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PRELIMINARY COMMUNICATION

DIMERIZATION OF ACRYLONITRILE TO 1,4-DICYANO-1-BUTENE WITH RUTHENIUM COMPLEXES

JAMES D. McCLURE, RAYMOND OWYANG AND LYNN H. SLAUGH
Shell Development Company, Emeryville, California 94608 (U.S.A.)

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A recent communication[1] has reported that a ruthenium complex, $RuCl_2(CH_2{=}CHCN)_3$, prepared by interaction of an ethanolic solution of $RuCl_3(H_2O)_3$ with excess acrylonitrile, catalyzes the conversion of acrylonitrile under a hydrogen atmosphere (300 psi) to a mixture of propionitrile, I (45%), and linear dimers, II [1,4-dicyano-1-butene (50%) and adiponitrile (4%)]. We indepently discovered this reaction and wish to report results bearing on the mechanism of the reaction.

The $RuCl_2(CH_2{=}CHCN)_4$*, III, catalyzed reaction of acrylonitrile in the presence of hydrogen** is affected significantly by tertiary amines. At 150 to 600 psi hydrogen pressure, the presence of *N*-methylpyrrolidine (10–20 moles per mole of ruthenium complex) produces a 2 to 3-fold increase in the conversion of acrylonitrile to I and II (Table 1). The dimer yield (based on converted acrylonitrile)*** is un-

TABLE 1

EFFECT OF ADDED TERTIARY AMINE
750 mmoles of acrylonitrile and 0.5 mmole of $RuCl_2(CH_2{=}CHCN)_4$ at 110°[a]

Amine (10 mmoles)	Hydrogen pressure (psi)	Time (h)	Conversion (%)	Yield (%)[b]	
				Propionitrile	Dimer[c]
None	150	10	15–22	33–36	62–65
N-Methylpyrrolidine	150	10	45–65	32–35	63–66
None	600	3	38–40	50	50
N-Methylpyrrolidine	600	3	86–88	45–50	50–53

[a] Acrylonitrile was stabilized with hydroquinone in all experiments. [b] Based on converted acrylonitrile. [c] 45% *Cis*-, 45% *trans*-1,4-dicyano-1-butene, 9–10% adiponitrile, and less than 1% 2-methyleneglutaronitrile.

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* Prepared from $RuCl_3(H_2O)_3$ and excess acrylonitrile at 115°. The elemental analysis of the product varied somewhat and indicated that in some experiments a mixture of $RuCl_2(CH_2{=}CHCN)_4$, III, and $RuCl_2(CH_2{=}CHCN)_3(H_2O)$, IV, was obtained. However, no distinction between the catalytic behavior of III and mixtures of III and IV was observed.

** The catalysts are inactive in absence of hydrogen.

*** Throughout this manuscript yields of products are based on converted acrylonitrile.

effected by the presence of the amine. It should be noted, however, that dimer yield at 150 psi hydrogen pressure* is higher (65%) than that observed at 600 psi (52%) and that only in the presence of amine are good conversions (45–65%) to I and II observed at the lower pressure. Several experiments have also been performed in the presence of *N*-methylpyrrolidine using deuterium (80 psi) in place of hydrogen. The rate of reaction of acrylonitrile is about three times slower with deuterium while product composition is unchanged.

In Table 2 are summarized the results of several experiments in which the nature of the ligands bonded to the ruthenium** has been varied. The highest yield of dimer (65–66%) is obtained with a catalyst containing three or four bonded acrylonitrile molecules. The presence of two or more Ph_3P ligands on the ruthenium reduces dimer yield to 33–37%. Proceeding from $(Ph_3P)_3RuCl_2$ to $RuCl_3(AsPh_3)_2$ to $RuCl_2(Ph_3Sb)_4$ gives increasingly higher yields of the dimer. Acrylonitrile appears to replace all of the Ph_3Sb ligands on the ruthenium in the latter catalyst since the ruthenium complex isolated after termination of the reaction showed no significant aromatic absorption in its infrared spectrum. The complex isolated from the $(Ph_3P)_3RuCl_2$ catalyzed reaction still contains bonded Ph_3P. Hence the trend in product composition observed above appears to arise from the fact that Ph_3As and Ph_3Sb are weaker bonding ligands than Ph_3P and are less able to compete with acrylonitrile for ligand sites on the ruthenium.

TABLE 2

EFFECT OF LIGAND VARIATIONS

100 mmoles of acrylonitrile, 0.2 mmole Ru catalyst, 4 mmoles of *N*-methylpyrrolidine, and 20 ml of acetone solvent under 80 psi hydrogen pressure maintained at 110–115° for 5 hours

Catalyst or catalyst precursor	Conversion (%)	Yield (%)	
		Propionitrile	Dimer
$RuCl_2(CH_2{=}CHCN)_4$ or $RuCl_2(CH_2{=}CHCN)_3(H_2O)$	53	33	65–66
$RuCl_3(H_2O)_3$	43	45–50	50
$RuCl_2(PPh_3)_3$ (Ref. 2)	42	55–65	33–37
$RuCl_2(PPh_3)_2(CH_2{=}CHCN)_2$[a]	45	55–65	33–37
$RuCl_3(AsPh_3)_2(CH_3OH)$ (Ref. 2)	35	42–48	48–53
$RuCl_2(SbPh_3)_4$ (Ref. 2)	33	33–39	60–63
$RuCl_3(H_2O)_3 + (CH_3)_2NCH_2CH_2N(CH_3)_2$	36	34–42	56
$Ru(acac)_3$	40	45	49
$Ru(OAc)_2(PPh_3)$[b]	42	55	35

[a] Prepared from $RuCl_2(PPh_3)_3$ and excess acrylonitrile in acetone diluent at 25°. [b] Prepared from $RuCl_2(PPh_3)_3$ and silver acetate in acetic acid at 100°.

The hydrogen requirement of the dimerization suggests that ruthenium hydride complexes are involved as intermediates. Reaction of $(Ph_3P)_3RuCl_2$, V[2], with hydrogen (80 psi) in the presence of *N*-methylpyrrolidine (10 moles/mole of ruthenium) at 25° affords $(Ph_3P)_3RuClH$, VI, in 95% yield as has been recently reported by Wilkinson and co-workers[3]. In the absence of amine, higher hydrogen

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* At 80 psi hydrogen pressure, the dimer yield is only very slightly higher than that observed at 150 psi.

** These catalysts have been reused several times with no apparent loss in activity.

pressures (600 psi) and higher temperatures (80°) are required to make the hydride formation proceed to completion. The non-catalytic reaction of VI with acrylonitrile[*] (50 moles/mole of VI) in benzene diluent in the presence of *N*-methylpyrrolidine at 25° affords propionitrile (80% yield, based on amount of VI introduced) and a mixture of 2-methyleneglutaronitrile (may contain some 2-methylglutaronitrile), adiponitrile, and 1,4-dicyano-1-butene in the ratio 6:2:1 (20% total yield). A similar experiment with V failed to give any dimeric products. A control experiment performed with Ph_3P and acrylonitrile in benzene solution showed that only a trace of 2-methyleneglutaronitrile was formed via simple phosphine catalysis at 25°. Both 2-methyleneglutaronitrile and 1,4-dicyano-1-butene are known to be formed[4] by such a reaction at 100°. From the reaction of VI with 1.5–2.0 molar equivalents of acrylonitrile at 40–60° a ruthenium complex, tentatively assigned the dimeric structure $[(Ph_3P)_2RuCl(CH_2{=}CHCN)]_2$, VII[**], has been isolated. VII is reconverted to VI on treatment with hydrogen and amine. In the presence of *N*-methylpyrrolidine and hydrogen, both VI and VII catalyze the reaction with acrylonitrile at 110–115° to give conversions and product compositions that are very similar to those observed with V (see Table 3). Furthermore, in the absence of amine[***] the product compositions observed with VI and VII are almost identical. The results strongly indicate that both VI and VII are intermediates in the acrylonitrile dimerization/hydrogenation with a $(Ph_3P)_3RuCl_2$ catalyst. A mechanistic scheme employing compounds similar to VI and VII, that is VIII and XI, respectively, as intermediates is formulated in a general manner for a halogen containing ruthenium catalyst (Next page).

In the catalytic experiments carried out in the presence of hydrogen, propionitrile formation may occur by reaction of IX or X with either VIII or with hydrogen. The higher propionitrile yield observed at higher hydrogen pressure with catalyst III suggests that the rate of reaction of X (or IX) with hydrogen increases with increasing hydrogen pressure. When propionitrile is formed by the reaction of IX or X with VIII, the ruthenium complex, XI, (similar to VII) is the co-product. Reconversion of XI to VIII which is essential to maintain catalytic activity is apparently promoted by the presence of a tertiary amine; hence, the accelerating effect of the *N*-methylpyrrolidine. Possibly an intermediate such as $L_2RuCl(NR_3)(CH_2{=}CHCN)$, XII, is formed by interaction of XI with *N*-methylpyrrolidine[5]. Conversion of XII to VIII by reaction with hydrogen[†] may be faster than the corresponding conversion of XI to VIII. If conversion of XI or $L_2Ru(CH_2{=}CHCN)Cl_2$ to VIII is slow and rate-determining even in the presence of amine, the deuterium isotope effect noted above

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[*] It should be emphasized that no hydrogen was present in this experiment.

[**] Found: C, 66.0; H, 4.9; N, 2.1; Cl, 4.8; P, 8.2. Calcd. for $C_{78}H_{66}P_4Cl_2N_2Ru_2$: C, 65.6; H, 4.64; N, 1.95; Cl, 4.97; P, 8.68. Dimeric nature of VII is provisional.

[***] In contrast to the results found with catalyst III, the yield of dimer observed with catalyst V increases in the presence of added *N*-methylpyrrolidine. The results suggest that the amine may be participating in the reaction by ligand formation with the ruthenium. Experiments carried out in the presence of a chelating diamine recorded in Table 2 are consistent with this interpretation.

[†] Another interpretation is that the *N*-methylpyrrolidine hydrochloride formed by the initial hydrogenolysis is involved in the conversion of XI to VIII:

$$2\,L_2RuCl(NR_3)(CH_2{=}CHCN) + R_3NHCl \rightarrow L_2RuClH(CH_2{=}CHCN) + L_2RuCl_2(CH_2{=}CHCN) + 3\,R_3N\,.$$

Experiments designed to establish this point are in progress.

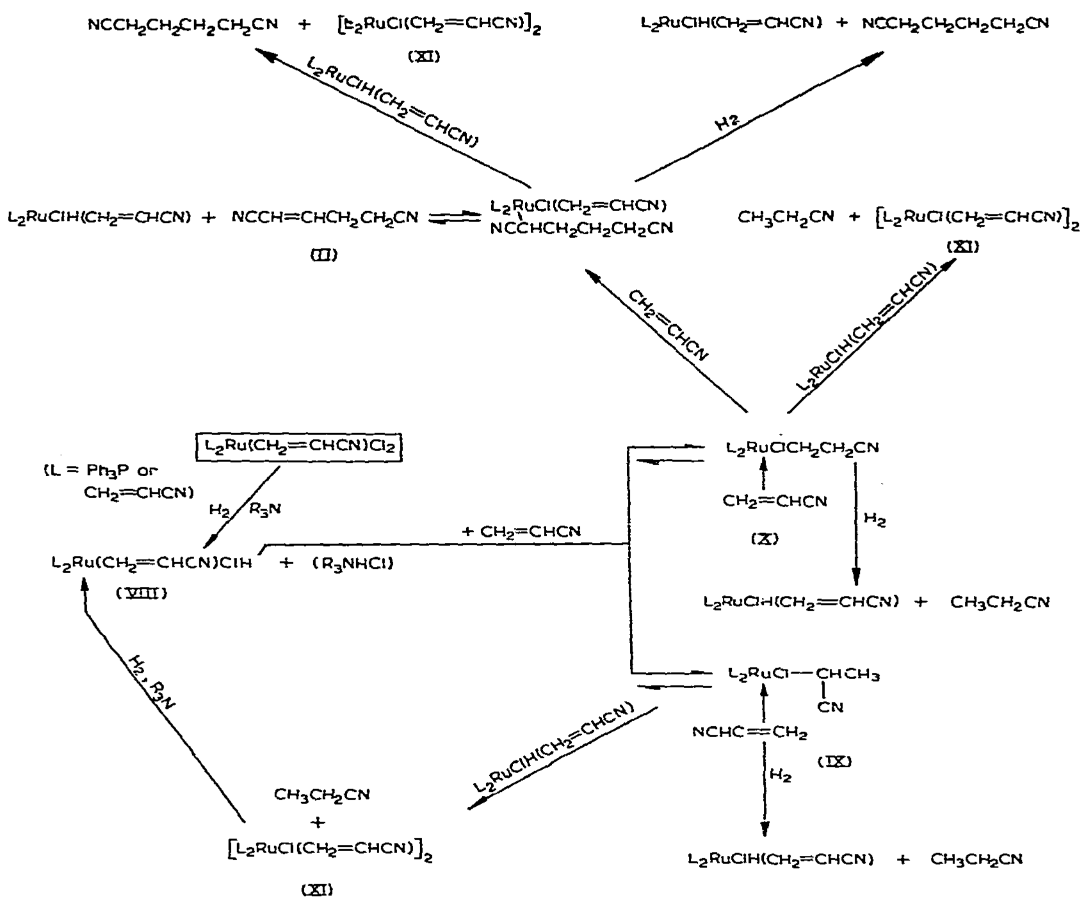

TABLE 3

DIMERIZATION/HYDROGENATION OF ACRYLONITRILE WITH CATALYSTS PREPARED FROM $(Ph_3P)_3RuCl_2$

200 mmoles of acrylonitrile. 0.3 mmole of ruthenium catalyst, and 20 ml of acetone maintained under 200 psi hydrogen pressure at 115° for 3 hours

Catalyst	Base	Conversion (%)	Yield (%)		
			Propionitrile	Linear dimer[a]	2-Methyleneglutaronitrile[b]
$(Ph_3P)_3RuCl_2$ (V)	*N*-Methylpyrrolidine (4 mmole)	58	65	33	2
$(Ph_3P)_3RuHCl$ (VI)	*N*-Methylpyrrolidine	64	66	32.5	1.5
$[(CH_2{=}CHCN)(Ph_3P)_2RuCl]_2$ (VII)	*N*-Methylpyrrolidine	61	69	28	2.5
$(Ph_3P)_3RuCl_2$		41	88.5	7.5	4
$(Ph_3P)_3RuHCl$		39	77	18	4
$[(CH_2{=}CHCN)(Ph_3P)_2RuCl]_2$		31	78	17	4

[a] 60–70% 1,4-dicyano-1-butene and 30–40% adiponitrile. [b] Almost all of the 2-methyleneglutaronitrile is formed by the competing Ph_3P catalyzed dimerization of acrylonitrile which produces a mixture of 70% 2-methyleneglutaronitrile and 30% 1,4-dicyano-1-butene at 115°.

can be explained. The fact that replacement of the hydrogen gas with deuterium fails to alter the relative amounts of I and II suggests that the reactivities of the two gases are nearly equal for the hydrogenolysis of IX and X.

1,4-Dicyano-1-butene is probably formed by an insertion of a π-bonded acrylonitrile into the sigma 2-cyanoethyl ruthenium bond of X followed by elimination of VIII. Insertion of π-bonded acrylonitrile into the ruthenium carbon bond of IX appears to be a very unfavorable reaction at 110–115° under hydrogen pressure since no significant amount of 2-methyleneglutaronitrile is formed under these conditions. However, the formation of the latter dimer from the stoichiometric reaction of VI with acrylonitrile shows that this insertion reaction can occur at 25° in the absence of hydrogen.

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