

The Catalytic Activity of Group VIB Carbene Complexes

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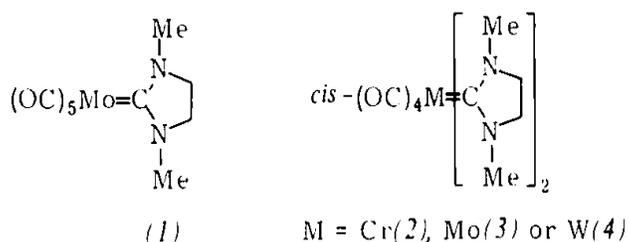
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Article:

The synthesis and properties of transition metal carbene complexes has been an area of fertile development with the preparation of many compounds being reported in the past few years⁽¹⁾. Interest is now being shown in the catalytic activity of complexes containing these novel ligands, especially as carbene complexes have been proposed as intermediates in metathesis⁽²⁾. We would like to report the results of our preliminary investigation of the activity of some Group VIB carbene complexes in metathesis, olefin polymerisation and hydrosilylation. The complexes (1-4)⁽³⁾ investigated contain the 1,3-dialkylimidazolidin-2-ylidene fragment derived from the corresponding electron-rich olefin.



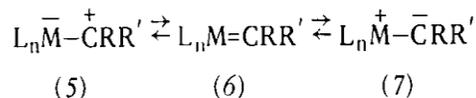
Metathesis

Our attempts to use the carbene complexes (1-4) as metathesis catalysts are summarised in Table 1. As can be seen, the complexes are inactive or weakly active alone for the metathesis of 1,7-octadiene. Complex (3) is inactive even after activation by support on alumina. The tungsten carbene (4) is only mildly active for the metathesis of norbornene, an olefin which readily undergoes metathesis. Norbornene is polymerised via ring opening metathesis by W(CO)₅CPh(OMe) at 50^o(4). Using EtAlCl₂ and n-Bu₄NCl as activators yields catalyst systems that are weakly active, (3), and moderately active, (1), for the metathesis of 1,7-octadiene to cyclohexene and ethylene. These systems would appear to be analogous to the Mo(CO)₅ py-EtAlCl₂- n-Bu₄ NCl systems which are active for metathesis⁽⁵⁾.

Although these results are largely negative, they do provide supporting evidence for the concept that a carbene must be nucleophilic in character in order to initiate, or take part in, olefin metathesis^(6,7).

Table 1. Attempted metatheses catalyzed by carbene complexes

Olefin	Catalyst	Conditions	Results
1,7-Octadiene	(3)-Al ₂ O ₃	130 ^o /20 h	No metathesis
Norbornene	(4)	THF, reflux/50 h	4% polymer
1,7-Octadiene	(3)-EtAlCl ₂ -n-Bu ₄ NCl	90 ^o /0.5 h	5% cyclohexene
1,7-Octadiene	(1)-EtAlCl ₂ -n-Bu ₄ NCl	100 ^o /2 h	40% cyclohexene



Possible resonance structures for transition metal carbenes.

According to this theory, carbenes in which resonance from (7) predominates, *i.e.* nucleophilic carbenes, are predicted to be active catalytically in metathesis, whereas those that are electrophilic in character (resonance structure 5) are likely to be inactive. In support of this concept $W(CO)_5CPh(OMe)$ is less active than $W(CO)_5CPh_2$ in metathesis, due to the more electrophilic character of the former caused by the stabilization of the electrophilic resonance structure (5) due to the heteroatom substituent on the carbene carbon. 1,3-Dialkylimidazolidin-2-ylidene carbenes have two heteroatom substituents on the carbene carbon, which are likely to increase the electrophilic character of the carbene, compared to carbenes having only one heteroatom substituent. These carbenes would be predicted, therefore, according to this theory, to have little catalytic activity for metathesis. The experimental results cited above are in agreement with, and supporting evidence for, the theories previously outlined^(6,7).

Polymerization of Methyl Methacrylate

The carbene complexes (2-4), in conjunction with carbon tetrachloride, have proven to be efficient catalysts for the polymerization of methyl methacrylate. The results are summarized in Table 2. No detailed kinetic investigations have been carried out, but it seems probable that the carbene complex- CCl_4 mixture serves to generate free radicals, as do the extensively investigated $M(CO)_6-CCl_4$ ($M = Cr, Mo$ or W) systems⁽⁸⁾. The substitution of carbonyl ligands by carbenes leads to catalysts which are more active at initiating polymerization of methyl methacrylate. $Mo(CO)_5py-CCl_4$ is more active than $Mo(CO)_6$, and in general the activity of $Mo(CO)_5L$ complexes towards CCl_4 depends on the nature of L , with activity decreasing in the order: O-compound > nitrile > N-base > P-compound > CO ⁽⁸⁾. Therefore, as these carbenes have been postulated to be good σ -donors⁽⁹⁾, perhaps somewhat like nitrogen or phosphorus bases, the increase in rate for the carbene complexes appears reasonable.

Table 2. Polymerisation of methyl methacrylate by *cis*- $M(CO)_4L_2-CCl_4$ ^{a)}

Catalyst	Temp. (°)	Rel. initiation
$Mo(CO)_6$	60	1
<i>cis</i> - $Mo(CO)_4L_2$	40	8
<i>cis</i> - $Mo(CO)_4L_2$	60	31
<i>cis</i> - $Cr(CO)_4L_2$	60	28
<i>cis</i> - $W(CO)_4L_2$	60	12

^{a)} Polymerisations carried out in neat methyl methacrylate. $[CCl_4] = 0.2 \text{ mol cm}^{-3}$; catalyst = $0.004 \text{ mol cm}^{-3}$. Rates measured by dilatometry. $L = \overline{CN(Me)CH_2CH_2}$.

Hydrosilylation

We have also utilized the $Cr(CO)_5CHNMe_2$ complex⁽¹⁰⁾ as a hydrosilylation catalyst for 1,3-dienes. For example 2,3-dimethyl-1,3-butadiene and triethylsilane give 50% yield of the 1,4-adduct, 1-triethylsilyl-2,3-dimethylbut-2-ene (based on the silane and calculated by quantitative g.l.c.) under u.v. irradiation with $Cr(CO)_5CHNMe_2$. Similar regiospecific addition is reported using $Cr(CO)_6$ ⁽¹¹⁾.

We have shown the Group VIB carbene complexes are active catalysts for a variety of reactions. We are continuing our studies of the reactions outlined above and will report in more detail later.

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