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Regioselective Mono- and Di-C-acylation of Tungsten Diazoalkane Complexes via Alkenyldiazenido Complexes[1)]

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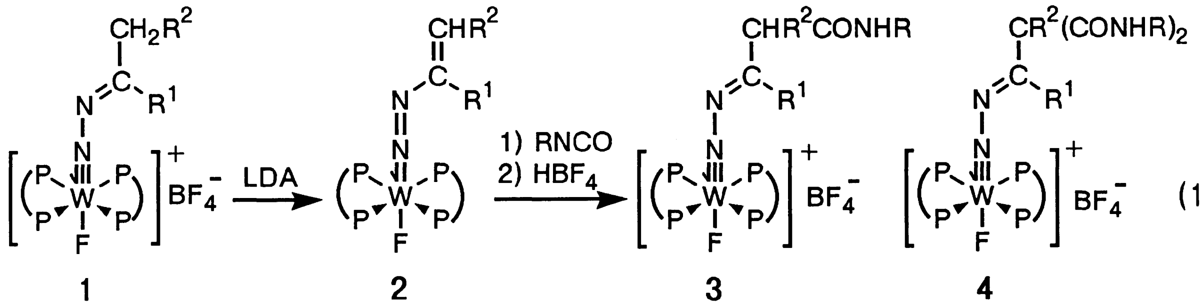
Tungsten alkenyldiazenido complexes reacted with isocyanates, isothiocyanate, and diphenylketene to give regioselectively α-acylated diazoalkane complexes after protonation. In the reaction of *trans*-[WF(NNCMe=CH_2)$(dpe)_2$] (dpe = Ph_2P-$CH_2CH_2PPh_2$) with excess aryl isocyanates, α,α-diacylated diazoalkane complexes such as *trans*-[WF{NN=CMeCH$(CONHPh)_2$}$(dpe)_2$][BF_4] were obtained, whose structure was determined by the X-ray analysis.

Diazoalkane complexes of molybdenum and tungsten having the M≡N-N=CRR' moiety (M=Mo,W) are readily derived from the corresponding dinitrogen complexes.2,3) However, there have been only a few reports on their chemical transformations.3,4) We have recently found that the deprotonation of tungsten diazoalkane complexes by a strong base provides a novel and general route to alkenyldiazenido complexes, and that the alkenyldiazenido ligands have high nucleophilicity to react with alkyl halides giving alkylated diazoalkane complexes.5) With a view to shedding light on the novel reactivities of the alkenyldiazenido complexes, reactions with heterocumulenes such as isocyanates were investigated. Here we describe the regioselective mono- and di-C-acylation of tungsten alkenyldiazenido complexes.

When an orange-red benzene solution of a tungsten alkenyldiazenido complex *trans*-[WF(NNCMe=CH_2)$(dpe)_2$]5) (**2a**), prepared by treatment of a benzene suspension of *trans*-[WF(NN=CMe_2)$(dpe)_2$][BF_4] (**1a**) with LDA, was allowed to react with PhNCO (1.1 equiv.) at r.t. for 20 h, the color of the solution changed to red. The reaction mixture was diluted with CH_2Cl_2 and washed with aqueous HBF_4. The resulting brownish green solution was dried over $MgSO_4$ and evaporated, and the residue was purified by gel-chromatography on Sephadex LH-20 and recrystalization from CH_2Cl_2/ether to give a C-acylated diazoalkane complex *trans*-[WF(NN=CMeCH_2CONHPh)$(dpe)_2$]-[BF_4] (**3a**) in 35% yield.6) The ^1H NMR spectrum7) of **3a** showed a methyl singlet at -0.50 ppm which is attributable to the methyl group held in a sandwich position relative to two dpe phenyl groups,2a,8) and this suggests that the acylation occurred regioselectively at the methyl group *cis* to the



(1)

lone pair on the nitrogen in complex **1a**. This regioselectivity probably arises from the steric effect of the dpe phenyl groups. In this reaction, no N-acylated complexes were isolated. Some other alkenyldiazenido complexes were similarly acylated by aryl and alkyl isocyanates and the results are summarized in Table 1.[7)] It should be noted that the deprotonation-acylation of *trans*-[WF(NN=CMeEt)(dpe)$_2$]BF$_4$ selectively occurred at the α-position of the ethyl group because of the same reason stated above.

When excess (5 equiv.) PhNCO was used in the reaction of **2a**, an α,α-diacylated diazoalkane complex *trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$][BF$_4$] **4a** was obtained in 51% yield after aqueous workup and purification analogous to those for **3a**. Although aryl isocyanates such as *p*-TolNCO and 1-NaphNCO reacted similarly to give the diacylated products, reaction with *t*-BuNCO resulted in the formation of the monoacylated complex only.

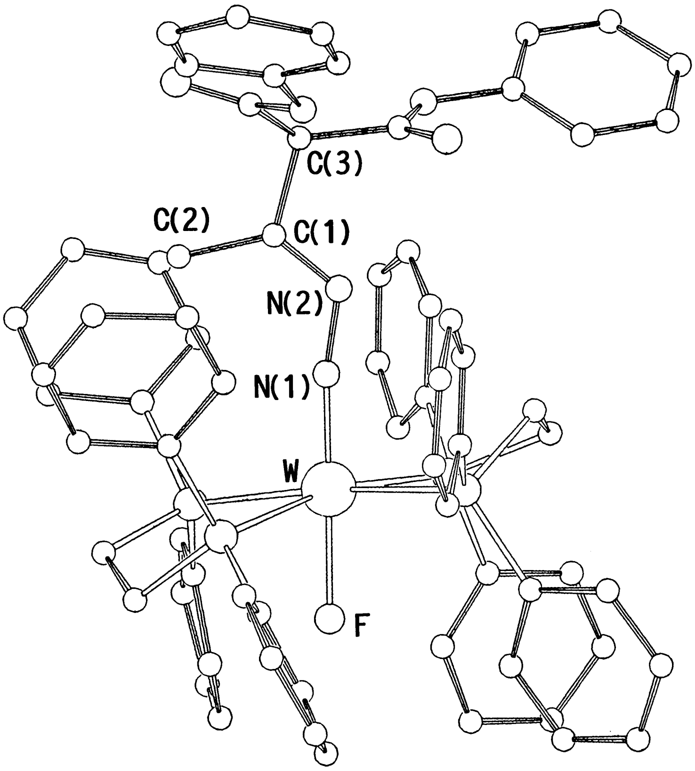
The α,α-diacylated structure of complex **4a** was not only supported by the ^{1}H NMR[7)] spectrum

Table 1. Acylation of **1** by Isocyanates[a)]

Substrate				Yield / %	
R^1	R^2	R	RNCO/**1**	**3**	**4**
Me	H	Ph	1.1	35	–
Me	H	Ph	5.0	–	51
Me	H	*p*-Tol	3.0	–	69[b)]
Me	H	1-Naph	3.0	–	66[c)]
Me	H	*t*-Bu	3.0	59	–
H	Me	*p*-Tol	3.0	50	–
H	Me	*t*-Bu	3.0	48	–
Me	Me	*p*-Tol	3.0	56	–
Me	Me	*t*-Bu	3.0	76	–

a) For reaction conditions, see text.
b) Reaction time, 1 h. c) Reaction time, 3 h.

but also confirmed by the X-ray analysis as depicted in Fig. 1.[9] The molecular structure is totally similar to those of known diazoalkane complexes *trans*-[WF(NN=CMeCH$_2$COMe)(dpe)$_2$][BF$_4$],[2a] *trans*-[WBr(NN=CHCH$_2$CH$_2$CH$_2$OH)(dpe)$_2$][PF$_6$],[8] and *trans*-[WBr(NN=CMe$_2$)(dpe)$_2$]Br.[8] The W-N-N linkage is almost linear and the methyl group is located in a sandwich position between two phenyl rings.

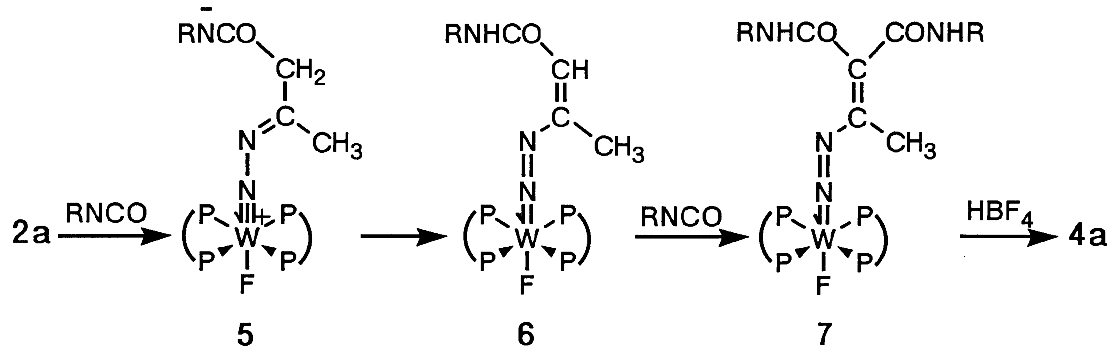


Selected bond lengths(Å) and angles(°):

W-N(1) = 1.77(1)
W-F = 1.96(1)
N(1)-N(2) = 1.33(2)
N(2)-C(1) = 1.30(3)
C(1)-C(2) = 1.48(3)
C(1)-C(3) = 1.54(3)
F-W-N(1) = 178.2(5)
W-N(1)-N(2) = 170.4(12)
N(1)-N(2)-C(1) = 122.2(16)

Fig. 1. An ORTEP drawing of *trans*-[WF{NN=CMeCH(CONHPh)$_2$}(dpe)$_2$]$^+$ (**4a**).

The α,α-diacylation is considered to proceed by the mechanism shown in Eq. 2. Complex **5**, which is formed by the first condensation of **2a** with PhNCO, undergoes intramolecular proton shift to give a new alkenyldiazenido complex **6**. This complex reacts with excess PhNCO to give a diacylated alkenyldiazenido complex **7**, and protonation of **7** by aqueous workup yields the diacylated diazoalkane complex **4a**.



(2)

Complex **2a** also reacted with phenyl isothiocyanate and diphenylketene to afford *trans*-$[WF(NN=CMeCH_2CSNHPh)(dpe)_2][BF_4]$ (67%) and *trans*-$[WF(NN=CMeCH_2COCHPh_2)(dpe)_2][BF_4]$ (80%), respectively. In these reactions, the acylation again occurred regioselectively, but no diacylated products were obtained. Further study on the reactivities of alkenyldiazenido complexes are in progress.

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6) A small amount of **4a** was detected in the reaction mixture by ^1H NMR.
7) Satisfactory ^1H NMR, IR, and analytical data have been obtained for the complexes reported here. Selected spectral and analytical data are as follows.
trans-$[WF(NN=CMeCH_2CONHPh)(dpe)_2][BF_4]$ (**3a**): ^1H NMR ($CDCl_3$) δ -0.50 (s, 3H, Me), 2.82 (s, 2H, CH_2), 9.06 (s, 1H, NH). IR (KBr) 1680 cm^{-1} ν(C=O). Anal. Found: C, 58.11; H, 4.64; N, 3.25%. Calcd for $C_{62}H_{59}N_3BF_5OP_4W$: C, 58.37; H, 4.66; N, 3.29%.
trans-$[WF\{NN=CMeCH(CONHPh)_2\}(dpe)_2][BF_4]$ (**4a**): ^1H NMR ($CDCl_3$) δ -0.39 (s, 3H, Me), 4.15 (s, 1H, CH), 9.37 (s, 2H, NH). IR (KBr) 1695 cm^{-1} ν(C=O). Anal. Found: C, 59.18; H, 4.66; N, 3.99%. Calcd for $C_{69}H_{64}N_4BF_5O_2P_4W$: C, 59.42; H, 4.62; N, 4.02%.
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9) Crystal data for complex **4a**: greenish brown blocks from CH_2Cl_2-MeOH-hexane, M = 1394.8, orthorhombic, space group $P2_12_12_1$, a = 13.764(4), b = 35.917(7), c = 12.986(4) Å, U = 6420(3) $Å^3$, Z = 4, D_{calcd} = 1.443 g/cm^3, D_{obsd} = 1.442 g/cm^3, μ(Mo Kα) = 48.06 cm^{-1}, R = 0.064, Rw = 0.077 for 5235 reflections ($|Fo| > 5\sigma(|Fo|)$). The conformation of complex **4a** in the crystal was determined based on the anomalous dispersion effects.

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