Ruthenium Complexes which catalyse the Dimerization of Acrylonitrile

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WE have recorded[1] the conversion of acrylonitrile into a mixture of propionitrile, adiponitrile, and 1,4-dicyanobut-1-ene by the use of hydrated ruthenium trichloride in alcohol under hydrogen. We now report the reactions of acrylonitrile using other ruthenium complexes as catalysts. Reactions were carried out at 130° under 3·7 atmos. of hydrogen in ethanol for 4 hr. The results are shown in the Table.

Dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV), $RuCl_2(C_{12}H_{18})$, and ruthenium(III) acetylacetonate exhibited catalytic activity similar to hydrated ruthenium trichloride. However, all reactions of acrylonitrile were inhibited by the use of dichloro(dicarbonyl)bis(pyridine)ruthenium(II), in which carbon monoxide and pyridine are strongly co-ordinated to the ruthenium atom. Propionitrile, in addition to small amounts of dimers of acrylonitrile, was mainly produced using dichlorotetrakis(triphenylphosphite)ruthenium(II), $RuCl_2[P(OPh)_3]_4$, and dichlorotetrakis(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_4$. Wilkinson *et al.* have reported[2] that the latter complex is dissociated in solution to solvated species $RuCl_2(PPh_3)_2(solvent)_2$ and $RuCl_2(PPh_3)_3(solvent)$, and it is an effective homogeneous catalyst for the hydrogenation of olefins and acetylenes. In the case of dichlorobis(triphenylphosphine)bis(acrylonitrile), $RuCl_2(PPh_3)_2an_2$, propionitrile was mainly formed, but the yields of dimers were much higher than those in the case of $RuCl_2(PPh_3)_4$. These results indicate that the co-ordination of more than two molecules of acrylonitrile to ruthenium atom may be required for the dimerization reaction.

TABLE

The dimerization of acrylonitrile and related reactions catalysed by ruthenium complexes: ruthenium complex, $7·75 \times 10^{-4}$mole; acrylonitrile, $1·5 \times 10^{-1}$mole; ethanol, 20 ml.

Ruthenium complex	an[a] conversion (%)	pn[b]	Yields of products (%) cis[c]	trans[d]	adn[e]
$RuCl_3,3H_2O$	59·5	22·6	16·5	18·5	2·7
$RuCl_2(C_{12}H_{18})$	92·2	34·3	20·9	22·7	3·8
Ru $acac_3$[f]	98·2	39·6	23·2	30·1	7·6
$RuCl_2(CO)_2\ py_2$[g]	2·2	2·9	—	—	—
$RuCl_2(P(OPh)_3)_4$[h]	44·7	21·0	—	—	—
$RuCl_2(PPh_3)_4$[h]	77·0	41·0	2·3	1·7	2·0
$RuCl_2(PPh_3)_2an_2$	51·0	24·3	7·3	5·9	2·9
Ru $acac_2(PPh_3)_2$[h]	92·9	18·0	1·1	2·6	2·6

[a] an = acrylonitrile, [b] pn = propionitrile, [c] *cis*-1,4-dicyano-1-butene, [d] *trans*-1,4-dicyano-1-butene, [e] adn = adiponitrile, [f] acac = acetylacetonate, [g] py = pyridine, [h] β-ethoxypropionitrile was also produced.

During the course of the catalysis of the dimerization of acrylonitrile by ruthenium complexes, three new ruthenium complexes were obtained.

The pale yellow crystalline complex, $RuCl_2[P(OPh)_3]_4$, was obtained by treating $RuCl_2(PPh_3)_4$ with an excess of $P(OPh)_3$ at room temperature in benzene (yield 80%).

The yellow crystalline complex, $RuCl_2(PPh_3)_2an_2$, was obtained by the reaction of a toluene solution of $RuCl_2(PPh_3)_4$ with acrylonitrile at room temperature (yield 90%). In the i.r. spectrum the C≡N stretching frequency was shifted to 2215 cm.$^{-1}$, a position lower than that in free acrylonitrile and the C=C stretching absorption at 1610 cm.$^{-1}$ and the C–H deformation absorption at 1410 and 962 cm.$^{-1}$ disappeared. The n.m.r. spectrum showed resonance bands at τ 1·7 and 5·8. This spectrum is similar to that of $W(CO)_3an_3$ in which[3] acrylonitrile is bonded to the metal through a C=C double bond. These observations indicate the co-ordination of acrylonitrile through the C=C double bond.

The orange crystalline complex, $Ru(PPh_3)_2acac_2$, was obtained by refluxing a toluene solution of Ru $acac_3$ and $AlEt_2(OEt)$ in the presence of PPh_3 for 2—3 hr. under nitrogen (yield 25%). In the i.r. spectrum the C–C stretching and C–CH_3 stretching frequency was shifted to 1260 cm.$^{-1}$, a position lower than that in ruthenium(III) acetylacetone.

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