Synthesis and Characterization of Alkenyldiazenido, Alkenylhydrazido(2-), and Diazoalkane Complexes of Tungsten and Molybdenum[1]

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Abstract: The dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ reacts with acetylacetone in methanol at 50 °C to give a novel alkenyldiazenido complex *mer*-$[W(acac)(NNCMeCHCOMe)(PMe_2Ph)_3]$ (acac = acetylacetonate) in moderate yield. Two possible mechanisms for the formation of this alkenyldiazenido complex are proposed. (1) Ligating dinitrogen is first protonated by acetylacetone to form the diazenido complex $[W(acac)(NNH)(PMe_2Ph)_3]$. The nucleophilic addition of the diazenido ligand to one of the carbonyl groups in acetylacetone followed by elimination of water results in the formation of the alkenyldiazenido complex. (2) The dinitrogen complex is converted into the hydrazido(2-) complex $[W(acac)(NNH_2)(PMe_2Ph)_3][acac]$ via the diazenido complex by protonation with acetylacetone. The condensation of this hydrazido(2-) complex with acetylacetone gives the diazoalkane complex $[W(acac)(NN{=}CMeCH_2COMe)(PMe_2Ph)_3][acac]$, which is readily transformed into the alkenyldiazenido complex by abstraction of the active methylene proton with the acetylacetonate anion in the outer coordination sphere. Analogous complexes with dpe ligands *trans*-$[MF(NNCMeCHCOMe)(dpe)_2]$ (M = W or Mo; dpe = $Ph_2PCH_2CH_2PPh_2$) are produced by treatment of the diazoalkane complexes *trans*-$[MF(NN{=}CMeCH_2COMe)(dpe)_2][BF_4]$ with sodium methoxide. Reactions of these alkenyldiazenido complexes with 1 equiv of HX gas (X = Cl or Br) cause the formation of the alkenylhydrazido(2-) complexes *mer*-$[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)_3]X$ and the diazoalkane complex *trans*-$[WF(NN{=}CMeCH_2COMe)(dpe)_2]Cl$ as crystals. The alkenylhydrazido(2-) structure of the former complex (X = Br) in crystalline form has been fully characterized by an X-ray diffraction method, whereas the NMR spectrum of a solution of this complex in CD_2Cl_2 or $CDCl_3$ shows the existence of an equilibrium between two diazoalkane structures and the alkenylhydrazido(2-) structure. On the other hand, the complex *trans*-$[WF(NN{=}CMeCH_2COMe)(dpe)_2]Cl$ exists in one diazoalkane form even in solution.

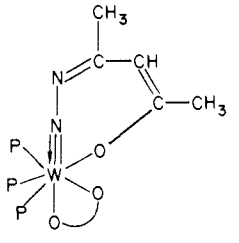
In relevance to biological nitrogen fixation, reactivities of a dinitrogen molecule coordinated to transition metals have attracted much attention.[3] Among many dinitrogen complexes of transition metals, molybdenum and tungsten dinitrogen complexes with tertiary phosphine ligands $[M(N_2)_2(L)_4]$ (M = Mo or W; L = tertiary phosphine) have proven to be excellent model complexes for the reduction of dinitrogen to ammonia and hydrazine.[4] Moreover, three classes of organo-nitrogen ligands such as diazenido (NNR),[5] hydrazido(2-) (NNRR'),[5] and diazoalkane (NN=CRR')[6] ligands can readily be derived from ligating dinitrogen in these complexes, which may lead to direct synthesis of organo-nitrogen compounds from dinitrogen and organic compounds.

Recently we have reported that alcohols or water react with *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) at 50 °C to give ammonia,[7,8] whereas

Scheme I

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{ROH} [W(OR)_2(NNH_2)(PMe_2Ph)_3] \xrightarrow{R'R''C=O} [W(OR)_2(NNCR'R'')(PMe_2Ph)_3] \xrightarrow{ROH} H_2NNCR'R'' \xrightarrow{R'R''CO} R'R''C{=}NN{=}CR'R''$$

ketazines are obtained as the major product in the presence of ketones.[7] The proposed pathway to ketazines involves hydrazido(2-) and diazoalkane complexes as key intermediates as shown in Scheme I. In the same paper,[7] we described that when acetylacetone was used as ketone in this reaction, the complex $[W(acac)(NNCMeCHCOMe)(PMe_2Ph)_3]$ (**2**) was isolated in moderate yield. Since the IR spectrum of complex **2** showed no bands assignable to ν(C=O) or ν(C=N) in the region of 1570-1725 cm^{-1} but a strong band at 1480 cm^{-1}, we tentatively proposed that complex **2** had the O-chelating cyclic diazo structure I. However, further investigations on the structure and chemical behaviors of complex **2** and the analogous complexes with dpe ligands (dpe = $Ph_2PCH_2CH_2PPh_2$) have disclosed that complex **2** has an alkenyldiazenido structure (II), which is formed from



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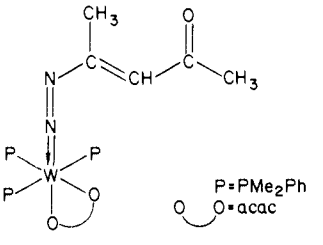

II

the nucleophilic reaction of a dinitrogen-derived diazenido (NNH) or hydrazido(2-) (NNH_2) ligand with one of the carbonyl groups in acetylacetone. We now report the details of the synthesis and characterization of the novel diazenido complexes of tungsten and

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(8) The formation of ammonia from complex **1** in refluxing methanol or ethanol was first reported by Chatt et al.; see ref 4a.

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Table I. The NMR Data for *mer*-[W(acac)(NNCMeCHCOMe)(PMe_2Ph)$_3$] (**2**)

nucleus	chemical shift (ppm)	assignment
$^1H^a$	1.19 (t, J_{PH} = 3.2 Hz, 6 H) 1.26 (t, J_{PH} = 3.2 Hz, 6 H)	CH_3P (trans)
	1.58 (d, J_{PH} = 8.2 Hz, 6 H)	CH_3P (unique)
	1.89 (s, 3 H)	CH_3CNN
	2.11 (s, 3 H)	CH_3CO (diazenido)
	2.01 (s, 3 H), 2.15 (s, 3 H)	CH_3CO (acac)
	5.49 (s, 1 H)	CCHC (acac)
	6.25 (s, 1 H)	CCHC (diazenido)
$^{13}C^a$	20.6, 26.4, 26.6, 31.2	CH_3C
	99.1	$CCHC$ (diazenido)
	101.2	$CCHC$ (acac)
	169.1	CNN
	190.0	C=O (diazenido)
	183.5, 184.0	COW (acac)
$^{31}P^b$	−2.12 (s, 1 P)	PMe_2Ph (unique)
	−2.65 (s, 2 P)	PMe_2Ph (trans)

[a] Relative to Me_4Si, CD_2Cl_2 solution, resonances assigned to phenyl groups are omitted. [b] Relative to H_3PO_4, CD_2Cl_2/CH_2Cl_2 solution.

molybdenum as well as hydrazido(2-) and diazoalkane complexes derived from them.

Results and Discussion

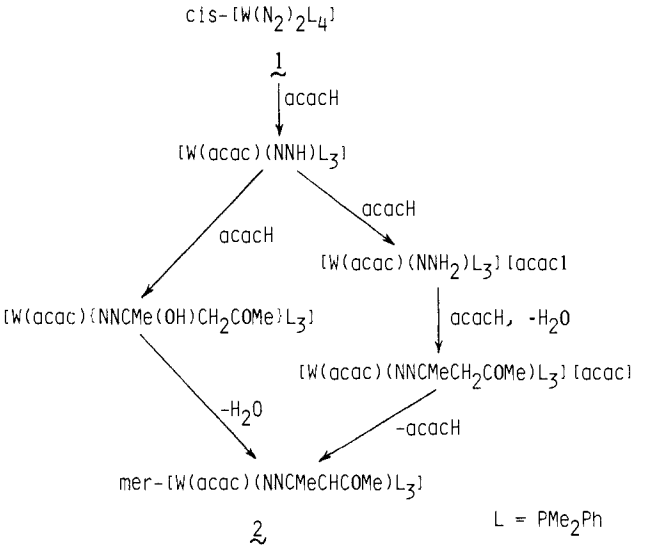
Formation of the Alkenyldiazenido Complex *mer*-[W(acac)(NNCMeCHCOMe)(PMe_2Ph)$_3$] (2). By treatment of complex **1** with acetylacetone in methanol or ethanol at 50 °C, the novel alkenyldiazenido complex **2** was isolated as green crystals in moderate yield (eq 1). We could not disclose the structure of

$$\underset{\mathbf{1}}{cis\text{-}[W(N_2)_2(PMe_2Ph)_4]} \xrightarrow{2acacH} \underset{\mathbf{2}}{mer\text{-}[W(acac)(NNCMeCHCOMe)(PMe_2Ph)_3]} \quad (1)$$

complex **2** itself by an X-ray analysis because suitable crystals were not available. However, the structure of the hydrazido(2-) complex *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]Br obtained from the reaction of complex **2** with HBr gas has been determined by an X-ray crystallographic analysis. It shows that tungsten is not linked to the carbonyl oxygen (vide infra), although ν(C=O) was not observed at around 1700 cm^{-1} in the IR spectrum of this hydrazido(2-) complex. This has led us to conclude that complex **2** has an alkenyldiazenido ligand without any interaction between tungsten and the carbonyl oxygen atom in spite of the lack of the band assignable to ν(C=O) at around 1700 cm^{-1} in its IR spectrum. Thus, a strong absorption band at 1480 cm^{-1} is due to the highly conjugated NNCMeCHCOMe ligand. Such low-stretching frequencies were also reported by Colquhoun et al. in the case of alkenyldiazenido complexes *trans*-[WBr(NNCR″CR′)(dpe)$_2$] (e.g., R = R′ = CN, R″ = H or Cl: ν(C=C/N=N) = 1500 cm^{-1}).[9]

The NMR data of complex **2** are summarized in Table I. In the ^1H NMR spectrum a set of peaks assigned to methyl protons of three PMe_2Ph ligands appears as two triplets and one doublet, which is consistent with meridional configuration of these ligands. The ^{31}P NMR spectrum shows two singlet peaks in the ratio of 2:1 as is expected for this structure.[10] Methyl and methine protons of diazenido and acac ligands are recorded as six singlets. For the assignment of these peaks, *mer*-[W(acac-d_7)(NNCMeCHCOMe)(PMe_2Ph)$_3$] (acac-d_7 = heptadeuterated acetylacetonate) was prepared from *mer*-[WCl_2(NNCMeCH$_2$COMe)(PMe_2Ph)$_3$] and $CD_3COCD_2COCD_3$ (vide infra), and the ^1H NMR spectrum of this complex was compared with that of complex **2**. Two methyl and methine resonances that disappeared are assigned to those of the acac ligand and the other three peaks tentatively to those of the diazenido ligand. As for two methyl resonances of the diazenido ligand, the peak at 2.11 ppm may be assigned to methyl protons of the acetyl group and the peak at 1.89 ppm to protons of the methyl group attached to the C–N moiety, since the methyl resonances of the acetyl groups in the diazoalkane complexes appear at 2.13 ppm for *mer*-[WBr_2(NN=CMeCH$_2$COMe)(PMe_2Ph)$_3$][6b] and at 2.2 and 2.1 ppm for M = Mo and W in *trans*-[MF(NN=CMeCH$_2$COMe)(dpe)$_2$][BF_4],[6a] respectively.

Scheme II



As already reported,[4a,7] the dinitrogen ligand in complex **1** is protonated by methanol or ethanol at 50 °C and finally converted into ammonia via the hydrazido(2-) ligand. However, in the presence of acetylacetone, which exists mainly in the enol form MeCOCH=C(OH)Me with both hydroxy and carbonyl groups in a molecule, the protonation seems to proceed not by alcohol but by acetylacetone, because the latter has a much lower pK_a value (9) than methanol (pK_a 16) or ethanol (pK_a 17). This is confirmed by the fact that complex **2** can also be prepared in moderate yield if complex **1** is treated with neat acetylacetone at 40 °C.

The mechanism proposed for the formation of complex **2** is shown in Scheme II, which involves two possible routes to complex **2**. The first step involves protonation at the terminal nitrogen atom by acetylacetone and the chelation of the resulting acac anion concurrent with dissociation of one dinitrogen and one PMe_2Ph ligand to afford the diazenido complex [W(acac)(NNH)(PMe_2Ph)$_3$]. Colquhoun et al. reported that the diazenido complexes [WX(NNH)(dpe)$_2$] (X = Br or F) are amenable to electrophilic attack by 2,4-dinitrofluorobenzene[11] or cyanoalkenyl chlorides[9] at the nitrogen atom. Thus, it may be reasonable to assume that nucleophilic attack of the diazenido ligand on one of the carbonyl groups in acetylacetone followed by dehydration leads to the formation of the alkenyldiazenido complex **2**. On the other hand, if further protonation of the diazenido complex proceeds rapidly to give the hydrazido(2-) complex [W(acac)(NNH$_2$)(PMe_2Ph)$_3$][acac], another route to complex **2** is plausible. The hydrazido(2-) complex condenses with acetylacetone to form the diazoalkane complex [W(acac)(NN=CMeCH$_2$COMe)(PMe_2Ph)$_3$][acac], which is readily converted into complex **2** by abstraction of the active methylene proton with the acetylacetonate anion in the outer coordination sphere. This is supported by the fact that the alkenylhydrazido(2-) complex *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]Cl, which exists in solution as a mixture of the hydrazido(2-) and the diazoalkane forms (vide supra), is nearly quantitatively transformed into complex **2** by treatment with 1 equiv of Na^+acac^- in methanol. We must await further investigations to elucidate which route is predominant for formation of complex **2**.

(9) Colquhoun, H. M.; Crease, A. E.; Taylor, S. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 736.

(10) For the extensive study on ^1H and ^{31}P NMR of octahedral W and Mo complexes with meridional PMe_2Ph ligands, see: Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766.

(11) Colquhoun, H. M. *J. Chem. Res., Synop.* **1979**, 325.

Table II. The NMR Data for *trans*-[MF(NNCMeCHCOMe)(dpe)$_2$] (**3**)

nucleus	chemical shift (ppm) M = W	chemical shift (ppm) M = Mo	assignment
$^1H^a$	1.60 (s, 3 H)	1.58 (s, 3 H)	CH_3CO
	0.35 (s, 3 H)	0.48 (s, 3 H)	CH_3CNN
	3.87 (s, 1 H)	4.09 (s, 1 H)	CCHC
	2.57 (m, 4 H), 2.91 (m, 4 H)	2.96 (m, 4 H), 2.55 (m, 4 H)	PCH_2CH_2P
$^{31}P^b$	33.92 (d, J_{PF} = 41.5 Hz)	47.52 (d, J_{PF} = 27.5 Hz)	dpe

[a] CD_2Cl_2 solution, relative to Me_4Si, phenyl protons are omitted. [b] C_6D_6 solution, relative to H_3PO_4.

Preparation of Alkenyldiazenido Complexes *trans*-[MF(NNCMeCHCOMe)(dpe)$_2$] (3, M = W or Mo). When the dinitrogen complexes *trans*-[M(N$_2$)$_2$(dpe)$_2$] (M = W or Mo) were treated with acetylacetone at temperatures up to 80 °C, most of the dinitrogen complexes were recovered unreacted. Thus, analogous alkenyldiazenido complexes with dpe ligands could not be prepared by the same method, as from complex **1**. However, if the diazoalkane complexes *trans*-[MF(NN=CMeCH$_2$COMe)(dpe)$_2$][BF$_4$] (**4**, M = W or Mo), which are prepared from *trans*-[M(N$_2$)$_2$(dpe)$_2$] according to eq 2,[6a] are

$$trans\text{-}[M(N_2)_2(dpe)_2] \xrightarrow{HBF_4} trans\text{-}[MF(NNH_2)(dpe)_2][BF_4] \xrightarrow{MeCOCH_2COMe,\ H^+} trans\text{-}[MF(NN{=}CMeCH_2COMe)(dpe)_2][BF_4] \quad (2)$$
$$\mathbf{4}$$

treated with sodium methoxide, the alkenyldiazenido complexes *trans*-[MF(NNCMeCHCOMe)(dpe)$_2$] (**3**, M = W or Mo) are obtained in good yields (eq 3). The IR spectra of complexes **3** shows a similar strong band to that of complex **2** at 1480 cm^{-1} characteristic of the conjugated alkenyldiazenido group.

$$trans\text{-}[MF(NN{=}CMeCH_2COMe)(dpe)_2][BF_4] \xrightarrow{NaOMe} trans\text{-}[MF(NNCMeCHCOMe)(dpe)_2] \quad (3)$$
$$\mathbf{3}$$
$$(M = W \text{ or } Mo)$$

The ^{1}H NMR data of complexes **3** are shown in Table II. The ^{31}P NMR spectra of complexes **3** exhibit a doublet resonance coupled with a fluorine nucleus by 41.5 Hz (M = W) or 27.5 Hz (M = Mo). This finding clearly shows that four phosphorus atoms of the dpe ligands are equivalent and complexes **3** have an octahedral configuration with the alkenyldiazenido and fluorine ligands in a trans position to each other. The phosphorus–fluorine coupling constant of complex **3** (M = Mo) corresponds very well to those of six-coordinate complexes *trans*-[MoF(NNH$_2$)(dpe)$_2$][BF$_4$] (30 Hz)[12] and *trans*-[MoF(NN=CHEt)(dpe)$_2$][BF$_4$] (30 Hz)[6a] observed in the ^{19}F NMR spectra.

The ^{1}H NMR spectra of complexes **3** are quite similar to each other. However, the resonances due to the methyl and methine protons of the alkenyldiazenido groups in complexes **3** are found at much higher field than those of complex **2**. This trend is especially noticeable for the methyl and methine protons attached to the carbon at the β-position from the terminal nitrogen atom. Previously we reported that the resonance assigned to the methyl protons attached to the C=N bond in complex **4** shifts to an unusually high field. This was explained by the shielding effect of the two phenyl rings on dpe ligands between which the methyl group occupies a constricted "sandwich" position.[6a] Appearance of the methyl and methine resonances of complexes **3** at relatively high field indicates the existence of the similar effect on the alkenyldiazenido ligand in complexes **3**.

Preparation and Characterization of the Alkenylhydrazido(2−) Complexes *mer*-[W(acac)(NNHCMeCHCOMe)(PMe$_2$Ph)$_3$]X (5, X = Cl or Br). The alkenyldiazenido complex **2** reacts with 1 equiv of HX gas (X = Cl or Br) in CH_2Cl_2 to give the alkenylhydrazido(2−) complexes *mer*-[W(acac)(NNHCMeCHCOMe)(PMe$_2$Ph)$_3$]X (**5**) (eq 4). Dark red crystals suitable for

$$mer\text{-}[W(acac)(NNCMeCHCOMe)(PMe_2Ph)_3] \xrightarrow{HX\ gas} mer\text{-}[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)_3]X \quad (4)$$
$$\mathbf{5}$$

X-ray diffraction were grown by mixing slowly an acetone solution of complex **5** (X = Br) with ether. The unit cell parameters and a summary of data collection and refinement information for complex **5** (X = Br) are shown in Table III. The perspective view of complex **5** is shown in Figure 1, and pertinent bond lengths and angles are given in Table IV. The complex **5** has an octahedral structure with three meridional phosphine ligands. The acac ligand coordinates to the metal in a bidentate fashion, and the alkenylhydrazido(2−) ligand occupies the trans position to one oxygen atom of the acac ligand.

The structure of the alkenylhydrazido(2−) ligand can be described as III on the basis of the result of the X-ray analysis. The

Table III. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for *mer*-[W(acac)(NNHCMeCHCOMe)(PMe$_2$Ph)$_3$]Br (**5**)

quantity	data
	$C_{34}H_{49}N_2O_3P_3WBr$
mol wt	889.95
a (Å)	14.934 (2)
b (Å)	23.285 (3)
c (Å)	10.926 (1)
V (Å^3)	3799.4
systematic absences	$h = 2n + 1$ for $h00$ $k = 2n + 1$ for $0k0$ $l = 2n + 1$ for $00l$
space group	$P2_12_12_1$
d_{calcd} (g/cm^3)	1.56
Z	4
F (000)	1632
cryst dimensns (mm)	0.19 × 0.26 × 0.48
linear abs coeff (cm^{-1})	34.83
data collectn method	2θ–θ scan
2θ–scan range (deg)	2.5–60.0
scan rate (2θ, deg/min)	2
scan range ($A + B\tan\theta$, deg)	A = 1.1, B = 0.45
no. of stand. reflctns	3 (0, 10, 0; 6, 0, 0; 0, 0, 2)
no. of unique data collctd	6041
no. of data used ($F_o \geq 3\sigma F_o$)	4374
data param ratio	11.0
final R value (%)	9.20

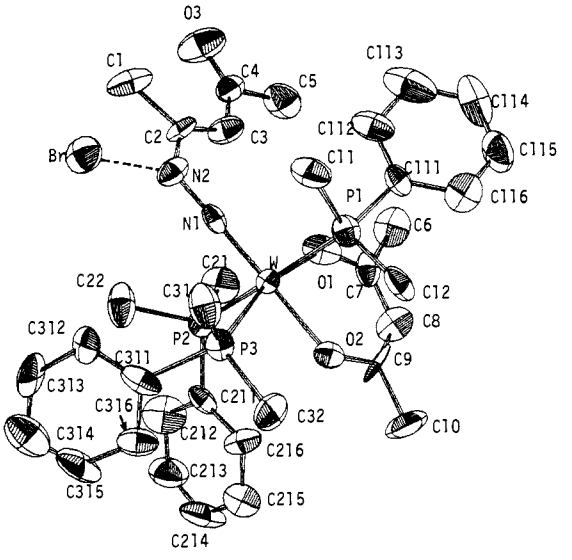


Figure 1. Perspective view of *mer*-[W(acac)(NNHCMeCHCOMe)(PMe$_2$Ph)$_3$]Br (**5**), with atom numbering.

(12) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694.

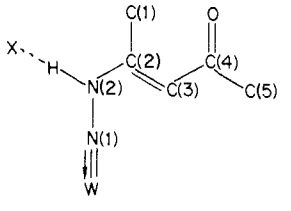
Table IV. Selected Bond Lengths and Angles for *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]Br (**5**)

	Bond Length (Å)		
W-P(1)	2.509 (7)	C(3)-C(4)	1.43 (4)
W-P(2)	2.543 (6)	C(4)-C(5)	1.57 (5)
W-P(3)	2.468 (7)	C(4)-O(3)	1.20 (4)
W-O(1)	2.082 (20)	O(1)-C(7)	1.27 (3)
W-O(4)	2.100 (17)	O(2)-C(9)	1.35 (3)
W-N(1)	1.793 (13)	C(6)-C(7)	1.52 (4)
N(1)-N(2)	1.375 (29))	C(7)-C(8)	1.41 (4)
N(2)-C(2)	1.40 (4)	C(8)-C(9)	1.37 (4)
C(1)-C(2)	1.55 (4)	C(9)-C(10)	1.51 (5)
C(2)-C(3)	1.33 (4)	N(2)-Br	3.192 (22)
	Bond Angle (deg)		
P(1)-W-P(2)	170.8 (2)	N(2)-C(2)-C(1)	106.2 (23)
P(1)-W-P(3)	93.0 (2)	N(2)-C(2)-C(3)	125.8 (27)
P(1)-W-O(1)	85.4 (6)	C(1)-C(2)-C(3)	128.0 (27)
P(1)-W-O(2)	85.6 (5)	C(2)-C(3)-C(4)	122.8 (26)
P(1)-W-N(1)	93.4 (6)	C(3)-C(4)-C(5)	113.0 (24)
P(2)-W-P(3)	96.0 (2)	O(3)-C(4)-C(3)	130.1 (27)
P(2)-W-O(1)	85.4 (6)	O(3)-C(4)-C(5)	116.8 (27)
P(2)-W-O(2)	93.7 (5)	W-O(1)-C(7)	134.7 (18)
P(2)-W-N(1)	87.7 (6)	W-O(2)-C(9)	130.2 (16)
P(3)-W-O(1)	164.6 (6)	O(1)-C(7)-C(6)	114.7 (25)
P(3)-W-O(2)	82.6 (5)	O(1)-C(7)-C(8)	123.9 (26)
P(3)-W-N(1)	95.3 (6)	O(2)-C(9)-C(8)	125.8 (26)
O(1)-W-O(2)	82.0 (7)	O(2)-C(9)-C(10)	112.0 (25)
O(1)-W-N(1)	100.1 (8)	C(6)-C(7)-C(8)	121.4 (26)
O(2)-W-N(1)	177.6 (8)	C(7)-C(8)-C(9)	123.2 (28)
W-N(1)-N(2)	176.4 (16)	C(8)-C(9)-C(10)	122.0 (28)
N(1)-N(2)-C(2)	115.6 (21)		

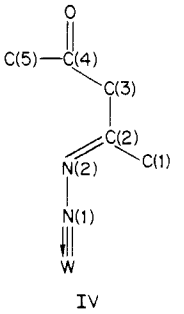
Table V. Comparison of Bond Distances and Angles for Alkenylhydrazido(2-) and Diazoalkane Ligands

bond	complex **5** (X = Br) (III)	complex **4** (IV)
	Distances (Å)	
N(1)-N(2)	1.375 (29)	1.317 (25)
N(2)-C(2)	1.40 (4)	1.300 (30)
C(2)-C(3)	1.33 (4)	1.525 (43)
C(3)-C(4)	1.43 (4)	1.490 (53)
C(4)-O(3)	1.20 (4)	1.198 (58)
	Angles (deg)	
N(1)-N(2)-C(2)	115.6 (21)	125.2 (19)
N(2)-C(2)-C(3)	125.8 (27)	121.5 (23)
C(2)-C(3)-C(4)	122.8 (26)	113.9 (29)

W-N(1)-N(2) linkage is essentially linear, and the angle of N(1)-N(2)-C(2) is around 120°. The N(1)-N(2) distance observed corresponds to the bond order of about 1.5. These features are commonly observed for alkylhydrazido(2-)[13] and (trimethylsilyl)hydrazido(2-)[14] complexes. The long N(2)-C(2) bond distance and the short C(2)-C(3) bond distance together with the sp^2 character of C(2), C(3), and C(4) atoms deduced from the bond angles around each atom are consistent with the structure III. Table V is for the comparison of the selected bond distances



III



IV

(13) (a) Day, V. W.; George, T. A.; Iske, S. D. A., Jr.; Wagner, S. D. *J. Organomet. Chem.* **1976**, *112*, C55. (b) March, F. C.; Mason, R.; Thomas, K. M. *J. Organomet. Chem.* **1975**, *96*, C43.

(14) Hidai, M.; Komori, K.; Kodama, T.; Jin, D.-M.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. *J. Organomet. Chem.* **1984**, *272*, 155.

Table VI. Chemical Shifts of Proton Resonances Characteristic of Structures III, IV, and V for Complexes **5**

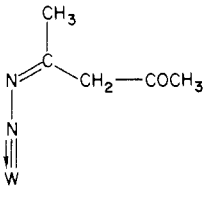
chemical shift (ppm)[a]						
III		IV		V		
X = Cl	X = Br	X = Cl	X = Br	X = Cl	X = Br	assignment
5.65	5.68	5.81	5.82	5.18	5.24	CCHC (acac)
6.14	6.16			5.90	6.01	CCHC
		3.52	3.76			CCH_2C
13.2	12.2[b]					NNH
				13.4	13.5[b]	OH

[a] $CDCl_3$ (X = Br) or CD_2Cl_2 (X = Cl) solution, relative to Me_4Si, all peaks are singlets. [b] Resonances disappeared slowly after the addition of D_2O.

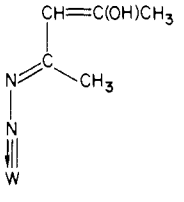
and angles of the alkenylhydrazido(2-) ligand in complex **5** with those of the diazoalkane ligand IV in complex **4**, which has the N(2)-C(2) double bond and the sp^3 C(3) atom. The C(4)-O(3) distance of 1.20 (4) Å in complex **5** is essentially the same as that in complex **4**, and the conjugated feature of the C(4)-O(3) double bond with the C(2)-C(3) double bond is not reflected in the bond distance. We previously reported that the steric hindrance caused by dpe ligands in complex **4** requires the restriction that the group attached to the C(2) atom in an anti position to the lone pair orbital of the N(2) atom must be smaller than the methyl group.[6a,15] Interestingly, in complex **5**, the larger group (acetylmethylidene) positions the space that the C(1) methyl group occupies in complex **4**. This indicates that a steric restriction is no longer encountered in the alkenylhydrazido(2-) complexes with monophosphine ligands.

The IR spectra of complexes **5** by a KBr method show the broad ν(NH) at 2700 cm^{-1} (X = Br) or 2730 cm^{-1} (X = Cl), which is characteristic of the hydrazido(2-) group strongly hydrogen-bonded to an anion. This interaction is also confirmed by the X-ray analysis as shown in Figure 1. Several strong bands also appear in the region that presumably relates to ν(C=O), ν(C=C), and ν(C=N) (X = Br: 1640, 1560, and 1500 cm^{-1}; X = Cl: 1710, 1640, 1560, and 1500 cm^{-1}). The weak band observed at 1710 cm^{-1} in complex **5** (X = Cl) may be due to the existence of the ketodiazoalkane isomer described below to some extent even in the solid form.

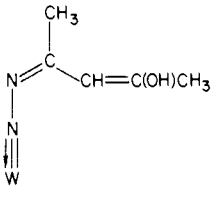
The ^1H and ^{31}P NMR spectra of complexes **5** show the complicated patterns that can be interpreted in terms of an equilibrium among alkenylhydrazido(2-) (III), keto-diazoalkane, and enol-diazoalkane complexes. Although the X-ray analysis has demonstrated that the keto-diazoalkane ligand in complex **4** has the structure described as IV, it is not yet certain whether it is also the case for the keto- and enol-diazoalkane ligands in complexes **5** (IV and V) or not (IV′ and V′). The ratio of these three isomers



IV′



V



V′

III:IV or IV′:V or V′ is estimated to be 3:1:1 for X = Br in $CDCl_3$ and 4:2:1 for X = Cl in CD_2Cl_2 on the basis of the intensity ratio of the methine proton resonances of these isomers. Tentative assignments of the methine and methylene protons are shown in Table VI together with those of the hydrazido(2-) and hydroxy protons. Resonances in the spectral region of methyl protons are so complicated that it is practically difficult to assign all peaks. The ^{31}P NMR spectrum of complex **5** (X = Br) in $CDCl_3$ shows three pairs of resonances, each of which is composed of two peaks with the intensity ratio of about 2:1. Among these, the one pair of resonances with the largest intensity at −5.67 and −5.00 ppm

(15) Head, R. A.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1980**, 1150.

Scheme III

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{HX\ aqueous/MeOH} \underset{\mathbf{1}}{}$$

$$mer\text{-}[WX_2(NNH_2)(PMe_2Ph)_3] \xrightarrow{acacH/CH_2Cl_2}$$

$$mer\text{-}[WX_2(NN{=}CMeCH_2COMe)(PMe_2Ph)_3] \xrightarrow{NEt_3/acacH/CH_2Cl_2}$$

$$mer\text{-}[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)_3]X \quad \mathbf{5}$$

(upfield from H_3PO_4) are assigned to mutually trans and the other unique phosphorus atoms in III, respectively.

As for the neutral diazoalkane complex *mer*-[WBr_2(NN=$CMeCH_2COMe$)(PMe_2Ph)$_3$], an equilibrium between equal amounts of keto and enol forms was observed by the ^{1}H NMR spectrum but no resonances due to the hydrazido(2-) isomer were detected.[6b,16] It seems plausible that the existence of the anion capable of making a hydrogen bonding with the hydrazido(2-) proton results in the isomerization of the diazoalkane ligand to the hydrazido(2-) ligand of type III. Thus, the above neutral diazoalkane complex without an outer-sphere anion favors the diazoalkane structure.

Complexes **5** can also be prepared via another route from the dinitrogen compelx **1** (Scheme III). As already reported,[6b] diazoalkane complexes *mer*-[WX_2(NN=$CMeCH_2COMe$)-(PMe_2Ph)$_3$] (X = Cl or Br) are formed by the condensation of hydrazido(2-) complexes with acetylacetone in CH_2Cl_2. When these diazoalkane complexes were treated with an excess of the acetylacetone/triethylamine mixture, metathetical replacement of one of the halide anions with an acac ligand takes place to give cationic complexes **5** with the other halide anion in the outer coordination sphere. Transformation of the diazoalkane ligand into the alkenylhydrazido ligand may take place via the simple internal proton migration from the carbon adjacent to the carbonyl group to the terminal nitrogen atom or via the abstraction of the acidic methylene proton by NEt_3 and the successive protonation at the terminal nitrogen atom by $HNEt_3^+$.

Treatment of the alkenylhydrazido(2-) complex **5** (X = Cl) with a large excess of triethylamine or sodium methoxide in CH_2Cl_2 regenerates alkenyldiazenido complex **2**. This alternative route to complex **2** was useful for the assignment of the methyl and methine resonances in the ^{1}H NMR spectrum of complex **2**, since those of the diazenido and acac ligands could be distinguished from each other by preparing *mer*-[W(acac-d_7)(NNCMeCH-COMe)(PMe_2Ph)$_3$] from the diazoalkane complex *mer*-[WCl_2-(NN=$CMeCH_2COMe$)(PMe_2Ph)$_3$] and $CD_3COCD_2COCD_3$/NEt_3 (vide supra).

The conversion of the alkenyldiazenido complex **2** into the alkenylhydrazido(2-) complexes **5** by treatment with acids and the regeneration of complex **2** from complexes **5** by bases are the type of reactions commonly observed for the diazenido complexes *trans*-[MX(NNR)(dpe)$_2$][5] and [MX(NNCOR)(dpe)$_2$] (M = W or Mo).[5a,d] However, the data concerning the equilibrium in solution between the diazenido and hydrazido(2-) complexes have not yet been reported. The ^{1}H NMR spectrum of a mixture of the alkenyldiazenido complex **2** and [$HNEt_3$][Br] in $CDCl_3$ showed the existence of an equilibrium between complex **2** and three isomers of complex **5** (X = Br), that is hydrazido(2-), keto-diazoalkane, and enol-diazoalkane complexes (eq 5). The

$$\text{complex } \mathbf{2} + [HNEt_3][Br] \rightleftharpoons \text{three isomers of complex } \mathbf{5} + NEt_3 \quad (5)$$

equilibrium constant K = [three isomers of complex **5**][NEt_3]/[complex **2**][$HNEt_3^+$] was estimated to be about 4. It is of great interest that the alkenyldiazenido ligand has a stronger basicity than trialkylamine.

(16) In the ^{1}H NMR spectrum of *mer*-[WBr_2(NN=$CMeCH_2COMe$)-(PMe_2Ph)$_3$] in CD_2Cl_2 recorded at 400 MHz appears the singlet peak assignable to the OH proton of enol form at 12.6 ppm in addition to the resonances described in ref 6b.

Table VII. Atomic Parameters (×10^4) and Equivalent Isotropic Temperature Factors (×10)

atom	x	y	z	B_{eq}[a]
W	−1028.2 (5)	3426.6 (3)	3115.8 (7)	23
Br	−2604.0 (22)	3525.8 (13)	7598.3 (27)	49
P(1)	−2526.2 (40)	3135.0 (28)	2284.5 (59)	33
P(2)	583.3 (37)	3576.2 (27)	3793.7 (57)	31
P(3)	−1561.8 (42)	4401.1 (26)	3690.8 (60)	31
O(1)	−539 (10)	2715 (7)	2178 (18)	40
O(2)	−828 (10)	3320 (6)	1409 (15)	32
O(3)	−407 (18)	1104 (9)	5967 (24)	66
N(1)	−1236 (12)	3111 (7)	4586 (17)	28
N(2)	−1339 (13)	2861 (9)	5717 (18)	37
C(1)	−1194 (17)	2114 (13)	7167 (28)	51
C(2)	−1035 (20)	2294 (10)	5816 (18)	34
C(3)	−697 (18)	1979 (11)	4908 (25)	41
C(4)	−375 (17)	1408 (11)	5082 (21)	35
C(5)	38 (25)	1142 (12)	3891 (36)	58
C(6)	−56 (21)	1999 (15)	811 (30)	54
C(7)	−290 (15)	2620 (12)	1084 (23)	36
C(8)	−242 (21)	3047 (14)	171 (29)	50
C(9)	−517 (17)	3601 (12)	350 (14)	38
C(10)	−440 (27)	4052 (15)	−639 (32)	65
C(11)	−3402 (19)	3047 (12)	3491 (30)	48
C(12)	−3030 (19)	3596 (10)	1103 (28)	45
C(111)	−2521 (17)	2424 (11)	1617 (23)	39
C(112)	−2374 (17)	1938 (11)	2419 (32)	47
C(113)	−2418 (26)	1375 (14)	1978 (46)	81
C(114)	−2551 (16)	1294 (16)	637 (36)	65
C(115)	−2676 (26)	1756 (15)	−96 (30)	61
C(116)	−2643 (21)	2307 (13)	305 (29)	49
C(21)	1275 (21)	2895 (13)	3583 (32)	54
C(22)	688 (19)	3715 (17)	5476 (27)	57
C(211)	1309 (13)	4122 (9)	3110 (28)	32
C(212)	2202 (17)	4167 (15)	3604 (35)	58
C(213)	2716 (23)	4575 (13)	3017 (37)	61
C(214)	2528 (25)	4904 (12)	2060 (43)	69
C(215)	1659 (21)	4836 (13)	1569 (31)	54
C(216)	1041 (22)	4439 (10)	2084 (24)	45
C(31)	−2666 (19)	4451 (14)	4410 (29)	51
C(32)	−1709 (25)	4868 (13)	2354 (28)	56
C(311)	−873 (15)	4832 (9)	4787 (28)	39
C(312)	−1005 (22)	4764 (11)	6065 (21)	42
C(313)	−512 (22)	5114 (13)	6823 (26)	53
C(314)	138 (25)	5502 (13)	6398 (40)	66
C(315)	260 (20)	5542 (13)	5209 (37)	60
C(316)	−169 (18)	5213 (11)	4323 (30)	44

[a] $B_{eq} = {}^4/_3 \times (\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$.

Reaction of *trans*-[WF(NNCMeCHCOMe)(dpe)$_2$] (3) with HCl gas. Treatment of complex **3** (M = W) with 1.5 equiv of HCl gas in THF gives the diazoalkane complex *trans*-[WF(NN=$CMeCH_2COMe$)(dpe)$_2$]Cl (**6**) in good yield (eq 6). The IR

$$trans\text{-}[WF(NNCMeCHCOMe)(dpe)_2] \xrightarrow{HCl\ gas} trans\text{-}[WF(NN{=}CMeCH_2COMe)(dpe)_2]Cl \quad (6)$$
$$\mathbf{6}$$

spectrum of complex **6** shows strong bands at 1710 and 1580 cm^{-1} assignable to ν(C=O) and ν(C=N), respectively. The ^{1}H NMR spectrum shown in the Experimental Section as well as the IR spectrum of complex **6** are in good agreement with those of complex **4**, indicating that complex **6** exists in one diazoalkane form even in solution. Difference in the favored isomeric forms between complexes **5** and **6** may be due to the steric crowdedness. Since the organic group bonded to the nitrogen atom is located in the sterically crowded environment made by two dpe ligands in complex **6**, the structure IV which permitts the free rotation around the C(2)–C(3) and C(3)–C(4) bonds is much more favored than the strucures III or V having conjugated double bonds which tend to be coplanar.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. IR spectra were measured by Hitachi

Table VIII. Anisotropic Temperature Factors ($\times 10^5$)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	246 (2)	113 (1)	455 (4)	20 (2)	16 (5)	2 (3)
Br	626 (16)	213 (6)	923 (24)	54 (8)	174 (17)	−11 (10)
P(1)	255 (24)	176 (12)	768 (53)	−2 (14)	−48 (31)	−26 (21)
P(2)	216 (22)	189 (13)	696 (49)	21 (13)	−41 (29)	16 (21)
P(3)	357 (28)	128 (10)	706 (51)	71 (14)	−94 (34)	−25 (20)
O(1)	251 (66)	144 (29)	1400 (234)	54 (37)	53 (105)	29 (68)
O(2)	356 (81)	120 (26)	818 (141)	0 (36)	7 (88)	18 (52)
O(3)	847 (158)	229 (47)	1551 (287)	170 (71)	369 (186)	247 (101)
N(1)	335 (93)	89 (28)	709 (158)	17 (39)	−60 (96)	−114 (57)
N(2)	353 (92)	221 (46)	628 (163)	−12 (54)	90 (108)	93 (76)
C(1)	356 (127)	264 (61)	1347 (351)	34 (70)	118 (165)	362 (123)
C(2)	471 (113)	184 (43)	452 (150)	−13 (78)	163 (146)	121 (69)
C(3)	440 (126)	188 (53)	881 (240)	35 (68)	243 (150)	86 (96)
C(4)	401 (114)	179 (50)	647 (188)	−13 (61)	42 (133)	51 (80)
C(5)	745 (206)	158 (55)	1529 (405)	56 (87)	−86 (248)	−20 (124)
C(6)	470 (149)	313 (82)	1090 (315)	88 (93)	250 (187)	−74 (137)
C(7)	246 (95)	247 (59)	682 (198)	7 (62)	−70 (121)	−95 (94)
C(8)	510 (155)	252 (76)	1024 (292)	68 (86)	108 (184)	79 (122)
C(9)	507 (122)	338 (72)	−108 (95)	113 (75)	130 (87)	119 (66)
C(10)	813 (224)	318 (85)	1113 (328)	−129 (115)	20 (241)	382 (148)
C(11)	438 (131)	192 (55)	1337 (348)	−85 (73)	145 (178)	−23 (112)
C(12)	559 (145)	114 (40)	1275 (303)	−17 (62)	−560 (187)	−23 (91)
C(111)	349 (108)	206 (51)	839 (260)	−100 (63)	−160 (135)	−35 (90)
C(112)	310 (108)	169 (48)	1607 (363)	−26 (62)	248 (173)	−38 (113)
C(113)	873 (234)	247 (70)	2338 (579)	−166 (106)	927 (349)	−313 (188)
C(114)	142 (93)	433 (97)	1825 (444)	32 (78)	−428 (178)	−232 (175)
C(115)	801 (219)	304 (84)	970 (283)	−106 (107)	130 (214)	−267 (127)
C(116)	523 (156)	222 (62)	1095 (309)	135 (83)	37 (186)	−4 (115)
C(21)	551 (167)	226 (62)	1342 (339)	96 (82)	225 (197)	−88 (124)
C(22)	356 (121)	461 (103)	834 (257)	−79 (95)	17 (157)	−204 (140)
C(211)	234 (74)	123 (34)	1035 (219)	−24 (42)	−139 (147)	−78 (98)
C(212)	250 (108)	322 (79)	1709 (430)	45 (77)	301 (183)	11 (154)
C(213)	689 (181)	244 (65)	1422 (375)	−145 (91)	274 (259)	10 (156)
C(214)	733 (194)	179 (57)	2144 (549)	−200 (90)	−9 (313)	117 (162)
C(215)	586 (166)	213 (60)	1299 (376)	−31 (84)	9 (202)	−13 (121)
C(216)	594 (136)	160 (41)	975 (264)	14 (80)	168 (210)	142 (88)
C(31)	379 (129)	299 (74)	1106 (305)	34 (82)	−140 (176)	−173 (130)
C(32)	852 (223)	228 (63)	872 (258)	25 (99)	−365 (206)	146 (111)
C(311)	273 (112)	85 (33)	1569 (324)	40 (48)	25 (151)	−60 (89)
C(312)	566 (136)	206 (49)	628 (182)	38 (87)	256 (171)	−168 (81)
C(313)	740 (177)	294 (68)	602 (200)	144 (92)	−407 (187)	73 (121)
C(314)	697 (202)	168 (60)	2110 (534)	75 (96)	−152 (282)	−126 (146)
C(315)	402 (136)	192 (59)	2117 (505)	−137 (75)	−391 (229)	16 (146)
C(316)	446 (133)	129 (44)	1350 (327)	35 (64)	129 (180)	83 (106)

215 and Shimadzu IR 400 spectrometers, and NMR spectra were measured by a JEOL GX-400 spectrometer. Complexes *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**),[17] *trans*-$[WF(NN{=}CMeCH_2COMe)(dpe)_2][BF_4]$ (**4**),[6a] and *mer*-$[WCl_2(NN{=}CMeCH_2COMe)(PMe_2Ph)_3]$[6b] were prepared according to the published methods.

Preparation of *mer*-[W(acac)(NNCMeCHCOMe)(PMe_2Ph)$_3$] (2). **(a)** An orange suspension of complex **1** (1.00 g, 1.26 mmol) in methanol (16 mL) and acetylacetone (4.0 mL, 39 mmol) was stirred for 24 h at 50 °C. The resultant purple solution was dried up in vacuo, and the residue was dissolved in ether (25 mL). The mixture was filtered, and hexane (25 mL) was added to the filtrate to precipitate green crystals. The product was filtered off, washed with hexane (10 mL × 2), and dried in vacuo (yield, 445 mg (44%)). Anal. Calcd for $C_{34}H_{47}N_2O_3P_3W$: C, 50.51; H, 5.86; N, 3.46. Found: C, 50.43; H, 6.23; N, 3.33.

(b) Complex **1** (254 mg, 0.321 mmol) was suspended in acetylacetone (5 mL), and the mixture was stirred for 13 h at 40 °C. The resultant dark brown solution was dried up in vacuo, and the residue was dissolved in ether (6 mL). The mixture was filtered, and hexane (6 mL) was added slowly to the filtrate to precipitate green crystals, which were filtered off, washed with hexane (4 mL × 2), and then dried in vacuo (yield, 116 mg (45%)). The product shows the same IR and ^1H NMR spectra as those of complex **2** prepared by method a.

Preparation of *trans*-[MF(NNCMeCHCOMe)(dpe)$_2$] (3). (a) M = W. A brown suspension of complex **4** (1:1 THF solvate, 249 mg, 0.198 mmol) in THF (5 mL) was stirred with sodium methoxide (21.9 mg, 0.405 mmol) overnight at room temperature. The resultant orange suspension was dried up in vacuo, and the residue was extracted with benzene (10 mL). The extract was concentrated in vacuo to about 4 mL, and hexane (6 mL) was added to precipitate orange crystals, which were filtered off, washed with hexane, and dried in vacuo. Complex **3** crystallizes as the 1:1 benzene solvate. The amount of benzene was determined quantitatively by GLC analysis by using a Ohkura Model 103 Gas Chromatograph (yield, 172 mg (74%)). Anal. Calcd for $C_{63}H_{61}N_2OP_4FW$: C, 63.64; H, 5.17; N, 2.36. Found: C, 62.98; H, 5.23; N, 2.31.

(b) M = Mo. A green-brown suspension of complex **4** (485 mg, 0.410 mmol) in THF (13 mL) was stirred with sodium methoxide (44 mg, 0.81 mmol) for 2 h at room temperature. The resultant orange solution was dried up in vacuo, and the residue was extracted with benzene (15 mL) for 3 h. The mixture was filtered, and the filtrate was concentrated to about 5 mL in vacuo. Hexane (8 mL) was added to the concentrated solution to precipitate dark red crystals, which were filtered off, washed with hexane (5 mL × 2), and dried in vacuo (yield, 368 mg (88%)). Anal. Calcd for $C_{57}H_{55}N_2OP_4FMo$: C, 66.93; H, 5.42; N, 2.74. Found: C, 67.82; H, 5.46; N, 2.77.

Preparation of *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]X (5). (a) X = Cl. Hydrogen chloride gas (0.26 mmol) was condensed at −196 °C in vacuo onto complex **2** (138 mg, 0.171 mmol) in CH_2Cl_2 (5 mL). The mixture was allowed to warm to room temperature and stirred for 30 min. The resultant red solution was concentrated to 2 mL in vacuo, and hexane (10 mL) was added with stirring to precipitate a reddish brown solid. The crude compound was filtered off, dried in vacuo, and then crystallized from acetone (5 mL)/ether (15 mL). Red crystals deposited were filtered off, washed with hexane (5 mL × 2), and then dried in vacuo (yield, 88 mg (58%)). Anal. Calcd for $C_{34}H_{48}N_2O_3P_3ClW$: C, 48.33; H, 6.73; N, 3.31; Cl, 4.20. Found: C, 48.24; H, 6.02; N, 3.28; Cl, 4.41.

(b) X = Br. The Br analogue was obtained in a similar way from complex **2** (418 mg, 0.517 mmol) and hydrogen bromide gas (0.671 mmol) as red crystals (yield, 262 mg, 57%)). Anal. Calcd for

(17) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074.

$C_{34}H_{48}N_2O_3P_3BrW$: C, 45.91; H, 5.44; N, 3.15; Br, 8.98. Found: C, 45.14; H, 5.43; N, 2.92; Br, 9.06.

Preparation of *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]Cl (5) from *mer*-[WCl_2(NNH$_2$)(PMe_2Ph)$_3$] via *mer*-[WCl_2(NN=CMeCH$_2$COMe)(PMe_2Ph)$_3$]. To a suspension of *mer*-[WCl_2(NNH$_2$)(PMe_2Ph)$_3$] (346 mg, 0.494 mmol) in CH_2Cl_2 (10 mL) was added acetylacetone (1.5 mL, 15 mmol) and hydrochloric acid (35% solution, 4 μL). The condensation reaction proceeds smoothly to give a dark red solution of *mer*-[WCl_2(NN=CMeCH$_2$COMe)(PMe_2Ph)$_3$] in 10 min. After the solution was stirred for 3 h, triethylamine (2.1 mL, 15 mmol) was added, and the mixture was then stirred overnight. The resultant black-yellow solution was dried up in vacuo, washed with ether (15 mL), and then extracted with acetone (15 mL). Addition of ether (40 mL) to the extract deposited red crystals of complex **5** (X = Cl), which were filtered off, washed with hexane repeatedly, and dried in vacuo (yield, 194 mg (46%)).

^{1}H NMR Study of *mer*-[W(acac-d_7)(NNCMeCHCOMe)(PMe_2Ph)$_3$]. $CD_3COCD_2COCD_3$ was obtained in satisfactory yield by refluxing $CH_3COCH_2COCH_3$ with D_2O in the presence of a catalytic amount of NaOH. The complex **5** with acac-d_7 ligand *mer*-[W(acac-d_7)(NNDCMeCHCOMe)(PMe_2Ph)$_3$]Cl was prepared according to the method described above from isolated *mer*-[WCl_2(NN=CMeCH$_2$COMe)(PMe_2Ph)$_3$] and excess $CD_3COCD_2COCD_3$/NEt_3 in CH_3OD. The complex **5** with acac-d_7 ligand was dissolved in CD_2Cl_2 and then treated with excess triethylamine (ca. 5 mol equiv). The ^{1}H NMR spectrum of this mixture was recorded directly and compared with that of complex **2**. The resonances of methyl and methine protons that disappeared by the replacement with acac-d_7 were assigned to those of acac ligands in complex **2**.

Investigation of an Equilibrium in Solution between *mer*-[W(acac)(NNCMeCHCOMe)(PMe_2Ph)$_3$] (2) and *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]Br (5) and Its Two Diazoalkane Isomers. A solution of [$HNEt_3$][Br] (12.8 mg, 0.0703 mmol) in $CDCl_3$ (0.6 mL) was added into a solution of complex **2** (8.9 mg, 0.011 mmol) in $CDCl_3$ (0.6 mL) charged in a NMR sample tube. The ^{1}H NMR spectrum of this mixture showed the existence of an equilibrium between complex **2** and three isomers of complex **5**, that is hydrazido(2−) and two diazoalkane isomers. The equilibrium constant K = [three isomers of complex **5**][NEt_3]/[complex **2**][$HNEt_3^+$] was calculated as follows. Each concentration of complex **2** and three isomers of complex **5** were estimated on the basis of the intensity ratio of the resonances of the methine protons in the four complexes, where the total amount of the complexes was 0.011 mmol. The concentration of NEt_3 was regarded as the sum of those of three isomers of complex **5** and that of $HNEt_3^+$ was determined by subtracting the concentration of NEt_3 from the initial concentration of $HNEt_3^+$.

Preparation of *trans*-[WF(NN=CMeCH$_2$COMe)(dpe)$_2$]Cl (6). Hydrogen chloride gas (0.164 mmol) was condensed onto complex **3** (1:1 benzene solvate, 130 mg, 0.109 mmol) in THF (8 mL). After being allowed to warm to room temperature, the mixture was stirred at room temperature for 40 min, and the resultant yellow-brown suspension was dried in vacuo. Crystallization of the green residue from CH_2Cl_2 (2 mL)/hexane (4 mL) gave green crystals, which were filtered off, washed with hexane (4 mL × 2), and then dried in vacuo. Complex **6** crystallizes as the 1:2 CH_2Cl_2 solvate. The amount of CH_2Cl_2 was determined by recording the ^{1}H NMR spectrum of complex **6** in $CDCl_3$ (yield, 131 mg (97%)): ^{1}H NMR ($CDCl_3$, relative to Me_4Si) 2.28 (s, 3 H, CH_3CO), −0.58 (s, 3 H, CH_3CNN), 2.93 (s, 2 H, CCH_2C), 2.75, 3.00 (br m, 4 H each, PCH_2CH_2P), 6.8−7.4 (m, 40 H, C_6H_5P), 5.30 ppm (s, 4 H, solvated CH_2Cl_2). Anal. Calcd for $C_{59}H_{60}N_2OP_4Cl_5FW$: C, 53.80; H, 4.59; N, 2.13. Found: C, 53.63; H, 4.62; N, 2.11.

Crystallographic Data. Dark red prism-like crystals of *mer*-[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)$_3$]Br were prepared as described above and sealed in a glass capillary under a nitrogen atmosphere. Data collection was carried out on an automatic Rigaku four-circle diffractometer, using LiF-monochromated Mo K_α radiation. The lattice parameters of the crystals were determined by a least-squares fit to the setting angles for 37 hand-centered reflections with $25° < 2\theta < 32°$. The intensity data were measured by the 2θ–θ scan mode, which prove the space group to be $P2_12_12_1$. In Table III are summarized the crystallographic data and details of data collection. Lorentz and polarization corrections were applied to the data, followed by absorption correction.

Determination and Refinement of the Structure. The crystal structure was solved by conventional Patterson synthesis to locate the tungsten atom. Fourier syntheses were then carried out for the location of the remaining atoms except for the hydrogen atoms. The positional parameters were refined by the block-diagonal least-squares technique.[18] Scattering factors and anomalous dispersion corrections for W, Br, and P atoms were taken from ref 19.

The quantity $w(|F_o| - |F_c|)^2$ was minimized and a weighting scheme was $w = 0.3$ for $F_o < 3.6$, $w = 1.0$ for $3.6 \le F_o < F_{max}$, and $w = (F_{max}/|F_o|)^2$ for $F_o \ge 8.9$. In the refinement, the R value was 0.092. The standard deviation of an observation of unit weight defined as $[w(|F_o| - |F_c|)^2/(N - M)]$ was 0.35, where N and M are defined as the number of reflections and the number of refined parameters, respectively. The positional parameters obtained from the last cycle of refinement are listed in Table VII with the associated deviations estimated from the inverse matrix. (See Table VIII also).

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

(18) The UNICS program for the M-280H (Hitachi) was employed at Tokyo University Computer Centre; Ueda's PAMI patterson program, Iwasaki's ANSFR-2 Fourier synthesis program, Ashida's HBLS-4 block-diagonal least-squares program, modified Johnson's ORTEP thermal ellipsoid plot program, and the lattice constant and absorption correction program in the X-ray system's program made by Stewert et al.

(19) (a) Cromer, D. T.; Waber, J. T. Table 2.2a In "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV. (b) Cromer, D. T.; Liberman, D. Table 2.3.1 In "International Tables for X-ray Crystallography"; Kynoch Press: Birmningham, 1974; Vol. IV.