Procatalysts for Carbenoid Transformations

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Treatment of $(CO)_5W{=}C(OMe)Ph$ with diazo compounds in the presence of alkenes provides a convenient methodology for the generation of an active catalyst for cyclopropanation.

Diazomethane reacts with the Fischer carbenes $(CO)_5W{=}C(OMe)R$ at 0 °C in the presence of pyridine to produce vinyl ethers in high yield.[1] These reactions presumably involve electrophilic addition of the metal carbene to the diazo compound, and they form vinyl ethers through the loss of dinitrogen and formation of a labile alkene complex of the highly electrophilic $(CO)_5W$. Nucleophilic displacement of the alkene from the pentacarbonyl tungsten complex [equation (1)] is responsible for the high yield of vinyl ethers obtained from these coupling transformations. In the absence of pyridine (pyr) or another comparable nucleophile, the alkene complex represents a potential source of $(CO)_5W$ which we had expected[2] to be an effective catalyst for carbenoid reactions of diazo compounds.

$$(CO)_5W{=}C(OMe)R \xrightarrow[(-N_2)]{H_2CN_2} (CO)_5W[H_2C{=}C(OMe)R] \xrightarrow{pyr} (CO)_5W(pyr) + H_2C{=}C(OMe)R \qquad (1)$$

Reactions of ethyl diazoacetate (EDA) with alkenes in the presence of $(CO)_5W{=}C(OMe)Ph$[3] occur at 35 °C to produce the corresponding cyclopropanes in moderate to good yields (Table 1). Generally less than 2 mol % of the Fischer carbene, based on EDA, was effective for these conversions, but reaction times were dependent on the alkene employed and on the molar ratio of alkene to diazo compound. With styrene, for example, complete loss of dinitrogen was observed within 6 h when [styrene]/[EDA] was 10, whereas 3 days were required when the same reaction was performed with a 100-fold excess of styrene. Furthermore, the carbenoid dimers, diethyl fumarate and diethyl maleate, were major competing by-products of these transformations. These observations, alkene inhibition and competitive carbene dimer formation, are consistent with the generation of the carbenoid intermediate derived from ethyl diazoacetate [equation (2), $Z = CO_2Et$] rather than the alternative electrophilic addition of the co-ordinated alkene to the diazo compound.

$$(CO)_5W(alkene) \underset{+alkene}{\overset{-alkene}{\rightleftharpoons}} (CO)_5W \xrightarrow[-N_2]{N_2CHZ} (CO)_5W{=}CHZ \qquad (2)$$

Stereoselectivities for these cyclopropanation reactions are also presented in Table 1, and the reported values are compared with those obtained with $Rh_2(OAc)_4$ catalysis.[4] As was previously suggested from comparative results with $(CO)_5WCHPh$ and $PhCHN_2/Rh_2(OAc)_4$ in which the *cis*(*syn*) cyclopropane isomer was often predominant,[5,6] these results demonstrate a comparable preference of both the tungsten and rhodium ethoxycarbonyl carbenes for the *trans*(*anti*) isomer (slope = 0.9 from a plot of these linearly related selectivities). Thus $(CO)_5W$ and $Rh_2(OAc)_4$ provide nearly identical environments for carbenoid addition from which we

Table 1. Cyclopropane product yields and stereoselectivities from reactions of representative alkenes (100 mmol) with ethyl diazoacetate (1.0 mmol) in the presence of $(CO)_5WC(OMe)Ph$ (0.015 mmol) at 35 °C.

Alkene	Yield, %	*trans*/*cis* (*E*/*Z*)[a]
2-Methoxypropene	70	0.9 [1.0]
2-Methoxybuta-1,3-diene[b]	46	0.8 [0.8][c]
Ethyl vinyl ether	38	1.4 [1.7]
Phenyl vinyl ether	28	1.2 [1.4]
Styrene	41	1.6 [1.6]
Cyclohexene[b]	33	3.5 [3.8]
Dihydropyran	32	5.4 [6.5]
Isoprene[b]	25	1.6 [1.7][d]
		0.8 [1.1][c]

[a] Numbers in square brackets are stereoselectivities for $Rh_2(OAc)_4$-catalysed reactions at 25 °C (ref. 4). [b] Reaction performed with a 10-fold excess of alkene and 10 mol % procatalyst. [c] Addition to the 1,2-double bond. [d] Addition to the 3,4-double bond.

can conclude that, in the absence of over-riding effects from metal ligands, nonmetal carbene substituents determine isomer predominance, and decreasing temperature enhances their influence.

Coupling between the methoxyphenylcarbene substituent of tungsten and EDA was evident in the product mixture from each cyclopropanation reaction. The yields of these isomeric products varied with the alkene employed but were generally between 50 and 90%. The stoicheiometric reaction performed in anhydrous nitromethane with pyridine employed in excess gave Ph(MeO)C=CHCO$_2$Et in 82% yield. In the absence of either pyridine or alkene, these products were obtained in less than 20% yield. Similar attempts to effect coupling and/or catalytic cyclopropanation with (CO)$_5$Cr=C(OMe)Ph were only marginally successful.

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