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Reactivities of Molybdenum and Tungsten Diazoalkane–Isocyanide Complexes Derived from Dinitrogen Complexes[1)]

Yuji Harada, Yasushi Mizobe, Takayuki Aoshima,[†] Hiroyuki Oshita,[†] and Masanobu Hidai[*,†]

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

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

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The diazoalkane–isocyanide complexes *cis,trans*-$[MX_2(NN{=}CMePh)(CNBu^t)(PMe_2Ph)_2]$ (**1a**: M = Mo, X = Cl; **1b**: M = W, X = Cl; **1c**: M = W, X = Br), readily derived from dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$, reacted with $AlMe_3$ at room temperature to give the aminocarbene–diazoalkane complexes *cis,trans*-$[MX_2(NN{=}CMePh)\{{=}C(Me)NHBu^t\}(PMe_2Ph)_2]$ (**2a**: M = Mo, X = Cl; **2b**: M = W, X = Cl; **2c**: M = W, X = Br) after hydrolysis. Treatment of **1b** with TfOH ($Tf = CF_3SO_2$) and then with Bu^tNC at room temperature resulted in the formation of a cationic bis(isocyanide)–diazoalkane complex *trans,trans*-$[WCl(NN{=}CMePh)(CNBu^t)_2(PMe_2Ph)_2]$ [OTf] (**3**). The detailed structures of **2b** and **3** have been determined by single-crystal X-ray analyses.

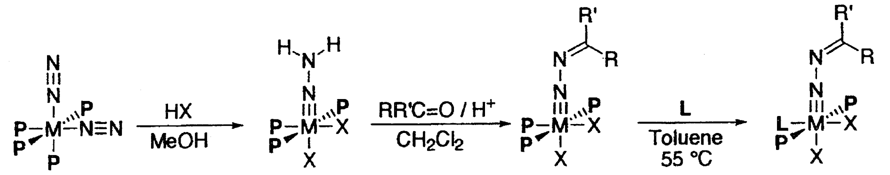
Development of chemical transformations of molecular nitrogen into organo-nitrogen compounds under mild conditions will be essential for a new generation of industrial nitrogen fixation. In this context, reactions to convert the N_2 coordinated in metal complexes into organo-nitrogen ligands have been drawing significant attention recently.[2)] We have previously reported the synthesis of the diazoalkane complexes *cis,mer*-$[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ (M = Mo, W; X = Cl, Br, I)[3)] and *trans*-$[MF(NN{=}CRR')(Ph_2PCH_2CH_2PPh_2)_2]^+$ from the bis(dinitrogen) complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$. This provides one of the most versatile methods to form organo-nitrogen ligands from the N_2 ligand (Scheme 1).[4)] Extensive studies on these diazoalkane complexes have subsequently revealed their novel reactivities including the conversion of the diazoalkane ligands into amines and azines[4a)] as well as a variety of other organo-nitrogen ligands.[4a—4c)]

More recently, we have also shown that the diazoalkane complexes *cis,mer*-$[MCl_2(NN{=}CRR')(PMe_2Ph)_3]$ (M = Mo, W) readily undergo the replacement of one of the PMe_2Ph ligands by various π-acceptor molecules to afford a series of new diazoalkane complexes *cis,trans*-$[MCl_2(NN{=}CRR')(L)(PMe_2Ph)_2]$ (L = CO, isocyanide, olefin, aldehyde, etc.) (Scheme 1).[5)] Interestingly, the latter complexes contain both a potentially reactive substrate and a diazoalkane ligand in mutually *cis* positions, and hence more detailed study on the reactivities of these ligands might lead to the exploitation of new methods for converting molecular nitrogen into nitrogenous compounds. We have now investigated the reactivities of the diazoalkane–isocyanide complexes *cis,trans*-$[MX_2(NN{=}CMePh)(CNBu^t(PMe_2Ph)_2]$ (**1**) in detail, since for certain isocyanide complexes reactions have been reported, in which isocyanide ligands interact with multiply bonded co-ligands such as carbynes.[6)] By treatment with $AlMe_3$ and subsequent hydrolysis, complexes **1** could be converted into novel aminocarbene–diazoalkane complexes *cis,trans*-$[MX_2(NN{=}CMePh)\{{=}C(Me)NHBu^t\}(PMe_2Ph)_2]$ (**2**), although attempts to liberate nitrogen-containing organic compounds from **2** have been unsuccessful. Here we wish to describe the preparation and characterization of **2** in detail, as well as a cationic bis(isocyanide)–diazoalkane complex *trans,trans*-$[WCl(NN{=}CMePh)(CNBu^t)_2(PMe_2Ph)_2][OTf]$ (**3**). A part of this work has appeared in a preliminary form.[7)]

Results and Discussion

Reaction of 1 with $AlMe_3$: Synthesis of Aminocarbene–Diazoalkane Complexes. Treatment of diazoalkane-isocyanide complexes **1** with 1 equiv of $AlMe_3$ in toluene at room temperature for 1 h and the subsequent hydrolysis resulted in the formation of a series of aminocarbene–diazoalkane complexes **2** (Scheme 2). These have been characterized spectroscopically and by elemental analysis. The structure of **2b** has been confirmed by X-ray analysis (vide infra). The nature of the halogen ligand significantly affects the yield of **2**. Thus, for W complexes the chloro complex **2b** was isolated in much higher yield (54%) than the bromo complex **2c** (19%), while for the preparation of the iodo analogue, the starting *cis,trans*-$[WI_2(NN{=}CMePh)(CNBu^t)(PMe_2Ph)_2]$ (**1d**) was recovered quantitatively under the same reaction conditions.

Spectroscopic data for **2** are summarized in Table 1. In the IR spectrum of **2**, two characteristic bands are observed in the regions of 3279—3298 and 1518—1530 cm^{-1}, the former being assignable to ν(N–H) of the aminocarbene ligand and the latter to ν(C=N) of the diazoalkane ligand.



M = Mo, W
X = Cl, Br, I
P = PMe2Ph

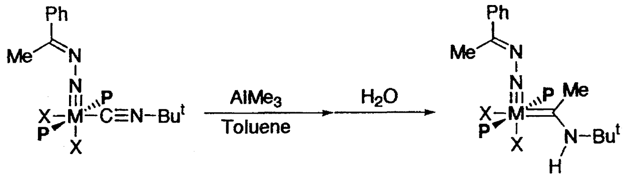
L = Isocyanide, Aldehyde, Olefin, CO, Alkyne, etc.

Scheme 1.

Table 1. IR and ^{1}H NMR Data for **2**

	M	X	IR[a)]	^{1}H NMR resonance[b)]
2a	Mo	Cl	ν(N–H) 3279	0.98 (s, 9H, N*Bu^t*)
			ν(C=N) 1518	1.84, 1.93 (t, 3H each, $J_{\mathrm{PH}} = 3.7$ Hz, P*Me*$_2$Ph)
				2.20 (s, 3H, N=C*Me*)
				2.89 (s, 3H, W=C*Me*)
				9.86 (s, 1H, N*H*)
2b	W	Cl	ν(N–H) 3298	1.03 (s, 9H, N*Bu^t*)
			ν(C=N) 1524	1.89, 1.96 (t, 3H each, $J_{\mathrm{PH}} = 3.9$ Hz, P*Me*$_2$Ph)
				1.98 (s, 3H, N=C*Me*)
				3.43 (t, 3H, $J_{\mathrm{PH}} = 1.6$ H, W=C*Me*)
				8.69 (s, 1H, N*H*)
2c	W	Br	ν(N–H) 3285	1.02 (s, 9H, N*Bu^t*)
			ν(C=N) 1530	1.98, 2.06 (t, 3H each, $J_{\mathrm{PH}} = 4.4$ Hz, P*Me*$_2$Ph)
				1.91 (s, 3H, N=C*Me*)
				3.35 (s, 3H, W=C*Me*)
				8.81 (s, 1H, N*H*)

a) cm^{-1}/KBr. b) ppm/C$_6$D$_6$. Reasonances of phenyl protons are omitted.



1a: M = Mo, X = Cl
1b: M = W, X = Cl
1c: M = W, X = Br

2a: M = Mo, X = Cl
2b: M = W, X = Cl
2c: M = W, X = Br

Scheme 2.

The ^{1}H NMR spectra of **2** show resonances due to the aminocarbene ligand in addition to those of the diazoalkane and PMe$_2$Ph ligands. The appearance of the methyl protons in two PMe$_2$Ph ligands as two triplets indicates that the two PMe$_2$Ph ligands are equivalent and present in mutually *trans* positions, where the two methyl groups in each PMe$_2$Ph ligand are inequivalent. As for the two signals arising from the methyl groups either attached to the carbene carbon or in the diazoalkane ligand, the signal in the lower field has been assigned to the former methyl group, since the chemical shift observed for the resonance ($\delta = 2.89$—3.43) is significantly larger if compared with the values of the methyl resonances of NN=CMePh ligands in the numerous diazoalkane complexes prepared previously ($\delta =$ ca. 2). In the spectrum of **2b**, a small coupling of the methyl protons with the two P nuclei was observed only for the lower-field resonance, which also supports this assignment.

Organic synthesis and catalysis using transition metal–carbene complexes have been the subject of great interest,[8,9] which has led to extensive studies on preparation of aminocarbene complexes. However, the synthetic routes involving the reaction of isocyanide complexes with AlR$_3$ are not precedented, although the conversion of coordinated isocyanides into aminocarbene ligands has already been demonstrated. This is initiated by the attack of nucleophiles such as RLi, amines, or alcohols on α-carbon.[10]

The precise mechanism of the present reaction is uncertain, but the initial step might be the adduct formation between **1** and AlMe$_3$ at the isocyanide N atom. This is supported by the result of the EHMO calculation on the model complex *cis*,*trans*-[WCl$_2$(NN=CH$_2$)(CNMe)(PH$_3$)$_2$], showing the presence of the highest electron density of HOMO on the N atom in the CNMe ligand. On the other hand, the ^{1}H NMR spectrum recorded immediately after mixing **1b** with an equimolar AlMe$_3$ in C$_6$D$_6$ showed the shift of the AlMe$_3$ resonances[11] to $\delta = -0.54$ and 3.10 with the intensity ratio of 2 : 1. The latter low-field signal is comparable to those assigned to the methyl groups attached to the carbene C atoms in **2**, indicating that one methyl group in the AlMe$_3$ bound to the N atom in the CNBu^t ligand migrates rapidly to the C atom attached to the metal center to form presumably an intermediate complex *cis*,*trans*-[WCl$_2$(NN=CMePh){=C(Me)N(AlMe$_2$)Bu^t}(PMe$_2$Ph)$_2$]. Upon addition of ca. 3 molar equiv of H$_2$O to this mixture, the signal at $\delta = -0.54$ arising from the AlMe$_2$ moiety disappeared and alternatively the

NH resonance emerged. For the product obtained by treatment of the reaction mixture of **1b** and $AlMe_3$ with D_2O, the IR spectrum showed ν(N–D) band at 2448 cm^{-1} instead of the ν(N–H) band observed at 3298 cm^{-1} for **2b**, while the NH resonance is no longer present in the ^{1}H NMR spectrum, demonstrating unequivocally that the amino proton in **2** has its origin in the added H_2O.

Structure of 2. The detailed structure of **2b** has been determined by the X-ray crystallography. The ORTEP drawing is depicted in Fig. 1, and selected bond distances and angles are summarized in Table 2. The X-ray analysis has unambiguously demonstrated the presence of the aminocarbene ligand *cis* to the diazoalkane ligand and *trans* to one of the chloride ligands in a slightly distorted octahedron. For the remaining four coordination sites, two chloride and PMe_2Ph ligands occupy mutually *cis* and *trans* positions, respectively.

In the diazoalkane ligand, the W–N–N linkage is essentially linear (171(1)°), while the N–N–C moiety is bent with the angle of 118(1)°. The W, N(2), N(3), and C(31)–C(38) atoms lie nearly on the same plane. The N(2)–N(3) and N(3)–C(31) bond lengths at 1.31(2) and 1.32(3) Å, respectively, are comparable to those in the related diazoalkane complexes reported previously (e.g., *cis,trans*-[$WCl_2(NN{=}CMePh)(\eta^2\text{-}p\text{-}MeC_6H_4CHO)(PMe_2Ph)_2$]: N–N, 1.29(2) Å; N–C, 1.27(2) Å).[5]

In the aminocarbene ligand, the W–C(1) distance at 2.05(2) Å is not exceptional if compared with the W–C double bond lengths observed in the W carbene complexes reported previously (e.g., [$WCl_2(O)(=CHBu^t(PMe_3)_2$]: 1.986(21) Å,[12] [$WCl_2(O)(=C(CH_2)_5)(PPh_2Me)_2$]: 1.980(12) Å,[13] [$WCl_2(NPh)(=CHC_6H_4\text{-}p\text{-}Me)(PPh_2Me)_2$]: 1.975(3) Å[14]). The C(1)–N(1) bond length of 1.35(3) Å is indicative of a bond order larger than unity, as is commonly observed in the other aminocarbene ligands (e.g., [$Cr(=CMeNHMe)(CO)_5$]: 1.33(3) Å[15]). The Me and Bu^t groups are bound to this multiply-bonded C–N moiety in a *syn* configuration. The W, C(1), C(2), and N(1) atoms are coplanar and this plane is perpendicular to the *xy* plane when the *z* axis is defined as coincident with the W–N(2) bond. The EHMO calculation of the model complex *cis,trans*-[$WCl_2(NN{=}CH_2)(=CHNH_2)(PH_3)_2$] (**2′**) has suggested that this geometry is favorable because of the occurrence of the effective overlap between the filled d$_{xy}$ orbital of the W atom (HOMO) and the empty p orbital of the sp^2 hybridized carbene carbon atom (Fig. 2). The equivalent nature of two PMe_2Ph ligands from the NMR criteria noted above is explained well by this orientation of the carbene ligand.

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

a) Bond length (Å)			
W–N(2)	1.77(2)	W–C(1)	2.05(2)
W–Cl(1)	2.536(6)	W–Cl(2)	2.503(6)
W–P(1)	2.487(6)	W–P(2)	2.470(6)
N(1)–C(1)	1.35(3)	N(2)–N(3)	1.31(2)
N(3)–C(31)	1.32(3)	C(31)–C(32)	1.48(2)
C(31)–C(33)	1.48(3)		
b) Bond angle (°)			
C1(1)–W–Cl(2)	83.3(2)	C1(1)–W–P(1)	85.3(2)
Cl(1)–W–P(2)	89.0(2)	Cl(1)–W–N(2)	96.8(5)
Cl(1)–W–C(1)	169.9(5)	Cl(2)–W–P(1)	87.3(2)
Cl(2)–W–P(2)	83.4(2)	Cl(2)–W–N(2)	176.8(5)
Cl(2)–W–C(1)	86.6(5)	P(1)–W–P(2)	169.6(2)
P(1)–W–N(2)	95.9(5)	P(1)–W–C(1)	93.7(5)
P(2)–W–N(2)	93.4(6)	P(2)–W–C(1)	90.4(5)
N(2)–W–C(1)	93.4(7)	C(1)–N(1)–C(3)	133(1)
W–N(2)–N(3)	171(1)	N(2)–N(3)–C(31)	118(1)
W–C(1)–N(1)	125(1)	W–C(1)–C(2)	122(1)
N(1)–C(1)–C(2)	113(1)	N(3)–C(31)–C(32)	124(2)
N(3)–C(31)–C(33)	115(1)	C(32)–C(31)–C(33)	121(2)

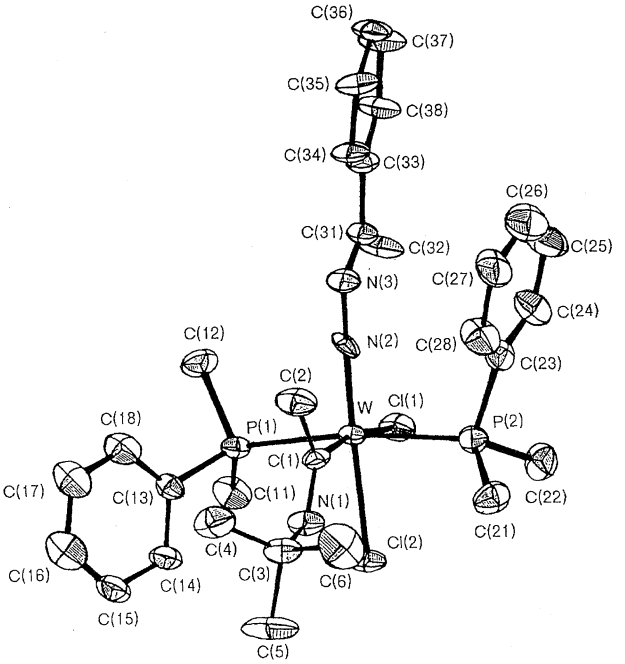


Fig. 1. Molecular structure of **2b**.

Analogous π-back donation from the d^2 metal center towards the direction *cis* to the metal-ligand multiple bond has been demonstrated previously in *cis,trans*-[$MCl_2(NN{=}CRR')(L)(PMe_2Ph)_2$] (M = Mo, W) shown above and [$WCl_2(E)(L)(PR_3)_2$] (E = S, O, NR′; L = olefins, Bu^{t}NC, etc.).[16]

It is also to be noted that ^{1}H NMR spectra of **2** exhibit only one set of resonances arising from the aminocarbene ligand at room temperature; this feature is essentially unaltered in

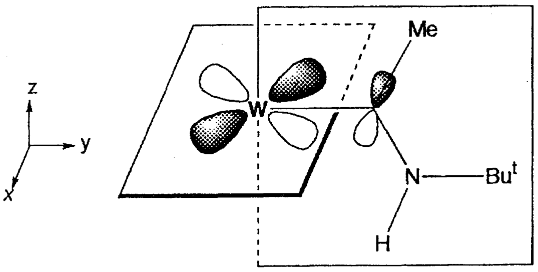


Fig. 2. Interaction of the d$_{xy}$ orbital of the W atom with the p orbital of the carbene carbon.

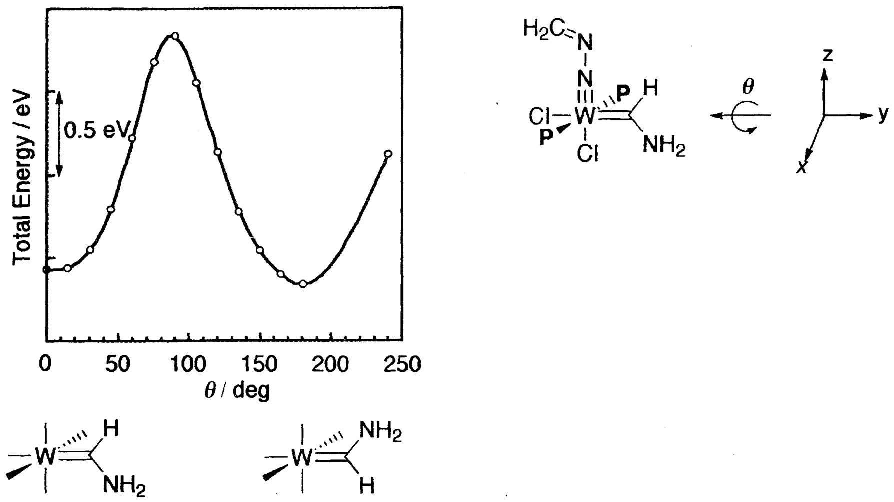
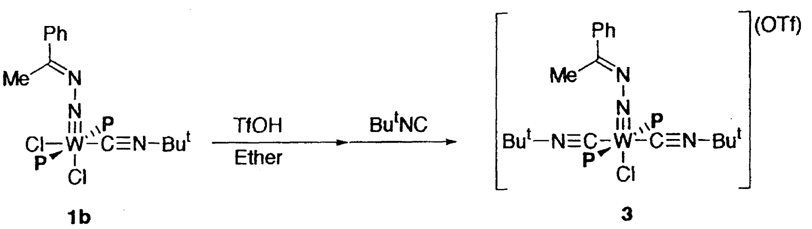


Fig. 3. Change in total energy for rotation of aminocarbene ligand around the *y* axis in *cis,trans*-[$WCl_2(NN{=}CH_2)({=}CHNH_2)(PH_3)_2$].



Scheme 3.

the temperature range from −60 to 100 °C for the spectrum of **2b**. This finding suggests that the solid state structure of the aminocarbene ligand shown in Fig. 2 is preserved in the solution state and the rotation around the W–C axis does not occur even at 100 °C. In the EHMO calculation of the model complex (**2′**), the rotation barrier was estimated to be ca. 1 eV (Fig. 3), which is consistent with the result of the variable temperature ^{1}H NMR spectrum study.

Reaction of 1b with TfOH Forming a Bis(isocyanide)–Diazoalkane Complex. Conversion of the coordinated isocyanide in **1** to an aminocarbyne ligand by protonation has also been attempted. Introduction of a carbyne ligand, viz., metal–carbon triple bond, *cis* to the diazoalkane ligand might open a new pathway to synthesize organo-nitrogen compounds via the coupling of these two ligands. As a convenient method to prepare aminocarbynes from isocyanides in the coordination sphere, reactions of certain isocyanide complexes with protic acids have been well documented.[17] However, treatment of diazoalkane-isocyanide complexes **1** with HCl gas resulted in the quantitative recovery of **1**.

Reaction of **1b** with TfOH also did not result in the formation of the expected aminocarbyne complex. However, a cationic complex containing two Bu^{t}NC ligands *trans,trans*-[$WCl(NN{=}CMePh)(Bu^tNC)_2(PMe_2Ph)_2$][OTf] (**3**) has been isolated in ca. 30% yield from the reaction mixture. As expected, subsequent treatment of this reaction mixture with Bu^{t}NC increased the yield of **3** to 50% (Scheme 3).

The detailed structure of **3** has been determined by the X-ray analysis. The ORTEP drawing is shown in Fig. 4, and bond distances and angles are summarized in Table 3. The geometry around the W center is essentially octahedral and two Bu^{t}NC and two PMe_2Ph ligands each occupy the mutually *trans* positions. The bonding parameters associated with the diazoalkane ligand in **3** are comparable to those in **2b**; the W–N–N linkage is essentially linear (172.6(4)°), while the N–N–C moiety is bent with the angle of 119.5(5)°. The C–N–C linkages in the isocyanide ligands are almost linear (178.2(6)°, 176.6(6)°), whereas the slightly bent C–N–C

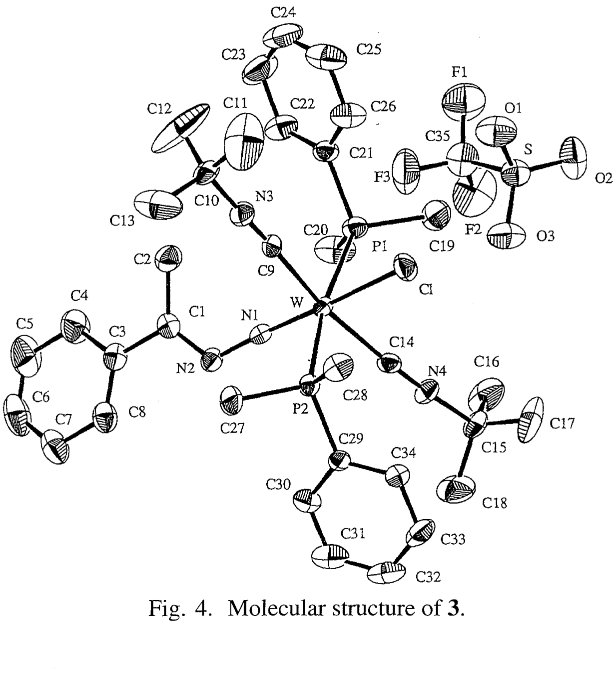


Fig. 4. Molecular structure of **3**.

Table 3. Selected Bond Lengths and Angles in **3**

a) Bond length (Å)			
W–Cl	2.436(1)	W–P(1)	2.519(2)
W–P(2)	2.496(1)	W–N(1)	1.744(4)
W–C(9)	2.093(5)	W–C(14)	2.135(5)
N(1)–N(2)	1.342(5)	N(2)–C(1)	1.287(6)
N(3)–C(9)	1.166(6)	N(3)–C(10)	1.453(6)
N(4)–C(14)	1.142(6)	N(4)–C(15)	1.445(6)
C(1)–C(2)	1.483(7)	C(1)–C(3)	1.484(7)
b) Bond angles (°)			
Cl–W–P(1)	85.61(5)	Cl–W–P(2)	86.34(5)
Cl–W–N(1)	174.8(1)	Cl–W–C(9)	83.1(1)
Cl–W–C(14)	86.6(1)	P(1)–W–P(2)	170.71(5)
P(1)–W–N(1)	97.3(1)	P(1)–W–C(9)	94.1(1)
P(1)–W–C(14)	85.2(1)	P(2)–W–N(1)	91.1(1)
P(2)–W–C(9)	89.5(1)	P(2)–W–C(14)	89.7(1)
N(1)–W–C(9)	92.3(2)	N(1)–W–C(14)	98.0(2)
C(9)–W–C(14)	169.7(2)	W–N(1)–N(2)	172.6(4)
N(1)–N(2)–C(1)	119.5(5)	N(2)–C(1)–C(2)	124.7(5)
N(2)–C(1)–C(3)	116.9(5)	C(2)–C(1)–C(3)	118.4(5)
C(9)–N(3)–C(10)	178.2(6)	C(14)–N(4)–C(15)	176.6(6)
W–C(9)–N(3)	177.3(5)	W–C(14)–N(4)	177.0(5)

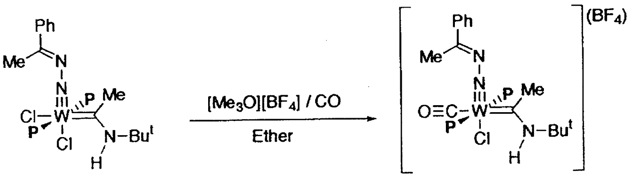
moieties (156(1)°) are found in the bis(isocyanide) complex of molybdenum *trans*-[Mo(CNMe)$_2$(dppe)$_2$].[18]

The ^{1}H NMR and IR spectra for **3** correspond well to the X-ray structure. Thus, in the ^{1}H NMR spectrum the Bu^t protons in the two Bu^{t}NC ligands and the methyl protons in the two PMe$_2$Ph ligands were recorded as one singlet and one triplet, respectively. The IR spectrum showed two characteristic bands at 2133 and 1522 cm^{-1}, the former of which is assignable to ν(NC) in the CNBu^t ligands and the latter to ν(C=N) in the diazoalkane ligand.

In the present reaction forming **3** from **1b**, substitution of the weakly coordinating OTf anion of the Cl ligand *trans* to the CNBu^t ligand is taking place. The Cl ligand might be removed as HCl through interaction with HOTf and the generated vacant site is presumably occupied by CNBu^t rather than the OTf anion. The reaction course observed here might relate to that affording *mer*-[WCl(NN=CMe$_2$)(CO)(PMe$_2$Ph)$_3$][ZnCl$_3$(dioxane)] from the reaction of *cis,mer*-[WCl$_2$(NN=CMe$_2$)(PMe$_2$Ph)$_3$] with ZnCl$_2$ (dioxane) under CO.[19]

Reaction of 2b with [Me$_3$O][BF$_4$]: Synthesis of a Cationic Aminocarbene–Diazoalkane Complex. As unambiguously demonstrated, complexes **2** contain both diazoalkane and carbene ligands in mutually *cis* positions. Though a number of diazoalkane complexes and carbene complexes have appeared in the literature, the complexes having both of these ligands are quite rare. To our knowledge, the only precedented example of this type is a dinuclear Mo complex [Cp(CO)$_3$MoMo(CAr$_2$)(NNCAr$_2$)Cp] (Cp = η^5-C$_5$H$_5$; Ar = 4-MeC$_6$H$_4$).[20] However, reactivities of this complex are unknown.

The reactivities of **2** have therefore been investigated extensively, but any intriguing reactions such as the coupling of the diazoalkane and carbene ligands to give organo-nitrogen compounds have not yet been exploited. For example, neither thermolysis nor chemical reduction of **2b** proceeded cleanly, giving a small amount of PhMeC=CMePh as an only characterizable product. It is to be noted, however, that we have found the reaction of **2b** with [Me$_3$O][BF$_4$] under CO results in the formation of the cationic aminocarbene–diazoalkane complex *trans,trans*-[WCl(NN=CMePh){=C(Me)-NHBu^t}(CO)(PMe$_2$Ph)$_2$] [BF$_4$] (**4**) in high yield (Eq. 1).



2b **4**

(1)

Complex **4** was characterized by the spectroscopic and analytical data. The ν(CO) value of 1977 cm^{-1} is in good agreement with that of the cationic diazoalkane complex *mer*-[WCl(NN=CMe$_2$)(CO)(PMe$_2$Ph)$_3$]$^+$ (1977 cm^{-1}).[19] In contrast to the appearance of only one ν(C=N) band for the neutral complexes **2**, the cationic complex **4** shows two ν(C=N) bands at 1543 and 1524 cm^{-1}. Since the ν(C=N) values of the NN=CMePh ligands invariably fall in the range of 1510—1530 cm^{-1} for various diazoalkane complexes of tungsten,[4,5,21] the latter band at 1524 cm^{-1} should be assigned to ν(C=N) in the diazoalkane ligand. Hence, the former band at 1543 cm^{-1} may be assigned to ν(C=N) in the aminocarbene ligand, which is comparable to the ν(C=N) values in the other aminocarbene complexes reported previously.[8c,8d,9c] In the IR spectra of **2**, these two ν(C=N) bands are presumably overlapping, which may be supported by the unusually large intensities of these bands for **2**.

Complex **4** may be formed through the exchange of the Cl ligand by the weakly coordinating BF$_4$ anion. It is to be noted that **4** was not obtained by the anion metathesis under CO using other BF$_4$ salts such as NaBF$_4$ and formation of **4** from **2b** is probably enhanced by the liberation of MeCl.

Experimental

General. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and distilled by common procedures, and degassed before use. Bu^{t}NC, TfOH, AlMe$_3$ (2 M hexane solution, 1 M = 1 mol dm^{-3}), and [Me$_3$O][BF$_4$] were obtained commercially and used without further purification. The diazoalkane complex **1b** was prepared by a modified literature method.[5] IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer, and ^{1}H NMR spectra were obtained by a JEOL EX-270 spectrometer. Elemental analyses were done by a Perkin–Elmer 2400II CHN analyzer at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. The EHMO calculations were performed as previously reported[5] by the use of the parameters which appeared in the literature.[22]

Preparation of the Diazoalkane–Isocyanide Complexes *cis, trans*-[MX$_2$(NN=CMePh)(CNBu^t)(PMe$_2$Ph)$_2$] (1a: M=Mo, X=Cl; 1b: M=W, X=Cl; 1d: M=W, X=I). New diazoalkane-isocyanide complexes **1a**, **1c**, and **1d** were prepared in a similar way to that of **1b**.[5)]

1a: Color: Brown. Yield: 92%. Found: C, 52.06; H, 5.98; N, 5.68%. Calcd for $C_{29}H_{39}N_3P_2Cl_2Mo$: C, 52.90; H, 6.00; N, 6.06%. IR (KBr) ν(CN) 2104, ν(C=N) 1520 cm^{-1}; ^{1}H NMR (C_6D_6) δ=2.02, 1.99 (t, J_{P-H}=3.7 Hz, 6H each, P*Me*$_2$Ph), 1.57 (t, 3H, J_{P-H}=0.9 Hz, NNC*Me*Ph), 0.97 (s, 9H, ^{t}*Bu*NC).

1c: Color: Brown. Yield: 51%. Found: C, 41.58; H, 4.71; N, 5.08%. Calcd for $C_{29}H_{39}N_3P_2Br_2W$: C, 41.70; H, 4.71; N, 5.03%. IR (KBr) ν(CN) 2127, ν(C=N), 1526 cm^{-1}; ^{1}H NMR (C_6D_6) δ=2.18, 2.14 (t, J_{P-H}=3.7 Hz, 6H each, P*Me*$_2$Ph), 1.46 (s, 3H, NNC*Me*Ph), 1.17 (s, 9H, ^{t}*Bu*NC).

1d: Color: Brown. Yield: 84%. Found: C, 38.83; H, 4.52; N, 3.07%. Calcd for $C_{32}H_{41}N_2P_3I_2W$: C, 39.05; H, 4.20; N, 2.85%. IR (KBr) ν(CN) 2116, 2039, ν(C=N), 1520 cm^{-1}; ^{1}H NMR (C_6D_6) δ=2.34, 2.30 (t, J_{P-H}=3.7 Hz, 6H each, P*Me*$_2$Ph), 1.66 (s, 3H, NNC*Me*Ph), 1.07 (s, 9H, ^{t}*Bu*NC).

Preparation of *cis, trans*-[WCl$_2$(NN=CMePh){=C(Me)NH-Bu^t}(PMe$_2$Ph)$_2$] (2b). To a solution of **1b** (500 mg, 0.670 mmol) in toluene (20 ml) was added $AlMe_3$ in hexane solution (0.37 ml, 0.74 mmol) and the mixture was stirred at room temperature for 1 h, during which the pale brown solution turned dark brown. On treatment of the resultant solution with H_2O (0.05 ml, 2.8 mmol), a green solid precipitated. This was removed by filtration and the filtrate was evaporated to dryness. The residual solid was recrystallized from CH_2Cl_2–hexane to yield brown crystals of **2b**, which were filtered off, washed with hexane, and then dried in vacuo (276 mg, 54%). Found: C, 47.29; H, 5.68; N, 5.66%. Calcd for $C_{30}H_{43}N_3P_2Cl_2W$: C, 47.26; H, 5.70; N, 5.51%.

Complexes *cis,trans*- [MoCl$_2$(NN=CMePh){=C(Me)NHBu^t}-(PMe$_2$Ph)$_2$] (**2a**) and *cis,trans*- [WBr$_2$(NN=CMePh){=C(Me)-NHBu^t}(PMe$_2$Ph)$_2$] (**2c**) were prepared by essentially the same method as that for **2b**.

2a: Color: Brown. Yield: 30%. Found: C, 48.43; H, 5.88; N, 5.25%. Calcd for $C_{31}H_{45}N_3P_2Br_2Mo$: C, 49.03; H, 5.97; N, 5.53%.

2c: Color: Brown. Yield: 19%. Found: C, 42.33; H, 5.09; N, 4.94%. Calcd for $C_{30}H_{43}N_3Br_2P_2W$: C, 41.70; H, 4.80; N, 5.17%.

Preparation of *trans, trans*-[WCl(NN=CMePh)(CNBu^t)$_2$-(PMe$_2$Ph)$_2$][OTf] (3). To an orange suspension of **1b** (93.4 mg, 0.125 mmol) in ether (8 ml) was added TfOH (15 µl, 0.17 mmol) and the mixture was stirred at −78 °C for 5 h. To a resultant green suspension was added Bu^{t}NC (0.020 ml, 0.18 mmol) and the mixture was continuously stirred at room temperature for 10 h. A green solid which precipitated was collected by filtration and recrystallized from CH_2Cl_2–hexane. Resulting green crystals of **3** were filtered off, washed with hexane, and then dried in vacuo (35.6 mg, 60%). Found: C, 41.93; H, 5.19; N, 5.22%. Calcd for $C_{35}H_{48}O_3N_4P_2SClF_3W \cdot CH_2Cl_2$: C, 42.06; H, 4.90; N, 5.45%. IR (KBr) ν(CN) 2134, ν(C=N) 1522 cm^{-1}; ^{1}H NMR (THF-d_8) δ=2.47 (s, 3H, NN=C*Me*Ph), 2.05 (t, J_{P-H}=4.0 Hz, 12H, P*Me*$_2$Ph), 1.73 (s, 18H, *Bu^t*NC).

Table 4. X-Ray Crystallographic Data for **2b** and **3**

	2b	**3**
(a) Crystal data		
Empirical formula	$C_{30}H_{43}N_3P_2Cl_2W$	$C_{35}H_{48}N_4O_3P_2SF_3ClW$
Formula weight	762.37	943.09
Crystal color	Brown	Green
Crystal dimension/mm	0.3×0.3×0.1	0.2×0.2×0.3
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	12.619(20)	13.105(5)
b/Å	13.700(16)	25.392(1)
c/Å	10.739(12)	14.113(4)
α/deg	94.52(10)	
β/deg	104.56(12)	115.94(2)
γ/deg	68.51(10)	
Vol/Å^3	1672(4)	4223(1)
Z	2	4
d(calcd)/g cm^{-3}	1.514	1.408
μ(Mo $K\alpha$)/cm^{-1}	38.07	30.84
F(000)	764	1780
(b) Data collection		
Radiation	Mo$K\alpha$ (λ=0.7093 Å)	Mo $K\alpha$ (λ=0.7107 Å)
Monochromator	Graphite	Graphite
Temperature	Room temperature	Room temperature
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan rate/deg min^{-1}	16	16
$2\theta_{\max}$/deg	60	55
No. of unique reflections	10475	9914
Transmittion factor	1.003—1.075	0.843—1.000
(c) Structure solution and refinements		
No. of data used	5037 ($I>5\sigma(I)$)	6064 ($I>3\sigma(I)$)
No. of variables	344	451
R, R_w	0.080, 0.093	0.036, 0.023

Preparation of *trans*-[WCl(NN=CMePh){=C(Me)NHBu^t}(CO)($PMe_2Ph)_2$][BF_4] (4). To a suspension of **2b** (102 mg, 0.133 mmol) in ether (10 ml) was added [Me_3O][BF_4] (22 mg, 0.15 mmol) under CO and the mixture was stirred at room temperature for 2 h, during which the brown suspension turned to a green suspension. A green solid precipitated was collected by filtration and recrystallized from CH_2Cl_2–hexane to yield purple crystals of **4**, which were filtered off, washed with hexane, and then dried in vacuo (82.2 mg, 73%). Found: C, 42.55; H, 5.10; N, 4.93%. Calcd for $C_{31}H_{43}N_3OBF_4ClP_2W\cdot0.5CH_2Cl_2$: C, 42.79; H, 5.02; N, 4.75%. IR (KBr) ν(N–H) 3250, ν(CO) 1977, ν(C=N) 1543 (aminocarbene) and 1524 (diazoalkane) cm^{-1}; ^1H NMR (CD_2Cl_2) $\delta=9.6$ (br, 1H, N*H*), 2.9 (s, 3H, W=C*Me*), 1.55 (s, 3H, NN=C*Me*Ph), 1.97, 1.91 (t, $J_{P-H}=4.0$ Hz, 6H each, P*Me*$_2$Ph), 1.26 (s, 9H, CN*Bu*^{t}).

X-Ray Crystallographic Studies of 2b and 3. X-Ray diffraction studies were carried out at room temperature using the single crystals of **2b** and **3** sealed in grass capillaries under N_2 and transferred to a Rigaku AFC 5R or a Rigaku AFC 7R diffractometer for **2b** and **3**, respectively. The orientation matrices and unit cell parameters were derived from the least-squares fit of 25 machine-centered reflections with $35°<2\theta<40°$. No significant decay in the intensities of three standard reflections was observed during data collections. Intensity data were corrected for the Lorentz and polarization effects and for absorption. Crystallographic data are summarized in Table 4.

Structure solution and refinements were performed using the UNIX-III program package[23] at The Computer Center, The Uni-

Table 5. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **2b**

Atom	x	y	z	B_{eq}
W	0.1460(1)	0.7444(1)	0.7843(1)	2.9
Cl(1)	-0.0139(4)	0.9248(4)	0.7581(5)	4.8
Cl(2)	-0.0240(4)	0.6831(4)	0.7337(5)	4.8
P(1)	0.1329(4)	0.7557(4)	1.0125(5)	3.6
P(2)	0.1206(4)	0.7384(4)	0.5484(5)	4.2
N(1)	0.213(1)	0.508(1)	0.793(2)	4.5
N(2)	0.266(1)	0.788(1)	0.811(1)	4.2
N(3)	0.362(1)	0.806(1)	0.820(2)	4.0
C(1)	0.251(1)	0.589(1)	0.800(2)	3.6
C(2)	0.384(2)	0.554(2)	0.826(2)	5.4
C(3)	0.275(2)	0.390(1)	0.798(2)	4.6
C(4)	0.374(2)	0.349(2)	0.913(3)	7.1
C(5)	0.179(2)	0.350(2)	0.808(3)	8.6
C(6)	0.310(3)	0.350(2)	0.676(3)	8.9
C(11)	-0.011(2)	0.826(2)	1.044(2)	5.7
C(12)	0.219(2)	0.829(2)	1.106(2)	5.6
C(13)	0.186(1)	0.634(1)	1.101(2)	3.7
C(14)	0.111(2)	0.578(2)	1.090(2)	4.9
C(15)	0.152(2)	0.485(2)	1.162(2)	6.1
C(16)	0.263(2)	0.446(2)	1.239(3)	6.7
C(17)	0.336(2)	0.500(2)	1.245(3)	7.2
C(18)	0.296(2)	0.593(2)	1.178(2)	5.8
C(21)	0.129(2)	0.613(2)	0.469(2)	6.0
C(22)	-0.014(2)	0.830(2)	0.451(2)	6.5
C(23)	0.236(2)	0.769(2)	0.507(2)	4.9
C(24)	0.221(2)	0.871(2)	0.478(3)	7.2
C(25)	0.316(3)	0.891(3)	0.457(3)	8.9
C(26)	0.421(3)	0.815(3)	0.469(3)	9.8
C(27)	0.439(2)	0.716(3)	0.498(3)	8.3
C(28)	0.344(2)	0.690(2)	0.514(3)	7.3
C(31)	0.355(1)	0.904(1)	0.817(2)	3.9
C(32)	0.246(2)	0.995(1)	0.813(3)	5.8
C(33)	0.466(1)	0.918(1)	0.820(2)	3.9
C(34)	0.567(1)	0.830(2)	0.812(2)	5.2
C(35)	0.669(2)	0.848(2)	0.804(3)	6.7
C(36)	0.672(2)	0.945(2)	0.809(2)	6.0
C(37)	0.576(2)	1.029(2)	0.820(3)	7.7
C(38)	0.469(2)	1.018(2)	0.823(3)	6.8

Table 6. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **3**

Atom	x	y	z	B_{eq}
W	0.12992(2)	0.065759(8)	−0.16103(2)	2.887(7)
Cl	0.0168(1)	0.06118(6)	−0.0628(1)	4.88(7)
S	0.4893(2)	0.22836(7)	0.2997(1)	5.15(8)
P(1)	0.2088(1)	0.14978(6)	−0.0608(1)	3.90(6)
P(2)	0.0481(1)	−0.02209(5)	−0.2346(1)	3.24(6)
F(1)	0.5552(4)	0.3194(2)	0.2651(4)	11.0(3)
F(2)	0.6766(4)	0.2592(2)	0.2987(4)	11.5(3)
F(3)	0.5346(4)	0.2623(2)	0.1497(3)	10.6(3)
O(1)	0.3759(3)	0.2464(2)	0.2425(4)	7.5(2)
O(2)	0.5382(4)	0.2409(2)	0.4095(3)	8.5(3)
O(3)	0.5117(4)	0.1767(2)	0.2753(4)	7.5(3)
N(1)	0.1993(3)	0.0688(2)	−0.2418(3)	3.1(2)
N(2)	0.2457(3)	0.0653(2)	−0.3095(3)	3.7(2)
N(3)	−0.0970(4)	0.1204(2)	−0.3410(4)	4.4(2)
N(4)	0.3293(4)	0.0082(2)	0.0443(3)	4.2(2)
C(1)	0.2394(4)	0.1049(2)	−0.3689(4)	3.6(2)
C(2)	0.1823(5)	0.1554(2)	−0.3696(5)	5.6(3)
C(3)	0.2939(5)	0.0989(2)	−0.4409(4)	4.2(3)
C(4)	0.3234(6)	0.1419(3)	−0.4825(6)	6.8(4)
C(5)	0.3760(7)	0.1360(3)	−0.5482(7)	8.7(5)
C(6)	0.4009(7)	0.0882(4)	−0.5700(6)	7.9(5)
C(7)	0.3722(6)	0.0445(3)	−0.5314(5)	6.6(4)
C(8)	0.3196(5)	0.0501(2)	−0.4652(5)	4.8(3)
C(9)	−0.0156(4)	0.1019(2)	−0.2748(4)	3.3(2)
C(10)	−0.1985(5)	0.1448(2)	−0.4211(5)	4.9(3)
C(11)	−0.2846(6)	0.1464(4)	−0.3835(7)	16.6(7)
C(12)	−0.1671(7)	0.1983(3)	−0.4363(7)	16.9(6)
C(13)	−0.2340(7)	0.1171(3)	−0.5171(5)	16.1(6)
C(14)	0.2612(5)	0.0277(2)	−0.0290(4)	3.5(2)
C(15)	0.4166(5)	−0.0135(2)	0.1401(4)	4.5(3)
C(16)	0.5006(6)	0.0295(3)	0.1945(5)	8.2(4)
C(17)	0.3596(6)	−0.0330(3)	0.2046(5)	9.5(5)
C(18)	0.4740(5)	−0.0575(3)	0.1117(5)	8.2(4)
C(19)	0.2264(5)	0.1484(2)	0.0737(4)	6.5(3)
C(20)	0.3499(5)	0.1643(2)	−0.0476(5)	6.7(3)
C(21)	0.1273(5)	0.2096(2)	−0.1122(4)	4.0(3)
C(22)	0.1601(6)	0.2479(2)	−0.1632(6)	6.4(4)
C(23)	0.0931(8)	0.2923(3)	−0.2035(7)	8.8(5)
C(24)	−0.0037(8)	0.2976(3)	−0.1918(7)	8.5(5)
C(25)	−0.0375(6)	0.2613(3)	−0.1426(7)	7.8(4)
C(26)	0.0279(6)	0.2166(2)	−0.1026(6)	6.5(4)
C(27)	0.0138(5)	−0.0272(2)	−0.3731(4)	5.3(3)
C(28)	−0.0838(4)	−0.0401(2)	−0.2312(4)	5.0(3)
C(29)	0.1419(5)	−0.0784(2)	−0.1764(4)	3.3(2)
C(30)	0.2240(5)	−0.0914(2)	−0.2094(5)	4.5(3)
C(31)	0.2974(5)	−0.1323(3)	−0.1640(6)	6.2(4)
C(32)	0.2910(6)	−0.1606(2)	−0.0842(6)	6.3(3)
C(33)	0.2130(6)	−0.1473(2)	−0.0479(5)	6.0(3)
C(34)	0.1385(5)	−0.1055(2)	−0.0929(4)	4.6(3)
C(35)	0.5661(7)	0.2685(3)	0.2506(6)	6.8(4)

versity of Tokyo for **2b** or the teXsan crystallographic software package for **3**.[24] The W atom in **2b** was found by the direct-methods program SHELXS 86, while the heavy atom positions in **3** were determined by the use of the Patterson methods program DIRDIF92 PATTY.[25] Remaining non-hydrogen atoms were located by the subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by block-diagonal or full-matrix least-squares techniques for **2b** and **3**, respectively. Hydrogen atoms were placed at the calculated positions and included with fixed parameters at the final stages of refinements. Final coordinates of non-hydrogen atoms in **2b** and **3** are collected in Tables 5 and 6, respectively.[26]

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26) Hydrogen atom coordinates, anisotropic thermal parameters of non-hydrogen atoms, extensive bond distances and angles, and the complete $F_o - F_c$ data for these compounds are deposited as Document No. 71006 at the Office of the Editor of Bull. Chem. Soc. Jpn.