Conjugate Additions of Organocuprates to α,β-Unsaturated Diazoalkane Complexes of Molybdenum and Tungsten: β-Monoalkylation and α,β-Difunctionalization of α,β-Unsaturated Diazoalkane Ligands[1]

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β-Alkylation of α,β-unsaturated diazoalkane complexes [MF(NN=CHCR=CHR¹)(dpe)₂]X (1, M = W, Mo; X = BF_4, PF_6; dpe = $Ph_2PCH_2CH_2PPh_2$) by lithium dimethyl- or diphenylcuprates $LiCuR^2_2$ leads to the formation of the alkenyldiazenido complexes [MF(N=NCH=CRCHR¹R²)(dpe)₂] (2). Protonation of 2 at the α-carbon of the alkenyldiazenido ligands produced β-monoalkylated diazoalkane complexes in moderate to high yields. Complexes 2 also reacted with alkyl halides or isocyanates to give the corresponding α-alkylated or acylated diazoalkane complexes, respectively, in good yields, and these reactions provide a method for the α,β-difunctionalization of 1. Hydrolysis of the diazoalkane complexes obtained by the above method in alkaline THF–H_2O under air yielded the corresponding aldehydes. Reaction of α,β-acetylenic diazoalkane complexes [WF(NN=CHC≡CR¹)(dpe)₂]X (6) with $LiCuR^2_2$ followed by protonation or treatment with I_2 gave [WF(NN=CHCH=CR¹R²)(dpe)₂]X or [WF(NN=CHCI=CR¹R²)(dpe)₂]X, respectively.

Introduction

The chemical transformation of dinitrogen and related complexes has been attracting continuing and widespread interest.[2] We have previously reported that the diazoalkane complexes [MF(NN=CR¹CHR²R³)(dpe)₂][BF_4] (M = W, Mo) can be obtained by the protonation of *trans*-[M(N₂)₂(dpe)₂] with HBF_4 followed by condensation with the carbonyl compounds $R^1COCHR^2R^3$.[3] This reaction is one of the most simple potential methods for the formation of organic ligands having a C–N bond from ligating dinitrogen. We have investigated the reactivities of the diazoalkane complexes and recently found that their deprotonation by a strong base such as lithium diisopropylamide leads to the generation of alkenyldiazenido complexes of type [MF(N=NCR¹=CR²R³)(dpe)₂].[4] The latter complexes show a strong nucleophilicity at the terminal carbon of the alkenyldiazenido ligands and react with several electrophiles such as alkyl halides, heterocumulenes, and aldehydes to provide the corresponding *C*-alkylated, acylated, and Aldol-type condensed diazoalkane complexes, respectively.

An alternative route to alkenyldiazenido complexes may be provided by β-alkylation of α,β-unsaturated diazoalkane complexes using organometallic reagents. Further reaction of the resulting alkenyldiazenido complexes with electrophiles would lead to a new series of diazoalkane complexes functionalized at both the α- and β-positions. On the basis of this idea, we have investigated the reaction of α,β-unsaturated diazoalkane complexes with cuprates and the subsequent α-functionalization of the resulting alkenyldiazenido complexes.

Results and Discussion

Generation of Alkenyldiazenido Complexes via Conjugate Addition of Cuprates to α,β-Unsaturated Diazoalkane Complexes. α,β-Unsaturated diazoalkane complexes [MF(NN=CHCR=CHR¹)(dpe)₂]X (1: M = W, Mo; X = BF_4, PF_6) reacted with the dimethyl- or diphenylcuprates $LiCuR^2_2$[5] in THF to give air- and moisture-sensitive orange-red solutions, whose color is characteristic of alkenyldiazenido complexes. The reaction seemed to be completed within 30 min at −20 °C, judging from the disappearance of complexes 1, which are slightly soluble in THF. The formation of alkenyldiazenido complexes [MF(N=NCH=CRCHR¹R²)(dpe)₂] (2) (Scheme 1) was unambiguously confirmed by the spectroscopic data for the crude product of **2d** and isolation of relatively stable **2g**.

The IR spectrum of the reaction product from [WF(NN=CHCH=CHPh)(dpe)₂][PF_6] (1c) and $LiCuPh_2$ showed a strong absorption at 1451 cm^{-1} assignable to ν(N=N) and a weak absorption at 1599 cm^{-1} assignable to ν(C=C). The ^1H NMR spectrum showed signals due

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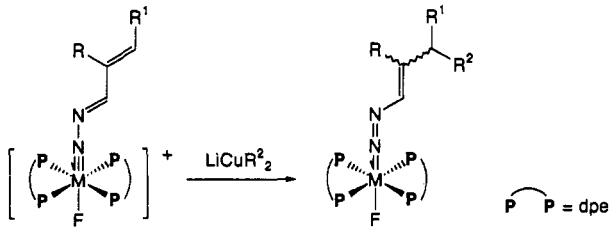
Scheme 1



	M	R	R^1
1a	W	H	H
1b	W	H	Me
1c	W	H	Ph
1d	Mo	H	Me
1e	W	Et	H

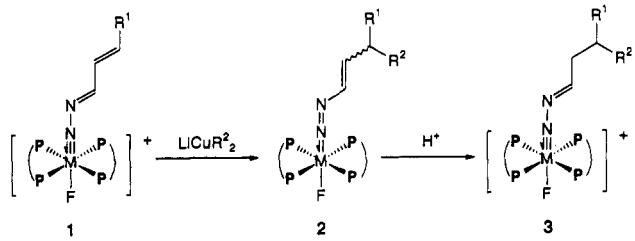
	M	R	R^1	R^2
2a	W	H	H	Me
2b	W	H	Me	Me
2c	W	H	Me	Ph
2d	W	H	Ph	Ph
2e	Mo	H	Me	Me
2f	Mo	H	Me	Ph
2g	W	Et	H	Me

to the vinyl protons of the alkenyldiazenido ligand $-N{=}NCH{=}CHCHPh_2$ in the region of δ 3.8–5.5, revealing the existence of the *Z* and *E* isomers in a ratio of 4.5:1.[6] These spectroscopic data were analogous to those for other alkenyldiazenido complexes generated by α-deprotonation of diazoalkane complexes[4] and supported the formation of $[WF(N{=}NCH{=}CHCHPh_2)(dpe)_2]$ (**2d**). Furthermore, $[WF(N{=}NCH{=}CEt_2)(dpe)_2]$ (**2g**), obtained by the reaction of $[WF(NN{=}CHCEt{=}CH_2)(dpe)_2][BF_4]$ (**1e**) with $LiCuMe_2$, could be isolated in 59% yield by recrystallization from C_6H_6/hexane. The IR spectrum of **2g** showed strong absorptions assignable to ν(N=N) (1460 cm^{-1}) and ν(C=C) (1551 cm^{-1}), and the ^1H NMR spectrum exhibited resonances due to one vinyl proton at δ 5.03 and two inequivalent ethyl groups (see Experimental Section). These spectra for **2g** were similar to those for $[WF(N{=}NCH{=}CMe_2)(dpe)_2]$,[4] whose structure was previously determined by the single-crystal X-ray diffraction method. Interestingly, the elemental analysis revealed that **2g** was isolated as an adduct with LiI, which is in sharp contrast to the previously isolated alkenyldiazenido complexes formed by the α-deprotonation of diazoalkane complexes. Although other alkenyldiazenido complexes were not stable enough for purification and characterization, the above results support that the reaction of the α,β-unsaturated diazoalkane complexes **1** with cuprates effectively generates alkenyldiazenido complexes **2**.

β-Monoalkylation of α,β-Unsaturated Diazoalkane Complexes. Analogously to the alkenyldiazenido complexes prepared by the α-deprotonation of diazoalkane complexes,[4] complexes **2** are considered to have a nucleophilicity at the terminal carbon of the alkenyldiazenido group. The C-protonation of **2** provides a facile route to the β-alkylation and β-arylation of complex **1**. In fact, when a solution of **2** generated from **1** and cuprates was treated with saturated aqueous NH_4BF_4, a rapid reaction occurred (Scheme 2) and the corresponding β-monoalkylated cationic diazoalkane complexes $[MF(NN{=}CHCH_2CHR^1R^2)(dpe)_2][BF_4]$ (**3**) were isolated in moderate to high yields (Table 1). It is worth mentioning that only the β-alkylated complex **3** (conjugate addition

(6) (*Z*)-**2d**: δ 3.87 (dd, 1 H, J = 9.3, 7.2 Hz, N=NCH=C*H*), 5.25 (d, 1 H, J = 7.2 Hz, C*H*Ph_2), 5.50 (d, 1 H, J = 9.3 Hz, N=NCH). (*E*)-**2d**: δ 4.03 (d, 1 H, J = 9.9 Hz, C*H*Ph_2), 5.09 (dd, 1 H, J = 13.0, 9.9 Hz, N=NCH=C*H*), 5.25 (d, 1 H, J = 13.0 Hz, N=NCH). The predominant formation of (*Z*)-alkenyldiazenido complexes was also found in the deprotonation of the diazoalkane complexes.[4a,b]

Scheme 2



product) was obtained; the product expected from alkylation at the carbon atom of the C=N group (1,2-addition product) was not formed at all. In addition, the facts that no starting complex **1** was recovered and complexes **3** were obtained in high yields strongly support the nearly quantitative formation of **2** in the reaction of **1b** or **1c** with cuprates. However, yields of **3** were lower in the case of **1a**, which has no alkyl substituent, and the molybdenum complex **1d**.

Although the conjugate addition to **1** was highly regioselective when cuprates were used as the alkylating reagent, similar reactions of **1** with alkyllithium or alkylmagnesium bromide did not show such a selectivity. The reaction of **1b** and MeLi at −20 °C followed by protonation resulted in the formation of a complex mixture containing small amounts of **1b** and **3b**. When MeMgBr was used, **1b** was recovered in 53% yield.

It should be pointed out that, in the reaction of an α,β-unsaturated aldehyde with a dialkylcuprate, the conjugate-addition product is obtained in a good yield only when the reaction is conducted in the presence of trimethylsilyl chloride, which traps the intermediate enolate formed by the conjugate addition, to avoid side reactions.[7] In the reaction of **1**, the bulky Ph groups of dpe ligands are considered to contribute to the exclusive formation of **3** by preventing the alkenyldiazenido ligand from undesirable side reactions.

α,β-Difunctionalization of α,β-Unsaturated Diazoalkane Complexes. Alkenyldiazenido complexes **2**, prepared from **1** and cuprates, also reacted with other electrophiles (Scheme 3), and one-pot α,β-difunctionalization of **1** was achieved in good yields (Table 2). Thus, the reaction of **2b** or **2e**, prepared by the β-methylation of **1b** or **1d**, respectively, with an excess amount of alkyl halides gave the α-alkylated products $[MF(NN{=}CHCHR^3CHMe_2)(dpe)_2][BF_4]$ (**4**). In this second alkylation step, the regioselectivity for the C-alkylation was fairly high, and N-alkylated products either were not found or were obtained only in small amounts.[8] Reactions of **2c** and **2d** with MeI were also attempted, but the C-methylated complexes were not obtained, probably because of steric congestion by the bulky 1-phenylethyl and diphenylmethyl groups, respectively.

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(8) When **2b** was treated with MeI or EtI, the N-alkylated product (*E*)-$[WF(NNMeCH{=}CHCHMe_2)(dpe)_2][BF_4]$ (**10a**) or (*E*)-$[WF(NNEtCH{=}CHCHMe_2)(dpe)_2][BF_4]$ (**10b**), respectively, was obtained in up to 10% yield. **10a**: brown crystals; ^1H NMR ($CDCl_3$) δ 0.56 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.49 (m, 1 H, C*H*Me_2), 1.92 (s, 3 H, NNMe), 2.5–3.0 (m, 8 H, CH_2 of dpe), 3.62 (dd, 1 H, J = 14.0, 7.9 Hz, NNCH=C*H*), 4.53 (d, 1 H, J = 14.0 Hz, NNCH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1648 cm^{-1} (C=C). **10b**: brown crystals; ^1H NMR ($CDCl_3$) δ 0.18 (t, 3 H, J = 7.0 Hz, CH_2*Me*), 0.56 (d, 6 H, J = 6.4 Hz, CH*Me*$_2$), 1.41 (m, 1 H, C*H*Me_2), 2.38 (q, 2 H, J = 7.0 Hz, $NNCH_2$), 2.5–3.0 (m, 8 H, CH_2 of dpe), 3.68 (dd, 1 H, J = 14.3, 8.1 Hz, NNCH=C*H*), 4.45 (d, 1 H, J = 14.3 Hz, NNCH), 6.8–7.3 (m, 40 H, Ph of dpe); IR 1641 cm^{-1} (C=C).

Table 1. β-Alkylation of the α,β-Unsaturated Diazoalkane Complexes $[MF(NN{=}CHCH{=}CHR^1)(dpe)_2]^+$ [a]

substrate	cuprate	product	yield (%)[b]
1a[c]	$LiCuMe_2$	$[WF(NN{=}CHCH_2CH_2Me)(dpe)_2][BF_4]$ (**3a**)	36
1b[c]	$LiCuMe_2$	$[WF(NN{=}CHCH_2CHMe_2)(dpe)_2][BF_4]$ (**3b**)	80
1b[c]	$LiCuPh_2$	$[WF(NN{=}CHCH_2CHMePh)(dpe)_2][BF_4]$ (**3c**)	97
1c[d]	$LiCuMe_2$	$[WF(NN{=}CHCH_2CHMePh)(dpe)_2][BF_4]$ (**3c**)	75
1c[d]	$LiCuPh_2$	$[WF(NN{=}CHCH_2CHPh_2)(dpe)_2][BF_4]$ (**3d**)	90
1d[c]	$LiCuMe_2$	$[MoF(NN{=}CHCH_2CHMe_2)(dpe)_2][BF_4]$ (**3e**)	55
1d[c]	$LiCuPh_2$	$[MoF(NN{=}CHCH_2CHMePh)(dpe)_2][BF_4]$ (**3f**)	61

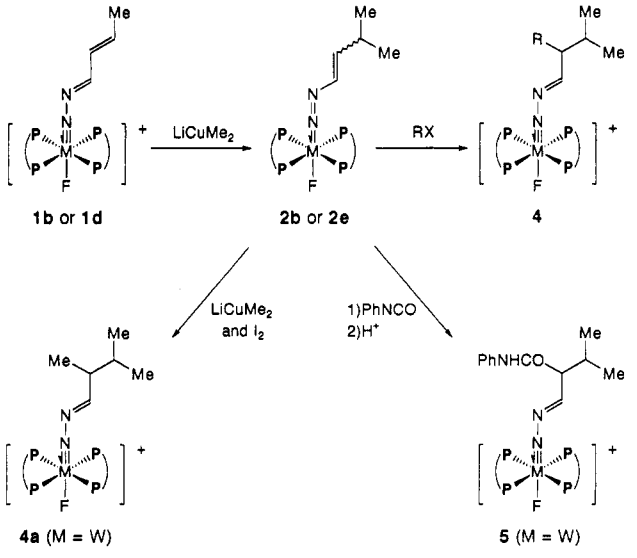
[a] Cuprate:diazoalkane complex = 1.5. For reaction conditions, see Experimental Section. [b] Yields are based on the starting diazoalkane complexes. [c] Tetrafluoroborate. [d] Hexafluorophosphate.

Table 2. β-Methylation–α-Alkylation and –α-Acylation of the Diazoalkane Complexes $[MF(NN{=}CHCH{=}CHMe)(dpe)_2][BF_4]$ [a]

substrate	electrophile[b]	product	yield (%)[c]
1b	MeI (3.6)	$[WF(NN{=}CHCHMeCHMe_2)(dpe)_2][BF_4]$ (**4a**)	65
1b	EtI (6.0)	$[WF(NN{=}CHCHEtCHMe_2)(dpe)_2][BF_4]$ (**4b**)	62
1b	$PhCH_2Br$ (3.6)	$[WF(NN{=}CHCH(CH_2Ph)CHMe_2)(dpe)_2][BF_4]$ (**4c**)	78
1b	(1) PhNCO (3.6), (2) NH_4BF_4 (aq)	$[WF(NN{=}CHCH(CONHPh)CHMe_2)(dpe)_2][PF_6]$ (**5**)[d]	50
1d	$PhCH_2Br$ (5.0)	$[MoF(NN{=}CHCH(CH_2Ph)CHMe_2)(dpe)_2][BF_4]$ (**4d**)	62

[a] For reaction conditions, see Experimental Section. [b] Ratios of electrophile to starting diazoalkane complex are given in parentheses. [c] Yields are based on the starting diazoalkane complexes. [d] Isolated as the hexafluorophosphate after anion exchange.

Scheme 3



α-Acylation of **2** was also carried out by using complex **2b** and an excess amount of PhNCO. After protonation and anion exchange, the α-acylated product **5** was obtained in 50% yield.

It is known that enolates derived from α,β-unsaturated carbonyl compounds and organocopper reagents often need special modification to achieve the α-functionalization[9] such as changing the countercation[10] or reaction solvent[11] after conjugate addition or trapping the intermediate enolate as a silyl enol ether.[12] However, these additional procedures are not required in the present α,β-difunctionalization of diazoalkane complexes **1**.

We have already reported that the alkenyldiazenido complexes formed by the deprotonation of diazoalkane complexes undergo an oxidative coupling reaction by the treatment with I_2.[4a] Nevertheless, addition of I_2 to the reaction mixture of **1b** and 2 equiv of $LiCuMe_2$ did not result in the oxidative coupling of **2b** but the methylation of **2b** to give **4a** in high yield (78%, Scheme 3). This reaction is considered to be an oxidative cross-coupling reaction between the alkenyldiazenido complex and the organocopper reagent, although the coupling reactions on the copper atom are known in the oxidation of homo- and heterocuprates with O_2.[13] When this reaction was conducted using 1–1.5 equiv of $LiCuMe_2$ with **1b**, the yield of **4a** was decreased but neither oxidative dimerization nor iodination of **2b** was observed.[14] This indicates that the methyl group comes from the excess amounts of $LiCuMe_2$ rather than CuMe formed by the reaction of $LiCuMe_2$ and **1b**.

Reaction of α,β-Acetylenic Diazoalkane Complexes with Cuprates. α,β-Acetylenic diazoalkane complexes $[WF(NN{=}CHC{\equiv}CR^1)(dpe)_2]X$ (**6**: X = BF_4, PF_6) also reacted with cuprates $LiCuR^2_2$ to give α,β-unsaturated diazoalkane complexes $[WF(NN{=}CHCH{=}CR^1R^2)(dpe)_2]X$ (**8**: X = BF_4, PF_6) in high yields by protonation (Scheme 4, Table 3). The reaction intermediates generated from **6** and cuprates are thought to be the allenyldiazenido complexes $[WF(N{=}NCH{=}C{=}CR^1R^2)(dpe)_2]$ (**7**); however, their high instability prevented spectroscopic characterization.

On the other hand, treatment of complex **7b** with I_2 gave the α-iodo α,β-unsaturated diazoalkane complex $[WF(NN{=}CHCI{=}CPh_2)(dpe)_2][BF_4]$ (**9a**) in 52% yield (Scheme 4). It has been reported that an allenolate, generated from an α,β-acetylenic ester and cuprate, is also iodinated by I_2[15] analogously to the reaction of **7b** and I_2. This reactivity of **7b** is essentially different from that of alkenyldiazenido complex **2** toward I_2. Moreover, similar halogenation of complex **7** was also achieved by using

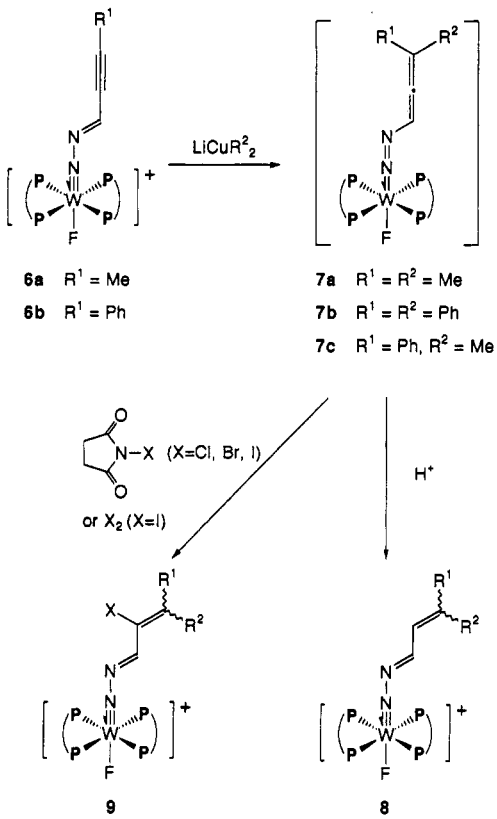
(9) For a review of α,β-difunctionalization of α,β-unsaturated carbonyl compounds, see: Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *39*, 225.
(10) Heng, K. K.; Smith, R. A. J. *Tetrahedron* **1979**, *35*, 425.
(11) (a) Coats, R. M.; Sandefur, L. O. *J. Org. Chem.* **1974**, *39*, 275. (b) Boeckman, R. K., Jr. *J. Org. Chem.* **1973**, *38*, 4450.
(12) (a) Patterson, J. W., Jr.; Fried, J. H. *J. Org. Chem.* **1974**, *39*, 2506. (b) Binkley, E. S.; Heathcock, C. H. *J. Org. Chem.* **1975**, *40*, 2156.
(13) Oxidative coupling reactions of organocopper reagents have been reported, where O_2 or copper(II) salts were usually used for the oxidizing reagents. For dimerization: (a) Whitesides, G. M.; San Filippo, J., Jr.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302. (b) Camus, A.; Marsich, N. *J. Organomet. Chem.* **1972**, *46*, 385. For cross-coupling reaction to form a C—C bond: (c) Whitesides, G. M.; Fischer, W. F., Jr.; San Filippo, J., Jr.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. (d) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003. For a cross-coupling reaction to form a C—N bond: (e) Yamamoto, H.; Maruoka, K. *J. Org. Chem.* **1980**, *45*, 2739. (f) Iwao, M.; Reed, J. N.; Snieckus, V. *J. Am. Chem. Soc.* **1982**, *104*, 5531.
(14) When the reaction mixture of **1b** and 1 equiv of $LiCuMe_2$ was treated with I_2, **4a** was obtained in 44% yield and **1b** was recovered in 30% yield.
(15) (a) Corey, E. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 1851. (b) Klein, J.; Levene, R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1971.

Table 3. Conjugate Addition of the α,β-Acetylenic Diazoalkane Complexes $[WF(NN{=}CHC{\equiv}CR^1)(dpe)_2]^+$ [a]

substrate	cuprate	electrophile[b]	product	yield (%)[c]
6a[d]	$LiCuMe_2$	H^+ [c]	$[WF(NN{=}CHCH{=}CMe_2)(dpe)_2][BF_4]$ (**8a**)	85
6b[f]	$LiCuPh_2$	H^+ [c]	$[WF(NN{=}CHCH{=}CPh_2)(dpe)_2][PF_6]$ (**8b**)[g]	70
6b[f]	$LiCuPh_2$	I_2 (1.6)[h]	$[WF(NN{=}CHCI{=}CPh_2)(dpe)_2][BF_4]$ (**9a**)	52
6b[f]	$LiCuPh_2$	NBS (3.6)[i]	$[WF(NN{=}CHCBr{=}CPh_2)(dpe)_2][BF_4]$ (**9b**)	56
6b[f]	$LiCuPh_2$	NCS (3.6)[i]	$[WF(NN{=}CHCCl{=}CPh_2)(dpe)_2][BF_4]$ (**9c**)	52
6b[f]	$LiCuMe_2$	NIS (3.6)[j]	$[WF(NN{=}CHCI{=}CMePh)(dpe)_2][BF_4]$ (**9d**)	75 (Z/E = 1)[k]

[a] Reaction conditions for β-alkylation step: cuprate:diazoalkane complex = 1.5, −20 °C, 40 min. [b] Ratios of electrophile to starting diazoalkane complex are given in parentheses except for H^+ (large excess). [c] Yields are based on the starting diazoalkane complexes. [d] Tetrafluoroborate. [e] By addition of saturated aqueous NH_4BF_4 at −20 °C. [f] Hexafluorophosphate. [g] Isolated as the hexafluorophosphate after anion exchange. [h] Room temperature, 20 h. [i] −30 °C, 1.5 h. [j] β-Alkylation step: −78 °C, 1.5 h. Treatment with NIS: −78 °C, 1 h. [k] Determined by the ^1H NMR spectrum of the crude product.

Scheme 4



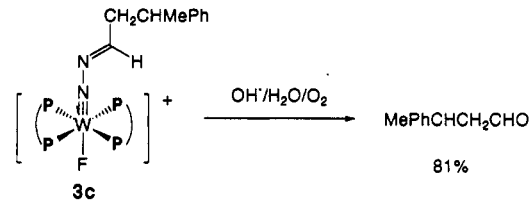
N-iodo-, *N*-bromo-, and *N*-chlorosuccinimide (NIS, NBS, NCS; Scheme 4, Table 3).[16] In the reaction of complex **7c** and NIS, the formation of two stereoisomers of complex **9d** were observed, but no selectivity was observed (Z/E = 1) even at −78 °C.

Hydrolysis of Diazoalkane Complexes. Liberation of organic compounds from the diazoalkane complexes is an interesting reaction, because a variety of chemical conversions of diazoalkane ligands were proved to be feasible by the method described above. Here, we have investigated the liberation of the aldehydes by hydrolysis of the diazoalkane complexes under basic conditions in detail.

Complexes **3c** and **4a** are essentially inert toward acid-promoted hydrolysis. Conversely, treatment of a THF solution of **3c** with aqueous NaOH efficiently generated 3-phenylbutyraldehyde (81%) at room temperature under air after 40 min, although the reaction mixture was heterogeneous (Scheme 5). Under the same conditions,

(16) In these halogenation reactions, cuprates should be prepared from the corresponding copper(I) halides to avoid the halogen scrambling. When a solution of **7b** prepared from **6b**, CuI, and LiPh was treated with 3.6 equiv of NBS, **9a** and **9b** were obtained in the ratio of 1:3.

Scheme 5



no more than 48% 2,3-dimethylbutyraldehyde was generated from **4a** even after 12 h, probably due to the steric effect of the diazoalkane ligand. A higher reaction temperature only accelerated the reaction, but the yield of the aldehyde was not improved in the range 20–55 °C. However, use of aqueous *n*-$Bu_4N(OH)$, which makes a homogeneous solution with THF, increased the yield of 2,3-dimethylbutyraldehyde from **4a** to 60% at 45 °C (after 20 min).

Interestingly, the yields of aldehydes were extremely lowered (28% from **3c**; 22% from **4a**) when the reactions were carried out under a nitrogen atmosphere. Furthermore, no hydrazido(2−) complex $[WF(NNH_2)(dpe)_2]^+$ was recovered from the hydrolysis reaction mixtures under air, but the formation of the dioxide of dpe was observed. These facts indicate that the base-promoted hydrolysis of the diazoalkane ligands is accompanied by the oxidative liberation of dpe from the tungsten center, although the detailed mechanism is not clear.

Since diazoalkane complexes are easily obtained by the condensation reaction of carbonyl compounds and hydrazido(2−) complexes, conjugate addition of cuprates to α,β-unsaturated diazoalkane complexes followed by the reaction with electrophiles and the base-promoted hydrolysis of the resulting diazoalkane complexes provide an unique method for the functionalization of α,β-unsaturated aldehydes.

Experimental Section

All of the reactions except for the hydrolysis reactions of diazoalkane complexes were carried out under a nitrogen atmosphere. Solvents were dried and distilled under nitrogen before use. Solutions of organometallic reagents (methyllithium in ether, phenyllithium in cyclohexane/ether, methylmagnesium bromide in ether), copper(I) salts, I_2, and other organic reagents were commercially obtained and used without further purification. Diazoalkane complexes **1** and **6** were prepared from the dinitrogen complexes *trans*-$[M(N_2)_2(dpe)_2]$ (M = W, Mo) and the corresponding aldehydes (**1a–e**, **6b**) or aldehyde diethylacetal (**6a**) by following the established procedure.[3a] Cuprates were generated in situ from a THF suspension of CuI and 2 equiv of the corresponding organolithium reagents at −10 °C or below.

^1H NMR spectra were recorded on a JEOL JNM-GX-400 (400 MHz) or JEOL JNM-EX-270 (270 MHz) spectrometer. Amounts

of the solvated molecules of the reaction products were determined by ^{1}H NMR. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer by the KBr method. Quantitative GLC analyses were carried out on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. Elemental analyses were performed at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of the Alkenyldiazenido Complex [WF(N=NCH=CEt$_2$)(dpe)$_2$]·LiI (2g·LiI). To a benzene (5 mL)–ether (7 mL) solution of $LiCuMe_2$ prepared from CuI (48.3 mg, 0.254 mmol) and MeLi (0.51 mmol in ether) at −20 °C was added diazoalkane complex **1e** (300 mg, 0.254 mmol) at this temperature, and the mixture was stirred for 1.5 h. The resulting orange-red reaction mixture was slowly concentrated to 5 mL in vacuo. Hexane (3 mL) was added dropwise to the mixture with stirring, and the yellow solid precipitated was filtered off by using a glass-fiber filter paper. Hexane (15 mL) was added to the filtrate, and the orange-red crystals that deposited were collected, washed with a small amount of hexane, and then dried in vacuo. Alkenyldiazenido complex **2g** was isolated as the adduct with LiI (187 mg, 59%): ^{1}H NMR (THF-d_8) δ 0.73 (t, 3 H, J = 7.4 Hz, Me), 0.93 (t, 3 H, J = 7.4 Hz, Me), 1.73 (q, 2 H, J = 7.4 Hz, CH_2), 2.13 (q, 2 H, J = 7.4 Hz, CH_2), 2.3–2.6 (m, 8 H, CH_2 of dpe), 5.03 (s, 1 H, N=NCH), 7.0–7.5 (m, 40 H, Ph); IR 1551 (C=C), 1460 cm^{-1} (N=N). Anal. Calcd for $C_{58}H_{59}N_2WIP_4FLi$: C, 55.97; H, 4.78; N, 2.25; I, 10.20. Found: C, 56.78; H, 5.34; N, 1.93; I, 11.20. Copper was not detected by EPMA.

β-Alkylation and β-Arylation of α,β-Unsaturated Diazoalkane Complexes. The following procedure for the reaction of **1b** and $LiCuPh_2$ is representative. To 10 mL of a THF solution of $LiCuPh_2$, prepared from CuI (45.7 mg, 0.240 mmol) and PhLi (0.48 mmol in cyclohexane/ether), was added **1b**·CH_2Cl_2 (200 mg, 0.160 mmol) at −20 °C. After the mixture was stirred at the same temperature for 30 min, the resulting orange-red solution was quenched with 3 mL of saturated aqueous NH_4BF_4. The solution immediately turned green. Dichloromethane (20 mL) was added to the reaction mixture, and the organic layer was washed repeatedly with aqueous NH_4BF_4 (5%, 50 mL × 4), dried over $MgSO_4$, and evaporated to dryness. The dark green residue was purified by gel chromatography (Sephadex LH-20; eluent MeOH–CH_2Cl_2) and recrystallized from CH_2Cl_2–MeOH–ether. [WF(NN=CHCH$_2$CHMePh)(dpe)$_2$][BF_4] (**3c**) was obtained as dark green crystals (193 mg, 97%): ^{1}H NMR ($CDCl_3$) δ 1.01 (d, 3 H, J = 7.0 Hz, Me), 1.57 (br t, J = 5.8 Hz, 2 H, CH_2), 2.52 (m, 1 H, C*H*MePh), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.57 (t, 1 H, J = 4.4 Hz, NN=CH), 6.8–7.4 (m, 45 H, Ph); IR 1575 cm^{-1} (C=N). Anal. Calcd for $C_{62}H_{60}N_2WP_4F_5B$: C, 59.73; H, 4.85; N, 2.25. Found: C, 59.08; H, 4.75; N, 2.37.

[WF(NN=CHCH$_2$CH$_2$Me)(dpe)$_2$][BF_4]·1.5CH_2Cl_2 (3a·1.5CH_2Cl_2): pale green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 0.76 (t, 3 H, J = 7.2 Hz, Me), 1.12 (sextet, 2 H, J = 7.2 Hz, CH_2Me), 1.26 (dt, 2 H, J = 7.2, 5.0 Hz, NN=CHCH_2), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.51 (t, 1 H, J = 5.0 Hz, NN=CH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1574 cm^{-1} (C=N). Anal. Calcd for $C_{57.5}H_{59}N_2WCl_3P_4F_5B$: C, 53.21; H, 4.58; N, 2.16. Found: C, 53.48; H, 4.70; N, 2.05.

[WF(NN=CHCH$_2$CHMe$_2$)(dpe)$_2$][BF_4]·THF (3b·THF): green crystals from THF–ether; ^{1}H NMR ($CDCl_3$) δ 0.69 (d, 6 H, J = 6.4 Hz, Me), 1.18 (br t, J = 6.1 Hz, 2 H, CH_2), 1.36 (m, 1 H, C*H*Me$_2$), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.54 (t, 1 H, J = 5.5 Hz, NN=CH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1574 cm^{-1} (C=N). Anal. Calcd for $C_{61}H_{66}N_2WP_4F_5OB$: C, 58.30; H, 5.29; N, 2.23. Found: C, 57.78; H, 5.12; N, 2.23.

[WF(NN=CHCH$_2$CHPh$_2$)(dpe)$_2$][BF_4]·CH_2Cl_2 (3d·CH_2Cl_2): green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 2.03 (br t, J = 5.9 Hz, 2 H, CH_2), 2.5–2.7 (m, 4 H, CH_2 of dpe), 2.7–2.9 (m, 4 H, CH_2 of dpe), 3.76 (t, 1 H, J = 7.5 Hz, C*H*Ph$_2$), 5.64 (t, 1 H, J = 4.4 Hz, NN=CH), 6.8–7.4 (m, 50 H, Ph); IR 1574 cm^{-1} (C=N). Anal. Calcd for $C_{68}H_{64}N_2WCl_2P_4F_5B$: C, 58.60; H, 4.63; N, 2.01. Found: C, 58.64; H, 4.82; N, 1.97.

[MoF(NN=CHCH$_2$CHMe$_2$)(dpe)$_2$][BF_4]·0.5CH_2Cl_2 (3e·0.5CH_2Cl_2): green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 0.67 (d, 6 H, J = 6.4 Hz, Me), 1.30–1.40 (m, 3 H, CH_2C*H*Me$_2$), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.45 (t, 1 H, J = 5.2 Hz, NN=CH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1570 cm^{-1} (C=N). Anal. Calcd for $C_{57.5}H_{59}N_2MoClP_4F_5B$: C, 60.62; H, 5.22; N, 2.46. Found: C, 60.66; H, 5.34; N, 2.41.

[MoF(NN=CHCH$_2$CHMePh)(dpe)$_2$][BF_4] (3f): green crystals from CH_2Cl_2–MeOH–ether; ^{1}H NMR ($CDCl_3$) δ 1.00 (d, 3 H, J = 6.7 Hz, Me), 1.67–1.82 (m, 2 H, CH_2), 2.50 (m, 1 H, C*H*MePh), 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.51 (t, 1 H, J = 5.0 Hz, NN=CH), 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, 63.97; H, 5.22; N, 2.52.

[WF(NN=CHCH=CMe$_2$)(dpe)$_2$][BF_4]·0.5CH_2Cl_2 (8a·0.5CH_2Cl_2): green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 3 H, *cis*-Me), 1.59 (s, 3 H, *trans*-Me), 2.6-2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.39, 5.82 (each d, 1 H, J = 10.3 Hz, NN=CHCH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1630 (C=C), 1518 cm^{-1} (C=N). Anal. Calcd for $C_{57.5}H_{57}N_2WClP_4F_5B$: C, 56.37; H, 4.69; N, 2.29. Found: C, 56.04; H, 4.78; N, 2.32.

[WF(NN=CHCH=CPh$_2$)(dpe)$_2$][PF_6] (8b): green crystals from THF–ether; ^{1}H NMR ($CDCl_3$) δ 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 6.13 (dd, 2 H, J = 8.2, 1.2 Hz, *o* H of *cis*-Ph), 6.07, 6.21 (each d, 1 H, J = 10.1 Hz, NN=CHCH), 6.8–7.4 (m, 48 H, Ph); IR 1586, 1570 (C=C), 1505 cm^{-1} (C=N). Anal. Calcd for $C_{67}H_{60}N_2WP_5F_7$: C, 58.96; H, 4.43; N, 2.05. Found: C, 58.94; H, 4.56; N, 2.21.

α,β-Dialkylation of α,β-Unsaturated Diazoalkane Complexes. The following procedure is representative. An orange-red solution of the alkenyldiazenido complex **2b** was prepared from **1b**·CH_2Cl_2 (200 mg, 0.160 mmol) and 1.5 equiv of $LiCuMe_2$ in THF at −20 °C. Methyl iodide (36 μL, 0.58 mmol) was added to the solution, and the reaction mixture was stirred for 19 h at room temperature. The dark brown mixture was quenched with 3 mL of saturated aqueous NH_4BF_4 followed by aqueous workup similar to that for β-monoalkylation. The residue was purified by gel chromatography (Sephadex LH-20; eluent MeOH–CH_2Cl_2) and recrystallized from THF–ether. [WF(NN=CHCHMeCHMe$_2$)(dpe)$_2$][BF_4]·0.5THF (**4a·0.5THF**) was obtained as green crystals (128 mg, 65%): ^{1}H NMR ($CDCl_3$) δ 0.56 (d, 3 H, J = 6.7 Hz, Me), 0.62 (d, 3 H, J = 6.7 Hz, Me), 0.68 (d, 3 H, J = 6.7 Hz, Me), 1.24–1.33 (m, 2 H, C*H*MeC*H*Me$_2$), 2.5–3.0 (m, 8 H, CH_2 of dpe), 5.84 (d, 1 H, J = 4.3 Hz, NN=CH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1574 cm^{-1} (C=N). Anal. Calcd for $C_{60}H_{64}N_2WP_4F_5O_{0.5}B$: C, 58.37; H, 5.22; N, 2.27. Found: C, 58.09; H, 5.42; N, 2.26.

[WF(NN=CHCHEtCHMe$_2$)(dpe)$_2$][BF_4] (4b): green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 0.54 (d, 3 H, J = 7.0 Hz, CH*Me*), 0.55 (d, 3 H, J = 7.0 Hz, CH*Me*), 0.60 (t, 3 H, J = 7.2 Hz, CH_2*Me*), 1.02 (m, 1 H, CH_2), 1.11 (m, 1 H, NN=CHC*H*), 1.19 (m, 1 H, CH_2), 1.41 (m, 1 H, C*H*Me$_2$), 2.6–3.0 (m, 8 H, CH_2 of dpe), 5.96 (d, 1 H, J = 5.5 Hz, NN=CH), 6.8–7.4 (m, 40 H, Ph of dpe); IR 1572 cm^{-1} (C=N). Anal. Calcd for $C_{59}H_{62}N_2WP_4F_5B$: C, 58.44; H, 5.15; N, 2.31. Found: C, 58.06; H, 5.06; N, 2.28.

[WF(NN=CHCH(CH$_2$Ph)CHMe$_2$)(dpe)$_2$][BF_4]·CH_2Cl_2 (4c·CH_2Cl_2): green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 0.58 (d, 3 H, J = 7.0 Hz, Me), 0.60 (d, 3 H, J = 6.7 Hz, Me), 1.45–1.56 (m, 2 H, NN=CHC*H*CH), 2.24 (dd, 1 H, J = 14.0, 6.9 Hz, CH_2), 2.39 (dd, 1 H, J = 14.0, 7.2 Hz, CH_2), 2.5–3.0 (m, 8 H, CH_2 of dpe), 6.03 (d, 1 H, J = 4.0 Hz, NN=CH), 6.81 (d, 2 H, J = 6.7 Hz, *o* H of CH_2*Ph*), 6.9–7.4 (m, 43 H, Ph); IR 1572 cm^{-1} (C=N). Anal. Calcd for $C_{65}H_{66}N_2WCl_2P_4F_5B$: C, 57.41; H, 4.89; N, 2.06. Found: C, 57.59; H, 5.03; N, 1.93.

[MoF(NN=CHCH(CH$_2$Ph)CHMe$_2$)(dpe)$_2$][BF_4]·0.5CH_2Cl_2 (4d·0.5CH_2Cl_2): pale green crystals from CH_2Cl_2–ether; ^{1}H NMR ($CDCl_3$) δ 0.57 (d, 3 H, J = 7.0 Hz, Me), 0.69 (d, 3 H, J = 7.0 Hz, Me), 1.50 (m, 1 H, C*H*Me$_2$), 1.71 (m, 1 H, NN=CHC*H*), 2.19 (dd, 1 H, J = 14.2, 7.0 Hz, CH_2), 2.36 (dd, 1 H, J = 14.2, 7.3

Hz, CH_2), 2.5–3.0 (m, 8 H, CH_2 of dpe), 5.95 (d, 1 H, J = 4.6 Hz, NN=CH), 6.81 (d, 2 H, J = 6.7 Hz, *o* H of CH_2Ph), 6.9–7.4 (m, 43 H, Ph); IR 1563 cm^{-1} (C=N). Anal. Calcd for $C_{64.5}H_{65}N_2MoClP_4F_5B$: C, 63.02; H, 5.33; N, 2.28. Found: C, 63.71; H, 5.43; N, 2.32.

β-Alkylation–α-Acylation of 1b. To a THF solution of an alkenyldiazenido complex **2b**, generated from **1b**·CH_2Cl_2 (200 mg, 0.160 mmol) and $LiCuMe_2$ (1.5 equiv) at −10 °C, was added PhNCO (62 μL, 0.57 mmol). After it was stirred for 19 h at room temperature, the reaction mixture was quenched with 3 mL of saturated aqueous NH_4BF_4. After workup and purification similar to that for β-monoalkylation, a green oil was obtained. Anion exchange by using aqueous NH_4PF_6 (5%, 50 mL × 4) and recrystallization from CH_2Cl_2–hexane gave [WF(NN=CHCH(CONHPh)$CHMe_2$)(dpe)$_2$][PF_6] (**5**) as green crystals (109 mg, 50%): ^1H NMR ($CDCl_3$) δ 0.60 (d, 3 H, J = 6.7 Hz, Me), 0.88 (d, 3 H, J = 6.7 Hz, Me), 1.71 (m, 1 H, C*H*Me_2), 2.70 (dd, 1 H, J = 9.5, 7.0 Hz, NN=CHC*H*), 2.5–3.0 (m, 8 H, CH_2 of dpe), 6.21 (d, 1 H, J = 7.0 Hz, NN=CH), 6.8–7.3 (m, 41 H, Ph), 7.35 (t, 2 H, J = 7.6 Hz, *m* H of NH*Ph*), 7.82 (d, 2 H, J = 7.6 Hz, *o* H of NH*Ph*), 8.39 (s, 1 H, NH); IR 3390, 1686, 1538 (CONH), 1601 cm^{-1} (C=N). Anal. Calcd for $C_{64}H_{63}N_3WP_5F_7O$: C, 56.44; H, 4.66; N, 3.09. Found: C, 55.97; H, 4.66; N, 3.26.

Reaction of 2b and I_2 in the Presence of $LiCuMe_2$. To a THF solution of **2b** prepared from **1b**·CH_2Cl_2 (200 mg, 0.160 mmol) and 2 equiv of $LiCuMe_2$ was added I_2 (162 mg, 0.64 mmol) at −70 °C. The reaction mixture was slowly warmed to 0 °C over 8 h with stirring and quenched with diluted aqueous HCl. The resultant solution was washed successively with aqueous $Na_2S_2O_3$ (5%, 50 mL × 2) and aqueous NH_4BF_4 (5%, 50 mL × 4), dried over $MgSO_4$, and evaporated. The MeOH extract of the residue was purified by gel chromatography (Sephadex LH-20; eluent MeOH–CH_2Cl_2), followed by recrystallization from CH_2Cl_2–MeOH–ether. Complex **4a** was obtained as pale green crystals without solvate molecules (149 mg, 78%).

β-Alkylation–α-Halogenation of α,β-Acetylenic Diazoalkane Complexes. The following procedure is representative. To a stirred THF solution (10 mL) of $LiCuPh_2$, prepared from CuI (46.6 mg, 0.222 mmol) and PhLi solution (0.44 mmol), was added **6b** (190 mg, 0.148 mmol) at −20 °C. After the mixture was stirred for 40 min at the same temperature, I_2 (62 mg, 0.24 mmol) was added to the resulting reddish brown solution and stirring was continued for a further 20 h at room temperature. The reddish brown reaction mixture was quenched with 3 mL of diluted aqueous HCl, and CH_2Cl_2 (20 mL) was added. The organic layer was washed successively with aqueous $Na_2S_2O_3$ (5%, 40 mL × 2) and aqueous NH_4BF_4 (5%, 40 mL × 4), dried over $MgSO_4$, and evaporated. The residue was extracted with MeOH and recrystallized twice from CH_2Cl_2–ether. [WF(NN=CHCl=CPh_2)(dpe)$_2$][BF_4] (**9a**) was obtained as yellow-green crystals (111 mg, 52%): ^1H NMR ($CDCl_3$) δ 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 5.67 (s, 1 H, NN=CH), 6.01 (d, 2 H, J = 7.6 Hz, *o* H of Ph (*cis* to CH=NN)), 6.68 (t, 2 H, J = 7.6 Hz, *m* H of Ph (*cis* to CH=NN)), 6.8–7.4 (m, 46 H, Ph); IR 1528 (C=C), 1505 cm^{-1} (C=N). Anal. Calcd for $C_{67}H_{59}N_2WIP_4F_5B$: C, 56.17; H, 4.15; N, 1.96; I, 8.86. Found: C, 55.87; H, 4.16; N, 1.97; I, 9.27.

[WF(NN=CHCBr=CPh_2)(dpe)$_2$][BF_4] (9b): yellow-green crystals from CH_2Cl_2–ether; ^1H NMR ($CDCl_3$) δ 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 6.03 (d, 2 H, J = 7.7 Hz, *o* H of Ph (*cis* to CH=NN)), 6.16 (s, 1 H, NN=CH), 6.71 (t, 2 H, J = 7.7 Hz, *m* H of Ph (*cis* to CH=NN)), 6.8–7.4 (m, 46 H, Ph); IR 1547 (C=C), 1512 cm^{-1} (C=N). Anal. Calcd for $C_{67}H_{59}N_2WBrP_4F_5B$: C, 58.08; H, 4.29; N, 2.02; Br, 5.77. Found: C, 57.89; H, 4.28; N, 2.16; Br, 5.79.

[WF(NN=CHCCl=CPh_2)(dpe)$_2$][BF_4] (9c): green crystals from CH_2Cl_2–ether; ^1H NMR ($CDCl_3$) δ 2.6–2.8 (m, 4 H, CH_2 of dpe), 2.8–3.0 (m, 4 H, CH_2 of dpe), 6.04 (dd, 2 H, J = 8.0, 0.9 Hz, *o* H of Ph (*cis* to CH=NN)), 6.27 (s, 1 H, NN=CH), 6.74 (t, 2 H, J = 8.0 Hz, *m* H of Ph (*cis* to CH=NN)), 6.8–7.4 (m, 46 H, Ph); IR 1541 (C=C), 1506 cm^{-1} (C=N). Anal. Calcd for $C_{67}H_{59}N_2WClP_4F_5B$: C, 60.00; H, 4.43; N, 2.09; Cl, 2.64. Found: C, 59.83; H, 4.44; N, 2.68; Cl, 2.98.

(*E*)-[WF(NN=CHCl=CMePh)(dpe)$_2$][BF_4] ((*E*)-9d):[17] green crystals from MeOH–ether–hexane; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H, Me), 2.6–3.0 (m, 8 H, CH_2 of dpe), 5.60 (s, 1 H, NN=CH), 6.10 (d, 2 H, J = 7.6 Hz, *o* H of Cl=CMe*Ph*), 6.75 (t, 2 H, J = 7.6 Hz, *m* H of Cl=CMe*Ph*), 6.8–7.4 (m, 41 H, Ph); IR 1549 (C=C), 1507 cm^{-1} (C=N). Anal. Calcd for $C_{62}H_{57}N_2WIP_4F_5B$: C, 54.33; H, 4.19; N, 2.04. Found: C, 54.46; H, 4.32; N, 2.07.

(*Z*)-[WF(NN=CHCl=CMePh)(dpe)$_2$][BF_4]·CH_2Cl_2 ((*Z*)-9d·CH_2Cl_2):[17] green crystals from CH_2Cl_2–ether; ^1H NMR ($CDCl_3$) δ 0.97 (s, 3 H, Me), 2.7–2.9 (m, 4 H, CH_2 of dpe), 2.9–3.1 (m, 4 H, CH_2 of dpe), 5.48 (s, 1 H, NN=CH), 6.8–7.4 (m, 45 H, Ph); IR 1572 (C=C), 1512 cm^{-1} (C=N). Anal. Calcd for $C_{63}H_{59}N_2WICl_2P_4F_5B$: C, 51.99; H, 4.09; N, 1.92. Found: C, 52.20; H, 4.08; N, 1.95.

Hydrolysis of Diazoalkane Complexes. The following procedure is typical. To a solution of diazoalkane complex **3c** (48.3 mg, 0.0387 mmol) in THF (3 mL) was added aqueous NaOH (0.25 M, 1 mL), and the mixture was stirred vigorously under air at room temperature. The color of the organic layer gradually changed to reddish brown. The yield of 3-phenylbutyraldehdye was determined by GLC at 15–20-min intervals.

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(17) Recrystallization of the mixture of (*E*)- and (*Z*)-**9d** from CH_2Cl_2–MeOH–ether gave pure *E* and *Z* isomers as green prisms and green needles, respectively. The geometrical structures of (*E*)- and (*Z*)-**9d** were determined by the chemical shift of the resonance due to the phenyl (ortho and meta protons, (*E*)-**9d**) or methyl group ((*Z*)-**9d**). The protons of the phenyl or methyl group *cis* to the CH=NN group around the C=C double bond were expected to exhibit a high-field shift, caused by the shielding effect of the Ph groups of a dpe ligand.[3a]