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Tetrahedron Letters 47 (2006) 5167–5170

Tetrahedron Letters

The first example of tungsten-based carbene generation from WCl_6 and atomic carbon and its use in olefin metathesis

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Received 11 January 2006; revised 1 May 2006; accepted 10 May 2006
Available online 5 June 2006

Abstract—We describe a new route for the synthesis of tungsten-based carbenes generated by the reaction of WCl_6 with atomic carbon in a carbon arc reactor. The active species formed under these conditions, $[W]=CCl_2$, was found to catalyze olefin metathesis reactions of 1-octene, 2-octene and 1-heptene. We also evaluated the mechanism of formation of $[W]=CCl_2$ within the WCl_6/C system at the DFT level.

Olefin metathesis is an extremely useful reaction which has recently found a very wide range of application in the development of new medicines, biologically active compounds, polymeric materials and in industrial syntheses.[1] Catalyst systems for olefin metathesis reactions almost always contain a transition metal compound. There is much evidence to show that these catalyst systems act through the initial formation of metal carbene complexes which initiate and then propagate the reaction. The accepted metal carbene metallacyclobutane mechanism for olefin metathesis was first proposed by Yves Chauvin and his student Jean-Louis Hérisson in 1971.[2] From 1980 onwards, well-defined carbene complexes of Ta, Mo, W, Re, Ru have been reported which act as initiators without the need for activation by heat, light or co-catalyst.[1]

On the other hand, the reaction of carbon vapor with organic substrates in a carbon arc reactor can lead to the formation of carbenes via several pathways including single bond insertion and/or double bond addition.[3] These reactions involve a great deal of excess energy and are thus highly exothermic.

In this work we intended to generate a tungsten carbene species, which would be active in olefin metathesis reactions, via combination of a high energy C atom with WCl_6. Thus, the carbon arc reactor described by Skell and co-workers was used.[4] The ends of two high purity graphite rods were drilled and filled with powdered WCl_6. Then, an arc was struck intermittently between the graphite rods and the tungsten carbene intermediates were condensed on the walls of the reactor which was cooled by liquid nitrogen at 77 K. When the graphite rods had been used up, vaporized olefin was transferred into the reactor (without arcing to prevent the reaction of atomic carbon with the olefin). Liquid nitrogen was removed and the reactor was allowed to warm to room temperature. At room temperature, the olefin and tungsten carbene reacted. After 30 min, the contents of the reactor were dissolved in chloroform and the solution was concentrated by rotary evaporation and then analyzed by GC/MS.[5]

The results are given in Table 1 (see also the Supplementary data). The main metathesis product obtained from 1-heptene and 2-octene was 6-dodecene and that from 1-octene was 7-tetradecene. The metathetic activity obtained with the WCl_6/C system led to the formation of these products. When we repeated the same procedure without using WCl_6 we did not obtain any metathesis products.

Previously, information regarding the nature of the initiating metal carbene has been obtained in many cases[1] by examining the first-formed products in the reactions of olefins. The terminal groups in polymers formed by ROMP (ring opening metathesis polymerization) also

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Keywords: Carbon arc; Olefin metathesis; WCl_6; DFT.

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doi:10.1016/j.tetlet.2006.05.054

Table 1. GC/MS analyses of the metathesis products obtained

Reactants	Relative area of products (%)			
	Metathesis product	Side products		
		Chlorinated compounds	Isomerization[a]	Others[b]
1-Octene	7-Tetradecene 31.86	2-Chlorooctane 29.66	2-Octene (*Z*/*E*) 13.82/4.13 3-Octene (*Z* or *E*) 3.96/2.73	13.82
2-Octene	6-Dodecene 2.85	2-Chlorooctane 66.41 2- or 3-Chlorooctene 10.17	—	20.57
1-Heptene	6-Dodecene 6.57	2-Chloroheptane 64.43 2-Chloroheptane 12.61	2-Heptene 3.74 3-Heptane 3.84	8.79

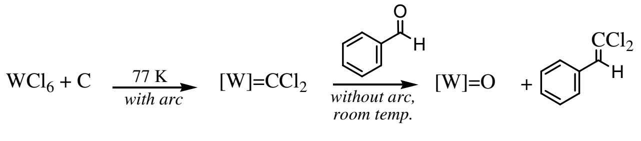
[a] Cis and trans-isomers.

[b] Oxygenated compounds which could not be exactly clarified.

carry information about the initiating carbene. Furthermore, it has been shown that the initiating species has a dichlorocarbene ligand, $[W]=CCl_2$, since the dichlorocarbene moiety has been identified in the products of reaction of preirradiated $W(CO)_6/CCl_4/h\nu$ with 1-ethoxynorbornene.[6] However, in the reaction with 4-octene and 7-tetradecene, no $RCH=CCl_2$ moiety was detected from cross-metathesis[7] and in the reaction with 2-pentene there was again no evidence for metathesis initiation by $[W]=CCl_2$.[8] In the last case it appeared that $[W]=CCl_2$ was destroyed before it could react with the substrate and the metathesis reaction was initiated from the surface of a precipitate; the nature of the initiating species is not clear. In the presence of benzaldehyde as a carbene trap, polymerization was inhibited and the main product was 2-benzylidenenorbornene. Similarly, the carbene ligands generated in the systems $W(CO)_6/CCl_4/h\nu$ and $W(CO)_6/Ph_2CCl_2/h\nu$ have been identified as $=CCl_2$ and $=CPh_2$, respectively, from the products of reaction with 2-ethoxynorbornene.[9]

With respect to this work, we presumed that the active species for our reaction was $[W]=CCl_2$ and we thus used benzaldehyde as a carbene trap to catch the tungsten–carbene species. As seen in Scheme 1, the formation of β,β-dichlorostyrene was detected by GC/MS analysis and this confirmed our supposition on the structure of tungsten carbene.

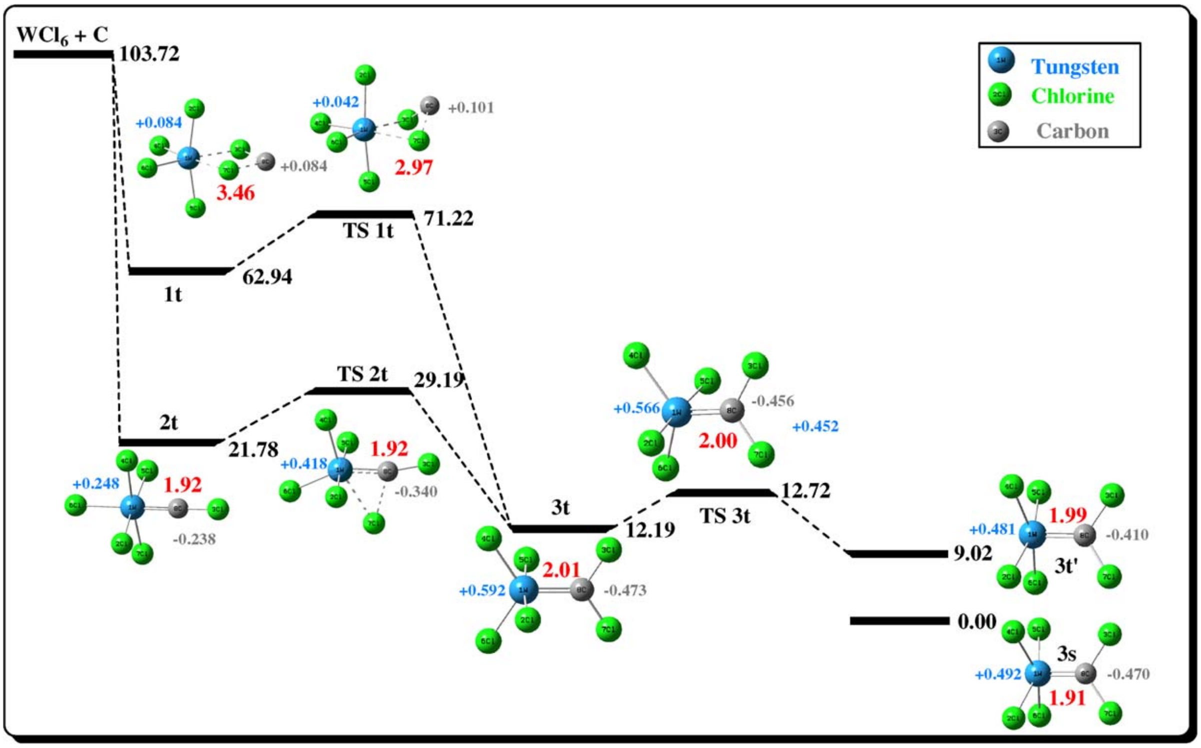
To gain insight into the mechanism of formation of $[W]=CCl_2$ from WCl_6 and a C atom, we performed molecular modeling calculations using GAUSSIAN 03.[10] The B3LYP[11] density-functional method[12] was used in combination with the LANL2DZ[13] basis set. The structures of all the carbene intermediates and transition states were optimized (see also Supplementary data). Geometries, relative energies, W–C bond lengths and the charges on W and C atoms for the structures found on the potential energy surface of the WCl_6/C atom system are given in Scheme 2.



Scheme 1.

In the triplet state, complex **1t** was transformed into the more stable structure **3t** with trigonal bipyramidal geometry and a 2.01 Å W═C bond, which is a double bond within experimental results,[14] through **TS1t** with an activation energy of 8.28 kcal mol^{-1}. From the structure **1t** to the structure **3t**, the W–C bond distance decreased steadily from 3.46 to 2.01 Å and a W═C double bond formed. The charge on the W atom increases from −0.037 to +0.592 and the charge on the C atom decreases from 0.00 to −0.473. Another pathway leading to **3t** starts with structure **2t**. Since we could not localize any complex, which could lead to the structure **2t**, we assumed that it had formed directly from WCl_6 and a C atom via insertion of the highly energetic C atom into the W–Cl bond. Then, through **TS2t** with an activation energy of 7.41 kcal mol^{-1}, it has formed **3t** and with a geometric isomerization and an activation energy of 0.53 kcal mol^{-1}, the tungsten–carbene **3t** adopted its least energetic form, **3t′**, through **TS3t**. In the singlet state, neither **1s**, nor **2s** could be localized. All calculations gave only one significant zero order stationary point corresponding to the structure **3s**, which is very similar to **3t′**. When we compare **3s** with **3t′**, we can see that the geometries are nearly the same and are square pyramidal, but the W═C bond distance is shorter and polarization of the W═C bond is higher for the singlet state. According to these calculations, we assumed that the active species, $[W]=CCl_2$, has a five coordinate square pyramidal geometry as in **3s**, which has a nucleophilic carbon atom bonded to the electrophilic metal.

In summary, we have found a new route for the synthesis of metathetic active tungsten based carbene intermediates in the reaction of a C atom with WCl_6. Current studies using other olefins are under way and will be reported in due course.



Scheme 2.

Acknowledgement

This research was supported by the TUBITAK (Scientific and Technical Research Council of the Turkish Republic) under Grant 104T402.

Supplementary data

Detailed spectral data for GC/MS analyses and computational data for DFT calculations are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.05.054.

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