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(Acetonitrile)pentacarbonyltungsten as a Catalytic Component for Olefin Metathesis

Since the initial report of olefin metathesis with heterogeneous catalysts (*1*) and the subsequent disclosure of homogeneous catalysts for this reaction (*2*), a plethora of other systems have been reported. Most of the previous research is summarized in the reviews by Bailey (*3*), Calderon (*4*) and Hughes (*5*). Preparation of heterogeneous systems entail a suitable thermal activation of oxides or carbonyls of tungsten, molybdenum or rhenium on an alumina or silica support. Most homogeneous catalysts require a compound of tungsten, molybdenum or rhenium mixed with a compound of aluminum, lithium, tin or magnesium. Catalysts exceptional to these patterns have been derived by the thermal activation of either (toluene) tricarbonyltungsten (*6*) or tungsten hexacarbonyl (*7*) with no other metallic component. Herein we report certain results with acetonitrile tungsten complexes as they bear directly on their capabilities as homogeneous catalysts and indirectly on the nature of the active site for metathetical catalysis.

All mixing of catalytic components and injections of olefins were done inside a glove box (Vacuum Atmospheres Corp.) under an atmosphere of prepurified nitrogen. No differences were observed when a control reaction was run in an argon atmosphere. All equipment was dried prior to insertion into the entry chamber. Reactions were carried out in 15 ml glass vials (Pierce Co.) fitted with Viton seals crimped with aluminum caps. The caps were perforated to permit the introduction of syringe needles.

Qualitative and quantitative analyses by gas–liquid partition chromatography were performed with a Hewlett-Packard Model 5750 chromatograph with a dual flame detector containing a 22 ft × 1/8 in. copper tube packed with β,β'-oxydipropionitrile on alumina. Pressures of the helium carrier stream, the hydrogen and the air were 50, 13 and 35 psi, respectively. The column was kept at room temperature. Typical temperatures for the injection port and flame detector were 170 and 130°C, respectively. Cyclohexane was used as the internal standard.

Olefins of 99% purity were supplied by Chemical Samples Co. Olefins were passed through a column of alumina under a nitrogen atmosphere to remove peroxides prior to any reaction. Ethylaluminum dichloride was used as a 25% solution in hexane (Texas Alkyls Corp.). Spectral grade benzene (Merck) was used and stored over molecular sieves in the glove box.

In a typical metathesis 2.0 mg of sublimed $W(CO)_5CH_3CN$, prepared by the method of Strohmeier and Schönauer (*8*), in 2.0 ml of benzene and 110 μl of 0.2 *M* $EtAlCl_2$ solution in hexane–benzene were mixed under nitrogen. After 1 hr 2.74 mmol of olefin were injected and the vial was sealed. Injection of $EtAlCl_2$ caused the initially clear, yellow solution to become colorless with a slight turbidity. Purified cyclohexane was added as an internal standard (about 50 mg). After the desired reaction time, usually 1 hr, the reaction was terminated by injection of 50 μl of ethanol.

(Acetonitrile)pentacarbonyltungsten ($W(CO)_5CH_3CN$) and ethylaluminum dichloride ($EtAlCl_2$) were found to be a catalytic combination for the metathesis of *cis*-2-pentene to 2-butene and 3-hexene in benzene at room temperature. The olefin/tungsten ratios were adjusted from 1000:1 to 340:1 to give conversion/selectivity values of 12%/45% and 36%/70%, respectively. Conversion is defined as the mole percent of starting olefin that has reacted; selectivity is the mole percent of reacted starting olefin that has been converted to metathesis products. Reaction times ranged from 5 min to 24 hr at conversion/selectivity values of 23%/78% and 64%/58%, respectively. The aluminum/tungsten ratios in these experiments were 4:1. *Trans/cis* ratios for these pentene reactions were 3:2 for 2-butene, 2:1 for 2-pentenes and 4:1 for 3-hexenes. Comparable values were noted for the *cis*-2-hexene metathesis to 2-butene and 4-octene. Results of the variation of metal ratios are given in Table 1. Catalytic activity commenced at an Al/W ratio of 3:1.

When aluminum chloride was used in place of ethylaluminum dichloride, the metathesis proceeded with 52% conversion of *cis*-2-pentene at a 77% selectivity. The Al/W ratio was 19:1 but little significance can be attached to this value due to the limited solubility of aluminum chloride in benzene. Higher ratios afforded alkylation of benzene. Although both components are air-stable, the catalytic combination was sensitive to air. Replacement of $EtAlCl_2$ with tetrabutyltin or butyllithium did not give metathesis.

Attempts to metathesize 1-pentene or 2-methyl-2-butene with the $W(CO)_5$-$CH_3CN/EtAlCl_2$ system were unsuccessful at the following ratios: Al/W, 4:1; olefin/W, 500:1. The analyses of the 1-pentene mixtures indicated only starting material after 16 hr, whereas those of the 2-methyl-2-butene mixtures showed neither starting material nor other low-boiling olefin.

When the 2-pentene was added to $W(CO)_5CH_3CN$ in benzene prior to the addition of $EtAlCl_2$ (Al/W = 4:1), metathesis took place in trace amounts only. The addition of 1-pentene or acetonitrile prior to the addition of 2-pentene in an otherwise actively catalytic mixture inhibited metathesis.

The striking change in conversion of 2-pentene at an Al/W ratio of 3:1 prompted an infrared examination of benzene solutions of $W(CO)_5CH_3CN$ and $EtAlCl_2$ at different Al/W ratios and devoid of olefin. Significant changes were observed and are summarized in Table 2. Again, the Al/W ratio of 3:1 produced a striking effect.

The $W(CO)_5CH_3CN$ spectrum is characterized by bands at 1930(m), 1945(vs) and 2080(w) cm^{-1}. As the amount of $EtAlCl_2$ increased, the strong 1945 cm^{-1}

TABLE 1

METATHESIS OF *cis*-2-PENTENE WITH $W(CO)_5CH_3CN/EtAlCl_2$[a]

Mole ratio, Al/W[b]	% Conversion of 2-pentene	% Selectivity to 2-butene and 3 hexene
1	0	—
2	0	—
3	43	85
4	31	84
7	31	87
10	39	92

[a] Reaction conditions: 3 mmole olefin in 2.0 ml of benzene with olefin/tungsten ratio of 500:1 for 1 hr at room temperature. All reactions were carried out in a nitrogen atmosphere.

[b] Catalytic mixtures were used after 1 hr standing.

TABLE 2

INFRARED ABSORPTIONS IN CARBONYL REGION OF BENZENE SOLUTIONS OF $W(CO)_5CH_3CN/EtAlCl_2$[a]

Al/W ratio	Frequencies (cm^{-1})			
0:1	1930(m)	1945(vs)	—	2080(w)
1:1	1930(sh,m)	1945(vs)	1980(w)	—
2:1	1930(sh,w)	1945(s)	1980(m)	—
3:1	—	1945(m)	1980(vs)	—
4:1	—	1945(m)	1980(vs)	—

[a] Spectra were taken 1 hr after mixing of components.

peak of the complex was diminished and a peak at 1980 cm^{-1} became predominant at Al/W = 3:1. The 1945 cm^{-1} peak broadened at medium intensity and was adjacent to weak and poorly resolved shoulders at 1900 and 1920 cm^{-1}. Additional amounts of $EtAlCl_2$ produced no further changes in peak positions or intensity ratios. The strong 1980 cm^{-1} band in these spectra was due to the presence of tungsten hexacarbonyl because the hexacarbonyl was isolated from two such mixtures and the addition of authentic $W(CO)_6$ to these mixtures did not cause peak broadening.

Parallel spectral changes in the ultraviolet region were noted wherein the 230 and 246(sh) nm bands of $W(CO)_5CH_3CN$ were replaced by the 228 and 290 nm bands of $W(CO)_6$ in addition to the loss of the yellow visible band of the pentacarbonyl.

Tungsten hexacarbonyl was not a catalyst for metathesis. Under the conditions of the $W(CO)_5CH_3CN$ experiments in benzene, $W(CO)_6$ and $EtAlCl_2$ were not a catalytic combination in olefin/tungsten ratios of 1000:1, 500:1, 160:1 and 100:1. Catalysis, however, took place in chlorobenzene (*9*). Herisson (*7*) reported that $W(CO)_6$ and $EtAlCl_2$ or $AlCl_3$ were catalytic combinations in chlorobenzene. This special effect of chlorobenzene may also be noted in Herisson's results with a thermally treated (160°C) $W(CO)_6$, wherein catalysis took place in that solvent but not in toluene, heptane or decalin. We noted further than when $W(CO)_6$ was irradiated in octane and the solvent along with excess starting material were removed at 60°C *in vacuo*, a portion of the resulting residue in benzene was catalytic for the metathesis of *cis*-2-pentene with 50% conversion and 80% selectivity provided that $EtAlCl_2$ were present.

These results suggest the formation of an unstable $W(CO)_5$ species which is able to disproportionate to $W(CO)_6$ and a species of lower carbonyls. A similar inorganic disproportionation in an olefin metathesis has been reported by Doyle (*10*) for a molybdenum system. We are examining currently the possibility that the lower carbonyl moiety complexed to an aluminum component may be the active site for metathesis is these reactions.

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