Metathesis

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The Triple-Bond Metathesis of Aryldiazonium Salts: A Prospect for Dinitrogen Cleavage

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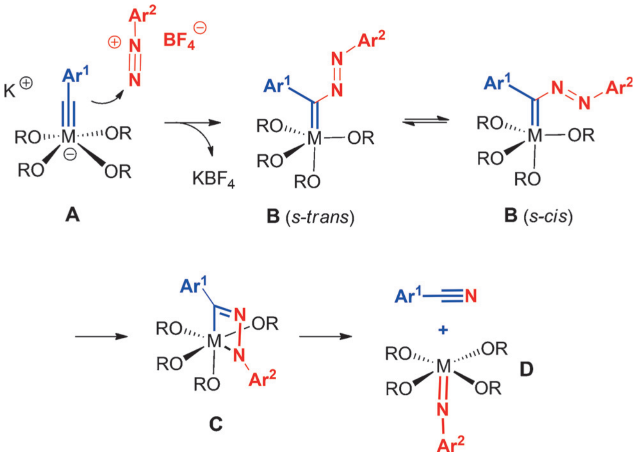
Dedicated to Professor R. R. Schrock on the occasion of his 70th birthday

***Abstract:** The {N_2} unit of aryldiazonium salts undergoes unusually facile triple-bond metathesis on treatment with molybdenum or tungsten alkylidyne ate complexes endowed with triphenylsilanolate ligands. The reaction transforms the alkylidyne unit into a nitrile and the aryldiazonium entity into an imido ligand on the metal center, as unambiguously confirmed by X-ray structure analysis of two representative examples. A tungsten nitride ate complex is shown to react analogously. Since the bonding situation of an aryldiazonium salt is similar to that of metal complexes with end-on-bound dinitrogen, in which {N_2}→M σ donation is dominant and electron back donation minimal, the metathesis described herein is thought to be a conceptually novel strategy toward dinitrogen cleavage devoid of any redox steps and, therefore, orthogonal to the established methods.*

The chemistry of aryldiazonium salts is largely dominated by two distinct reactivity modes:[1,2] loss of N_2 by heterolytic or homolytic pathways or attack of a suitable nucleophile at the terminal N atom with formation of an azo derivative.[3] Metal catalysts or promoters enhance these inherent patterns by oxidative insertion into the weak C–N bond by single-electron transfer, or by end-on coordination to the Ar-N_2^+ unit with formation of (transient) diazenido complexes.[4–6] We now report a fundamentally different transformation which is, to the best of our knowledge, without precedent in the literature.

Specifically, we conceived a metathetic cleavage of the $+{>}N{\equiv}N$ bond of aryldiazonium salts that might occur preferentially over nitrogen extrusion, even though the latter process is extremely facile. This expectation arose from the properties of Schrock alkylidynes, which comprise transition-metal centers in their highest possible oxidation state.[7,8] Therefore, such complexes will neither serve as single-electron donors nor will they undergo formal oxidative insertion reactions. By virtue of the nucleophilicity of the alkylidyne C atom, however, they might engage the terminal N atom of the diazonium unit in a way that mimics the behavior of conventional nucleophiles (Scheme 1).[1] Rather than giving ordinary azo compounds, Fischer carbene complexes of type **B** are expected to form.[9] If the barrier for *s-trans*/*s-cis* isomerization is low, such intermediates might evolve into a metallacycle of type **C**, which would ultimately furnish a nitrile and an arylimido-metal complex **D** upon formal [2+2] cycloreversion. We reasoned that this pathway could be promoted by not using neutral Schrock alkylidynes but rather the corresponding negatively charged ate complexes **A**: in this case, Coulombic attraction is expected to result in an increased affinity to a cationic aryldiazonium partner, which in turn will favor substrate uptake. Moreover, a salt by-product (KBF_4 in Scheme 1) will be formed concomitantly, which should pay valuable thermodynamic dividends. From a conceptual viewpoint, it is noteworthy that the consequent metathesis event gains a "unimolecular" character, different from the canonic [2+2] mechanism.[10–12]



Scheme 1. Conceived metathetic cleavage of an aryldiazonium salt; the escorting ions and the derived salt (here KBF_4) are arbitrarily chosen; M = Mo, W.

It was previously shown that molybdenum alkylidyne ate species such as **2** endowed with triarylsilanolate ligands are highly competent catalysts for alkyne metathesis (Scheme 2).[12–15] However, we attribute the reactivity of **2** to its demonstrated equilibrium under the reaction conditions with the neutral alkylidyne **3**, which exhibits excellent catalytic performance even in highly demanding synthetic applications. Furthermore, the formation of ate complexes is fully reversible upon coordination of donor ligands such as 1,10-phenanthroline, which affords adduct **4** in high yield.[13,14] Since the proposed cleavage of a diazonium salt was thought to require an intact ate complex, we initially avoided the use of **2**, instead resorting to more stable variants. Formal replacement of molybdenum by an inherently more Lewis-

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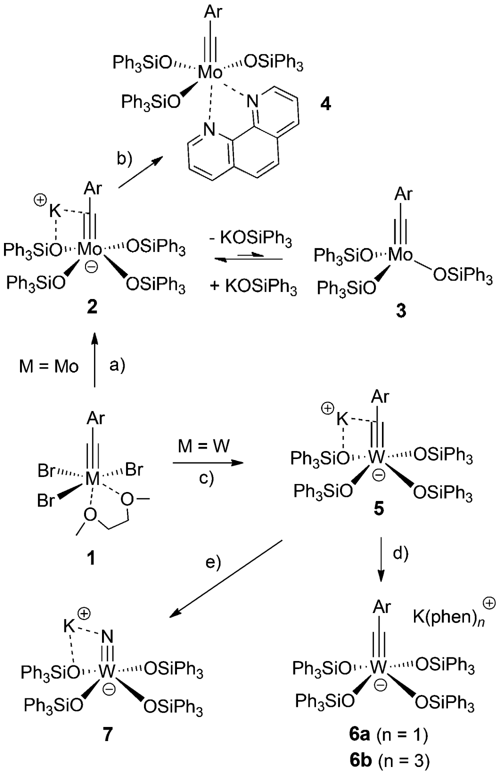


Scheme 2. Preparation of different ate complexes for the metathesis of aryldiazonium salts: a) Ph_3SiOK, toluene, 0°C→RT, 68%, see Ref. [14]; b) phen, toluene, 84%, see Ref. [14]; c) Ph_3SiOK, toluene, 58%; d) phen (1 or 3 equiv), toluene, 90% ($n=1$), 81% ($n=3$); e) propionitrile (5 equiv), toluene, 60°C, 70%. Ar = 4-$MeOC_6H_4$-; phen = 1,10-phenanthroline.

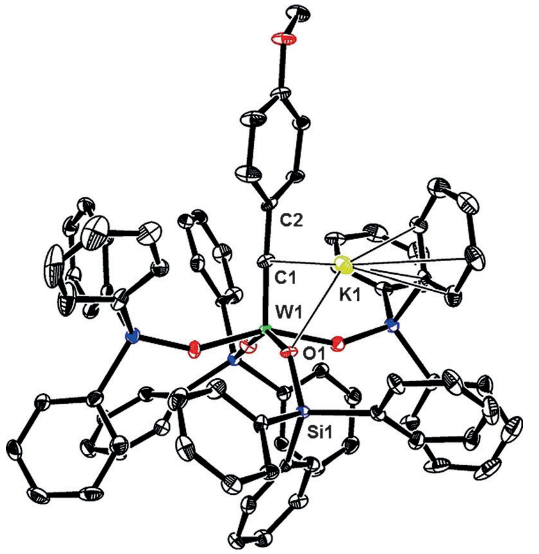


Figure 1. Structure of the tungsten alkylidyne ate complex **5**; cocrystallized CH_2Cl_2 is not shown for clarity; color code: W = green, O = red, Si = blue, K = yellow.

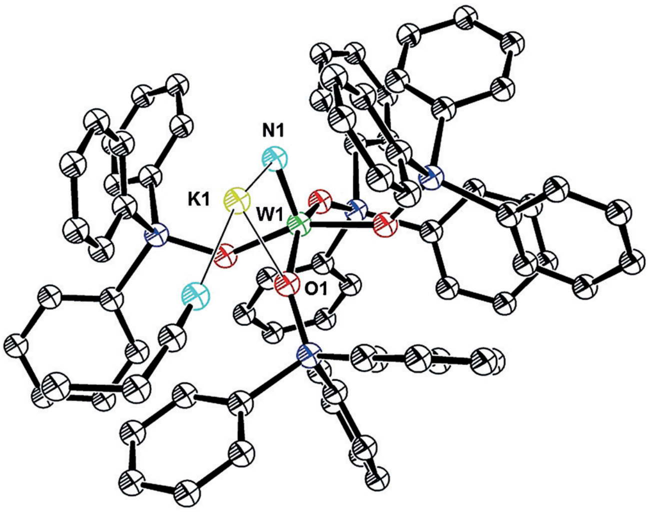


Figure 2. Structure of the tungsten nitride ate complex **7**·EtCN in the solid state; color code: W = green, O = red, Si = blue, K = yellow, N = cyan.

acidic tungsten center proved effective. Thus, the addition of Ph_3SiOK to a solution of **1** (M = W) in toluene furnished the analogous ate complex **5**, which shows no signs of dissociation of the fourth silanolate unit in solution. Complex **5** even persists in the presence of (excess) 1,10-phenantroline, which fails to bind the tungsten center but rather chelates the escorting potassium cation in the resulting complexes **6a** ($n=1$) and **6b** ($n=3$). Stoichiometric nitrile metathesis[16,17] allowed **5** to be converted in good yield into the corresponding nitride ate complex **7**,[18] which crystallizes with an equivalent of propionitrile ligated to the potassium counterion (**7**·EtCN).

The structure of complex **5** in the solid state is depicted in Figure 1, and those of the derived phenanthroline adducts **6a** and **6b** are contained in the Supporting Information. As expected, **5** adopts a square-pyramidal coordination geometry, with the alkylidyne forming the apex and the silanolates the basal plane. The W≡C distance at 1.769(7) Å is slightly longer than that of neutral alkylidyne complexes of this element[19] and the W1-C1-Ar unit is almost linear (177.1(6)°). The potassium counterion is held in place by weak contacts to an oxygen atom, the negatively polarized alkylidyne C atom, and the π cloud of one of the lateral phenyl rings. The structure of complex **7**·EtCN is largely similar (Figure 2); the key contacts to the escorting cation are now made by one of the silanolate O atoms and the terminal N atom, indicative of the nucleophilicity of the nitrido group.

Next, the reactivity of the tungsten alkylidyne ate complex **5** toward aryldiazonium salts was examined. Addition of a bright pink solution of **5** in CH_2Cl_2 to a solution of diazonium tetrafluoroborate **8b** (R = 4-*tert*-butyl) in the same solvent at −78°C leads to an instantaneous appearance of an intense purple color, which is tentatively ascribed to the formation of a carbene complex of type **B**, which comprises a diazenido substructure as an "azo-like" chromophore.[20] If the ate complex is instead added dropwise to the diazonium salt solution at 0°C, the purple color appears upon contact and fades within seconds. The mixture gradually turns yellow upon stirring; GC analysis after 30 min indicated 4-*tert*-

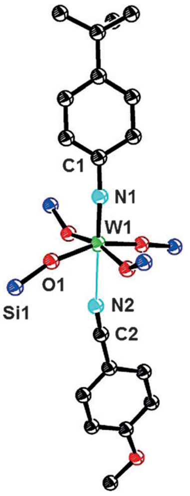
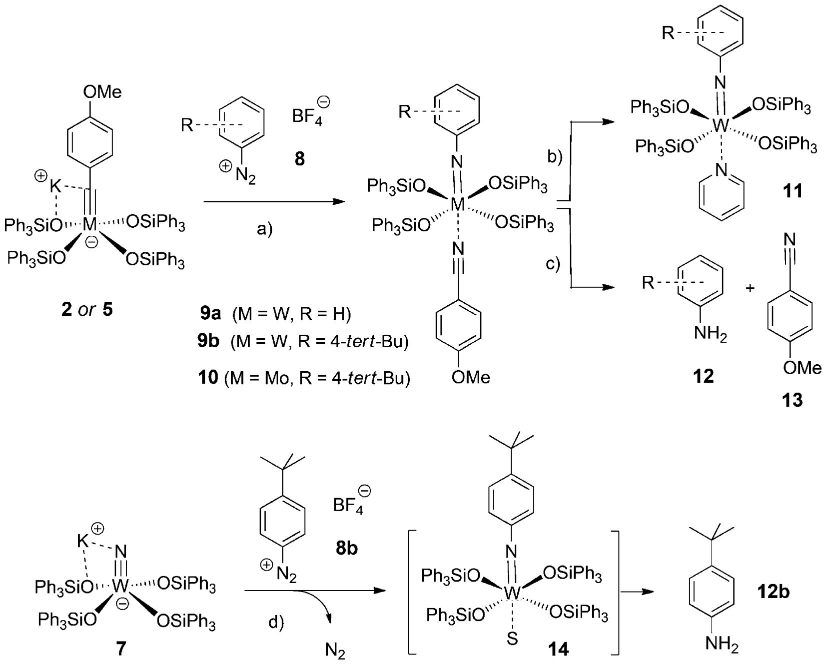


Figure 3. The structure of complex **9b** in the solid state; only the core region is depicted for clarity (for the entire structure, see the Supporting Information); color code: W = green, O = red, Si = blue, K = yellow, N = cyan.



Scheme 3. a) **8**, CH_2Cl_2, 0 °C→RT, 84 % (**9a**), 84 % (**9b**), 81 % (**10**); b) pyridine, 82 % (**11c**, R = 4-MeO), 71 % (**11d**, R = 4-F); c) H_2O, 73 % (**12e**, R = 2-Br), 60 % (**12f**, R = 2,6-dibromo), 51 % (**12g**, R = 2-phenyl); d) **8b**, CH_2Cl_2, −20 °C→RT, then H_2O, 72 %.

butylaniline (**12b**) and 4-$MeOC_6H_4CN$ (**13**) had formed as the only volatile organic products.[21] These compounds, as well as the recorded NMR spectra, are consistent with the formation of the tungsten imido complex **9b** by a purported metathesis reaction. Its presence and constitution was ultimately proven by single-crystal X-ray diffraction (Figure 3). **9b** features the expected N-aryl substituent derived from the diazonium salt and also ligates the substituted benzonitrile originating from the former alkylidyne unit; it is coordinated to the tungsten center *trans* to the imido group to complete a quasioctahedral ligand sphere. The interaction with the Lewis-acidic metal site leads to a slight elongation of the nitrile bond (N2-C2 1.160(8) Å).[22] As expected, the W=N-Ar group is slightly tilted (167.4(4)°) and the W=N bond length of 1.749(5) Å falls into the typical range.[23] In any case, the presence of both predicted fragments in a single complex proves that the [N≡N] unit of the aryldiazonium salt must have been cleaved by a formal triple-bond metathesis event. The use of ^{15}N-labeled diazonium salts confirmed these conclusions (for details, see the Supporting Information).

A selection of other aryldiazonium salts were cleaved analogously, thus showing that this novel reactivity mode is general (Scheme 3). In some cases, the imido complexes were best isolated after exchange of the nitrile by pyridine; alternatively, the crude material was hydrolyzed and the amount of the released aniline **12** and 4-methoxybenzonitrile (**13**) determined. Importantly, the reaction is not confined to the tungsten complex **5**. Specifically, the nitrido ate complex **7** was found to react analogously with release of N_2 (not detected). Although no single crystals of the expected imido complex **14** have been obtained so far (it lacks the stabilizing nitrile present in **9b**), the high yield of the corresponding aniline **12b** after hydrolytic work up leaves no doubt that a metathetic cleavage of the substrate must have taken place.[24] Furthermore, the molybdenum ate complex **2** proved equally competent, even though it is capable of reverting to the neutral alkylidyne **3** (see above);[13,14] the resulting product complex **10** was unambiguously characterized by X-ray diffraction and found to be isostructural to **9b** (see the Supporting Information). A control experiment proved that it is the ate complex **2** which accounts for the observed N_2 cleavage: thus, treatment of **8b** with authentic **3**[14] was unproductive, despite the remarkable performance of this particular neutral alkylidyne in regular alkyne metathesis.[25–27]

Although the metathesis of alkynes has gained considerable momentum in recent years,[12,28] not least because of the excellent application profile of **2** and relatives, the reactions typically require ambient temperature or higher.[29] In contrast, the metathesis of the aryldiazonium salts with **2**, **5**, or **7** proceeds even at ≤ −20 °C. This ease is even more remarkable when compared to the difficulty of cleaving the -C≡N bond, which limits the preparative significance of nitrile metathesis at this stage.[16] The ease can be attributed to a match between the properties of the diazonium substrates and the early transition metal alkyidyne ate complexes as reaction partners. Facile and likely irreversible nucleophilic attack leads to an intermediate which is uniquely poised for metathetic transformation to result in full N-N scission, with only a single bond rotation from *s-trans* to *s-cis* as the kinetic barrier. The robustness of this reactivity is reflected in the successful transformation of even fairly hindered diazonium derivatives (see Scheme 3).

This auspicious reactivity profile is, therefore, believed to provide opportunities beyond the aryldiazonium series. Such substrates can be thought of as consisting of a [N≡N] "ligand" acting as a σ donor to an aryl cation partner, with very little π character in the resulting C−N bond.[30,31] This bonding situation is analogous to that of certain (cationic) N_2-ligated metal complexes in which σ donation of the end-on-bound dinitrogen to the metal center is the dominant interaction, whereas electron back donation from the metal into the π* orbital of the N_2 ligand is minimal.[32–34] The net effect is a polarization of the {N≡N} unit, arguably increasing its susceptibility to nucleophilic attack by an alkylidyne (or nitride).[35] The transfiguration of the newly discovered mode of triple bond metathesis into a (stoichiometric) nitrogen cleavage process is, therefore, a tempting prospect.[36] Under this proviso, the reaction would be orthogonal to the established means of dinitrogen activation in that it does not comprise any redox steps;[37] it might excel in kinetic terms if the favorable reactivity profile observed with aryldiazonium salts were even partly retained. Finally, such a process would obviate ammonia as the product of N_2 fixation and allow nitrogen to be "stitched" directly into an organic product.[38] Although attempts to reduce this tantalizing prospect to practice will almost certainly require a broad screening campaign in view of the vast number of dinitrogen complexes that might qualify as possible substrates, efforts along these lines seem worthwhile and are underway in our laboratory.

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