Journal of Organometallic Chemistry, 300 (1986) 249–262
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ON THE TRAIL OF METATHESIS CATALYSTS

RICHARD R. SCHROCK
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139 (U.S.A.)
(Received September 24th, 1985)

It was in the fall of 1973 that Geoffrey Wilkinson made one of his too-infrequent visits to the Central Research Department at E.I. duPont de Nemours and Company. On this occasion he announced that he had prepared hexamethyltungsten. At the time I was interested in adding the dianion of cyclooctatetraene to early transition metals in order to provide complexes of potential catalytic interest [1], and in the process had rediscovered Juvinall's preparation of $TaMe_3Cl_2$ [2]. Since the C_8H_8 complexes I obtained did not appear to be potentially interesting catalysts, I decided to try to prepare pentamethyltantalum by adding methyllithium to $TaMe_3Cl_2$. Pentamethyltantalum, like hexamethyltungsten, turns out to be an unpredictable and potentially vicious material when isolated as a solid, owing to its ready decomposition to give methane and (under some conditions) hydrogen [3]. Since $Zr(CH_2Ph)_4$ and $Ti(CH_2Ph)_4$ had been known for several years [4], I was not surprised to find that pentabenzyltantalum could be prepared, and that it was a relatively stable red crystalline species [3b,5]. I was surprised when I attempted to extend the list of pentaalkyls to pentaneopentyltantalum.

Trineopentyltantalum dichloride was prepared straightforwardly, and upon addition of 2 equivalents of neopentyllithium to it in pentane a lovely orange solution was produced, from which a low melting orange crystalline product could be isolated virtually quantitatively [6a]. Its mass spectrum revealed that it was not pentaneopentyltantalum, but a compound whose mass was consistent with the formulation $Ta(CHBu^t)(CH_2Bu^t)_3$. Paul Meakin was kind enough to run a ^{13}C NMR spectrum of $Ta(CHBu^t)(CH_2Bu^t)_3$ that same night; I asked him to be sure to extend the window to 300 ppm downfield of TMS. He called the next morning to tell me that there was indeed a most peculiar doublet located at 250 ppm with a coupling constant of only 90 Hz. Since this was the first "carbene" complex that did not contain some sort of stabilizing substituent(s) (usually O or N) [7], I did not think the low "olefinic" carbon-hydrogen coupling constant was especially significant. Extensive studies did not result in any firm conclusions regarding the mechanism of formation of $Ta(CHBu^t)(CH_2Bu^t)_3$, and it is still uncertain whether $Ta(CH_2Bu^t)_4Cl$ spontaneously loses neopentane or is dehydrohalogenated by a fifth equivalent of a lithium reagent to give the final product [6b]. The salient feature of the reaction in either case is removal of an α-hydrogen from one neopentyl group by another

0022-328X/86/$03.50

neopentyl group, a reaction that could be interpreted as deprotonation of one alkyl ligand by the strongly basic α-carbon atom of a second. This point of view was supported to some extent by the finding that $Ta(CHBu^t)(CH_2Bu^t)_3$ reacted with butyllithium to give a lithiated derivative in which the lithium atom was bound to a "carbyne" carbon atom, and in which the Ta–C–Li angle was approximately 95° [8]. We did not realize at the time that the lithium atom had more or less taken the place of the α-proton in the $CHBu^t$ ligand, and that the low value for J(CH) therefore resulted from a high % p character in the CH bond. I was following Schmidbaur's work on the reactions of main group ylides with late transition metal complexes [9] and was attracted to the possibility that $Ta(CHBu^t)(CH_2Bu^t)_3$ was a tantalum ylide, i.e. a neopentylidene complex, according to IUPAC nomenclature, instead of a "t-butylcarbene" complex.

It was Grant Urry who pointed out that $Ta(CHBu^t)(CH_2Bu^t)_3$ should react in a Wittig sense with carbonyl functionalities. $Ta(CHBu^t)(CH_2Bu^t)_3$ does indeed react extremely rapidly not only with aldehydes and ketones, but also with esters and amides to give mixtures of the expected Wittig-type products, along with the white precipitate of the polymeric trineopentyltantalum oxide [10]. Shortly before this time Fred Tebbe, my lab mate, had discovered what is now known as Tebbe's reagent, $[TiCp_2(CH_2AlMe_2Cl)]$, by treating titanocene dichloride with trimethylaluminum [11]. He soon showed that "$TiCp_2(CH_2)$" could be generated by adding a base to $TiCp_2(CH_2AlMe_2Cl)$ in order to remove $AlMe_2Cl$, and that it too reacted with carbonyl functionalities to give Wittig-type products. This reaction has been developed recently as a relatively convenient method of preparing vinyl ethers from esters [12].

In the process of developing the chemistry of methyl tantalum complexes, and in keeping with the tradition at duPont in cyclopentadienyl chemistry, I prepared $TaCp_2Me_3$ by treating $TaMe_3Cl_3$ with TlCp. By analogy with the reaction that Tebbe discovered I treated $TaCp_2Me_3$ with excess $AlMe_3$ in toluene. An insoluble orange oil formed immediately, but it gradually redissolved over a period of several hours to produce a compound with the formula $TaCp_2(CH_2AlMe_3)(CH_3)$. This species could be viewed as a trimethylaluminum adduct of $TaCp_2(CH_2)(CH_3)$. By analogy with phosphorus chemistry I reasoned that it should be possible to make $[TaCp_2Me_2]^+$ and deprotonate it to give the parent methylene complex. The cation could be prepared by the reaction between $TaCp_2Me_3$ and trityltetrafluoroborate in dichloromethane. Deprotonation of $[TaCp_2Me_2]^+ BF_4^-$ with the relatively exotic base $Me_3P{=}CH_2$ [9] produced $TaCp_2(CH_2)(CH_3)$ in high yield [13].

I spent most of the rest of my time at duPont under the mistaken impression that I could prepare a wide variety of alkylidene complexes by deprotonating cationic d^0 alkyl complexes. That might have been and may still be possible under carefully controlled conditions, but the problem is that the conjugate acid of every anion I tried was a poorer acid than the tantalum cation.

The controversy concerning the olefin metathesis reaction was at full strength about this time [14]. It had been virtually proven that alkylidene exchange via (most likely) a metallacyclobutane intermediate was the key reaction, although it seemed most reasonable at the time, given the "reducing" conditions under which most catalysts were prepared, that the metal was reduced in the process. Yet Fischer-type carbene complexes reacted in the expected manner only stoichiometrically. I began to suspect that "high oxidation state" alkylidene complexes might be relatively common, and in fact might be the active species in metathesis reactions catalyzed by Mo, W, and Re, either homogeneously or heterogeneously.

The research that I began upon moving to MIT first focused upon the relatively unsaturated complex, $TaCp(CHBu^t)Cl_2$, and analogs. $TaCp(CHBu^t)Cl_2$ reacts rapidly with terminal olefins to give products of rearrangement of an intermediate tantalacyclobutane complex, plus tantalacyclopentane complexes formed from the incipient tantalum(III) complex and two equivalents of olefin [15]. This finding ultimately led to the discovery of monopentamethylcyclopentadienyltantalum complexes that would dimerize olefins to a mixture of only two dimers via a mechanism whose key step was shown to consist of contraction of a metallacyclopentane to metallacyclobutane ring system, followed by rearrangement of the MC_3 ring to the olefin [16].

We then discovered even simpler, readily prepared, neopentylidene complexes. For example, $Ta(CHBu^t)(THF)_2Cl_3$ could be prepared simply by treating $Ta(CH_2Bu^t)_2Cl_3$ with THF [17]. The reaction of a wide variety of Ta and Nb complexes of this family with olefins was explored in some depth. We discovered that rearrangement of MC_3 rings could be slowed down by replacing halides with t-butoxide ligands [18], and we finally observed productive metathesis of *cis*-2-pentene starting with $M(CHBu^t)(OBu^t)_2(PMe_3)Cl$ (M = Nb or Ta). To my knowledge this was the first time that productive metathesis of a simple olefin starting with a well-characterized carbenoid complex had been observed. The story was not complete, however, because the intermediate ethylidene and propylidene complexes rearranged to give ethylene and propylene before they could be observed. We were certain, however, that we were on the right track.

What sort of tungsten complexes should we seek as metathesis catalysts? We thought that $W(CHBu^t)(OBu^t)_4$ was a reasonable choice. Having no idea how to go about making such a species we tried the long shot of substituting an oxo ligand on tungsten with a neopentylidene ligand on tantalum (eq. 1). The result was a

$$Ta(CHBu^t)(PMe_3)_2Cl_3 + W(O)(OBu^t)_4 \rightarrow Ta(OBu^t)_4Cl + W(O)(CHBu^t)(PMe_3)_2Cl_2 \quad (1)$$

quantitative yield of $W(O)(CHBu^t)(PMe_3)_2Cl_2$ [19]. An X-ray structural study [20] (Fig. 1) showed that the oxo and neopentylidene ligands were *cis* to one another, and that the neopentylidene ligand lay in the OWC plane. This must be true in order that the π-bonding in the neopentylidene ligand does not have to compete with the π-bonding of the oxo ligand, a notoriously good π-electron donor. The value for J(CH) in the neopentylidene ligand was relatively high, consistent with the relatively small $W{-}C_\alpha{-}C_\beta$ angle of 141.1(16). We were pleased to find that $W(O)(CHBu^t)(PMe_3)_2Cl_2$ is indeed a catalyst for the metathesis of terminal, as well as internal olefins (in benzene), but only in the presence of a trace of $AlCl_3$. The new alkylidene complexes could be observed; in several cases, including $W(O)(CH_2)(PMe_3)_2Cl_2$, they could be isolated [21a]. In the presence of one equivalent of $AlCl_3$ in dichloromethane $W(O)(CHCMe_3)(PEt_3)_2Cl_2$ yielded a complex that appeared to be $[W(O)(CHCMe_3)(PEt_3)_2Cl]^+ AlCl_4^-$, and in the presence of two equivalents of $AlCl_3$ an analogous dicationic species [19]. Both the mono- and di-cationic species will metathesize terminal and internal olefins in dichloromethane slowly (up to ~ 100 turnovers in 24 h) and appeared to be more stable than the catalyst consisting

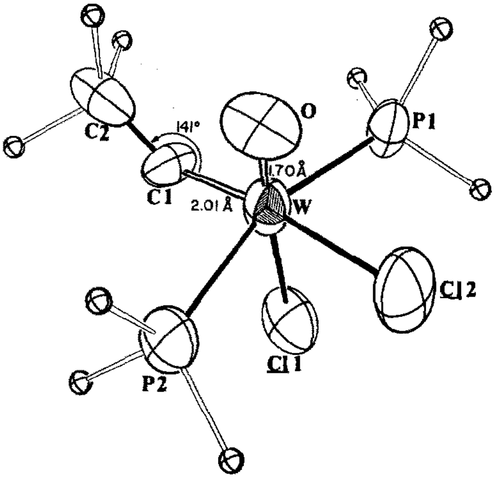


Fig. 1. A drawing of $W(O)(CHCMe_3)(PMe_3)_2Cl_2$ (30% ellipsoids). Hydrogen atoms are omitted and carbon atoms of the methyl groups are reduced for clarity.

of $W(O)(CHCMe_3)(PMe_3)_2Cl_2/AlCl_3$ in benzene [21b]. The cationic system was not studied in any detail due to its "classical" nature and our conviction that simpler systems free of Lewis acid could be found. At this time we suspected that loss of at least one phosphine ligand was required in order for the olefin to coordinate to the metal. $W(O)(CHCMe_3)(PEt_3)Cl_2$ could be isolated, in fact, and it would metathesize *cis*-2-pentene, but activity was short-lived [22]. We had not yet come to grips with the problem of how to prepare an active, long-lived catalyst. It should be one of relatively low coordination number (4 or 5), but one that will not decompose bimolecularly, or rearrange to an olefin complex.

In the meantime we tried to prepare alkylidene complexes directly by treating $MoCl_5$ or WCl_6 with neopentyllithium [23]. We were able to isolate neopentylidyne complexes of the type $M(CBu^t)(CH_2Bu^t)_3$ in low yield. The yields have since been improved to ~30% for $Mo(CBu^t)(CH_2Bu^t)_3$ [24] and ~50% for $W(CBu^t)(CH_2Bu^t)_3$ [25] on a relatively large scale. Any neopentylidene ligand which is formed during the reaction apparently is deprotonated to give a neopentylidyne complex that ultimately is alkylated to give the observed products. It is best to maintain the highest possible oxidation state of the metal in order to obtain a good yield of product, although we showed that in the initial reaction between WCl_6 and $LiCH_2Bu^t$ the metal is first reduced to W^{III}. Clearly alkylidynetungsten(VI) complexes could be formed under "reducing" conditions.

A key to the development of the neopentylidyne chemistry was the discovery of the reaction shown in eq. 2 (dme = 1,2-dimethoxyethane). One of our first goals was

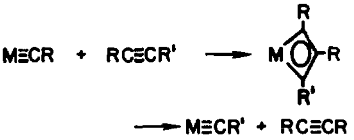
$$M(CBu^t)(CH_2Bu^t)_3 \xrightarrow[\text{dme}]{3\ \text{HCl}} M(CBu^t)(dme)Cl_3 \qquad (2)$$

to reprotonate the neopentylidyne ligand to give a neopentylidene complex. We showed that $W(CBu^t)(dme)Cl_3$ or $[W(CBu^t)Cl_4]^-$ could be treated with one equivalent of water in the presence of phosphines and NEt_3 to give the oxoneopentylidene species we had isolated previously [26]. We could also prepare analogous imidoneopentylidene complexes similarly, and showed that the amidoneopentylidyne intermediates could be isolated and transformed smoothly into the imidoneopentylidene complexes upon heating or by treatment with NEt_3 (eq. 3) [26]. It would be

$$W(CBu^t)(NHR)L_2Cl_2 \xrightarrow{\Delta} W(CHBu^t)(NR)L_2Cl_2 \qquad (3)$$

nearly three years before we expanded upon this important observation. We did show that the imido and neopentylidene complexes also were catalysts for the metathesis of *cis*-2-pentene, but again only in the presence of $AlCl_3$ [27].

At this point we became captivated by the possibility that we could design a catalyst for the metathesis of acetylenes, a rare and inefficient reaction [28], but one whose principles were likely to be analogous to the olefin metathesis reaction, as Katz recognized in 1975 [29] (eq. 4). Since we had found that t-butoxide ligands were beneficial as far as olefin metathesis by tantalum complexes was concerned, we decided that $W(CBu^t)(OBu^t)_3$ would be a good candidate as an acetylene metathesis catalyst. Its preparation was straightforward, but we were not prepared for the results of the first exploratory reaction of it with several equivalents of 3-heptyne; the equilibrium mixture of acetylenes appeared virtually instantaneously. That morning we repeated the reaction again and again, consuming large quantities of 3-heptyne, until we were all convinced that $W(CBu^t)(OBu^t)_3$ did indeed catalyze the metathesis of 3-heptyne at a spectacular rate. We could show that the expected alkylidyne complexes were present under catalytic conditions and we could isolate several of them easily by adjusting conditions. We were happy to find that the presence of β-protons did not destabilize the alkylidyne complex [30].



(4)

We saw no evidence for tungstenacyclobutadiene intermediates in the $W(CR)(OBu^t)_3$ catalyst system. We had shown that a tungstenacyclobutadiene complex could be prepared from $W(CBu^t)(dme)Cl_3$ and one equivalent of 2-butyne or 3-hexyne, and that it had a beautifully simple pseudo-trigonal bipyramidal structure, with the virtually symmetric, planar ring in the equatorial plane (Fig. 2) [31a]. How this formally 12-electron complex could exist as a monomer was puzzling. We did note that the entire C_3 fragment was tightly bound to the metal ($W-C_\alpha \approx 1.86$ Å; $W-C_\beta \approx 2.12$ Å) and that a great deal of electron density therefore must be delivered to the metal. We found out that these species failed miserably as metathesis catalysts, although the reason why, the formation of penta-substituted cyclopentadienyl complexes, was interesting in its own right [31].

We began to look for a simpler method of preparing $W(CR)(OBu^t)_3$ catalysts, as well as for other examples of catalytically active species. It was clear that $W(CR)(OBu^t)_3$ complexes did not decompose to $RC\equiv CR$ and $W_2(OBu^t)_6$, in spite of what appeared to be a favorable formation of the "strong" $W\equiv W$ bond. Therefore, on a whim I decided to try the reverse reaction (eq. 5). I was as surprised as everyone

$$RC\equiv CR + W_2(OBu^t)_6 \rightarrow 2W(CR)(OBu^t)_3 \qquad (5)$$

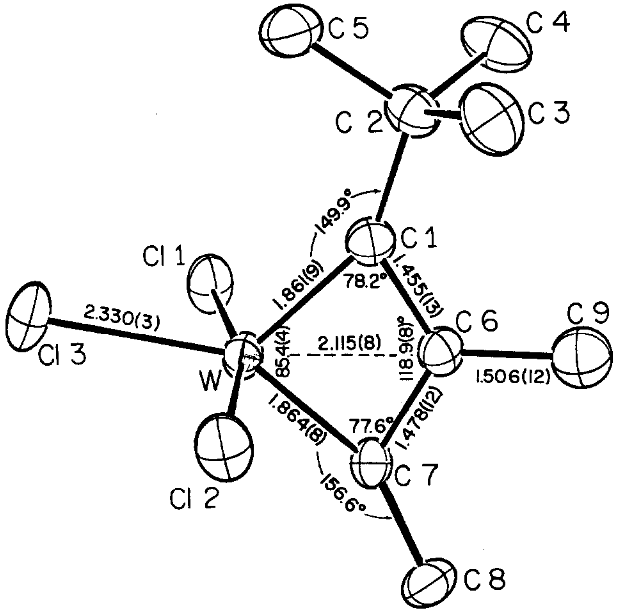
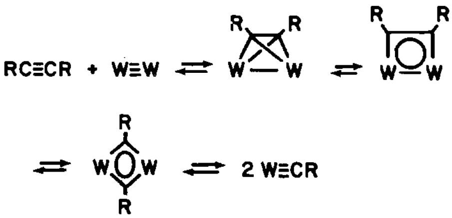


Fig. 2. ORTEP II drawing (30% ellipsoids) of $W(CBu^tCMeCMe)Cl_3$ with hydrogen atoms omitted.

else that the reaction that I gave a 1% chance of working did in fact work extremely well [32]. Ultimately we showed that a variety of acetylenes, even functionalized ones, could be "cleaved" in this manner. Many of the reactions were successful only in the presence of pyridine and/or quinuclidine, and in many of those cases only adducts of the type $W(CR)(OBu^t)_3(Base)$ could be isolated. We came up with the theory that (i) a planar 1,3-dimetallacyclobutadiene intermediate was required; (ii) this species could be cleaved by pyridine, and (iii) quinuclidine was an especially efficient trap for certain alkylidyne complexes, especially the parent methylidyne complex. After Chisholm showed that a mixture of $W_2(OBu^t)_6(HC{\equiv}CH)(py)$ and $W_2(OBu^t)_6(D^{13}C{\equiv}^{13}CD)(py)$ yielded two parts of $W_2(OBu^t)_6(D^{13}C{\equiv}CH)(py)$, probably via formation of intermediate $W(CH)(OBu^t)_3(py)$ and $W(^{13}CD)(OBu^t)_3(py)$ [33], it became clear that all of the equilibria in eq. 6 were potentially important in



(6)

the general case. Since the cleavage reaction had to compete with many other irreversible reactions involving addition of more acetylene to one of the $W_2(CR)_2$ isomers, it became less surprising that the reaction appeared to work so well for $W_2(OBu^t)_6$, the W≡W analog of the extremely efficient $W(CR)(OBu^t)_3$ metathesis catalyst. We now know that the cleavage of an acetylene by $W_2(OR)_6$ works also for

$OR = OPr^i$ [34], $OCMe_2(CF_3)$ [34], and O-2,6-$C_6H_3Me_2$ [27]. The observation that tetrahedral WC_3 arrays (η^3-cyclopropenyl complexes) could be formed by adding ligands such as pyridine or TMEDA to tungstenacyclobutadiene complexes [31b] further convinced us that the chemistry of certain complexes containing WC_3 and W_2C_2 arrangements were closely linked.

The search for other examples of acetylene metathesis catalysts led us to $M(CBu^t)[OCMe_2(CF_3)]_3$, $M(CBu^t)[OCMe(CF_3)_2]_3$, and $M(CBu^t)(DIPP)_3$ (DIPP = 2,6-diisopropylphenoxide) where M = Mo or W. We chose these three alkoxides first because they are relatively bulky, and second because they are relatively electron-withdrawing compared to the t-butoxide ligand. We began to feel that maximizing the electrophilicity of the metal without forming a cationic complex would prove to be as important as adjusting the steric properties of the alkoxide ligands. The efficiency of the various Mo and W complexes as metathesis catalysts varied greatly. In several tungsten systems we could observe and isolate triethylmetallacyclobutadiene complexes and measure the rate at which they reacted with 3-hexyne-d_{10}. For example, $W(C_3Et_3)(DIPP)_3$ could be prepared as shown in eq. 7. Its reaction

$$W(CBu^t)(DIPP)_3 \xrightarrow[-\,Bu^tC\equiv CEt]{+\,2EtC\equiv CEt} W(C_3Et_3)(DIPP)_3 \qquad (7)$$

with 3-hexyne-d_{10} was independent of the concentration of added 3-hexyne-d_{10} and relatively slow ($\Delta H^{\ddagger} = 26.1(4)$, $\Delta S^{\ddagger} = 15.2(15)$) [35]. In the case of $W(C_3Et_3)[OCMe(CF_3)_2]_3$ the reaction was independent of 3-hexyne-d_{10}, but extremely fast [36]. Interestingly, the reaction between $W(C_3Et_3)[OCH(CF_3)_2]_3$ and 3-hexyne-d_{10} was rapid, but first order in 3-hexyne-d_{10} [36], a clear indication of the tremendous importance of steric factors; the $OCH(CF_3)_2$ ligand is too small to force 3-hexyne out of the WC_3Et_3 ring system, and also too small to prevent 3-hexyne from attacking the relatively electrophilic metal. Studies in the Mo system confirmed the importance of electronic and steric tuning of the catalyst [24]; Mo $(CBu^t)(OBu^t)_3$ does not react with internal acetylenes, but $Mo(CBu^t)[OCMe_2(CF_3)]_3$ reacts slowly, and $Mo(CBu^t)[OCMe(CF_3)_2]_3$ and $Mo(CBu^t)(DIPP)_3$ react rapidly. Only in the DIPP system can a triethylmetallacyclobutadiene complex be observed, and it is unstable toward loss of 3-hexyne to give isolable $Mo(CEt)(DIPP)_3$.

The structures of $W(C_3Et_3)(DIPP)_3$ [35], $W(C_3Et_3)[OCH(CF_3)_2]_3$ [36], and $W(CBu^t_2H)[OCH(CF_3)_2]_3$ [37] are all quite similar to each other, and to that of $W(CBu^tCMeCMe)Cl_3$. In $W(C_3Et_3)(DIPP)_3$ (Fig. 3) there is some statistically significant distortion of the ring as if 3-hexyne were being extruded from it, as the reaction of $W(C_3Et_3)(DIPP)_3$ with 3-hexyne-d_{10} demands must be the case.

We thought it important that the only metallacyclobutadiene complexes that are acetylene metathesis catalysts are pseudo trigonal bipyramids containing a planar equatorial WC_3 ring. We had shown that cyclopentadienylneopentylidyne complexes reacted with internal acetylenes to give fluxional, bent metallacyclobutadiene complexes that did not metathesize acetylenes [38]. We also knew that η^3-cyclopropenyl complexes were the preferred tautomers in certain circumstances [39,40], and that they too were not metathesis catalysts. We began to suspect that pseudo-trigonal bipyramidal metallacyclobutane complexes might be ideal intermediates in olefin metathesis catalyst systems, and began to formulate the ligand combination that might be successful.

In the meantime we had continued to explore the possible routes to alkylidene

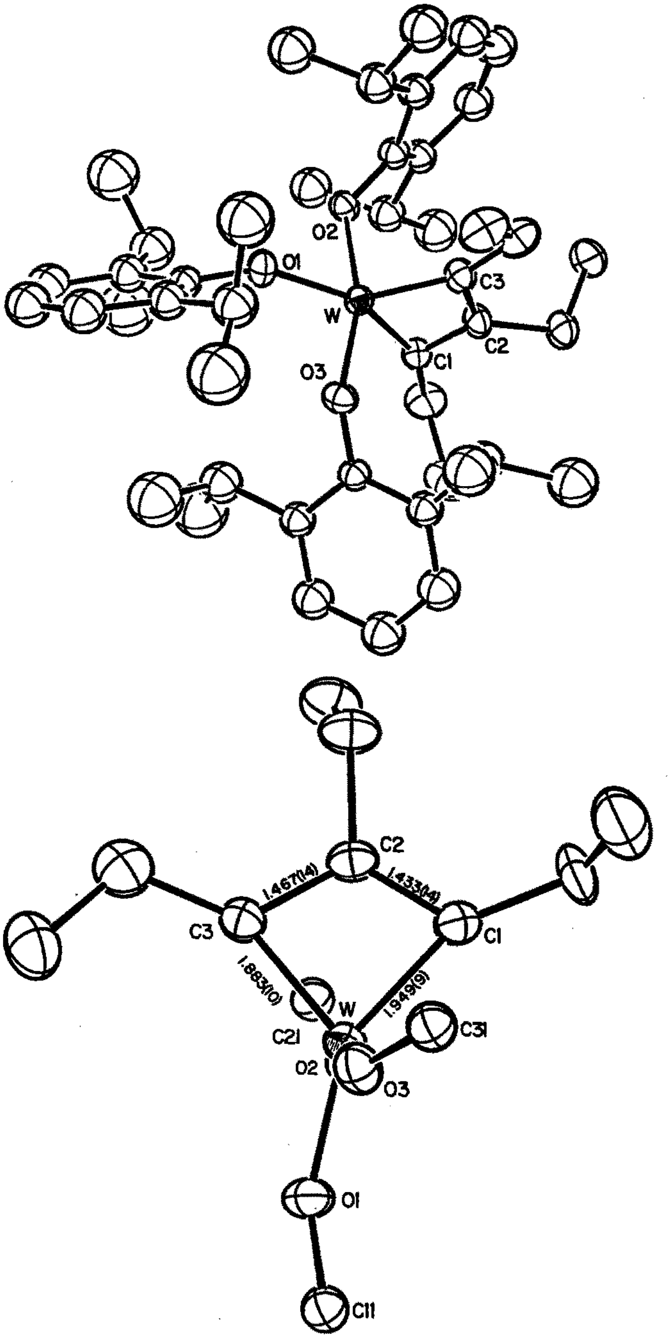
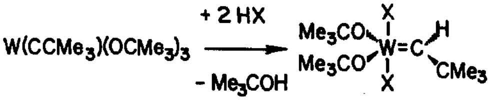


Fig. 3. (a) ORTEP II drawing of $W(C_3Et_3)(DIPP)_3$ (30% ellipsoids); (b) a top view of the WC_3 ring (phenyl rings omitted except for *ipso* carbon).

complexes. Protonation of alkylidyne complexes seemed to be a reasonable approach. We could show that five-coordinate trigonal bipyramidal complexes of the type $W(CHBu^t)(OBu^t)_2X_2$ could be prepared [41] (eq. 8), but they were disappoint-



(8)

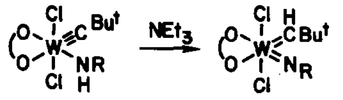
X = Cl, Br, $MeCO_2$, $PhCO_2$, OPh,
OC_6F_5, O-p-C_6H_4Cl

ingly unreactive toward ordinary olefins in the absence of a Lewis acid. In the presence of $AlCl_3$, however, they would metathesize *cis*-2-pentene extremely rapidly. Such systems are variations of the $W(CHBu^t)(OCH_2Bu^t)_2X_2/MX_y$ (X = halide; MX_y = Lewis acid) systems that have been developed by Osborn in the last several years [42]. He could show that cationic species are present, that at least one alkoxide in $W(CHBu^t)(OCHBu^t)_2X_2$ is replaced by X, that new alkylidene complexes are observable at low temperature upon treating $W(CHBu^t)(OCH_2Bu^t)_2X_2/AlX_3$ with *cis*-2-pentene, and that such systems are extremely efficient catalysts for the metathesis of *cis*-2-pentene.

We continued to be intrigued by the prospect of preparing active, Lewis acid-free, pseudo-tetrahedral, neutral olefin metathesis catalysts. We decided to model the acetylene metathesis systems as closely as possible. Four-coordination could be achieved only if an oxo or imido ligand were present, but an oxo ligand was unacceptable from a steric point of view. We came up with two targets, $W(CHBu^t)(N\text{-}2,6\text{-}C_6H_3Pr^i_2)(DIPP)_2$ (cf. $W(CBu^t)(DIPP)_3$), and $W(CHBu^t)(N\text{-}2,6\text{-}C_6H_3Pr^i_2)[OCMe(CF_3)_2]_2$ (cf. $W(CBu^t)[OCMe(CF_3)_2]_3$). In order to prepare these species we went back to the amido/neopentylidyne to imido/neopentylidene approach. The complex shown in eq. 9 forms smoothly and in high yield. Treating it with NEt_3 afforded the useful intermediate shown in eq. 10 from which

(9)

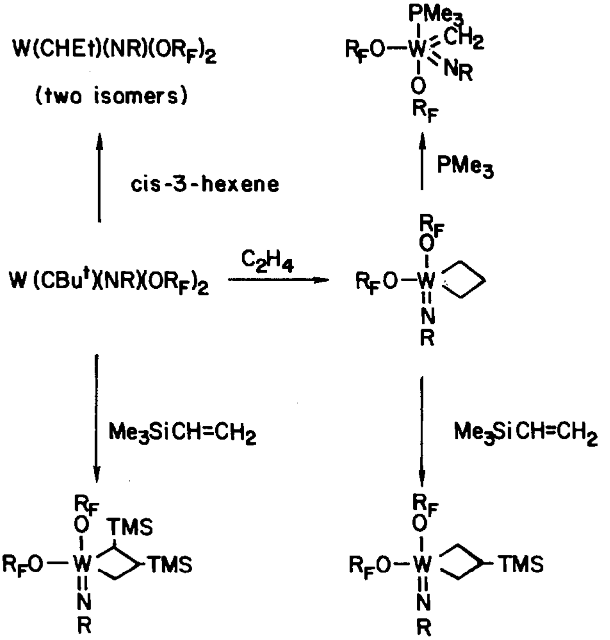
R = 2,6-$C_6H_3Pr^i_2$



(10)

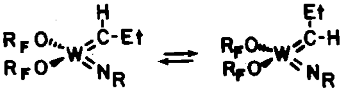
the yellow-orange, crystalline derivatives $W(CHBu^t)(NR)(DIPP)_2$ and $W(CHBu^t)(NR)(OR_F)_2$ ($OR_F = OCMe(CF_3)_2$) could be prepared. Dme coordinates to the $W(CHBu^t)(NR)(OR_F)_2$ complex, but it appears to be only weakly bound, probably for steric reasons.

$W(CHBu^t)(NR)(OR_F)_2$ reacts rapidly with olefins to yield either new alkylidene complexes or tungstenacyclobutane complexes. A few examples are shown in Scheme 1. One of the key reactions is that with 3-hexene to yield $W(CHEt)(NR)(OR_F)_2$ over a period of a few minutes at 25°C. If a mixture of $W(CHBu^t)(NR)(OR_F)_2$ and $W(CHEt)(NR)(OR_F)_2$ is prepared and observed by ^1H NMR over a period of 24 h the ratio of the two complexes remains constant, i.e. the propylidene complex does



Scheme 1. Some reactions of $W(CHBu^t)(NR)(OR_F)_2$ ($R = 2,6\text{-}C_6H_3Pr^i_2$; $OR_F = OCMe(CF_3)_2$).

not rapidly rearrange to propylene. From the point of view of the structure of $W(CHEt)(NR)(OR_F)_2$ it is interesting to note that two propylidene H_α signals are observed and their ratio varies with conditions. Since we believe the molecule must be a monomer, the structure must be one in which the alkylidene ligand lies in the same plane as W and N and is turned one way or the other, viz.:



Although the apparently slow rotation of the alkylidene ligand on the chemical time scale in a pseudo-tetrahedral species was unexpected, there is one precedent. $Re(NBu^t)_2(CHBu^t)(CH_2Bu^t)$ shows four different t-butyl groups by ^1H NMR and an AB pattern for the methylene protons in the neopentyl ligand [43]. In both $W(CHBu^t)(NR)(OR_F)_2$ and $Re(NBu^t)_2(CHBu^t)(CH_2Bu^t)$ one orientation of the neopentylidene is preferred, although it is not obvious which.

Tungstenacyclobutane complexes are either in equilibrium with the alkylidene complex and the olefin, or they react very quickly with an incoming ligand, we do not know which at this juncture. The X-ray structure of the bis-TMS derivative (Fig. 4) shows it to be a distorted trigonal bipyramidal species with the ring in the equatorial plane. The W–C_α bond lengths are much shorter than one would expect for "normal" W–C single bonds (cf. the shorter-than-expected W–C_α bonds in tungstenacyclobutadiene complexes) and the β-carbon is tipped up out of the equatorial plane so that the dihedral angle between the C(11)–W–C(13) plane and C(11)–C(12)–C(13) plane is ~ 25°. We suspect that bending of the ring to this extent requires little energy, and could result from steric interaction between the

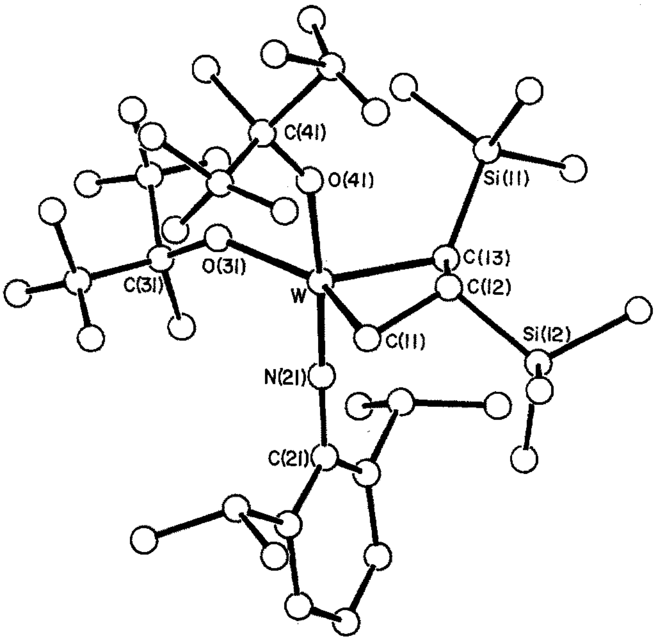


Fig. 4. A drawing of the structure of $W[CH(SiMe_3)CH(SiMe_3)CH_2](N\text{-}2,6\text{-}C_6H_3Pr^i_2)[OCMe(CF_3)_2]_2$ using atoms of equal radii (hydrogen atoms omitted). (W–C(13) 2.066(11) Å; W–C(12) 2.372(11) Å; W–C(11) 2.099(11) Å; C(11)–W–C(13) 82.3(4)°; C(11)–C(12)–C(13) 116.1(8)°; W–C(11)–C(12) 78.0(6)°).

β-TMS group and the bulky $2,6\text{-}C_6H_3Pr^i_2$ group in the imido ligand. This structure should be compared with those of the titanium metallacyclobutane complexes discovered by Grubbs, where relatively planar rings are found, perhaps in part because of the restriction imposed by the two Cp rings [44]. We now suspect that the extent of bending the ring may not be as important as it was for some time postulated to be [14].

$W(CHBu^t)(NR)(OR_F)_2$ is a very active catalyst for the metathesis of *cis*-2-pentene. Hundreds of turnovers are observed in minutes without any apparent loss of activity. New alkylidene complexes can be observed by ^1H NMR at any point. The activity of a system after 24 h is qualitatively the same as it was initially. We feel it likely that we will observe some deactivation eventually, but hope that it might be due primarily to reactions of the catalyst with water.

The metathesis of functionalized olefins has been a desirable goal ever since metathesis catalysts were first discovered, and much progress has been made, primarily with $SnMe_4$ activated W and Re systems [45]. We hope to be able to probe in detail the reactions between complexes of the type $W(CHR')(NR)(OR_F)_2$ in order to determine what problems are associated with what functionalities under what circumstances. The absence of a Lewis acid co-catalyst, and the apparently moderated Lewis acidity of the tungsten center, both favor preserving the functionality.

Methyl oleate is an especially attractive functionalized olefin to metathesize or cross-metathesize due to its ready availability in large quantities and the utility of the metathesis products as pheromone precursors, plasticizers, etc. $W(CHBu^t)$-

$(NR)(OR_F)_2$ does metathesize 100–200 equivalents of methyl oleate at 25°C to equilibrium in ~ 1 h. The expected cleavage products, $Bu^tCH{=}CH(CH_2)_7CO_2Me$ and $Bu^tCH{=}CH(CH_2)_7$ Me are formed and were identified by GC/MS. No new metallacycles or new alkylidene complexes are observed, however, and the catalyst is deactivated by conversion to $W(O)(NR)(OR_F)_2$. Although $W(CHBu^t)(NR)(OR_F)_2$ will not react readily with ethyl acetate, $W(CHEt)(NR)(OR_F)_2$ will (probably simply a steric phenomenon). Therefore, we propose that $W[CH(CH_2)_7CO_2Me]$-$(NR)(OR_F)_2$ and $W[CH(CH_2)_7Me](NR)(OR_F)_2$ form slowly from $W(CHBu^t)$-$(NR)(OR_F)_2$ and methyl oleate, and react much more readily with the ester functionality in methyl oleate than does $W(CHBu^t)(NR)(OR_F)_2$. Metathesis of olefins in which the carbonyl group is far removed from the double bond then boils down to finding a way to increase the rate of reaction of the alkylidene ligand with the C=C bond while minimizing or eliminating its reaction with the C=O bond. Since these two reactions are related it is not yet clear how this can be done simply by varying sterics and electronics of the NR and alkoxide ligands. Nevertheless, this is obviously the direction to go.

We have come a long way, from the exotic to the applied, but the story is not yet finished. Now that we have virtually total control of the catalyst, and can determine exactly what is wrong with reactions involving certain olefins, we should be able to answer a number of important mechanistic questions in the near future, as well as develop highly active, practical catalysts.

Acknowledgements

I thank all the Ph.D. and post-doctoral students over the years who through their convictions, diligence, and dedication have made these advances possible, especially Dr. Colin Schaverien, who made the most recent discovery [46]. I also thank the National Science Foundation for past and continuing support for research on multiple metal–carbon bonds. I apologize to others I have not mentioned whose findings undoubtedly contributed to our thinking about the metathesis problem over the years; their contributions can be found in recent review articles [14]. A detailed survey of early transition metal alkylidene complexes is about to appear [47].

References

1 (a) L.J. Guggenberger and R.R. Schrock, J. Am. Chem. Soc., 97 (1975) 6693; (b) R.R. Schrock, L.J. Guggenberger, and A.D. English, ibid., 98 (1976) 903.
2 G.L. Juvinall, J. Am. Chem. Soc., 86 (1964) 4202.
3 (a) R.R. Schrock and P. Meakin, J. Am. Chem. Soc., 96 (1974) 5288; (b) R.R. Schrock, J. Organomet. Chem., 122 (1976) 209.
4 (a) U. Zucchini, U. Giannini, E. Albizzati, and R. D'Angelo, J. Chem. Soc. D, (1969) 1174; (b) U. Giannini and U. Zucchini, J. Chem. Soc. Chem. Commun., (1968) 940; (c) R.R. Schrock and G.W. Parshall, Chem. Rev., 76 (1976) 243.
5 V. Malatesta, K.U. Ingold and R.R. Schrock, J. Organomet. Chem., 152 (1978) C53.
6 (a) R.R. Schrock, J. Am. Chem. Soc., 96 (1974) 6796; (b) R.R. Schrock and J.D. Fellmann, ibid., 100 (1978) 3359.
7 D.J. Cardin, B. Cetinkaya and M.F. Lappert, Chem. Rev., 72 (1972) 545.
8 R.R. Schrock and L.J. Guggenberger, J. Am. Chem. Soc., 97 (1975) 2935.
9 H. Schmidbaur, Adv. Organomet. Chem., 14 (1976) 205.

10 R.R. Schrock, J. Am. Chem. Soc., 98 (1976) 5399.
11 F.N. Tebbe, G.W. Parshall and G.S. Reddy, J. Am. Chem. Soc., 100 (1978) 3611.
12 S.H. Pine, R. Zahler, R.H. Evans and R.H. Grubbs, J. Am. Chem. Soc., 102 (1980) 3270.
13 R.R. Schrock and P.R. Sharp, J. Am. Chem. Soc., 100 (1978) 2389.
14 R.H. Grubbs, Chapter 54 in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Vol. 8, 1982.
15 C.D. Wood, S.J. McLain and R.R. Schrock, J. Am. Chem. Soc., 101 (1979) 3210.
16 (a) S.J. McLain, C.D. Wood and R.R. Schrock, J. Am. Chem. Soc., 101 (1979) 4558; (b) S.J. McLain, J. Sancho and R.R. Schrock, ibid., 102 (1980) 5610.
17 G.A. Rupprecht, L.W. Messerle, J.D. Fellmann and R.R. Schrock, J. Am. Chem. Soc., 102 (1980) 6236.
18 S.M. Rocklage, J.D. Fellmann, G.A. Rupprecht, L.W. Messerle and R.R. Schrock, J. Am. Chem. Soc., 103 (1981) 1440.
19 J.H. Wengrovius and R.R. Schrock, Organometallics, 1 (1982) 148.
20 M.R. Churchill, A.L. Rheingold, W.J. Youngs, R.R. Schrock and J.H. Wengrovius, J. Organomet. Chem., 204 (1981) C17.
21 (a) R.R. Schrock, S. Rocklage, J.H. Wengrovius, G. Rupprecht and J. Fellmann, J. Molec. Catal., 8 (1980) 73; (b) J.H. Wengrovius, Ph.D. Thesis, MIT, 1981.
22 J. Wengrovius, R.R. Schrock, M.R. Churchill, J.R. Missert and W.J. Youngs, J. Am. Chem. Soc., 102 (1980) 4515.
23 D.N. Clark and R.R. Schrock, J. Am. Chem. Soc., 100 (1978) 6774.
24 L.G. McCullough, J.C. Dewan, R.R. Schrock, and J.S. Murdzek, J. Am. Chem. Soc., 107 (1985) 5987.
25 R.R. Schrock, D.N. Clark, J. Sancho, J.H. Wengrovius, S.M. Rocklage and S.F. Pedersen, Organometallics, 1 (1982) 1645.
26 S.M. Rocklage, R.R. Schrock, M.R. Churchill and H.J. Wasserman, Organometallics, 1 (1982) 1332.
27 Unpublished observations.
28 (a) F. Pennella, R.L. Banks and G.C. Bailey, J. Chem. Soc., Chem. Commun., (1968) 1548; (b) J.A. Moulijn, H.J. Reitsma and C. Boelhouwer, J. Catal., 25 (1972) 434; (c) A. Mortreux, J.C. Delgrange, M. Blanchard and B. Labochinsky, ibid., 2 (1977), 73; (d) S. Devarajan, O.R.M. Walton and G.J. Leigh, J. Organomet. Chem., 181 (1979) 99.
29 T.J. Katz, J. Am. Chem. Soc., 97 (1975) 1592.
30 (a) J.H. Wengrovius, J. Sancho and R.R. Schrock, J. Am. Chem. Soc., 103 (1981) 3932; (b) J. Sancho and R.R. Schrock, J. Molec. Catal., 15 (1982) 75.
31 (a) S.F. Pedersen, R.R. Schrock, M.R. Churchill and H.J. Wasserman, J. Am. Chem. Soc., 104 (1982) 6808; (b) R.R. Schrock, S.F. Pedersen, M.R. Churchill and J.W. Ziller, Organometallics, 3 (1984) 1574.
32 (a) R.R. Schrock, M.L. Listemann and L.G. Sturgeoff, J. Am. Chem. Soc., 104 (1982) 4291; (b) M.L. Listemann and R.R. Schrock, Organometallics, 4 (1985) 74.
33 M.H. Chisholm, K. Folting, D.M. Hoffman and J.C. Huffman, J. Am. Chem. Soc., 106 (1984) 6794.
34 J.H. Freudenberger, S.F. Pedersen and R.R. Schrock, Bull. Soc. Chim. Fr., (1985) 349.
35 M.R. Churchill, J.W. Ziller, J.H. Freudenberger and R.R. Schrock, Organometallics, 3 (1984) 1554.
36 J.H. Freudenberger, R.R. Schrock, M.R. Churchill, A.L. Rheingold and J.W. Ziller, Organometallics, 3 (1984) 1563.
37 M.R. Churchill and J.W. Ziller, J. Organomet. Chem., 286 (1985) 27.
38 M.R. Churchill, J.W. Ziller, L. McCullough, S.F. Pedersen and R.R. Schrock, Organometallics, 2 (1983) 1046.
39 (a) M.R. Churchill, J.C. Fettinger, L.G. McCullough and R.R. Schrock, J. Am. Chem. Soc., 106 (1984) 3356; (b) M.R. Churchill, J.W. Ziller, S.F. Pedersen and R.R. Schrock, J. Chem. Soc., Chem. Commun., (1984) 485.
40 R.R. Schrock, J.S. Murdzek, J.H. Freudenberger, M.R. Churchill and J.W. Ziller, Organometallics, in press.
41 J.H. Freudenberger and R.R. Schrock, Organometallics, 4 (1985) 1937.
42 (a) J. Kress, M. Wesolek, J.-P. LeNy and J.A. Osborn, J. Chem. Soc., Chem. Commun., (1981) 1039; (b) J. Kress, M. Wesolek and J.A. Osborn, ibid., (1982) 514.
43 D.S. Edwards, L.V. Biondi, J.W. Ziller, M.R. Churchill and R.R. Schrock, Organometallics, 2 (1983) 1505.
44 D.A. Straus and R.H. Grubbs, Organometallics, 1 (1982) 1658.

45 (a) J.C. Mol, J. Molec. Catal., 15 (1982) 35; (b) R.H.A. Bosma, G.C.N. Van den Aardweg and J.C. Mol, J. Organomet. Chem., 255 (1983) 159; (c) J.C. Mol, Chemtech, 13 (1983) 250; (d) R.H.A. Bosma, G.C.N. Van den Aardweg and J.C. Mol, J. Organomet. Chem., 280 (1985) 115.
46 C. Schaverien and R.R. Schrock, submitted.
47 (a) R.R. Schrock in P.S. Braterman, (Ed.), Reactions of Coordinated Ligands, Plenum, 1986; (b) see also R.R. Schrock, Science, 219 (1983) 13.