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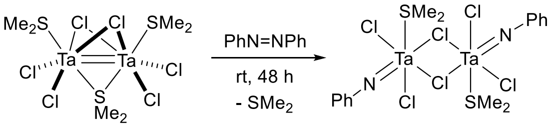
Metathesis Cleavage of an N=N Bond in Benzo[*c*]cinnolines and Azobenzenes by Triply-bonded Ditungsten Complexes†

Hideaki Ikeda, Kohei Nishi, Hayato Tsurugi,* and Kazushi Mashima*

A metathesis reaction of a W≡W bond and an N=N bond was observed by reacting a W-W triply-bonded W(III)$_2$ complex, $(^t\text{BuO})_3\text{W}\equiv\text{W}(\text{O}^t\text{Bu})_3$ (1), with benzo[*c*]cinnoline derivatives to form biphenyl-linked dinuclear (imido)tungsten complexes 2—4. When azobenzene was used as the substrate, a *trans* to *cis* isomerization induced by blue-LED light was essential prior to the metathesis cleavage of the N=N bond by the W≡W bond of $(\text{Me}_2\text{N})_2(\text{TfO})\text{W}\equiv\text{W}(\text{OTf})(\text{NMe}_2)_2$ (6), affording the corresponding imido-bridged dinuclear tungsten complexes 7—9.

Transition metal-mediated metathesis reactions have been extensively investigated and alkene and alkyne metathesis reactions are used to construct natural and pharmaceutical organic componds.[1] Notably, dinuclear metal complexes containing metal-metal triple bonds, especially W≡W complexes, are known to facilitate metathesis reactions of alkynes and nitriles, by which metal-alkylidyne and metal-nitride species are generated through cleavage of the C≡C and C≡N bonds of the substrates.[2] In contrast, metathesis-type cleavage of azo compounds is little explored, except for group 5 metal dinuclear complexes: Cotton *et al.* reported that a Ta=Ta bond of $[\text{Cl}_2(\text{Me}_2\text{S})\text{Ta}]_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)$ reacted with an N=N bond of azobenzene to give a dinuclear imidotantalum complex with doubly chloride-bridged ligands (eq 1).[3a] Herein we report that the W≡W scaffold in $\text{X}_2\text{YW}\equiv\text{WX}_2\text{Y}$ complexes (X = Y = O^{t}Bu; X = NMe$_2$, Y = OTf) could cleave an N=N bond of azo compounds *via* a metathesis pathway to afford dinuclear (imido)tungsten complexes as schematically shown in Figure 1. A *cis*-conformation of the N=N moiety in azo compounds was found to be crucial for the azo compounds to approach the ditungsten core to generate side-on bound μ-(η^2,η^2)-azo species as the plausible intermediate before cleaving the N=N bond.



(1)

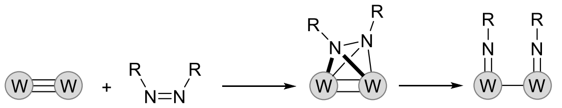
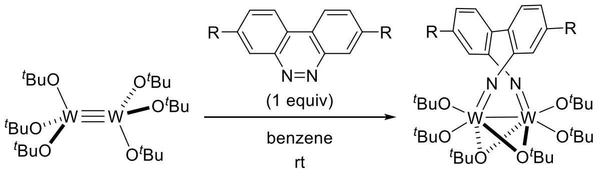


Fig. 1 Metathesis cleavage of N=N bond by W≡W bond.

Metathesis cleavage of an N=N bond occurred upon treating $(^t\text{BuO})_3\text{W}\equiv\text{W}(\text{O}^t\text{Bu})_3$ (**1**) with a cyclic azo compound, benzo[*c*]cinnoline, in benzene to afford biphenyl-bridged (phenylimido)tungsten complex **2** as red-colored microcrystals in quantitative yield (eq 2). In the ^{1}H NMR spectrum, one set of signals for the aryl moiety was observed at δ 7.32, 7.08, 7.02, and 6.91, suggesting a symmetric structure in solution. All the butoxy ligands were detected as one broad signal, and the integral ratio of the aromatic and butoxy protons indicated that the complexation reaction of **1** and benzo[*c*]cinnoline occurred in a 1:1 ratio. The overall molecular structure was clarified by an X-ray diffraction study (*vide infra*). After quenching **2** with H$_2$O, 1,1'-biphenyl-2,2'-diamine was obtained in the reaction mixture, suggesting the formula of the biphenyl-linked bimetallic (phenylimido)tungsten complex.[4] Thus, to the best of our knowledge, this is the first example of metathesis cleavage of an N=N bond using metal-metal triple bonds.

The ORTEP drawing of **2** is shown in Figure 2. The N=N bond of benzo[*c*]cinnoline is cleaved to form biphenyl-linked bimetallic (phenylimido)tungsten complex **2**. Thus, the distance of N1 and



(2)

1

2: R = H
3: R = Me
4: R = OMe

Department of Chemistry, Graduate School of Engineering Science,
Osaka University, Toyonaka, Osaka 560-8531, Japan
E-mail: mashima@chem.es.osaka-u.ac.jp; tsurugi@chem.es.osaka-u.ac.jp

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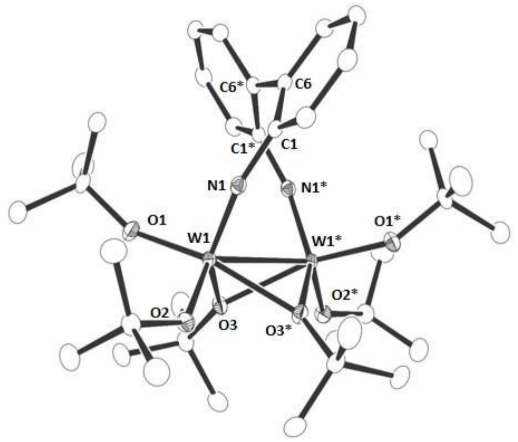
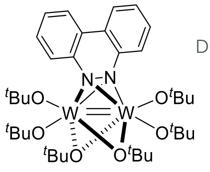


Fig. 2 ORTEP drawing of complex **2** with 50% thermal ellipsoid. All the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]; W1—W1* : 2.6782(5), W1—N1 : 1.7642(12), N1—N1* : 3.0926(17), W1—O1 : 1.8822(15), W1—O2 : 1.9276(11), W1—O3 : 2.0301(10), W1-N1-C1 : 162.87(11).

N1* (3.0926(17) Å) is reasonably elongated similarly to that of a normal N—N single bond.[5] The W—N1 bond length (1.7642(12) Å) and the W-N-C_{ipso} angle (162.87(11)°) are consistent with the terminal 6-electron donor imido ligands to early-transition metal centers with a high oxidation state.[6] The bond length of two tungsten atoms is 2.6782(5) Å, which is in the typical range for a W—W single bond.[7] Complex **2** has two types of *tert*-butoxido ligands, bridged and terminal ligands, and the bond length of W—O3 is slightly longer than that in terminal *tert*-butoxido ligands (W1—O1 = 1.8822(15) Å; W1—O2 = 1.9276(11) Å; W1—O3 = 2.0301(10) Å). The torsion angle of W1—W1* and C6—C6* ([W1]—[centroid of W1—W1*]—[centroid of C6—C6*]—[C6]) is 79.7°, a value that suggests a perpendicular approach of the benzo[*c*]cinnoline to the ditungsten core (*vide infra*).

We further checked the effect of the substituent at the 3,8-positions of the benzo[*c*]cinnoline: both of 3,8-dimethyl- and 3,8-dimethoxy-benzo[*c*]cinnolines could be also applicable to the metathesis cleavage by $W_2(O^tBu)_6$ (**1**) to give the corresponding bis(imido) tungsten complexes **3** and **4** in quantitative yields, whose structures were characterized by ^1H and ^{13}C NMR analyses. In addition, protonolysis of **3** and **4** afforded the corresponding 4,4'-dimethyl- and 4,4’-dimethoxy-1,1'-biphenyl-2,2'-diamines.

For the mechanism of cleavage of the N=N bond, $(^tBuO)_2W\{\mu\text{-}(\eta^2,\eta^2)\text{-(benzo[}c\text{]cinnoline)}\}(\mu\text{-}O^tBu)_2W(O^tBu)_2$ species **A** is proposed to be an intermediate prior to cleavage of the N=N bond, in which the W-W bond and N-N bond were perpendicular. A similar perpendicular coordination mode was observed for some dinuclear μ-(η^2,η^2)-(benzo[*c*]cinnoline) complexes of diniobium,[8] diiron,[9] and dizirconium[10] (Figure 3), in which the N=N bond was reduced to a single bond *via* two-electron transfer from two metal centers.



A

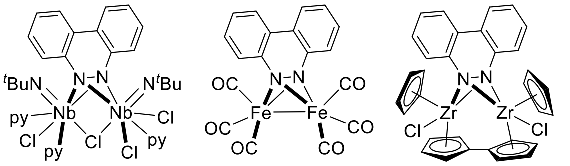


Fig. 3 Reported dinuclear μ-(η^2,η^2)-(benzo[*c*]cinnoline) complexes.

A linear azo compound, azobenzene, did not react with ditungsten complexes **1** and $(Me_2N)_3W{\equiv}W(NMe_2)_3$ (**5**), probably due to the difficult approach of the *trans* isomer to the ditungsten core. We accordingly used a ditungsten complex, $(Me_2N)_2(TfO)W{\equiv}W(OTf)(NMe_2)_2$ (**6**), bearing a labile triflate ligand and blue-LED irradiation conditions. When **5** was mixed with azobenzene in the presence of 2 equiv of Me_3SiOTf in benzene, complex **6** was formed, but no reaction was observed. Irradiation with 450-470 nm blue-LED light, however, led to the formation of phenylimido-bridged tungsten complex **7** (Scheme 1). Without the addition of Me_3SiOTf, we detected no reaction product from the reaction mixture, suggesting that the vacant site was indispensable for the NMe_2-bound ditungsten complex **5**. In addition, coordination of *in situ*-generated *cis*-azobenzene to the ditungsten core of **6** might proceed to generate **B**, similarly to the reaction of **1** with benzo[*c*]cinnoline, forming **A**. Because complex **7** was sparingly soluble and no signal was detectable in the ^1H NMR spectrum, structural determination was performed by the X-ray diffraction study (Figure 4). Complex **7** contains two W—W units linked by two bridging triflate ligands. Similar to complex **2**, the distance of N1 and N2 (2.819(7) Å) indicates complete scission of the N=N bond of azobenzene.[5] Phenylimido ligands asymmetrically bridge two tungsten atoms: one of four W—N bonds in the bridging phenylimido ligands is significantly elongated (W1—N1 = 2.106(5) Å) compared with other reported dinuclear tungsten(V) μ-imido complexes due to the *trans* influence of the electron-donating NMe_2 ligand,[6b,11] while the other W—N bonds of the μ-phenylimido moiety (W1—N2 = 1.988(5) Å; W2—N1 = 1.897(5) Å; W2—N2 = 1.931(5) Å) are shorter due to the presence of terminal and bridging triflate ligands in their *trans* position. In addition to the two μ-phenylimido ligands, one dimethylamido ligand bridges two tungsten centers. The W1—W2 bond length of 2.5255(4) is shorter than that in complex **2** as well as previously isolated and structurally characterized dinuclear tungsten(V) complexes due to the presence of three bridging ligands, two μ-phenylimido and one dimethylamido.[6b,6c,7,11] The dihedral angle of W1-N1-W2 and W1-N2-W2 planes is 135.3°, which is typical for the butterfly structure of doubly μ-arylimido-bridged bimetallic complexes.[12,13]

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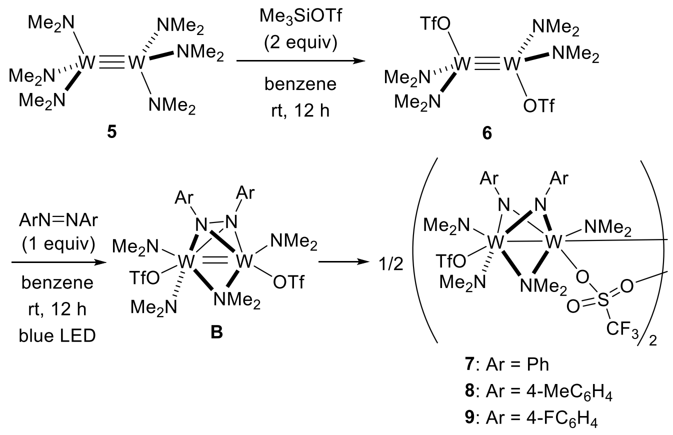

Scheme 1. Metathesis cleavage of the N=N bond of azobenzenes.

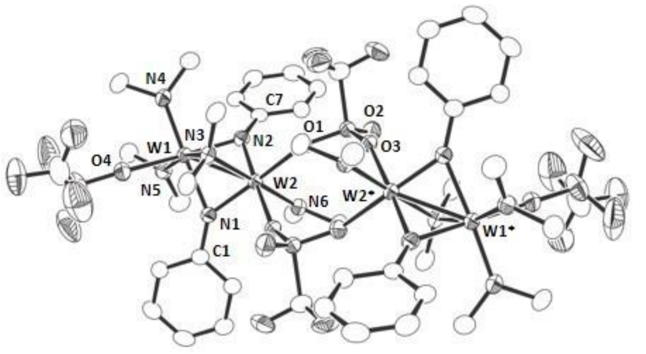

Fig. 4 ORTEP drawing of complex **7** with 50% thermal ellipsoid. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and bond angles [°]; W1—W2 : 2.5255(4), W1—N1 : 2.106(5), W1—N2 : 1.988(5), W2—N1 : 1.897(5), W2—N2 : 1.931(5), N1—N2 : 2.819(7), W1-N1-W2 : 78.04(17), W1-N2-W2 : 80.22(18), N1-W1-N4 : 170.67(19)

Under the same reaction conditions, N=N bond cleavage of substituted azobenzenes proceeded as follows: 4,4'-dimethylazobenzene and 4,4'-difluoroazobenzene reacted with **5** under blue-LED irradiation in the presence of Me_3SiOTf to afford corresponding tungsten complexes **8** and **9** as dark-red microcrystals in high yield (**8**: 71% yield; **9**: 83% yield). These complexes were characterized by elemental analysis. It is reasonable to assume that blue-LED light irradiation caused the isomerization of *trans*-azobenzene to the *cis* form.[14] In our experiments, after exposing a C_6D_6 solution of *trans*-azobenzene to blue-LED light for 2 h, *cis*-azobenzene was partially formed (19%), and all of the *cis*-azobenzene was rapidly consumed by adding the tungsten complex **5** and Me_3SiOTf.

In summary, we found that metathesis reactions of an N=N bond and a W≡W bond in $X_2YW{\equiv}WX_2Y$ complexes (**1**, X = Y = O^{t}Bu; **6**, X = NMe_2, Y = OTf) afforded the corresponding dinuclear bis(imido)ditungsten complexes **2—4**, and **7—9**, some of which were characterized by X-ray diffraction studies. The different reactivites of *trans* and *cis*-azobenzene indicated that μ-(η^2,η^2)-(N,N)-coordination was an important step for cleaving the N=N bond *via* a metathesis pathway.

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