The Reaction of Tungsten(VI) Alkylidyne Complexes with Inorganic Oxides: Involvement of the Resulting Alkylidene Ligand in Olefin Metathesis

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Although Schrock-type tungsten alkylidyne complexes react with inorganic oxides with formation of surface tungsten alkylidene species, the high catalytic activity of $W(CCMe_3)(CH_2CMe_3)_3/Nb_2O_5$ for the metathesis of *Z*-pent-2-ene does not seem to be correlated to the concentration of the alkylidene ligand, measured by specific reactions.

In solution, Schrock-type alkylidene complexes can be synthesized *via* protonation of the corresponding tungsten alkylidyne complexes by Brønsted acids [eqn. (1)]. This type

$$W(CCMe_3)(OCMe_3)_3 + 2HX \rightarrow W(CHCMe_3)X_2(OCMe_3)_2 + Me_3COH \quad (1)$$

of reaction allowed Weiss *et al.*[2] to synthesize silica anchored tungsten alkylidene complexes, a new generation of 'well-defined' heterogeneous metathesis catalysts. The electron-withdrawing ligands, crucial for good catalytic activity,[3] would be provided by the surface siloxy groups. We have tried to extend this concept to other supports which are characterized by a stronger surface Brønsted acidity, such as *inter alia*, Nb_2O_5.[4] $W(CCMe_3)Np_3$ (Np = neopentyl) and $W(CCMe_3)Cl_3(dme)$, (dme = dimethoxyethane) are the precursor complexes.

These two alkylidyne precursor complexes[5] (in CH_2Cl_2 or hexane solution) react readily, at room temp., with the surface of $Nb_2O_5[573]$ (100 $m^2\ g^{-1}$, from Companhia Brasileira de Mineraçao i Metalurgia, Brazil, previously treated as described elsewhere[4]): a drastic colour change is observed for both the support and the solution, and neopentane or HCl, respectively, is detected (Table 1). The quantity of gas liberated does not correspond to a simple stoichiometry. Thus, the formation of at least two different types of surface complex must have occurred, involving a reaction between the surface protons and the alkyl or chlorine ligands. Interestingly, in the case of $W(CCMe_3)Np_3/Nb_2O_5$, the formation of 2,2,5,5-tetramethylhexane is observed.

The catalytic activity of the solids resulting from the interaction between these complexes and the surface of niobia was determined for the metathesis of *Z*-pent-2-ene; the initial turnover rates are reported in Table 1. As already observed by Weiss in the case of silica supported complexes,[2] it appears that $W(CCMe_3)Np_3/Nb_2O_5$ is far more active towards olefin metathesis than $W(CCMe_3)Cl_3/Nb_2O_5$. The order of decreasing activity is as follows: $W(CCMe_3)Np_3/Nb_2O_5 > W(CCMe_3)Cl_3/Nb_2O_5 > W(CCMe_3)Np_3/SiO_2 \gg W(CCMe_3)Cl_3/SiO_2$. Although the precise coordination sphere around W for the supported complexes is not determined, the fact that, in the latter case, amounts of HCl much lower than three mol/mol W are released strongly suggests that some chlorine ligands are still present in all of the surface complexes. Thus, the smaller catalytic activity of the solid $W(CCMe_3)Cl_3/Nb_2O_5$ is rather unexpected on the basis of the strong electron withdrawing properties of the chlorine ligands. This latter observation prompted us to investigate the relationship between the concentration of surface alkylidene species and the catalytic activity. For comparison purposes, we performed the same experiments with $W(CCMe_3)Np_3/SiO_2$.

In all cases, the presence of a surface neopentylidene ligand,

Table 1

	W(% wt.)	Colour	Evolved gas[a]	2,4,4-Trimethylpent-2-ene[b]	3,3-Dimethylbut-1-ene[c]	3-Methylbut-1-ene[d]	Initial turnover rate /min^{-1}[e]
$W(CCMe_3)Np_3$		Yellow–orange					
$/Nb_2O_5[573]$[f]	0.51	Dark-grey	1.4[g]	0.3	0.1	0.3	370
$/SiO_2[473]$	3.8	Yellow	1.3[g]	0.5	0.15	0.03	15
$W(CCMe_3)Cl_3(dme)$		Blue-purple					
$/Nb_2O_5[573]$	0.66	Pale-yellow	0.2[h]	0.8	0.4	0.01	60

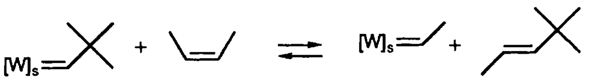
[a] After impregnation, mol/mol W. [b] mol/mol W, formed by a Wittig-type reaction with acetone. [c] mol/mol W, produced by an exchange reaction with allyl bromide. [d] mol/mol W, produced by reaction with *E*-2,5-dimethylhex-3-ene. [e] Metathesis of *Z*-pent-2-ene: [W]/[*Z*-pent-2-ene] = 1:1000; solvent: n-hexane; room temp. [f] [ ] Refers to the evacuation temperature, in K, of the support before impregnation. [g] Neopentene. [h] HCl.

obtained by protonation of the carbynic W≡C bond by the surface protons, [eqn. (1)], is demonstrated by the formation of 2,4,4-trimethylpent-2-ene when the solids are contacted with acetone (Table 1). This suggests that a Wittig-type reaction with a neopentylidene ligand on a surface W complex has occurred [eqn. (2)].

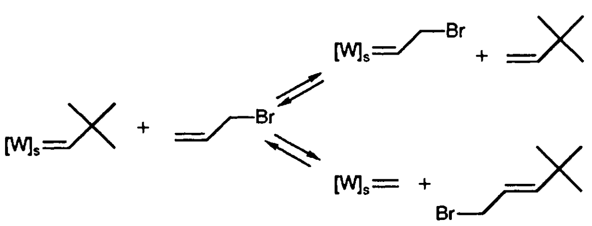
(2)

Interestingly, if one assumes that reaction (2) is quantitative, then the concentration of tungsten neopentylidene surface complexes varies as follows: $W(CCMe_3)Np_3/Nb_2O_5 < W(CCMe_3)Np_3/SiO_2 < W(CCMe_3)Cl_3/Nb_2O_5$. This sequence is quite different from that observed for the catalytic activity.

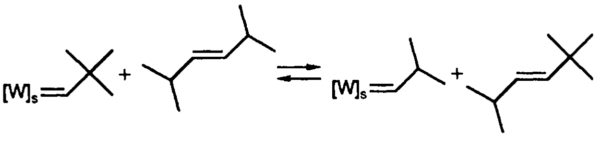
In order to establish the role of the neopentylidene ligand in the catalytic reaction (initiator or simple spectator), we determined the olefins that were first formed during the metathesis of *Z*-but-2-ene, allyl bromide and *E*-2,5-dimethylhex-3-ene, respectively. Participation of the neopentylidene ligand in the metathesis reaction *via* the metallacarbene mechanism of Chauvin,[6] would be demonstrated by the formation of 4,4-dimethylpent-2-ene, 3,3-dimethylbut-1-ene and 1-bromo-4,4-dimethylpent-2-ene, and 2,2,5-trimethylhex-3-ene, respectively [eqns. (3)–(5)].



(3)



(4)



(5)

In the case of but-2-ene, only trace amounts of the expected olefin (4,4-dimethylpent-2-ene) are formed.† The results concerning allyl bromide and *E*-2,5-dimethylhex-3-ene are summarized in Table 1. In both cases, the reaction of metathetical exchange is indeed observed, but the yield is much lower than that of the Wittig-type reaction with acetone.

In the case of allyl bromide, the reaction leads to equivalent amounts of 3,3-dimethylbut-1-ene for $W(CCMe_3)Np_3/Nb_2O_5$ and $/SiO_2$, while that for $W(CCMe_3)Cl_3/Nb_2O_5$ is much greater.‡ Most interesting is the reaction with the symmetric, sterically crowded *E*-2,5-dimethylhex-3-ene. In none of the cases do we detect the formation of the expected olefin, *i.e.* 2,2,5-trimethylhex-3-ene; instead, 3-methylbut-1-ene is formed, as the major product. Isobutene, C_7 olefins (5-methylhex-2-ene and 2,4-dimethylpent-2-ene) and trace amounts of propene are also detected. The yield of this reaction is highest in the case of $W(CCMe_3)Np_3/Nb_2O_5$.

When these results are considered as a whole, it is clear that surface neopentylidene concentration and catalytic activity are not always simply correlated. Thus, one can reasonably consider that in the cases of $W(CCMe_3)Np_3$/silica and $W(CCMe_3)Cl_3$/niobia, the neopentylidene ligand formed *via* the reaction with the surface is directly involved in the first step of the mechanism of the metathesis reaction. But in the case of $W(CCMe_3)Np_3$/niobia, the very high catalytic activity (it is the most active system) seems to be related to the presence of a surface complex, whose reaction with the olefin leads to the active carbenic complex. Although in this case a π-allyl mechanism would account for all the products formed by reaction with *E*-2,5-dimethylhex-3-ene,[7] many questions remain unanswered; if this mechanism operates, then the tungsten, initially in the formal oxidation state VI, must have been reduced prior to the formation of the hydrido π-allyl W complex. Studies are currently in progress in order to determine more accurately the coordination sphere of W in the surface complexes present on niobia.

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† But-1-ene (isomerisation product), propene, pentenes (products of cross-metathesis of but-1-ene and but-2-ene), ethylene and hex-3-ene (products of self-metathesis of but-1-ene) are also formed.

‡ 1-Bromo-4,4-dimethylpent-2-ene was not detected.