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Nucleophilic Reactions of Hydrazido(2-) Complexes of Molybdenum and Tungsten with Succinyl Dichloride and Phenyl Isocyanate†

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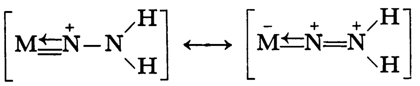
Nucleophilic attack of the $WNNH_2$ group in the hydrazido(2-) complex $[WF(NNH_2)(dpe)_2][BF_4]$ (dpe=$Ph_2PCH_2CH_2PPh_2$) on succinyl dichloride gives a novel ethanedioylhydrazido(2-) complex, $[WF(\overline{NNCOCH_2CH_2CO})(dpe)_2][BF_4]$. X-Ray structural analysis shows that the carbon, nitrogen, and oxygen atoms of the ethanedioylhydrazido(2-) ligand lie nearly in the same plane, indicating sp^2 character of the nitrogen atom bearing the two carbonyl groups. Phenyl isocyanate also undergoes nucleophilic attack by the hydrazido(2-) complex $[MBr(NNH_2)(dpe)_2]Br$ (M=Mo or W) to yield the phenylsemicarbazido(2-) type complex, $[MBr(NNHCONHPh)(dpe)_2]Br$. Treatment of the semicarbazido(2-) complex with triethylamine gives a new diazenido complex $[MBr(NNCONHPh)(dpe)_2]$.

Many hydrazido(2-) complexes containing the $MNNH_2$ moiety have been isolated by the reaction of dinitrogen complexes $[M(N_2)_2L_4]$ (M=Mo or W; L=phosphine) with acids.[1,2] These complexes are important intermediates in the reduction of ligating dinitrogen to both ammonia[3] and hydrazine.[4-6] The X-ray structural analyses of $[MoF(NNH_2)(dpe)_2][BF_4]$[2] and $[WCl(NNH_2)(dpe)_2][BPh_4]$[7] show that the M-N-N bond distances give a bond order greater than unity, the M-N bond distances being in line with considerable multiple bonding between the metal and nitrogen. This result is interpreted in terms of two resonance structures (i) and (ii). The basicity of the terminal nitrogen in the $MNNH_2$ moiety is, thus, expected to be weaker than that of hydrazine and amines. However, hydrazido(2-) complexes, $[MF(NNH_2)(dpe)_2][BF_4]$ and $[MX(NNH_2)(PMe_2Ph)_3]$ (M=Mo or W; X=Cl or Br), have been found to undergo condensation with a variety of aldehydes and ketones in a similar way to that for hydrazines, giving diazoalkane complexes containing the M≡N-N=CRR′ moiety.[8-11] In this paper, we wish to describe other nucleophilic reactions of hydrazido(2-) complexes with succinyl dichloride and phenyl isocyanate.



(i) (ii)

Experimental

All reactions were carried out under pure nitrogen atmosphere. Solvents were purified by the usual methods, thoroughly dried, and distilled under nitrogen atmosphere. Commercial succinyl dichloride, phenyl isocyanate, triethylamine, and sodium tetraphenylborate were used without further purification. The complexes *trans*-$[Mo(N_2)_2(dpe)_2]$[1,12] *trans*-$[W(N_2)_2(dpe)_2]$,[1] $[WF(NNH_2)(dpe)_2][BF_4]$,[9] $[MBr(NNH_2)(dpe)_2]Br$ (M=Mo or W),[1] and $[WBr(NNH)(dpe)_2]$[1] were prepared by the methods reported. IR spectra were determined with a Hitachi 215 spectrometer, ^1H-NMR spectra of the complexes $[MBr(NNHCONHPh)(dpe)_2]Br$ (M=Mo or W) with a Hitachi R-600 FT-spectrometer because of low solubility, and spectra of the other complexes with a JEOL PS-100 spectrometer. Analytical data are given in Table 1.

$[WF(\overline{NNCOCH_2CH_2CO})(dpe)_2][BF_4]$. To a yellow solution of $[WF(NNH_2)(dpe)_2][BF_4]$ (255 mg, 0.228 mmol) in dichloromethane (7.5 ml) was added succinyl dichloride (0.21 ml, 8 mol equiv.) at room temperature, and the mixture was stirred for 20 h. The red solution obtained was concentrated under reduced pressure to about half its volume, hexane (10 ml) then being added to precipitate the pinkish red crude product (246 mg, 90%). The product was recrystallyzed from chloroform–hexane (3—8 ml) and then chloroform–ether (3—6 ml) to give pure crystals which were dried *in vacuo* (97 mg, 35%). Suitable crystals for X-ray analysis were selected.

$[MoBr(NNHCONHPh)(dpe)_2]$. To a brown suspension of $[MoBr(NNH_2)(dpe)_2]Br$ (322 mg, 0.315 mmol) in tetrahydrofuran (10 ml) was added phenyl isocyanate (0.28 ml, 8 mol equiv.), and the mixture was stirred at refluxing temperature for 10 h. The green supension obtained was filtered off and the residue was crystallyzed from dichloromethane–hexane (15—15 ml). Green crystals were filtered off, washed with hexane, and then dried *in vacuo* (171 mg, 45%).

$[WBr(NNHCONHPh)(dpe)_2]Br$. This complex was prepared by the same method as described above for molybdenum analogue. From 219 mg of $[WBr(NNH_2)(dpe)_2]Br$ was obtained 114 mg of $[WBr(NNHCONHPh)(dpe)_2]Br$ as red crystals in 47% yield.

$[MoBr(NNCONHPh)(dpe)_2]$. To a stirred green suspension of $[MoBr(NNHCONHPh)(dpe)_2]$ (49 mg, 0.041 mmol) in tetrahydrofuran (3 ml) was added triethylamine (5.7 μl, 1 mol equiv.) After 2 h, to the orange homogeneous solution obtained was added ether (6 ml), affording orange crystals of $[MoBr(NNCONHPh)(dpe)_2]$ which were filtered off, washed with ether and dried *in vacuo* (23 mg, 50%).

$[WBr(NNCONHPh)(dpe)_2]$. *1)*: From 216 mg of $[WBr(NNHCONHPh)(dpe)_2]Br$ was obtained 64 mg of $[WBr(NNCONHPh)(dpe)_2]$ as orange crystals in 32% yield by the same method as described above for the molybdenum analogue.

2): To a yellow suspension of $[WBr(NNH)(dpe)_2]$ (95 mg, 0.087 mmol) in tetrahydrofuran (5 ml) was added phenyl isocyanate (76 μl, 8 mol equiv.) and the mixture was stirred at refluxing temperature for 2 h. From the brown solution obtained, red crystals of $[WBr(NNCONHPh)(dpe)_2]$ were precipitated by addition of ether, which were filtered off,

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† Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes 15. For part 14 of this series, see M. Hidai, T. Takahashi, I. Yokotake, and Y. Uchida, *Chem. Lett.*, **1980**, 645.

Table 1. Analytical and spectroscopic data of the new complexes

Complex	Found (Calcd)(%) C	H	N	IR (cm^{-1})[a] ν(C=O)	ν(N–H)	δ(N–H)	^1H-NMR δ/ppm[b]
$[WF(\overline{NNCOCH_2CH_2CO})(dpe)_2][BF_4]$	55.80 (56.12)	4.33 (4.37)	2.20 (2.34)	1720			2.0(s) $COC\underline{H}_2$
$[MoBr(NNHCONHPh)(dpe)_2]Br$	58.68 (58.96)	4.67 (4.62)	3.41 (3.50)	1715	3170 2730[c]	1530	1.5(s) $CON\underline{H}$ 11.7(s) $MNN\underline{H}$
$[WBr(NNHCONHPh)(dpe)_2]Br$	55.16 (54.94)	4.19 (4.31)	3.15 (3.26)	1710	3180 2800[c]	1540	1.5(s) $CON\underline{H}$ 10.5(s) $MNN\underline{H}$
$[WBr(NNDCONDPh)(dpe)_2]Br$	—	—	—	1700	2300 2150	1360	—
$[WBr(NNHCONHPh)(dpe)_2][BPh_4]$	64.05 (65.20)	4.82 (4.94)	2.60 (2.75)	1690	3300[d] 3380[d]	1530	4.7(s) $MNN\underline{H}$ 5.2(s) $CON\underline{H}$
$[MoBr(NNCONHPh)(dpe)_2]\cdot 1/2THF$[e]	62.47 (63.33)	5.23 (5.05)	3.60 (3.63)	1630	3380[d]	1510	5.6(s) $CON\underline{H}$
$[WBr(NNCONHPh)(dpe)_2]\cdot ether$[e]	58.67 (58.99)	4.69 (5.02)	3.28 (3.28)	1620	3400[d]	1510	5.7(s) $CON\underline{H}$

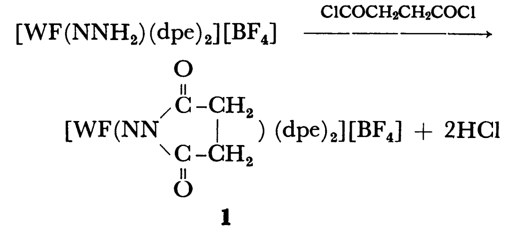
a) KBr disk. b) In CD_2Cl_2, relative to $SiMe_4$. s = Singlet. c) Broad. d) Nujol mulls, very weak. e) Determined from ^1H-NMR spectra.

washed with ether and then dried *in vacuo* (8 mg, 7%).

[WBr(NNHCONHPh)(dpe)₂][BPh₄]. A solution of $[WBr(NNHCONHPh)(dpe)_2]Br$ (280 mg, 0.217 mmol) in dichloromethane (18 ml) and a solution of sodium tetraphenylborate (297 mg, 4 mol equiv.) in dichloromethane–tetrahydrofuran (5—5 ml) were combined and stirred at room temperature. After 2 h, the reaction mixture was evaporated to dryness *in vacuo*, and the residue was extracted by dichloromethane (3 ml). Addition of hexane (5 ml) to the extract gave red crystalline solid of $[WBr(NNHCONHPh)(dpe)_2][BPh_4]$, which was filtered off, washed with hexane, and then dried *in vacuo* (221 mg, 67%).

Results and Discussion

Dinitrogen complexes $[M(N_2)_2(dpe)_2]$ and $[M(N_2)(RCN)(dpe)_2]$ (M=Mo or W; R=aryl) react with acyl or aroyl chlorides to give acyl- or aroyldiazenido complexes, $[MCl(NNCOR')(dpe)_2]$ (R'=acyl or aroyl), which, on treatment with hydrochloric acid, are converted into acyl- or aroylhydrazido(2-) complexes, $[MCl(NNHCOR')(dpe)_2]Cl$.[13,14] The latter complexes are also obtained by nucleophilic reactions of the hydrazido(2−) complex $[WCl(NNH_2)(dpe)_2]Cl$ with acyl halides.[15] We have found that the hydrazido (2−)complex $[WF(NNH_2)(dpe)_2][BF_4]$ reacts smoothly with succinyl dichloride to give ethanedioylhydrazido (2−) complex as follows.



$$[WF(NNH_2)(dpe)_2][BF_4] \xrightarrow{ClCOCH_2CH_2COCl} [WF(NN\begin{smallmatrix}C(=O)-CH_2\\ | \\ C(=O)-CH_2\end{smallmatrix})(dpe)_2][BF_4] + 2HCl$$

1

When an excess of succinyl dichloride was added to an orange solution of $[WF(NNH_2)(dpe)_2][BF_4]$ at room temperature, a red solution was obtained after *ca.* 20 h, from which pink crystals of $[WF(\overline{NNCOCH_2CH_2CO})(dpe)_2][BF_4]$ (**1**) were isolated. When adipoyl dichloride and phthaloyl dichloride were used instead of succinyl dichloride, no analogous products were obtained, probably because of steric effects. Treatment of another complex, $[WBr(NNH_2)(dpe)_2]Br$, with succinyl dichloride did not proceed satisfactorily under the same conditions. The lower reactivity of the latter is caused by the lower nucleophilicity of the terminal nitrogen atom relative to that of $[WF(NNH_2)(dpe)_2][BF_4]$, as estimated by the δ-value of the hydrazido protons in the ^1H-NMR spectra ($[WBr(NNH_2)(dpe)_2]Br$: 6.3 ppm;[1] $[WF(NNH_2)(dpe)_2][BF_4]$: 4.5 ppm[9]).

In the IR spectrum of **1**, a strong absorption band assignable to ν(C=O) was observed at 1720 cm^{-1}, higher by 25 cm^{-1} than that of succinimide. This shows that the carbonyl groups in complex **1** have no single bond character and the lone pair electrons on the terminal nitrogen atom do not flow over the carbonyl groups. Four succinyl protons appeared in the ^1H-NMR spectrum at 2.0 ppm as a singlet peak, indicating that four protons are completely equivalent.

X-Ray analysis was performed to determine the

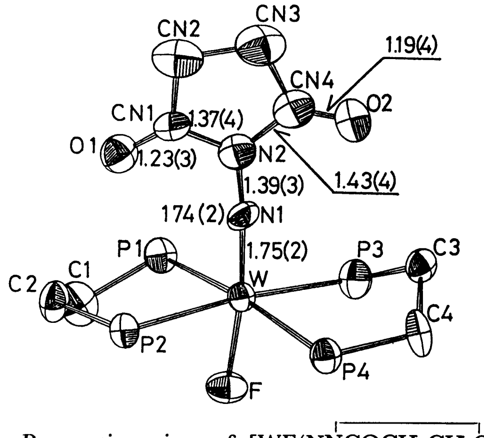
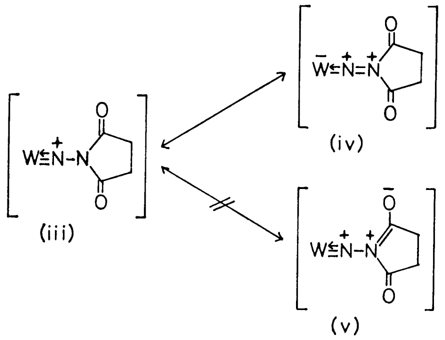


Fig. 1. Perspective view of $[WF(\overline{NNCOCH_2CH_2CO})(dpe)_2][BF_4]$. The shapes of the atoms on this drawing represent 50% probability contours of thermal motions. The bond angles are as follows: W-N1-N2=174.16°, N1-N2-CN1=120.50°, N1-N2-CN4=125.85°, CN1-N2-CN4=113.64°, N2-CN1-O1=122.01°, CN2-CN1-O1=123.99°, CN2-CN1-N2=113.86°.

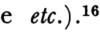
structure of ethanedioylhydrazido(2−) ligand. However, since a good crystal could not be obtained, the final residuals were R=0.109 and Rw=0.097 using block-diagonal least squares with anisotropic thermal factors for nonhydrogen atoms, and further refinement was no longer carried out.16)

Analysis shows that this complex has an octahedral geometry with the ethanedioylhydrazido(2−) ligand and fluoride anion in a trans position (Fig. 1). The W–N–N linkage is essentially linear. From the result of angle summations around the terminal nitrogen and two carbonyl carbon atoms, it is concluded that two nitrogen, four carbon, and two oxygen atoms lie in the same plane. This indicates that the terminal nitrogen atom is predominantly sp^2 hybridized. Considering the fact that the lone pair electrons on the terminal nitrogen do not flow over the carbonyl groups, the canonical structures (iv), rather than structure (v), might take part in the formation of structure (iii) to some extent.


(iii) (iv) (v)

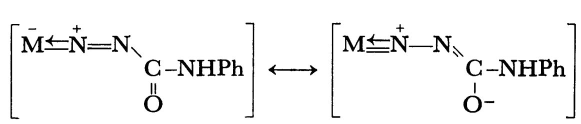
We have found that hydrazido(2−) complexes $[MBr(NNH_2)(dpe)_2]Br$ (M=Mo or W) react with phenyl isocyanate to give the semicarbazido type complexes [MBr(NNHCONHPh)$(dpe)_2$]Br.

The reaction is understood as the nucleophilic addition of the terminal nitrogen in the hydrazido(2−) ligand to the electron-defficient carbon in phenyl isocyanate.

When the hydrazido(2−) complexes $[MBr(NNH_2)(dpe)_2]Br$ suspended in tetrahydrofuran were treated with excess phenyl isocyanate at refluxing temperature for 10 h, the semicarbazido type complexes [MBr(NNHCONHPh)$(dpe)_2$]Br precipitated from the reaction mixture as a green (M=Mo) or red (M=W) solid. The complexes were obtained as pure crystals by crystallization from dichloromethane–hexane. In their IR spectra (Table 1), strong absorption bands characteristic of the amide group were observed (M=Mo: ν(C=O)=1715 cm^{-1}, δ(N–H)=1530 cm^{-1}; M=W: ν(C=O)=1710 cm^{-1}, δ(N–H)=1540 cm^{-1}). As regards the tungsten complex, frequencies assigned to ν(N–D) and δ(N–D) were observed on deuteration by D_2O. The shift to low frequency and the peak broadening of the N–H stretching bands are interpreted in terms of hydrogen bonding between the proton and bromide anion. This hydrogen bonding seems to be formed between the more electropositive hydrazido proton and bromide anion; the lower stretching band is due to the NH moiety in the NNH and the higher one to that in the amide group. The existence of hydrogen bonding is also supported by the result obtained from the ^1H-NMR spectra of these complexes (Table 1), that is, NNH protons were observed at 11.7 ppm for Mo and 10.5 ppm for W. The shift to a lower field from the usual NH region is due to the hydrogen bonding with bromide anion. Similar observations have been reported for $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$6) and $[WBr(NNH_2)L(PMe_2Ph)_3]Br$ (L=N-Me *etc.*).16) On the other hand, the amido protons appeared at relatively high field (M=Mo and W; 1.5 ppm) which may be explained by the shielding effect of the phenyl groups of dpe ligands. Analogous results have been found in the methyl protons of the complex, $[WF\{NN{=}C(C\underline{H}_3)CH_2COCH_3\}(dpe)_2][BF_4]\cdot THF$9) and $[WBr\{NN{=}C(C\underline{H}_3)CH_3\}(dpe)_2]Br$.18)

When the semicarbazido type complex [WBr(NNHCONHPh)$(dpe)_2$]Br was treated with excess sodium tetraphenylborate, anion exchange took place to afford the red complex [WBr(NNHCONHPh)$(dpe)_2][BPh_4]$. Since hydrogen bonding between NNH proton and the anion no longer exists in this complex, the NH stretching band in the IR spectrum and the NH resonance in the ^1H-NMR spectrum appear in the usual neutral NH region. The amido proton is observed at 5.2 ppm in the ^1H-NMR spectrum, lying in the common amido proton region. The cleavage of the hydrogen bonding might give rise to the conformational change, the amido proton being freed from the position shielded by the phenyl groups of dpe ligands. Spectroscopic data are summerized in Table 1.

The semicarbazido type complexes [MBr(NNHCONHPh)$(dpe)_2$]Br (M=Mo or W) easily react with a weak base such as triethylamine to afford the new diazenido complexes [MBr(NNCONHPh)$(dpe)_2$]. Strong absorption bands characteristic of the amide group were observed in the IR spectra, and amido protons appearing in the common amido region in the ^1H-NMR spectra. The relatively low ν(C=O) frequencies observed (M=Mo: 1630 cm^{-1}; M=W: 1620 cm^{-1}) as compared with the semicarbazido type complexes (M=Mo: 1715 cm^{-1}; M=W: 1710 cm^{-1}) can be explained by the large contribution of the structure (vii), which is formed by the electron flow from the metal to the carbonyl group.


(vi) (vii)

The combination of resonance structures has been proposed for the diazenido complex, [MoCl(NNCOPh)$(dpe)_2$].14,19) Spectroscopic data of the new diazenido complexes are also given in Table 1.

This diazenido complex, [WBr(NNCONHPh)$(dpe)_2$], can also be prepared by way of another route. The diazenido complex, $[WBr(NNH)(dpe)_2]$, obtained by the reaction of $[WBr(NNH_2)(dpe)_2]Br$ with triethylamine, reacts with phenyl isocyanate to give the complex [WBr(NNCONHPh)$(dpe)_2$]. This shows that the terminal nitrogen atom of the NNH ligand also has considerable nucleophilicity.20) These synthetic routes are summarized as follows.

$$\begin{tikzcd}
{[\mathrm{MBr(NNH_2)(dpe)_2]Br}} \arrow[r, "\mathrm{PhNCO}"] \arrow[d, "\mathrm{NEt_3}"'] & {[\mathrm{MBr(NNHCONHPh)\text{-}(dpe)_2]Br}} \arrow[d, "\mathrm{NEt_3}"'] \\
{[\mathrm{MBr(NNH)(dpe)_2]}} \arrow[r, "\mathrm{PhNCO}"] & {[\mathrm{MBr(NNCONHPh)\text{-}(dpe)_2]}}
\end{tikzcd}$$

As regards the nucleophilicity of the NNH ligand, Colquhoun has found that the NNH ligand in the complexes $[\mathrm{WX(NNH)(dpe)_2}]$ (X=F or Br) undergoes nucleophilic attack to 2,4-dinitrobenzene to give the dinitrophenylhydrazido complexes or, by successive deprotonation, dinitrophenyldiazenido complexes.21)

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16) The complex crystallized in the monoclinic space groups $P2_1/n$ with cell dimensions $a=17.92(1)$ Å, $b=18.26(1)$ Å, $c=17.59(1)$ Å, and $\beta=110.56(3)°$. Diffraction data were collected on a Rigaku automatic four-circle diffractometer; 4639 reflections ($|F_o|\geqq 3\sigma|F_o|$) were used in the structure solution and refinement. The structure was solved by the heavy atom method. The programs used for this analysis were UNICS and X-ray system, all calculations being carried out with a HITAC 8700/8800 computer.

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