dpe)$_2$WF(NN=CMeCH$_2$)}$_2$]I$_2$ (**14a**)	52
2b	I_2	C$_6$H$_6$, rt	*trans,trans*-[{(dpe)$_2$WF(NN=CHCHMe)}$_2$][BF$_4$]$_2$ (**14b**)	36 (3:1)
2b	I_2	THF, −78 °C	*trans,trans*-[{(dpe)$_2$WF(NN=CHCHMe)}$_2$][BF$_4$]$_2$ (**14b**)	60 (8.3:1)
2b	$CuCl_2$	C$_6$H$_6$, rt	*trans,trans*-[{(dpe)$_2$WF(NN=CHCHMe)}$_2$][BF$_4$]$_2$ (**14b**)	60 (2.1:1)
2h	I_2	C$_6$H$_6$, rt	*trans,trans*-[{(dpe)$_2$MoF(NN=CMeCH$_2$)}$_2$][BF$_4$]$_2$ (**14c**)	51
2i	I_2	C$_6$H$_6$, rt	*trans,trans*-[{(dpe)$_2$MoF(NN=CHCHMe)}$_2$][BF$_4$]$_2$ (**14d**)	22 (2.4:1)
2i	I_2	toluene, 0 °C	*trans,trans*-[{(dpe)$_2$MoF(NN=CHCHMe)}$_2$][BF$_4$]$_2$ (**14d**)	10 (3.6:1)

[a] For reaction conditions, see Experimental Section. [b] Yields are based on the starting diazoalkane complexes. Ratios of *threo*-**14**/*erythro*-**14** are given in parentheses. [c] rt = room temperature.

Table VI. Selected Bond Lengths and Angles of *threo*-**14b**·6(C_6H_6) (Estimated Standard Deviations Cited in Parentheses)

	Bond Lengths (Å)		
W-P(1)	2.530 (4)	W-P(2)	2.505 (4)
W-P(3)	2.501 (4)	W-P(4)	2.514 (4)
W-F(1)	1.996 (5)	W-N(1)	1.772 (8)
N(1)-N(2)	1.34 (2)	N(2)-C(1)	1.17 (4)
C(1)-C(2)	1.55 (3)		
	Bond Angles (deg)		
P(1)-W-P(2)	78.2 (1)	P(1)-W-P(3)	172.0 (1)
P(1)-W-P(4)	102.8 (1)	P(1)-W-F(1)	91.3 (2)
P(1)-W-N(1)	90.0 (4)	P(2)-W-P(3)	98.7 (1)
P(2)-W-P(4)	175.0 (1)	P(2)-W-F(1)	93.6 (3)
P(2)-W-N(1)	87.9 (4)	P(3)-W-P(4)	79.7 (1)
P(3)-W-F(1)	81.5 (2)	P(3)-W-N(1)	97.3 (4)
P(4)-W-F(1)	81.5 (3)	P(4)-W-N(1)	96.9 (4)
F(1)-W-N(1)	178.2 (5)	W-N(1)-N(2)	168.2 (14)
N(1)-N(2)-C(1)	120.5 (22)	N(2)-C(1)-C(2)	118.3 (25)

Scheme X



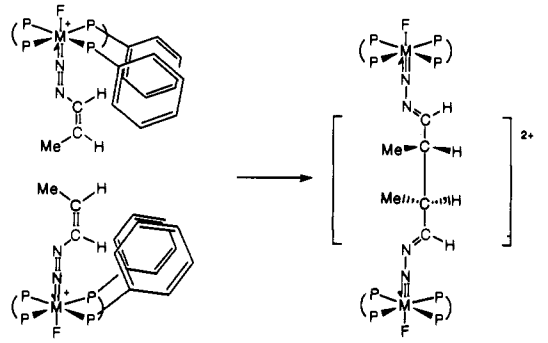
also be pointed out that the high-field shift of the methyl signals in the ^{1}H NMR of complexes *threo*-**14b** (δ 0.12) and *erythro*-**14b** (δ 0.11) is clearly ascribed to the structure where the μ-bis(diazo)alkane ligand is caged in the phenyl groups (Figure 3a).

Interestingly, the present oxidative coupling of alkenyldiazenido complexes is comparable with the oxidative coupling of ketone enolates by Cu(II) salts,[23] while enamines are reported to give α-haloiminium salts by reactions with halogens.[24] The former reaction is suggested to proceed through a single-electron-transfer followed by coupling of the radicals formed.[23a] With a view to obtaining information on the mechanism for the oxidative coupling of alkenyldiazenido complexes, cyclic voltammograms of isolable alkenyldiazenido complexes **2f** and **2g** were measured.

In THF–0.1 M n-Bu_4NBF_4, **2f** and **2g** showed the first oxidation waves at –0.33 V (irreversible, E_p) and at –0.50 V (reversible, $E_{1/2}$) vs Fc/Fc$^+$ couple (Fc = ferrocene), respectively (scan rate = 200 mV·s^{-1}). No reduction wave was observed up to –2.7 V vs Fc/Fc$^+$. Obviously these electrochemical data indicate that the alkenyldiazenido complexes are susceptible to one-electron oxidation. On the grounds of these results, a mechanism for the oxidative coupling of alkenyldiazenido complexes is proposed as shown in Scheme X. The first one-electron oxidation of complex **2** forms a 17-electron cationic W(III) species **15**. The terminal carbon atom of the C=C bond in **15** is considered to have a radical character owing to the conjugated double-bond system including the tungsten atom, and the radical coupling of two molecules of **15** yields the μ-bis(diazo)alkane complex **14**.

One rationale for the *threo*-selectivity is illustrated in Scheme XI. As described above, the predominant isomers of **2b** and **2i** are *Z*. As shown in the Scheme, the access of two molecules of *Z*-**15** with each other in a manner which minimizes steric interaction between the terminal methyl groups of the alkenyldiazenido ligands and the phenyl groups of the dpe ligands is expected to form the *threo*-isomer.

Scheme XI



Conclusion

A new series of tungsten and molybdenum alkenyldiazenido complexes has been prepared by the treatment of diazoalkane complexes, which can be readily derived from dinitrogen complexes, with a strong base such as LDA or $NaN(SiMe_3)_2$. This versatile synthetic method for alkenyldiazenido complexes enabled the systematic study of their properties and reactivities. Interesting reactivities such as the nucleophilic alkylation, acylation, Aldol-type condensation, and oxidative coupling were revealed. These novel reactions of the alkenyldiazenido complexes have realized a variety of chemical transformations of diazoalkane ligands. Future work will be focused on the transformation of diazoalkane ligands to nitrogen-containing organic compounds by taking advantage of the reactivities of alkenyldiazenido ligands.

Experimental Section

^{1}H NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer. IR spectra were recorded with a Shimadzu IR-408 or Shimadzu FTIR-8100M spectrometer by 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. LDA, $NaN(SiMe_3)_2$, I_2, $CuCl_2$, and other organic reagents except for diphenylketene were commercially obtained and used without further purification. Diphenylketene,[25] $Cr(\eta^6\text{-PhF})(CO)_3$,[26] and $Cr(\eta^6\text{-}p\text{-TolF})(CO)_3$[26] were prepared according to the published methods. Diazoalkane complexes **1** were prepared from the corresponding carbonyl compounds and dinitrogen complexes following the established literature procedure.[3]

Preparation of *trans*-[WF(NNCH=CMe$_2$)(dpe)$_2$]·(C_6H_6) (2f·C_6H_6). To a benzene (10 mL) suspension of **1f** (197 mg, 0.168 mmol) was added LDA (1.5 equiv, 1.5 M cyclohexane solution) dropwise at room temperature. The resulting orange-red solution was concentrated to one-third of its original volume, and hexane (15 mL) was added. The mixture was filtered through glass fiber filter paper. Orange crystals deposited from the filtrate were collected, washed with a small amount of hexane, and then dried in vacuo. **2f** was isolated as the mono C_6H_6 solvate (167 mg, 86%). ^{1}H NMR (C_6D_6) δ 1.92 (s, 3 H, NNCH=C*Me*$_2$), 2.22 (s, 3 H, NNCH=C*Me*$_2$), 2.3–2.5 (m, 8 H, CH_2 of dpe), 5.31 (s, 1 H, NNC*H*), 6.8–7.7 (m, 40 H, Ph); IR 1630 (C=C), 1418 cm^{-1} (N=N). Anal. Calcd for $C_{62}H_{61}N_2WP_4F$: C, 64.15; H, 5.30; N, 2.41. Found: C, 63.98; H, 5.38; N, 2.25. Other alkenyldiazenido complexes were prepared similarly, but only **2f** and **2g** could be isolated in analytically pure forms. **2a–e** and **2h,i** were identified spectroscopically.

***trans*-[WF(NNCMe=CH$_2$)(dpe)$_2$] (2a)**: ^{1}H NMR (C_6D_6) δ 1.46 (s, 3 H, NNCMe), 2.4–2.5 (m, 4 H, CH_2 of dpe), 2.7–2.8 (m, 4 H, CH_2 of dpe), 3.36 (s, 1 H, NNCMe=C*H*$_2$), 3.40 (s, 1 H, NNCMe=C*H*$_2$), 6.9–7.5 (m, 40 H, Ph); IR 1587 (C=C), 1390 cm^{-1} (N=N).

***trans*-[WF(NNCH=CHMe)(dpe)$_2$] (2b)**: ^{1}H NMR (C_6D_6) δ (*Z*-isomer) 2.32 (dd, J = 6.7, 1.2 Hz, 3 H, NNCH=CH*Me*), 3.62 (dq, J = 6.7, 7.0 Hz, 1 H, NNCH=C*H*Me), 5.78 (dq, J = 7.0, 1.2 Hz, 1 H, NNCH), (*E*-isomer) 1.90 (dd, J = 6.7, 1.4 Hz, 3 H, NNCH=CH*Me*), 4.71 (dq, J = 13.1, 6.7 Hz, 1 H, NNCH=C*H*Me), 5.49 (dq, J = 13.1,

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1.4 Hz, 1 H, NNCH), 2.3–2.6 (m, 8 H, CH_2 of dpe), 6.9–7.6 (m, 40 H, Ph); IR 1415 cm^{-1} (N=N, obscured by the absorption due to dpe).

***trans*-[WF(NNCH=CH_2)(dpe)$_2$] (2c)**: ^1H NMR (C_6D_6) δ 2.2–2.6 (m, 8 H, CH_2 of dpe), 3.12 (d, J = 7.5 Hz, 1 H, NNCH=CH_2), 4.37 (d, J = 15.0 Hz, 1 H, NNCH=CH_2), 6.00 (dd, J = 15.0, 7.5 Hz, 1 H, NNCH), 6.9–7.6 (m, 40 H, Ph). IR data could not be obtained because of its instability.

***trans*-[WF(NNCH=CHPh)(dpe)$_2$] (2d)**: ^1H NMR (C_6D_6) δ (*Z*-isomer) 4.40 (d, J = 8.1 Hz, 1 H, NNCH=C*H*Ph), 5.80 (d, J = 8.1 Hz, 1 H, NNCH), (*E*-isomer) 5.79 (d, J = 13.1 Hz, 1 H, NNCH=C*H*Ph), 6.78 (d, J = 13.1 Hz, 1 H, NNCH), 2.2–2.6 (m, 8 H, CH_2 of dpe), 6.9–8.2 (m, 45 H, Ph); IR 1582, 1567 (C=C), 1376 cm^{-1} (N=N).

***trans*-[WF{NNC=CH(CH_2)$_3CH_2$}(dpe)$_2$] (2e)**: ^1H NMR (C_6D_6) δ 1.4–1.8 (m, 8 H, NNC=CH(CH_2)$_3$CH_2), 2.3–2.8 (m, 8 H, CH_2 of dpe), 3.66 (broad s, 1 H, NNC=CH), 6.9–7.7 (m, 40 H, Ph); IR 1610 (C=C), 1405 cm^{-1} (N=N).

***trans*-[WF(NNCH=CPh_2)(dpe)$_2$] (2g)**: isolated in 72% yield as orange crystals. ^1H NMR (C_6D_6) δ 2.3–2.5 (m, 8 H, CH_2 of dpe), 6.60 (s, 1 H, NNCH), 6.9–7.6 (m, 48 H, Ph), 8.00 (d, J = 7.3 Hz, 2 H, Ph); IR 1550 (C=C), 1400 cm^{-1} (N=N). Anal. Calcd for $C_{66}H_{59}N_2WP_4F$: C, 65.68; H, 4.93; N, 2.32. Found: C, 66.50; H, 5.16; N, 1.85.

***trans*-[MoF(NNCMe=CH_2)(dpe)$_2$] (2h)**: ^1H NMR (C_6D_6) δ 1.22 (s, 3 H, NNCMe), 2.3–2.5 (m, 4 H, CH_2 of dpe), 2.7–2.9 (m, 4 H, CH_2 of dpe), 3.50 (s, 1 H, NNCMe=CH_2), 3.70 (s, 1 H, NNCMe=CH_2), 6.9–7.8 (m, 40 H, Ph); IR 1407 cm^{-1} (N=N).

***trans*-[MoF(NNCH=CHMe)(dpe)$_2$] (2i)**: ^1H NMR (C_6D_6) δ (*Z*-isomer) 2.03 (d, J = 6.9 Hz, 3 H, NNCH=CH*Me*), 3.76 (quint, J = 6.9 Hz, 1 H, NNCH=C*H*Me), 5.52 (d, J = 6.9 Hz, 1 H, NNCH), (*E*-isomer) 1.60 (d, J = 6.6 Hz, 3 H, NNCH=CH*Me*), 4.82 (dq, J = 13.1, 6.6 Hz, 1 H, NNCH=C*H*Me), 5.23 (d, J = 13.1 Hz, 1 H, NNCH), 2.3–2.6 (m, 8 H, CH_2 of dpe), 6.9–7.8 (m, 40 H, Ph); IR 1448 cm^{-1} (N=N).

Alkylation and Arylation Reactions of Alkenyldiazenido Complexes. The following procedure for the reaction of complex **2a** with MeI is representative. To an orange-red solution of **2a** in benzene prepared from **1a** (200 mg, 0.173 mmol) and LDA, was added MeI (63 mg, 0.44 mmol) at room temperature with stirring. Soon a brown precipitate started to separate out. After the reaction mixture was stirred for 70 min, CH_2Cl_2 (30 mL) was added to dissolve the precipitate, and the solution was washed repeatedly with aqueous NH_4BF_4 (5%, 30 mL × 3) and water (30 mL × 3), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by gel-chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2) and recrystallized from CH_2Cl_2–ether. ***trans*-[WF(NN=CMeEt)(dpe)$_2$][BF_4] (4a)** was obtained as red brown crystals (185 mg, 91%). ^1H NMR ($CDCl_3$) δ −0.69 (s, 3 H, NN=CMe), 0.97 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 1.53 (q, J = 7.3 Hz, 2 H, CH_2CH_3), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 6.9–7.3 (m, 40 H, Ph); IR 1590 cm^{-1} (C=N). Anal. Calcd for $C_{56}H_{56}N_2WP_4F_5B$: C, 57.46; H, 4.82; N, 2.39. Found: C, 57.40; H, 4.83; N, 2.45.

***trans*-[WF(NN=CMe-*n*-Pr)(dpe)$_2$][BF_4] (4b)**: brown crystals. ^1H NMR ($CDCl_3$) δ −0.71 (s, 3 H, NN=C*Me*), 0.93 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.34 (sextet, J = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 1.49 (t, J = 7.4 Hz, 2 H, NN=CMeCH_2), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 6.8–7.4 (m, 40 H, Ph); IR 1585 cm^{-1} (C=N). Anal. Calcd for $C_{57}H_{58}N_2WP_4F_5B$: C, 57.79; H, 4.94; N, 2.36. Found: C, 57.79; H, 4.92; N, 2.40.

***trans*-[WF{NN=CMeCH$_2$CH$_2$(*p*-C_6H_4-*i*-Pr)}(dpe)$_2$][BF_4] (4c)**: brown crystals. ^1H NMR ($CDCl_3$) δ −0.65 (s, 3 H, NN=C*Me*), 1.27 (d, J = 7.0 Hz, 6 H, CH*Me*$_2$), 1.82 (t, J = 8.0 Hz, 2 H, NN=CMeCH_2), 2.60 (t, J = 8.0 Hz, 2 H, NN=CMeCH$_2$CH_2), 2.7–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 2.93 (m, 1 H, C*H*Me$_2$), 6.8–7.4 (m, 44 H, Ph); IR 1585 cm^{-1} (C=N). Anal. Calcd for $C_{65}H_{66}N_2WP_4F_5B$: C, 60.58; H, 5.16; N, 2.17. Found: C, 59.88; H, 5.26; N, 2.26.

***trans*-[WF{NN=CMeCH$_2$[(η^6-Ph)Cr(CO)$_3$]}(dpe)$_2$][BF_4]·0.5(CH_2Cl_2) (4d·0.5(CH_2Cl_2))**: green crystals. ^1H NMR (CD_2Cl_2) δ −0.72 (s, 3 H, NN=C*Me*), 2.46 (s, 2 H, NN=CMeCH_2), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.01 (d, J = 5.8 Hz, 2 H, *o*-H of η^6-Ph), 5.40 (t, J = 5.8 Hz, 1 H, *p*-H of η^6-Ph), 5.56 (t, J = 5.8 Hz, 2 H, *m*-H of η^6-Ph), 6.7–7.4 (m, 40 H, Ph of dpe); IR 1966, 1887 (C=O), 1585 cm^{-1} (C=N). Anal. Calcd for $C_{64.5}H_{59}O_3N_2WCrClP_4F_5B$: C, 54.90; H, 4.09; N, 1.99. Found: C, 54.60; H, 4.42; N, 2.23.

***trans*-[WF{NN=CMeCH$_2$[(η^6-*p*-Tol)Cr(CO)$_3$]}(dpe)$_2$][BF_4]·0.5(CH_2Cl_2) (4e·0.5(CH_2Cl_2))**: green crystals. ^1H NMR (CD_2Cl_2) δ −0.72 (s, 3 H, NN=C*Me*), 2.24 (s, 3 H, C_6H_4*Me*), 2.39 (s, 2 H, NN=CMeCH_2), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.10 (d, J = 5.8 Hz, 2 H, *o*-H of η^6-*p*-Tol), 5.37 (d, J = 5.8 Hz, 2 H, *m*-H of η^6-*p*-Tol), 6.7–7.4 (m, 40 H, Ph of dpe); IR 1962, 1873 (C=O), 1588 cm^{-1} (C=N). Anal. Calcd for $C_{65.5}H_{61}O_3N_2WCrClP_4F_5B$: C, 55.20; H, 4.31; N, 1.97. Found: C, 55.45; H, 4.35; N, 2.20.

***trans*-[WF{NN=CCHMe(CH$_2$)$_3$CH$_2$}(dpe)$_2$][BF_4]·0.5(CH_2Cl_2) (4f·0.5(CH_2Cl_2))**: hygroscopic red-brown crystals. ^1H NMR ($CDCl_3$) δ −0.80, −0.29, 0.23, 0.65, 1.20, 1.68 (m × 6, 1 H × 6, NN=CCHMe-(CH_2)$_3$CH_2), 0.91 (m, 2 H, NN=CCHMe(CH_2)$_3$CH_2), 1.05 (d, J = 6.6 Hz, 3 H, NN=CCH*Me*), 1.50 (m, 1 H, NN=CCH), 2.5–3.2 (m, 8 H, CH_2 of dpe), 6.9–7.4 (m, 40 H, Ph); IR 1575 cm^{-1} (C=N). Anal. Calcd for $C_{59.5}H_{61}N_2WClP_4F_5B$: C, 57.03; H, 4.91; N, 2.24. Found: C, 57.64; H, 5.04; N, 2.07.

***trans*-[MoF(NN=CMeEt)(dpe)$_2$][BF_4] (4g)**: brown crystals. ^1H NMR ($CDCl_3$) δ −0.43 (s, 3 H, NN=CMe), 0.96 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.72 (q, J = 7.4 Hz, 2 H, NN=CMeCH_2), 2.6–2.9 (m, 4 H, CH_2 of dpe), 3.0–3.2 (m, 4 H, CH_2 of dpe), 6.8–7.4 (m, 40 H, Ph); IR 1575 cm^{-1} (C=N). Anal. Calcd for $C_{56}H_{56}N_2MoP_4F_5B$: C, 62.12; H, 5.21; N, 2.59. Found: C, 61.81; H, 5.26; N, 2.53.

***trans*-[MoF(NN=CMeCH$_2$CH$_2$Ph)(dpe)$_2$][BF_4] (4h)**: greenish brown crystals. ^1H NMR ($CDCl_3$) δ −0.37 (s, 3 H, NN=C*Me*), 2.01 (t, J = 7.9 Hz, 2 H, NN=CMeCH_2), 2.61 (t, J = 7.9 Hz, 2 H, CH_2Ph), 2.7–2.9 (m, 4 H, CH_2 of dpe), 2.9–3.2 (m, 4 H, CH_2 of dpe), 6.8–7.4 (m, 45 H, Ph); IR 1570 cm^{-1} (C=N). Anal. Calcd for $C_{62}H_{60}N_2MoP_4F_5B$: C, 64.26; H, 5.22; N, 2.42. Found: C, 63.74; H, 5.28; N, 2.39.

***trans*-[WF(NN=CMeCHMeEt)(dpe)$_2$][BF_4]·0.5(CH_2Cl_2) (5·0.5-(CH_2Cl_2))**: red-brown crystals. ^1H NMR ($CDCl_3$) δ −0.70 (s, 3 H, NN=C*Me*), 0.83 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.87 (d, J = 6.9 Hz, 3 H, CH*Me*Et), 1.20 (m, 2 H, CH_2CH$_3$), 1.66 (sextet, J = 6.9 Hz, 1 H, C*H*MeEt), 2.6–3.1 (m, 8 H, CH_2 of dpe), 6.8–7.4 (m, 40 H, Ph); IR 1577 cm^{-1} (C=N). Anal. Calcd for $C_{58.5}H_{61}N_2WClP_4F_5B$: C, 56.61; H, 4.95; N, 2.26. Found: C, 56.13; H, 4.91; N, 2.21.

Reactions of Alkenyldiazenido Complexes with Heterocumulenes. The following procedure is representative. To a benzene solution of **2a** prepared from **1a** (199 mg, 0.172 mmol) and LDA was added PhNCO (90 μL, 0.83 mmol), and the reaction mixture was stirred for 20 h at room temperature. The color of the solution changed to red-brown. CH_2Cl_2 (30 mL) was added to the reaction mixture, and the solution was washed with aqueous NH_4BF_4 (5%, 30 mL × 3) and water (30 mL × 3) and dried over $MgSO_4$. During the aqueous workup, the solution turned green. The solvents were evaporated, and the residue was purified by gel-chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2) and recrystallization from CH_2Cl_2–MeOH–hexane to give *trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF_4] (**7a**) as greenish brown crystals (123 mg, 51%). ^1H NMR ($CDCl_3$) δ −0.39 (s, 3 H, NN=C*Me*), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 4.15 (s, 1 H, NN=CMeC*H*), 6.7–7.4 (m, 46 H, Ph), 7.79 (d, J = 7.6 Hz, 4 H, *o*-H of NH*Ph*), 9.37 (s, 2 H, NH); IR 1695, 1535 cm^{-1} (CONH). Anal. Calcd for $C_{69}H_{64}O_2N_4WP_4F_5B$: C, 59.42; H, 4.62; N, 4.02. Found: C, 59.18; H, 4.66; N, 3.99.

***trans*-[WF(NN=CMeCH$_2$CONHPh)(dpe)$_2$][BF_4] (6a)**: gray green microcrystals. ^1H NMR ($CDCl_3$) δ −0.50 (s, 3 H, NN=C*Me*), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.82 (s, 2 H, NN=CMeCH_2), 2.9–3.1 (m, 4 H, CH_2 of dpe), 6.8–7.4 (m, 43 H, Ph), 7.85 (d, J = 7.9 Hz, 2 H, *o*-H of NH*Ph*), 9.06 (s, 1 H, NH); IR 1683, 1545 cm^{-1} (CONH). Anal. Calcd for $C_{62}H_{59}ON_3WP_4F_5B$: C, 58.37; H, 4.66; N, 3.29. Found: C, 58.11; H, 4.64; N, 3.25.

***trans*-[WF(NN=CMeCH$_2$CONH-*t*-Bu)(dpe)$_2$][BF_4] (6b)**: greenish brown crystals. ^1H NMR ($CDCl_3$) δ −0.52 (s, 3 H, NN=C*Me*), 1.41 (s, 9 H, *t*-Bu), 2.58 (s, 2 H, NN=CMeCH_2), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.2 (m, 4 H, CH_2 of dpe), 6.8–7.4 (m, 40 H, Ph), 6.91 (s, 1 H, NH); IR 1672, 1535 cm^{-1} (CONH). Anal. Calcd for $C_{60}H_{63}ON_3WP_4F_5B$: C, 57.39; H, 5.06; N, 3.35. Found: C, 57.10; H, 5.02; N, 3.32.

***trans*-[WF(NN=CHCHMeCONH-*p*-Tol)(dpe)$_2$][BF_4] (6c)**: greenish brown crystals. ^1H NMR ($CDCl_3$) δ 0.96 (d, J = 6.7 Hz, 3 H, NN=CHCH*Me*), 2.32 (s, 3 H, C_6H_4*Me*), 2.5–3.0 (m, 8 H, CH_2 of dpe), 3.06 (m, 1 H, NN=CHC*H*), 6.07 (d, J = 5.2 Hz, 1 H, NN=CH), 6.8–7.4 (m, 42 H, Ar), 7.71 (d, J = 8.2 Hz, 2 H, *o*-H of *p*-Tol), 8.84 (s, 1 H, NH); IR 1687, 1535 cm^{-1} (CONH). Anal. Calcd for $C_{63}H_{61}ON_3WP_4F_5B$: C, 58.67; H, 4.77; N, 3.26. Found: C, 58.43; H, 4.85; N, 3.23.

***trans*-[WF(NN=CHCHMeCONH-*t*-Bu)(dpe)$_2$][BF_4] (6d)**: dark brown crystals. ^1H NMR ($CDCl_3$) δ 0.95 (d, J = 6.7 Hz, 3 H, NN=CHCH*Me*), 1.38 (s, 9 H, *t*-Bu). 2.5–3.0 (m, 8 H, CH_2 of dpe), 2.78 (m, 1 H, NN=CHC*H*), 6.08 (d, J = 4.6 Hz, 1 H, NN=CH), 6.78 (s, 1 H, NH), 6.8–7.4 (m, 40 H, Ph); IR 1672 (CONH), 1587 (C=N), 1540 cm^{-1} (CONH). Anal. Calcd for $C_{60}H_{63}ON_3WP_4F_5B$: C, 57.39; H, 5.06; N, 3.35. Found: C, 56.85; H, 5.02; N, 3.09.

***trans*-[WF(NN=CMeCHMeCONH-*p*-Tol)(dpe)$_2$][BF_4]·0.5(CH_2Cl_2) (6e·0.5(CH_2Cl_2))**: brown crystals. ^1H NMR ($CDCl_3$) δ −0.55 (s, 3 H, NN=C*Me*), 1.14 (d, J = 6.9 Hz, 3 H, NN=CMeCH*Me*), 2.31 (s, 3 H, C_6H_4*Me*), 2.5–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of

Table VII. Crystallographic Data for Complexes **2f**·C_6H_6, **7a**, and **14b**·6(C_6H_6)

complex	**2f**·C_6H_6	**7a**	**14b**·6(C_6H_6)
formula	$C_{62}H_{61}N_2WP_4F$	$C_{69}H_{64}O_2N_4WP_4F_5B$	$C_{146}H_{142}N_4W_2P_8F_{10}B_2$
mol wt	1160.92	1394.84	2779.85
cryst size (mm^3)	0.25 × 0.20 × 0.85	0.95 × 0.50 × 0.25	0.70 × 0.30 × 0.15
cryst system	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$C2/c$
a (Å)	13.398 (8)	13.764 (4)	32.899 (3)
b (Å)	19.051 (13)	35.917 (7)	13.091 (1)
c (Å)	11.950 (8)	12.986 (4)	32.866 (4)
α (deg)	98.30 (7)		
β (deg)	114.54 (5)		109.782 (7)
γ (deg)	81.81 (6)		
V (Å^3)	2734 (3)	6420 (3)	13320 (2)
Z	2	4	4
d(calc) (g·cm^{-3})	1.410	1.443	1.386
d(obsd) (g·cm^{-3})	1.39 (22 °C)	1.44 (22 °C)	1.39 (22 °C)
μ (cm^{-1})	23.15	19.96	19.21
no. of data, $\|F_o\| > 5\sigma(F_o)$	7725	5235	7959
R	0.070	0.064	0.077
R_w	0.082	0.069	0.078

dpe), 3.24 (q, J = 6.9 Hz, 1 H, NN=CMeC*H*), 6.7–7.4 (m, 42 H, Ar), 7.76 (d, J = 8.6 Hz, 2 H, *o*-H of *p*-Tol), 8.94 (s, 1 H, NH): IR 1690, 1535 cm^{-1} (CONH). Anal. Calcd for $C_{64.5}H_{64}ON_3WClP_4F_5B$: C, 57.55; H, 4.79; N, 3.12. Found: C, 57.53; H, 5.00; N, 3.02.

***trans*-[WF(NN=CMeCHMeCONH-*t*-Bu)(dpe)$_2$][BF$_4$]·0.5(CH$_2$Cl$_2$) (6f·0.5(CH$_2$Cl$_2$))**: greenish brown crystals. ^{1}H NMR ($CDCl_3$) δ –0.52 (s, 3 H, NN=C*Me*), 1.16 (d, J = 7.0 Hz, 3 H, NN=CMeCH*Me*), 1.36 (s, 9 H, *t*-Bu), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 2.91 (q, J = 7.0 Hz, 1 H, NN=CMeC*H*), 6.80 (s, 1 H, NH), 6.8–7.4 (m, 40 H, Ph); IR 1670 (CONH), 1585 (C=N), 1540 cm^{-1} (CONH). Anal. Calcd for $C_{61.5}H_{66}ON_3WClP_4F_5B$: C, 56.29; H, 5.07; N, 3.20. Found: C, 55.77; H, 5.29; N, 3.02.

***trans*-[MoF(NN=CMeCH$_2$CONHPh)(dpe)$_2$][BF$_4$] (6g)**: pale brown powder. ^{1}H NMR ($CDCl_3$) δ –0.24 (s, 3 H, NN=C*Me*), 2.6–2.9 (m, 4 H, CH_2 of dpe), 2.98 (s, 2 H, NN=CMeC*H*$_2$), 3.0–3.2 (m, 4 H, CH_2 of dpe), 6.8–7.4 (m, 43 H, Ph), 7.85 (d, J = 7.7 Hz, 2 H, *o*-H of NH*Ph*), 9.09 (s, 1 H, NH); IR 1685, 1545 cm^{-1} (CONH). Anal. Calcd for $C_{62}H_{59}ON_3MoP_4F_5B$: C, 62.69; H, 5.01; N, 3.54. Found: C, 62.64; H, 5.21; N, 3.53.

***trans*-[MoF(NN=CHCHMeCONHPh)(dpe)$_2$][BF$_4$] (6h)**: green crystals. ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 6.7 Hz, 3 H, NN=C*Me*), 2.5–3.0 (m, 8 H, CH_2 of dpe), 3.21 (m, 1 H, NN=CHC*H*), 5.93 (d, J = 4.9 Hz, 1 H, NN=CH), 6.8–7.5 (m, 43 H, Ph), 7.82 (d, J = 7.6 Hz, 2 H, *o*-H of NH*Ph*), 8.95 (s, 1 H, NH); IR 1685, 1540 cm^{-1} (CONH). Anal. Calcd for $C_{62}H_{59}ON_3MoP_4F_5B$: C, 62.69; H, 5.01; N, 3.54. Found: C, 62.01; H, 5.06; N, 3.26.

***trans*-[WF{NN=CMeCH(CONH-*p*-Tol)$_2$}(dpe)$_2$][BF$_4$] (7b)**: green crystals. ^{1}H NMR ($CDCl_3$) δ –0.41 (s, 3 H, NN=C*Me*), 2.31 (s, 6 H, C_6H_4*Me*), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 4.09 (s, 1 H, NN=CMeC*H*), 6.7–7.4 (m, 44 H, Ar), 7.66 (d, J = 8.5 Hz, 4 H, *o*-H of *p*-Tol), 9.33 (s, 2 H, NH); IR 1692, 1525 cm^{-1} (CONH). Anal. Calcd for $C_{71}H_{68}O_2N_4WP_4F_5B$: C, 59.93; H, 4.82; N, 3.94. Found: C, 59.46; H, 4.82; N, 3.83.

***trans*-[WF{NN=CMeCH(CONH-1-Naph)$_2$}(dpe)$_2$][BF$_4$] (7c)**: green crystals. ^{1}H NMR ($CDCl_3$) δ –0.23 (s, 3 H, NN=C*Me*), 2.5–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 4.54 (s, 1 H, NN=CMeC*H*), 6.7–8.3 (m, 54 H, Ar), 9.94 (s, 2 H, NH); IR 1695, 1532 cm^{-1} (CONH). Anal. Calcd for $C_{77}H_{68}O_2N_4WP_4F_5B$: C, 61.86; H, 4.58; N, 3.75. Found: C, 60.70; H, 4.80; N, 3.56.

***trans*-[MoF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$]·0.5(CH$_2$Cl$_2$) (7d·0.5(CH$_2$Cl$_2$))**: greenish brown crystals. ^{1}H NMR ($CDCl_3$) δ –0.10 (s, 3 H, NN=C*Me*), 2.6–2.8 (m, 4 H, CH_2 of dpe), 3.0–3.3 (m, 4 H, CH_2 of dpe), 4.29 (s, 1 H, NN=CMeC*H*), 6.7–7.5 (m, 46 H, Ph), 7.79 (d, J = 7.6 Hz, 4 H, *o*-H of NH*Ph*), 9.33 (s, 2 H, NH); IR 1695, 1540 cm^{-1} (CONH). Anal. Calcd for $C_{69.5}H_{65}O_2N_4MoClP_4F_5B$: C, 61.86; H, 4.86; N, 4.15. Found: C, 62.05; H, 4.99; N, 4.31.

***trans*-[WF(NN=CMeCH$_2$CSNHPh)(dpe)$_2$][BF$_4$] (11a)**: brown crystals. ^{1}H NMR ($CDCl_3$) δ –0.45 (s, 3 H, NN=C*Me*), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 3.31 (s, 2 H, NN=CMeC*H*$_2$), 6.8–7.4 (m, 43 H, Ph), 8.03 (d, J = 7.6 Hz, 2 H, *o*-H of NH*Ph*), 10.52 (s, 1 H, NH); IR 1590 cm^{-1} (C=N). Anal. Calcd for $C_{62}H_{59}N_3WSP_4F_5B$: C, 57.65; H, 4.60; N, 3.25; S, 2.48. Found: C, 56.86; H, 4.59; N, 2.95; S, 2.75.

***trans*-[MoF(NN=CMeCH$_2$CSNHPh)(dpe)$_2$][BF$_4$]·0.5(CH$_2$Cl$_2$) (11b·0.5(CH$_2$Cl$_2$))**: brown crystals. ^{1}H NMR ($CDCl_3$) δ –0.19 (s, 3 H, NN=C*Me*), 2.7–2.9 (m, 4 H, CH_2 of dpe), 3.0–3.2 (m, 4 H, CH_2 of dpe), 3.49 (s, 2 H, NN=CMeC*H*$_2$), 6.8–7.4 (m, 43 H, Ph), 8.02 (d, J = 7.3 Hz, 2 H, *o*-H of NH*Ph*), 10.54 (s, 1 H, NH); IR 1575 cm^{-1} (C=N). Anal. Calcd for $C_{62.5}H_{60}N_3MoClSP_4F_5B$: C, 60.23; H, 4.85; N, 3.37; S, 2.57. Found: C, 60.50; H, 4.90; N, 3.37; S, 2.33.

***trans*-[WF(NN=CMeCH$_2$COCHPh$_2$)(dpe)$_2$][BF$_4$] (12)**: yellow brown crystals. ^{1}H NMR ($CDCl_3$) δ –0.61 (s, 3 H, NN=C*Me*), 2.6–3.1 (m, 8 H, CH_2 of dpe), 3.03 (s, 2 H, NN=CMeC*H*$_2$), 5.38 (s, 1 H, COC*H*Ph$_2$), 6.7–7.5 (m, 50 H, Ph); IR 1715 (C=O), 1588 cm^{-1} (C=N). Anal. Calcd for $C_{69}H_{64}ON_2WP_4F_5B$: C, 61.35; H, 4.78; N, 2.07. Found: C, 61.35; H, 5.07; N, 2.04.

Reactions of Alkenyldiazenido Complexes with Aldehydes. The following procedure is representative. To a benzene solution of **2c** prepared from **1c** (200 mg, 0.175 mmol) and LDA was added pivalaldehyde (40 μl, 0.37 mmol). The resulting brown solution was stirred for 1 h at room temperature. After aqueous workup similar to that for the reactions with heterocumulenes, purification by gel-chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2) and recrystallization from MeOH–ether gave *trans*-[WF(NN=CHCH=CH-*t*-Bu)(dpe)$_2$][BF$_4$] (**13a**) as green crystals (133 mg, 62%). ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H, *t*-Bu), 2.5–3.0 (m, 8 H, CH_2 of dpe), 5.26 (d, J = 9.3 Hz, 1 H, NN=CH), 5.38 (d, J = 15.6 Hz, 1 H, CH=C*H*-*t*-Bu), 5.49 (dd, J = 9.3, 15.6 Hz, 1 H, NN=CHC*H*), 6.8–7.4 (m, 40 H, Ph); IR 1628 (C=C), 1535 cm^{-1} (C=N). Anal. Calcd for $C_{59}H_{60}N_2WP_4F_5B$: C, 58.53; H, 5.00; N, 2.31. Found: C, 57.83; H, 4.90; N, 2.29.

***trans*-[WF(NN=CHCH=CHPh)(dpe)$_2$][PF$_6$] (13b)**: green crystals. ^{1}H NMR ($CDCl_3$) δ 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H,CH_2 of dpe), 5.63 (d, J = 7.6 Hz, 1 H, NN=CH), 6.24 (d, J = 15.2 Hz, 1 H, CH=C*H*Ph), 6.29 (dd, J = 7.6, 15.2 Hz, 1 H, NN=CHC*H*), 6.8–7.5 (m, 45 H, Ph); IR 1615 (C=C), 1528 cm^{-1} (C=N). Anal. Calcd for $C_{61}H_{56}N_2WP_5F_7$: C, 56.85; H, 4.38; N, 2.17. Found: C, 57.36; H, 4.58; N, 2.21.

Oxidative Coupling of Alkenyldiazenido Complexes. The following procedure is representative. To a benzene solution of **2b** prepared from **1b** (200 mg, 0.173 mmol) and LDA was added I_2 (54 mg, 0.21 mmol) at room temperature. The color of the solution immediately changed to brown, and a brown precipitate started to separate out. $CuCl_2$ (47 mg, 0.35 mmol) caused a similar but slower reaction. The reaction mixture was further stirred for 2 h. CH_2Cl_2 (30 mL) was added to the reaction mixture, and the solution was washed with aqueous $Na_2S_2O_3$ (5%, 50 mL × 2; omitted in the reactions with $CuCl_2$) and then aqueous NH_4BF_4 (5%, 50 mL × 4) and dried over $MgSO_4$. ^{1}H NMR analysis of the crude product revealed that the *threo*/*erythro* ratio was 2.1:1. Purification by gel-chromatography (Sephadex LH-20; eluent, MeOH–CH_2Cl_2) and recrystallization from CH_2Cl_2–ether gave *trans*,*trans*-[(dpe)$_2$WF(NN=CHCHMeCHMeCH=NN)WF(dpe)$_2$][BF$_4$]$_2$ (**14b**) as greenish brown crystals (130 mg, 60%). ^{1}H NMR ($CDCl_3$) δ (*threo*-isomer) 0.12 (d, J = 6.7 Hz, 6 H, Me), 1.25 (m, 2 H, C*H*Me), 5.94 (d, J = 3.1 Hz, 2 H, NN=CH), (*erythro*-isomer) 0.11 (d, J = 6.7 Hz, 6 H, Me), 1.16 (m, 2 H, C*H*Me), 6.03 (d, J = 4.6 Hz, 2 H, NN=CH), 2.5–3.0 (m, 16 H, CH_2 of dpe), 6.8–7.5 (m, 80 H, Ph); IR 1572 cm^{-1} (C=N). Anal. Calcd for $C_{110}H_{106}N_4W_2P_8F_{10}B_2$: C, 57.17; H, 4.62; N, 2.42. Found: C, 56.54; H, 4.67; N, 2.61. Crystals of *threo*-**14b**·6(C_6H_6) suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2–C_6H_6.

***trans*,*trans*-[(dpe)$_2$WF(NN=CMeCH$_2$CH$_2$CMe=NN)WF(dpe)$_2$]I$_2$·2(CH$_2$Cl$_2$) (14a·2(CH$_2$Cl$_2$))**: greenish brown crystals. ^{1}H NMR ($CDCl_3$) δ –0.45 (s, 6 H, Me), 1.54 (s, 4 H, NN=CCH$_2$), 2.7–2.9 (m, 8 H, CH_2 of dpe), 2.9–3.1 (m, 8 H, CH_2 of dpe), 6.9–7.5 (m, 80 H, Ph); IR 1585 cm^{-1} (C=N). Anal. Calcd for $C_{112}H_{110}N_4W_2I_2Cl_4P_8F_2$: C, 52.52;

H, 4.33; N, 2.19. Found: C, 52.71; H, 4.42; N, 2.26.

***trans,trans*-[(dpe)$_2$MoF(NN=CMeCH$_2$CH$_2$CMe=NN)MoF(dpe)$_2$][BF$_4$]$_2$·2(CH$_2$Cl$_2$) (14c·2(CH$_2$Cl$_2$))**: greenish brown crystals. ^{1}H NMR (CDCl$_3$) δ -0.17 (s, 6 H, Me), 1.64 (s, 4 H, NN=CCH$_2$), 2.7-2.9 (m, 8 H, CH$_2$ of dpe), 2.9-3.1 (m, 8 H, CH$_2$ of dpe), 6.8-7.5 (m, 80 H, Ph); IR 1570 cm^{-1} (C=N). Anal. Calcd for $C_{112}H_{110}N_4Mo_2Cl_4P_8F_{10}B_2$: C, 58.36; H, 4.81; N, 2.43. Found: C, 57.92; H, 4.94; N, 2.46.

***trans,trans*-[(dpe)$_2$MoF(NN=CHCHMeCHMeCH=NN)MoF(dpe)$_2$][BF$_4$]$_2$·CH$_2$Cl$_2$ (14d·CH$_2$Cl$_2$)**: greenish brown crystals. ^{1}H NMR (CDCl$_3$) δ (*threo*-isomer) -0.02 (d, J = 7.0 Hz, 6 H, Me), 1.55 (m, 2 H, C*H*Me), 5.88 (d, J = 2.8 Hz, 2 H, NN=CH), (*erythro*-isomer) 0.06 (d, J = 6.1 Hz, 6 H, Me), 1.25 (m, 2 H, C*H*Me), 5.94 (d, J = 4.6 Hz, 2 H, NN=CH), 2.6-3.0 (m, 16 H, CH$_2$ of dpe), 6.8-7.5 (m, 80 H, Ph); IR 1567 cm^{-1} (C=N). Anal. Calcd for $C_{111}H_{108}N_4Mo_2Cl_2P_8F_{10}B_2$: C, 60.04; H, 4.90; N, 2.52. Found: C, 60.32; H, 5.03; N, 2.57.

Collection of Diffraction Data and Structure Refinements. Diffraction data were collected on Rigaku AFC-6A (for **2f**·C$_6$H$_6$ and **7a** at The Kanagawa University) and Rigaku AFC-5 (for *threo*-**14b**·6(C$_6$H$_6$) at The University of Tokyo) four-cycle automated diffractometers with Mo Kα (λ = 0.7107 Å) radiation and a graphite monochromator. In each case, crystal sealed in a glass capillary under argon was used, and data were collected at room temperature. Empirical absorption and Lorentz-polarization corrections were made. Selected crystallographic data are summarized in Table VII.

Structure solution and refinement were performed by using the UNIX-III program at the computer center of The University of Tokyo.[27] Tungsten atoms in the asymmetric units were found by the direct-methods program MULTAN or SHELXS86. Subsequent block-diagonal least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms, which were refined by using anisotropic temperature factors taken from ref 28. The hydrogen atoms of **2f**·C$_6$H$_6$ and **7a** except for the NH hydrogens of **7a** were placed at the calculated positions and included in the final stage of refinement with isotropic thermal parameters. The hydrogens of *threo*-**14b**·6(C$_6$H$_6$) and the NH hydrogens of **7a** were not included in the structure refinement. The absolute structure of complex **7a** in the crystal was determined based on the anomalous dispersion effects. In the structure refinement of *threo*-**14b**·6(C$_6$H$_6$), difference Fourier maps showed six peaks of comparable electron density assignable to F atoms in a BF_4^- anion. These six peaks were refined as disordered F atoms with an atom multiplicity of 0.67. The difference maps also suggested that the positions of C(2) and C(3) are disordered to a minor extent, and this is probably the reason why the bond lengths and angles concerning these atoms include unusual values. An attempt to refine the minor disordered form was unsuccessful. The most intense residual peaks in the final difference Fourier maps are as follows: **2f**·C$_6$H$_6$, 0.89 e/Å^3, close to a P(2) atom; **7a**, 2.16 e/Å^3, close to a tungsten atom; *threo*-**14b**·6(C$_6$H$_6$), 3.20 e/Å^3, close to a tungsten atom.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, bond lengths and angles for **2f**·C$_6$H$_6$, **7a**, and *threo*-**14b**·6(C$_6$H$_6$) (23 pages); tables of observed and calculated structure factors for **2f**·C$_6$H$_6$, **7a**, and *threo*-**14b**·6(C$_6$H$_6$) (118 pages). Ordering information is given on any current masthead page.

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Electronic Structure of Paramagnetic Clusters of Transition Metal Ions. 2. Crystal and Molecular Structure, Single Crystal EPR Spectra, and Magnetic Properties of $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6](PF_6)$

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Abstract: The X-ray crystal structure of $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6](PF_6)$ (PEt_3 = triethylphosphine) has shown that the crystals are rhombohedric, space group $R\bar{3}$, with a = 11.713 (6) Å, α = 92.15 (4)°, and isomorphous to the homologous iron cluster. The cluster possesses one unpaired electron, and its electronic structure has been investigated through UV-visible electronic absorption spectra, magnetic susceptibility measurements in the temperature range 4.2-300 K, and fluid and frozen solution and single-crystal EPR spectra. The experimental data have been rationalized using semiempirical models (ligand field and extended Hückel) and SCF-Xα-SW calculations. A comparison with the EPR spectra of the parent triclinic cluster $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)$ is carried out.

Introduction

Paramagnetic oligonuclear complexes of transition metals have been known for a long time, and although they are probably less numerous than diamagnetic complexes, their electronic structure has attracted the attention of researchers since the complexity of the spin structure and peculiar magnetic phenomena have always been considered a challenge to both theoreticians and experimentalists.[1-6] One of the best-known examples is copper(II) acetate hydrate, whose dinuclear nature was first recognized by Bleaney and Bowers in 1952 using EPR spectroscopy.[6] Chemists have synthesized a lot of compounds containing different metal atoms in the same molecule,[7] and also molecules in which the metal

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