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**Alkyne Metathesis by Molybdenum and Tungsten  
Alkylidyne Complexes**

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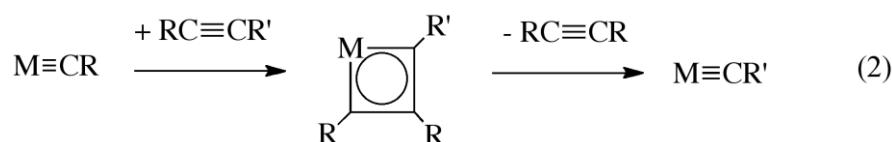
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In 1968 a paper was published by Penella, Banks, and Bailey<sup>1</sup> entitled "Disproportionation of Alkynes." In it they reported the conversion of 2-pentyne into a mixture of 2-butyne, 2-pentyne, and 3-hexyne (equation 1) employing a catalyst consisting of tungsten trioxide (6.8%) on silica that had been activated by treatment with dry air at 600 °C. The reaction was carried out in a fixed catalyst bed reactor at 200 to 450 °C. A few years later Mortreux showed that alkynes could be disproportionated by molybdenum oxide on silica.<sup>2</sup>



Disproportionation of alkynes by *homogeneous* tungsten catalysts was reported by Mortreux in 1974.<sup>3</sup> The catalyst consisted of molybdenum hexacarbonyl and resorcinol. A typical reaction employed *p*-tolylphenylacetylene in decalin containing Mo(CO)<sub>6</sub> and resorcinol in a sealed tube at 160 °C. Phenol and  $\alpha$ -naphthol were also effective in place of resorcinol.

In a 1975 paper concerning primarily the mechanism of alkene metathesis, Katz suggested<sup>4</sup> a mechanism for the alkyne metathesis reaction analogous to that proposed by Hérrison and Chauvin in 1971 for alkene metathesis,<sup>5</sup> namely a reaction between a metal-carbon triple bond and an alkyne to give an intermediate metallacyclobutadiene complex (equation 2). However, alkylidyne complexes known at that time, namely those prepared by Fischer<sup>6</sup> (e.g., Br(CO)<sub>4</sub>W $\equiv$ CPh), did not catalyze the metathesis of alkynes.



In 1974 the first high oxidation state alkylidene complex, Ta(CH-t-Bu)(CH<sub>2</sub>-t-Bu)<sub>3</sub>,<sup>7</sup> was reported, and the next year deprotonation of it to yield the first high oxidation state alkylidyne complex, [Li{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe}][Ta(C-t-Bu)(CH<sub>2</sub>-t-Bu)<sub>3</sub>].<sup>8</sup> Tantalum chemistry set the stage for the discovery of high oxidation state tungsten and molybdenum alkylidene and alkylidyne complexes.

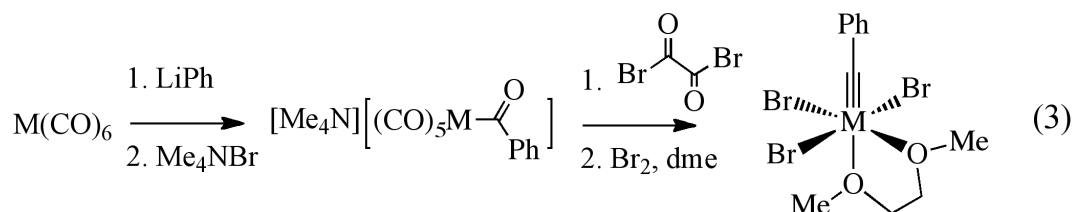
The method of preparing (t-BuCH<sub>2</sub>)<sub>3</sub>Ta=CH-t-Bu (treatment of Ta(CH<sub>2</sub>-t-Bu)<sub>3</sub>Cl<sub>2</sub> with two equivalents of LiCH<sub>2</sub>-t-Bu in pentane) led to exploratory reactions between tungsten or molybdenum chlorides and neopentyl reagents. In 1978 reactions between neopentyllithium and WCl<sub>6</sub> or MoCl<sub>5</sub> were reported to give compounds with the formula (t-BuCH<sub>2</sub>)<sub>3</sub>M $\equiv$ C-t-Bu in low yields (25% for M = W and 15% for M = Mo).<sup>9</sup> A reproducible route to (t-BuCH<sub>2</sub>)<sub>3</sub>W $\equiv$ C-t-Bu in relatively high yield (50%) made it possible to explore its chemistry in depth. One of the more remarkable reactions involving (t-BuCH<sub>2</sub>)<sub>3</sub>W $\equiv$ C-t-Bu is addition of three equivalents of HCl in

the presence of 1,2-dimethoxyethane to yield  $W(C-t-Bu)Cl_3(dme)$ .<sup>10</sup> Replacement of the three chlorides with lithium t-butoxide yielded  $W(C-t-Bu)(O-t-Bu)_3$ , which was found to metathesize  $RC\equiv CR'$  alkynes (e.g., 3-heptyne) rapidly at room temperature via  $W(CR)(O-t-Bu)_3$  and  $W(CR')(O-t-Bu)_3$  intermediates.<sup>11</sup>

The trichloride complex,  $W(C-t-Bu)Cl_3(dme)$ , served as a starting point for synthesizing a wide variety of  $W(C-t-Bu)X_3$  species, especially those in which X is a bulky alkoxide or aryloxy such as O-t-Bu,  $OCMe(CF_3)_2$ ,  $OCMe_2(CF_3)$ , O-2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, or O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. It became clear that bulky groups were required in order to maintain the monomeric nature of the trialkoxide alkylidyne complexes, which are 12 electron species if donation of electron density from alkoxide lone pairs is not included. Trigonal bipyramidal metallacyclobutadiene complexes could be observed and often isolated when the alkoxide is relatively electron withdrawing. For example, excess 3-hexyne reacts with  $W(C-t-Bu)(O-2,6-i-Pr_2C_6H_3)_3$  to yield t-BuC≡CEt and the tungstacyclobutadiene complex,  $W(C_3Et_3)(O-2,6-i-Pr_2C_6H_3)_3$ .<sup>12</sup> A wide variety of molybdenum neopentylidyne complexes of the type  $Mo(C-t-Bu)(OR)_3$  (OR = O-t-Bu,  $OCMe(CF_3)_2$ ,  $OCH(CF_3)_2$ ,  $OCMe_2(CF_3)$ , or O-2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) could be prepared from  $Mo(C-t-Bu)Cl_3(dme)$ ,<sup>13</sup> although development of Mo chemistry was limited by relatively low yields of the starting material,  $Mo(C-t-Bu)(CH_2-t-Bu)_3$ .

For nearly two decades Fürstner has explored organic applications of alkyne metathesis with well-defined alkylidyne complexes.<sup>14</sup> Fürstner found that trisamido Mo species prepared by Cummins<sup>15</sup> were catalyst precursors for the metathesis of alkynes in the presence of dichloromethane.<sup>16</sup> Among the products that could be identified from the reaction between dichloromethane and  $Mo(NAr_{Me}R)_3$  ( $Ar_{Me} = 3,5-C_6H_3$ , R = t-butyl) were  $MoCl(NAr_{Me}R)_3$  and  $Mo(CH)(NAr_{Me}R)_3$ . The latter was found to be relatively unreactive towards alkynes. One possibility is that some "mixed" (amido/chloro) species, e.g.,  $Mo(CH)(NAr_{Me}R)_{3-x}Cl_x$  where x = 1 or 2 is formed when  $Mo(NAr_{Me}R)_3$  reacts with dichloromethane and is the active catalyst.

Interest in Mo alkyne metathesis catalysts increased as a consequence of access to them via a "low oxidation state" approach pioneered by A. Mayr (equation 3)<sup>17</sup> and further elaborated recently by Tamm,<sup>18</sup> as well as the possibility of a more facile loss of an alkyne from a molybdacyclobutadiene intermediate and therefore higher alkyne metathesis activity. Both



tungsten and molybdenum alkylidyne complexes are now available on relatively large scales via the low oxidation state method.

Cummins devised routes to  $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R}'')_3$  species<sup>19</sup> and showed that addition of three equivalents of ROH to  $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R}'')_3$  led to  $\text{Mo}(\text{CR}')(\text{OR})_3$  complexes that were active for the metathesis of internal alkynes. Moore further improved the synthesis of  $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R}'')_3$  species through reactions between  $\text{Mo}(\text{NAr}_{\text{Me}}\text{R})_3$  and  $\text{R}'\text{CHCl}_2$  ( $\text{R}' = \text{H, Me, Et}$ ) in THF in the presence of excess Mg.<sup>20</sup> Addition of trifluoro-*o*-cresol or perfluoro-*t*-butanol to  $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R})_3$  led to active catalysts *in situ* that could be employed for a variety of internal alkyne metatheses. Typically an alkyne metathesis reaction is driven to completion through removal of a volatile product (e.g., 2-butyne or 3-hexyne) *in vacuo*. An alternative "precipitate driven" strategy, i.e., one where the unwanted symmetric alkyne product is *insoluble* and the desired product is *soluble*, was shown to be a viable alternative approach for certain reactions.<sup>21</sup> Moore also showed that molybdenum trisamido alkylidyne catalysts could be grafted onto a silica surface<sup>22</sup> to give catalysts with high activity and minimal leaching of the metal catalyst from the surface. Ligands that lead to highly active and selective alkyne metathesis catalysts typically have been aryloxides or siloxides,<sup>23</sup> although active catalysts have been prepared that employ, for example, imidazolin-2-iminato or phosphoraneiminato ligands.<sup>24</sup>

In general it has been challenging to metathesize terminal alkynes since acetylene itself often reacts destructively with alkylidyne catalysts. Initially some success was reported for tungsten catalysts; for example, Coutelier and Mortreux<sup>25</sup> found that  $\text{W}(\text{C-}t\text{-Bu})(\text{O-}t\text{-Bu})_3$  (4 mol%) in the presence of quinuclidine in toluene will metathesize 1-heptyne to 6-dodecyne (80-90% yield) at 80 °C in one minute. The most successful approach for metathesis of terminal alkynes is to employ molybdenum catalysts and to remove acetylene with molecular sieves.<sup>26</sup> Molecular sieves also have proven useful for removing 2-butyne in an alkyne metathesis reaction.<sup>23</sup>

Alkyne metathesis has lagged behind alkene metathesis in terms of applications, in part because alkenes are more available than alkynes and more common in organic synthesis. Also, since synthesis of *Z* olefins directly has become reality,<sup>27</sup> it is likely to be preferred over formation of a *Z* olefin through selective hydrogenation of an alkyne obtained in an alkyne metathesis reaction. However, impressive progress in the practical aspects of alkyne metathesis reactions, as well as applications,<sup>14</sup> guarantees that alkyne metathesis will continue to be useful for many transformations, obviously those in which a triple bond is the desired goal or those in which the alkyne is subjected to subsequent transformations other than hydrogenation to a *Z* olefin.

Alkyne metathesis is approximately 45 years old; alkene metathesis is approximately ten years older.<sup>28</sup> Alkyne and alkene metathesis have been intertwined closely in terms of discovery,

synthesis of well-defined catalysts, synthetic and mechanistic details, and applications to organic synthesis. It is also satisfying to see the synthetic connection between low oxidation state carbene and carbyne complexes obtained from Mo(CO)<sub>6</sub> or W(CO)<sub>6</sub> and high oxidation state alkylidyne complexes.

So what are the catalysts formed in the heterogeneous and homogeneous systems described at the beginning of this article? An overwhelming amount of evidence garnered since then in homogeneous systems would suggest that they are high oxidation state alkylidyne complexes. The original heterogeneous catalysts (WO<sub>3</sub> on silica) probably contain an alkylidyne "trialkoxo" species (in which the "alkoxides" are surface oxides), the alkylidyne ligand being formed from the alkyne itself, e.g., through "homolytic scission" in a reaction between the alkyne and a M≡M bond.<sup>29</sup> In the homogeneous systems a Mo(CR)(phenoxide)<sub>3</sub> complex is probably formed, with an initial M≡CH species arising from CO or an M≡CR species arising through homolytic scission of RC≡CR. Since modern alkyne metathesis catalysts can be quite active at room temperature, it seems highly likely that only a miniscule amount of catalyst is present at any given time in the "classical" catalyst systems. Therefore, what *exactly* these "classical catalysts" are and how they are formed seems likely to remain a mystery.

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