

Structure and reactivity of metathesis-active tungsta-carbenes

Lajos Bencze ^{*}, Robert Szilágyi

Department of Organic Chemistry, University of Veszprém, P.O.B. 158, Veszprém, Hungary

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Abstract

Experimental and theoretical studies revealed that the activity and selectivity of tungsta-carbene complexes change systematically with the structure of their alkylidene groups in olefin metathesis, CO coupling and Wittig reactions.

Keywords: Tungsten; Tungsta-carbene; Metathesis

It has been widely demonstrated that olefin metathesis reactions are initiated by transition metal–carbene complexes [1]. The catalytically active species can be prepared in advance, such as the well defined carbenes, and added to the reaction mixture, or can be generated in situ by the reaction of two to four precursors [2].

Choosing carbenes of the type WCl_4R , which act as catalysts in most WCl_6 -based catalyst compositions [3], calculations were made to determine the energetic and electronic properties of those complexes whose alkylidene groups appear most frequently in our work, including the well defined Osborn carbenes [1e,4].

Ab initio quantum chemical calculations were carried out with the STO-3G minimal basis set and Stevens–Basch–Krauss effective core potential for the net fragment charges of WCl_4 units balanced with the opposite charge on the carbene group (Table 1). The magnitude of the fragment charge is a function of the positive inductive effect of the alkylidene ligand. Binding energies for the C=W bond were also calculated for model compounds. The calculations were based on singlet complexes formed by the combination of triplet Cl_4W : and triplet R: units.

In studies of the catalyst systems $W(CO)_3Cl_2$ – $(AsPh_3)_2$ – $EtAlCl_2$ and WCl_6 – $SnMe_4$, we found previously that in the degenerate metathesis reaction of olefins $RCH=CH_2$, the chain carriers are the complexed alkylidenes $RCH=W$ ($R \neq H$) and not the complexed methylene $W=CH_2$ [5]. Cross-metathesis of cyclo-

olefins and linear-chain terminal olefins resulting mainly in non-symmetrical products such as $CH_2=CH(CH_2)_nCH=CHR$, showing also that the complexed alkylidenes are much preferred to complexed methylene, but when the latter is formed rapidly it reacts with olefins in a non-selective manner [5–7]. In other words, methylene-carbenes are less stable, less selective and more active than the identical types having longer chain alkylidene groups. The same is found for those thermally activated metathesis reactions in which the unicomponent $W(CO)_3L_2X_2$ catalysts are used as initiators [7].

Kress et al. [1e] reported that the activity of the well defined complexes $W(CHR)L_4$ changes with the L ligands and also changes as a function of the structure of the R group in the order of $R = Me > Et > ^iPr$.

Summing up the above observations, the latter order of activity can be extended to $R = H > Me > Et > Pr > ^iPr > \dots > ^tBu$, etc. This order is not complete and other groups might be also be inserted. However, it must be emphasized that the validity of this trend is limited to each individual catalytic system or carbene type considered, because the activities of the various catalytic species bearing the same alkylidene group are rarely the same owing to the different chemical environments of the central metal atom. More specifically, the activity of a complex methylene carbene formed in the WCl_6 – $SnMe_4$ -initiated metathesis of pent-1-ene is not necessarily equal to that formed in a WCl_6 – $EtAlCl_2$ – $EtOH$ -catalysed system, while the activity of the methylene complex in each system is greater than that of the butylidene complex.

^{*} Corresponding author.

It is interesting that the decrease in the catalytic activity of the alkylidene complexes seems to correlate with the increasing positive inductive effect of the R group; the latter can easily be estimated by elementary organic chemistry experiments.

The polarization of the carbon–metal double bond may be one of the determining factors in the catalytic activity, therefore. This suggestion seems to be supported by the observation that the carbene complex $[W = C_7H_8]$ generated by the reaction of norbornene and $W(CO)_3Cl_2(AsPh_3)_2$ initiates the ring-opening metathetical polymerization of the excess of norbornene, but it is reluctant to react with pent-2-ene. At the same time, the propagating carbene, having a different alkylidene ligand, undergoes a chain-transfer reaction with the linear-chain olefin. When an electron-withdrawing cocatalyst, e.g. $AlCl_3$, is added to the system, even the sluggish initiating carbene $[W = C_7H_8]$ triggers the homometathesis of pent-2-ene [8]. The addition of a Lewis acid-type cocatalyst increases the overall activity of the system, but leaves the relative order of activity among the different alkylidene complexes unchanged.

On the other hand, the decrease in the metathetical activity of the complexes is associated with increasing Wittig reactivity. In $W(CO)_3Cl_2(AsPh_3)_2$ -initiated reactions, carbene–CO coupling (c) [9] or Wittig reaction (w) (e.g. with PhCHO [10]) could be detected only with sluggish metathesis initiators and failed in more active cases. It should be noted that the reactions indicated in the second column in Table 1 refer to this system.

The metathetical activities of the $RWCl_4$ carbenes are much greater than those of the carbenes generated in the norbornene– $W(CO)_3Cl_2(AsPh_3)_2$ system, and the former are therefore not expected to undergo any Wittig or CO coupling reactions.





The third column of Table 1, listing the calculated charge on the WCl_4 fragments of $RWCl_4$ complexes, is intended only to demonstrate the electron-releasing effect of the given alkylidene fragments. The alkylidene groups are the only common features between the two catalyst systems and even the $C=W$ bond polarization might be reversed owing to the different environment of the central tungsten atom. Poor metathesis catalysts seem to have a larger charge on the WCl_4 fragment and higher activity, whereas the more active catalysts bear a smaller charge and are less selective. The dipole moments of the complexes vary in parallel with the fragment charges.

The sharp changes in the catalytic properties can be only partly attributed to the aforementioned polarization of the molecules, however. At the same time, the catalytic activity correlates with the binding energy very well: carbene complexes with weaker $W=C$ bonds are more reactive than the other, more stable complexes.

It might be concluded that the tungsta-carbene complexes having less electron-releasing and less strongly bonded alkylidene groups tend to be more active in metathesis reactions and less active in Wittig-type reactions. The thick arrow in Table 1 is aimed to indicate this tendency.

We believe that the most important finding of this

Table 1
Results of experimental studies and ab initio quantum chemical calculations

WCl_4R complex: R =	Reactions ^a				Net fragment charge on	Dipole moment (D) WCl_4 unit	C=W binding energy ($kcal\ mol^{-1}$)	
							SCF	MP2
	–			r	–0.63	10.134	–94.03	–162.53
	c	w	–	r	–0.58	9.636	–88.03	–155.45
	–			r	–0.55	9.189	–75.26	–146.20
$P=HC(CH_3CH_2)_2C=(E)$	c	–	(m)	r	–0.53	8.990	–76.07	–145.30
$(CH_3CH_2)_2C=(Z)$	c	–	(m)	r	–0.53	9.195	–76.28	–144.53
$CH_3CH_2CH_2(CH_3)C=$	c	–	(m)	r	–0.53	8.769	–75.76	–140.95
	–	w	–	r	–0.50	8.600	–73.77	–143.10
$CH_3CH_2CH_2CH_2CH=$	–	–	m	r	–0.48	7.832	–71.22	–164.49
$CH_3CH_2CH_2CH=$	–	–	m	r	–0.47	7.692	–70.85	–138.86
$CH_3CH_2CH=$	–	–	m	r	–0.46	–7.441	–70.40	–138.28
$CH_3CH=$	–	–	m	r	–0.43	6.948	–67.68	–133.28
$CH_2=$	–	–	m	r	–0.34	4.823	–52.04	–124.18

^a c, CO coupling detected; w, Wittig reaction detected; m, olefin metathesis detected; r, ring-opening metathesis polymerization detected; S, selectivity and stability; R, reactivity. Reaction data refer to unicomponent $W(CO)_3Cl_2(AsPh_3)_2$ -initiated systems.

work is that the relative reactivity of carbenes of the same type may be accurately qualified by determining the inductive effect of their alkylidene groups in the orthodox way [11]. The doubtless importance of these observations with respect to catalytic and stoichiometric reactions requires further study.

Supplementary material

Supplementary material is available on <http://mm1.vein.hu/molmod.html> World-Wide-Web server.

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