Regioselective Alkylation of Tungsten Diazoalkane Complexes *via* Alkenyldiazenido Complexes†

Youichi Ishii, Hidekazu Miyagi and Masanobu Hidai*

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

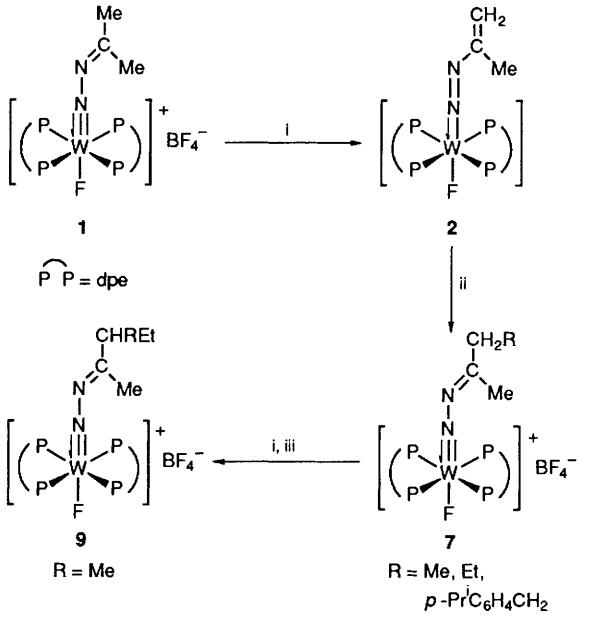
Tungsten alkenyldiazenido complexes, which are obtained by the deprotonation of diazoalkane complexes *trans*-[WF(NN=CRR')(dpe)$_2$][BF_4] (dpe = $Ph_2PCH_2CH_2PPh_2$) with lithium diisopropylamide (LDA) or $NaN(SiMe_3)_2$, undergo regioselective alkylation to give the *C*-alkylated diazoalkane complexes.

Diazoalkane complexes of molybdenum and tungsten,[2–6] which are readily obtained by protonation of the dinitrogen complexes with acids and subsequent reaction with carbonyl compounds,[2–4] have a unique conjugated structure including the central metal atom. However, little is known concerning their reactivity.[4,5,7,8] We have now found that the deprotonation of diazoalkane complexes with strong bases such as LDA provides a general route to alkenyldiazenido complexes. Here we describe the preparation and novel reactivity of tungsten alkenyldiazenido complexes.

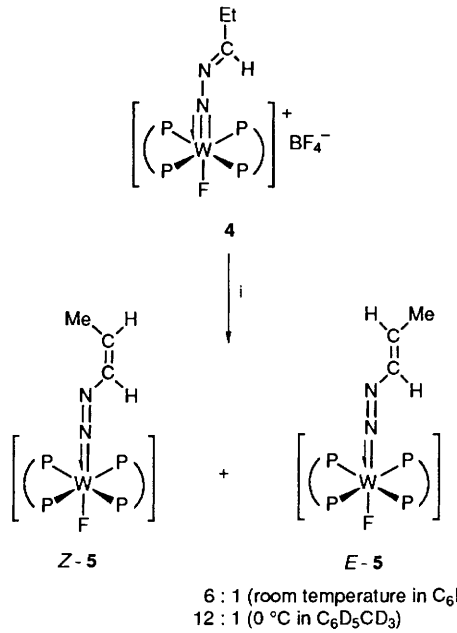
Treatment of a benzene suspension of a diazoalkane complex **1** with 1.5 equiv. of LDA or $NaN(SiMe_3)_2$ resulted in the formation of an orange-red solution. ^1H NMR analysis of the solution‡ and investigation of the reactivity of the resulting

† For Part 28 of the Series *Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes*, see ref. 1.

‡ Selected ^1H NMR (C_6D_6) data for **2**: δ 1.46 (s, 3H, NNC*Me*=CH_2), 3.36, 3.40 (2s, 1H × 2, NNCMe=CH_2). Satisfactory ^1H NMR and IR data have also been obtained for other alkenyldiazenido complexes, although analytically pure crystals could not be isolated owing to the instability of these complexes.

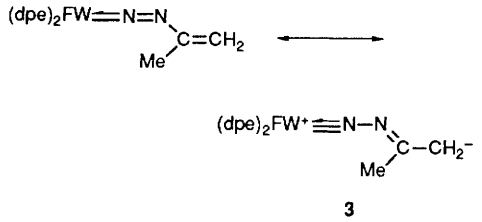


Scheme 1 *Reagents*: i, LDA or $NaN(SiMe_3)_2$; ii, RX (MeI, EtI, or *p*-$Pr^iC_6H_4CH_2Br$), then NH_4BF_4; iii, EtI, then NH_4BF_4



Scheme 2 *Reagent*: i, $NaN(SiMe_3)_2$

complex (*vide infra*) have revealed the quantitative formation of an alkenyldiazenido complex **2** by proton abstraction from the methyl group *cis* to the lone pair on the nitrogen in complex **1** (Scheme 1). Because the methyl group *trans* to the lone pair on the nitrogen is held in a sandwich position relative to two dpe phenyl groups, the other methyl group is exclusively attacked by LDA.[2,9] The IR spectrum showed ν (N=N) at 1390 cm^{-1} and ν (C=C) at 1587 cm^{-1}, which also supports the alkenyldiazenido structure. The ν (N=N) value of **2** is much lower than those of tungsten and molybdenum alkyldiazenido complexes reported,[10,11] suggesting that there is considerable contribution of a resonance structure **3** where the terminal carbon of the C=C bond is negatively charged (eqn. 1).



A striking feature of the deprotonation of diazoalkane complexes is the stereoselectivity with regard to the double bond formed. When a diazoalkane complex **4** was treated with $NaN(SiMe_3)_2$ at room temperature in C_6D_6, the products were a 6:1 mixture of two stereoisomeric alkenyldiazenido complexes, *Z*- and *E*-**5**.‡ Based on the coupling constants between the two sets of vinyl protons[12] (7.0 Hz and 13.1 Hz for the major and the minor isomers, respectively), the major product has been determined to be the *Z* isomer. Deprotonation at 0 °C in [$^2H_8$]toluene resulted in the increased *Z*:*E* ratio of 12:1 (Scheme 2). Some other alkenyldiazenido complexes *trans*-[WF(NNCH=CH_2)(dpe)$_2$], *trans*-[WF(NNCH=CHPh)(dpe)$_2$] and *trans*-[WF(NNC=$CH(CH_2)_3CH_2$)(dpe)$_2$] **6** have also been prepared in similar ways.‡

Alkenyldiazenido ligands may be regarded as a special kind of enamines and spectroscopic data of alkenyldiazenido complexes indicate that the terminal carbon of the alkenyl diazenido group is nucleophilic (*vide supra*). Thus, the reaction of an alkyl halide with an alkenyldiazenido complex is expected to give a new diazoalkane complex as a *C*-alkylation product, although *N*-alkylation has been reported in the case of alkyldiazenido complexes.[11,13] In fact, addition of an excess of alkyl halide (2–6 equiv.) to a benzene solution of complex **2** at room temperature resulted in a rapid change of colour from orange-red to brown, concurrent with precipitation of a *C*-alkylated cationic diazoalkane complex. After stirring for 3–24 h, anion exchange of I^- with BF_4^- followed by gel chromatography and recrystallization afforded **7** in 83–91% yield (Scheme 1). Similarly, treatment of **5** and **6** with MeI gives *trans*-[WF(NN=CHCHMe$_2$)(dpe)$_2$][BF_4] (82%) and *trans*-[WF(NN=CCHMe$(CH_2)_3CH_2$)(dpe)$_2$][BF_4]·½(CH_2Cl_2) **8** (73%), respectively,§ This illustrates that the sequential deprotonation–alkylation of a tungsten diazoalkane complex provides a facile *C*-alkylation method of the diazoalkane ligand.

Noteworthy is the fact that monoalkylated products were cleanly obtained in high yields, in contrast to the well known alkylation of enamines which often suffers from side reactions such as polyalkylation and *N*-alkylation.[14] Probably the bulky dpe ligands effectively prevent the undesired reactions and lead to the selective mono-*C*-alkylation. It should also be pointed out that the reactivity of the alkenyldiazenido group in the *C*-alkylation seems much higher than those of usual enamines. For comparison, cyclohexanone-pyrrolidine enamine was allowed to react with MeI under reaction conditions similar to those for the methylation of **6** (3 h), and GLC analysis after hydrolysis revealed that only 2% of 2-methylcyclohexanone was formed and 76% of cyclohexanone was recovered unchanged. The high nucleophilicity of the alkenyldiazenido complexes must reflect a substantial contribution of the resonance structure **3**.

From a synthetic point of view, it is interesting to mention that only *E*-isomers of diazoalkane complexes with regard to

§ The diazoalkane complexes obtained here are fully characterized by ^1H NMR, IR and elemental analyses. The *E*-stereochemistry with regard to the C=N bond was confirmed by its ^1H NMR spectrum which shows a high field shift of the resonance due to the Me group held in a sandwich position relative to two dpe phenyl rings.[2,9]

the C=N bond were obtained in the alkylations of complex **1**.§ This indicates the deprotonation–alkylation sequence proceeds regioselectively on the methyl group *cis* to the lone pair on the nitrogen in complex **1**. The high regioselectivity enables selective α,α-dialkylation by repeated deprotonation–alkylation reactions. For example, when **1** was successively alkylated with MeI and EtI, **9** was selectively obtained in 63% yield (Scheme 1). This makes a sharp contrast to the alkylation of carbonyl compounds *via* enamines and metalloenamines where α,α′-dialkylation usually occurs.[14]

In conclusion, the present study provides a novel regioselective alkylation method of diazoalkane ligands, which are readily derived from coordinated dinitrogen. Hydrolysis of the product is now under investigation and a preliminary trial of base promoted hydrolysis of **8** and **9** afforded 2-methylcyclohexanone and 3-methylpentan-2-one, respectively, in *ca.* 40% yield. These results suggest the potential utility of the diazoalkane complexes as a novel synthetic tool in the regioselective alkylation of carbonyl compounds.

The financial support by the Ministry of Education of Japan and the Asahi Glass Foundation of Engineering Technology is gratefully appreciated.

Received, 21st May 1990; Com. 0/02244F

References

1 H. Oshita, Y. Mizobe and M. Hidai, *Chem. Lett.*, 1990, 1303.
2 M. Hidai, Y. Mizobe, M. Sato, T. Kodama and Y. Uchida, *J. Am. Chem. Soc.*, 1978, **100**, 5740.
3 Y. Mizobe, Y. Uchida and M. Hidai, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1781.
4 P. C. Bevan, J. Chatt, M. Hidai and G. J. Leigh, *J. Organomet. Chem.*, 1978, **160**, 165.
5 R. Ben-Shoshan, J. Chatt, G. J. Leigh and W. Hussain, *J. Chem. Soc., Dalton Trans.*, 1980, 771.
6 P. C. Bevan, J. Chatt, A. A. Diamantis, R. A. Head, G. A. Heath and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1977, 1711.
7 C. J. Pickett, J. E. Tolhurst, A. Copenhaver, T. A. George and R. K. Lester, *J. Chem. Soc., Chem. Commun.*, 1982, 1071.
8 M. Hidai, S. Aramaki, K. Yoshida, T. Kodama, T. Takahashi, Y. Uchida and Y. Mizobe, *J. Am. Chem. Soc.*, 1986, **108**, 1562.
9 R. A. Head and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1980, 1150.
10 D. C. Busby, T. A. George, S. D. A. Iske, Jr. and S. D. Wagner, *Inorg. Chem.*, 1981, **20**, 22.
11 J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1977, 688.
12 J. Sauer and H. Prahl, *Chem. Ber.*, 1969, **102**, 1917.
13 W. Hussain, G. J. Leigh, H. Modh-Ali and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1986, 1473.
14 P. W. Hickmott, *Tetrahedron*, 1982, **38**, 1975.