**Supplementary Material Available:** Listings of experimental procedures for the syntheses of β-lactams, their spectral data, and structure determinations (15 pages). Ordering information is given on any current masthead page.

## Novel Arylation of Molecular Nitrogen via Bimetallic Activation: Reaction of Coordinated Dinitrogen with Coordinated Haloarene[1]

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*Received February 24, 1992*

C–N bond formation at coordinated dinitrogen has been attracting much attention in connection with direct synthesis of organo–nitrogen compounds from molecular nitrogen.[2] Of particular interest is the arylation of coordinated dinitrogen from both fundamental and industrial points of view. However, such reactions have rarely been reported in the literature. The only report dealing with the direct arylation of coordinated dinitrogen concerns the reaction of a molybdenum dinitrogen complex having a tetrathia macrocycle ligand with iodo- or bromoarenes to give aryldiazenido complexes.[3] More readily available molybdenum or tungsten dinitrogen complexes having phosphine ligands of the type $M(N_2)_2(L)_4$ (M = Mo or W; L = phosphine) have not been reported to undergo direct arylation.[4] In order to develop a novel method for arylation of coordinated dinitrogen, we have investigated reactions via bimetallic activation, i.e., reactions of coordinated dinitrogen with coordinated haloarenes. Coordination of haloarenes to transition metal complexes is known to be activated toward nucleophilic reactions.[5] Here we report that the bimetallic approach yields μ-aryldiazenido complexes.

Although an attempted reaction of $[W(N_2)_2(dpe)_2]$ (**1**, dpe = $Ph_2PCH_2CH_2PPh_2$) with $[Cr(p\text{-}FC_6H_4COOMe)(CO)_3]$ (**2**) failed to proceed, an anionic dinitrogen complex[6] $[^nBu_4N][W(NCS)(N_2)(dpe)_2]$ (**3a**) smoothly reacted with **2** in THF at room temperature to give a new complex which shows lower $\nu_{CO}$ (1948, 1867, 1857 cm$^{-1}$ (KBr)) than those of **2** (1991, 1902 cm$^{-1}$). The high reactivity of **3a** is attributable to strong back-donation from the anionic tungsten center to coordinated dinitrogen, which is reflected in the low $\nu_{NN}$ of **3a** (1860 cm$^{-1}$). Activation of the haloarene by the $Cr(CO)_3$ moiety must be essential for the reaction, since **3a** failed to react with noncoordinated $p\text{-}FC_6H_4COOMe$.

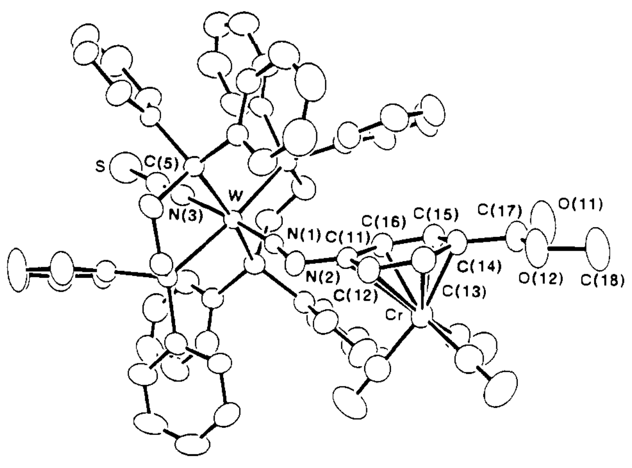
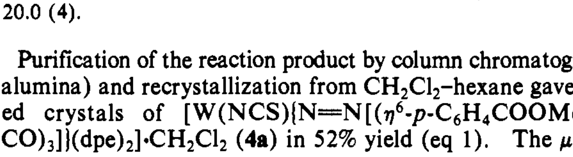


**Figure 1.** ORTEP view of the structure $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dpe)_2]$ (hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): W–N(1), 1.784 (4); N(1)–N(2), 1.314 (5); N(2)–C(11), 1.366 (6); Cr–C(11), 2.431 (5); Cr–C(12), 2.259 (5); Cr–C(13), 2.193 (5); Cr–C(14), 2.174 (5); Cr–C(15), 2.194 (5); Cr–C(16), 2.301 (5); W–N(1)–N(2), 164.9 (3); N(1)–N(2)–C(11), 120.0 (4).

Purification of the reaction product by column chromatography (alumina) and recrystallization from $CH_2Cl_2$–hexane gave dark red crystals of $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dpe)_2]\cdot CH_2Cl_2$ (**4a**) in 52% yield (eq 1). The μ-aryldiazenido structure is in good agreement with the above IR data as well as high-field shifted signals of the aromatic hydrogens in the $C_6H_4COOMeCr(CO)_3$ moiety in the $^1H$ NMR spectrum (δ ($C_6D_6$) 5.73, d, *J* = 7.3 Hz; 4.11, d, *J* = 7.3 Hz) and is further confirmed by an X-ray diffraction study.[7] As shown in Figure 1, **4a** has a significantly longer N=N bond (1.314 (5) Å) in comparison with similar singly bent diazenido complexes[4,8] (1.16–1.29 Å). It is more in the range of N–N bond lengths of hydrazido[8a,b,9] and diazoalkane[10] complexes (1.25–1.38 Å). Further, the Cr–C(11) bond (2.431 (5) Å) is longer than other Cr–arene carbon bonds (2.174 (5)–2.301 (5) Å). These data indicate the large contribution of resonance structure **5** (eq 2), whose zwitterionic structure is stabilized by the electron-withdrawing $Cr(CO)_3$.



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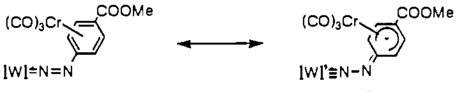

(2)

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[6] Although **3a** has been referred to as a thiocyanato in literature, its $\nu_{NCS}$ (2080 cm$^{-1}$) as well as the molecular structure of **4a** clearly indicates that it is an isothiocyanato: Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121.

[7] Crystal data: $M = 1422.89$; monoclinic, space group $P2_1/n$; $a = 24.135$ (3) Å, $b = 20.967$ (5) Å, $c = 12.273$ (5) Å, $\beta = 90.06$ (4)°; $V = 6210$ (5) Å$^3$; $Z = 4$; $D_{calcd} = 1.522$ g/cm$^3$, $D_{obsd} = 1.52$ g/cm$^3$; $\mu$(Mo K$\alpha$) = 23.31 cm$^{-1}$; $R = 0.034$, $R_w = 0.029$ for 7578 reflections with $I > 3.00\sigma(I)$.

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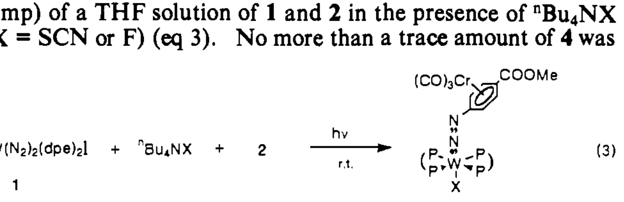
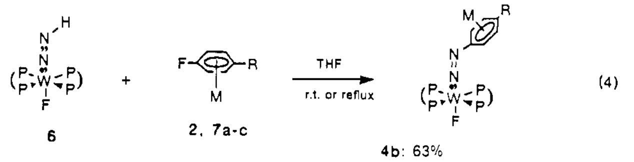
Complex **4** was also obtained by irradiation (tungsten-filament lamp) of a THF solution of **1** and **2** in the presence of $^nBu_4NX$ (X = SCN or F) (eq 3). No more than a trace amount of **4** was obtained in the absence of $^nBu_4NX$ or in the dark. Although the formation of $[^nBu_4N][WF(N_2)(dpe)_2]$ (**3b**) could not be confirmed, **3a** can be prepared by similar irradiation of **1** and $^nBu_4NSCN$ in THF.[6] Therefore in situ generated anionic dinitrogen complexes **3a** and **3b** are considered to be the intermediates which react with **2**. Since reaction 1 does not need irradiation, light probably liberates one of the dinitrogen ligands in **1**.



4a: X = NCS, 25%
4b: X = F, 24%

Alkylation of coordinated dinitrogen in complexes **1** and **3a** with alkyl halides has been considered to proceed by the attack of alkyl radical species generated from the halides on the dinitrogen ligands.[4,6,11] The facts which support the radical mechanism include the formation of organodiazenido or organohydrazido complexes having the *N*-tetrahydrofuranyl[11a] or *N*-benzyl[4] group in the reactions using THF or toluene as solvent, respectively. Such products are rationalized by considering the incorporation of THF$^\bullet$ and benzyl radicals generated by radical transfer between the solvent molecule and the initially formed alkyl radical. However, in reactions 1 and 3, no product incorporating the THF$^\bullet$ radical was isolated. Furthermore, in a reaction of **3a** with **2** in THF/toluene (2:1), we observed neither a decrease in the yield of **4a** (62%) nor formation of *N*-benzyl complexes due to the participation of benzyl radicals. These results strongly suggest that the observed arylation of the dinitrogen ligand proceeds not by a radical mechanism but by direct nucleophilic substitution at the coordinated haloarene. This is also in accord with the generally accepted reactivity of haloarene complexes.[5]

Finally, it should be pointed out that arylation of a diazenido or hydrazido complex derived from a dinitrogen complex can provide an indirect method of arylating dinitrogen. In spite of the well-documented nucleophilicity of diazenido and hydrazido complexes,[2a] such reactions have been investigated to a very limited extent; the only examples are reactions between $[WX(NNH_2)(dpe)_2]^+$ (X = Br, F, or $CF_3COO$) and 2,4-$(NO_2)_2C_6H_3F$.[12] We have now employed haloarene complexes **2** and **7a–c** in indirect dinitrogen arylation, which resulted in smooth reaction with a diazenido complex[13] $[WF(NNH)(dpe)_2]$ (**6**) at room temperature (**2**, **7b**, **7c**) or under THF reflux (**7a**) to give the corresponding $\mu$-aryldiazenido complexes **4b** and **8a–c** in good yields (eq 4). Spectroscopic and X-ray diffraction study[14] of these products revealed essentially the same type of $\mu$-aryldiazenido structure as that found for **4a**.



4b: 63%
8a: M = $Cr(CO)_3$, R = H, 63%
8b: M = $CpFe^+PF_6^-$, R = H, 84%
8c: M = $CpFe^+PF_6^-$, R = Me, 75%

As a conclusion, haloarene complexes have proved to be effective reagents for the direct and indirect arylation of coordinated dinitrogen. Novel reactivities of the unique $\mu$-aryldiazenido structure are now under investigation.

**Acknowledgment**. We thank Professor Yasuhiro Yamamoto and Dr. Tomoaki Tanase of Toho University for the X-ray diffraction analysis of **4a**.

**Supplementary Material Available:** Experimental details for the preparation of **4a** and **4b** and tables of positional parameters, anisotropic thermal coefficients, and bond lengths and angles for **4a** (13 pages); table of observed and calculated structure factors for **4a** (52 pages). Ordering information is given on any current masthead page.

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(14) The molecular structures of **4b** and **8c** were determined by X-ray diffraction analyses. The details will be reported elsewhere.

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## A Stable Solid That Generates Hydroxyl Radical upon Dissolution in Aqueous Solutions: Reaction with Proteins and Nucleic Acid

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*Received January 13, 1992*
*Revised Manuscript Received April 20, 1992*

Radiolysis, photolysis of peroxide species, and Fenton chemistry have all been used to generate hydroxyl radical (HO$^\bullet$) in aqueous solution. Access to radiolysis is limited by availability of a radioactive source ($^{60}Co$ or $^{137}Cs$) and, except in $N_2O$-saturated solution, generates a mixture of reactive species.[1] Photochemical HO$^\bullet$ generation methods involving hydrogen peroxide or alkyl hydroperoxides require irradiation at short wavelengths (254 nm) where the compounds targeted for reaction with HO$^\bullet$ often absorb.[2] Phthalimide hydroperoxides which generate HO$^\bullet$ from photoirradiation at longer wavelengths suffer from low photoefficiencies and require long irradiation times.[3] The iron–EDTA systems,[4] while sufficient for many purposes, become problematic in studies where addition of iron or hydrogen peroxide cannot be tolerated. The footprinting of DNA cleavage reagents such as bleomycin, which themselves utilize iron to effect cleavage, exemplifies this interference. The possible generation of oxidative species other than free HO$^\bullet$ [5] and quantitation of the amount of HO$^\bullet$ produced further complicate the use of these reagents. In this communication we describe the preparation and application of a solid which obviates the need for either sample irradiation or transition metal ion introduction while quickly generating an easily quantifiable amount of HO$^\bullet$. We demonstrate the convenient use of this solid to nonspecifically oxidize and cleave both DNA and protein.

A solid solution of potassium peroxonitrite (ONOOK) in potassium nitrate ($KNO_3$) can be generated by photolysis. Reagent grade $KNO_3$, a white crystalline solid, which has been crushed and sieved to between 250 and 420 $\mu m$ is irradiated in a rotating 3 × 28 cm quartz tube mounted parallel to three UV lamps. The solid $KNO_3$ is irradiated at 254 nm for 2 h while $N_2(g)$ flows through the tube to maintain the temperature at about 42 °C.

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