TRANSITION-METAL CATALYSIS IN ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALTS: DIMERIZATION OF PROPYLENE CATALYZED BY NICKEL COMPLEXES AND METATHESIS OF OLEFINS CATALYZED BY TUNGSTEN COMPLEXES.

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ABSTRACT
Room temperature molten salts based on aluminum chloride or ethylaluminum dichloride and 3-butyl-1-methyl imidazolium chloride have been used as solvents for the catalytic dimerization of propylene by nickel complexes and for the metathesis of olefins by tungsten complexes. Both these reactions were performed in a two-phase system. The role of the composition of the salt and the effect of the ligands coordinated on the metal have been studied. The existence of equilibria between the molten salt phase and the hydrocarbon phase was described.

INTRODUCTION
Two-phase catalysis is an attractive alternative to homogeneous and heterogeneous catalysis. Several reactions have tentatively been studied using this technique, and at least two of them have received industrial applications: the propylene hydroformylation reaction catalyzed by rhodium complexes dissolved in an aqueous phase (1) and the ethylene oligomerization catalyzed by nickel complexes dissolved in butanediol polar phase (2). Both these applications use protic coordination phases as catalyst solvents. However, such media could not be considered for the organometallic catalysts that are highly sensitive to protons or bases. For such catalysts, acidic room temperature molten salts based on aluminum trichloride or ethylaluminum dichloride (EtAlCl₂) and 3-butyl-1-methyl imidazolium chloride (BMIC) proved to be particularly suitable. They are good, noncoordinating solvents for many transition-metal complexes and do not dissolve aliphatic hydrocarbons. In addition, their acidity can be adjusted by varying their composition.

In this paper, we describe two reactions of petrochemical interest: the dimerization of propylene into isohexenes catalyzed by nickel complexes, and the metathesis of 2-pentene catalyzed by tungsten complexes.
EXPERIMENTAL

Air-sensitive compounds were manipulated in a glove box. Molten salts were prepared as previously described (3). Catalysis experiments were performed in a 100 mL double-walled glass reactor containing a stirring bar. The reactor was purged of air and moisture. The transition-metal complex (0.1 mmole), heptane (2 to 4 mL), molten salt (3 to 4 mL) and olefin were introduced successively into the reactor.

Dimerization. It was conducted in semi-batch experiments. An atmospheric pressure of propylene was maintained as the vapor phase. When the reactor was nearly full of liquid, the upper hydrocarbon phase was decanted and withdrawn and the experiment was started again up to 10 times with the same molten salt.

Metathesis. It was investigated in batch experiments. 2-Pentene (10 mL) was introduced under argon. 2-Pentene conversion was determined by the analysis (VPC) of the olefinic upper phase. After hydrocarbon phase withdrawals, the molten salt was reused several times.

The products were analyzed by conventional VPC techniques using an internal standard.

PROPYLENE DIMERIZATION

Dimerization of propylene was performed with NiCl$_2$2L complexes (L=trialkylphosphine). It is generally assumed that the formation of dimers results from a series of insertions into Ni-H and Ni-C bonds, thus affording various structures: n-hexenes, 2-methylpentenes, 2,3-dimethylbutenes. The presence of sterically demanding phosphines can modify the distribution of dimers by increasing the 2,3-dimethylbutene content.

Two types of molten salts were used: those based on EtAlCl$_2$ and those based on the AlCl$_3$/EtAlCl$_2$ mixture. Catalytic activity was observed only in melts where the total aluminum molar fraction was higher than 0.5. In both these systems, (EtAlCl$_2$)$_2$ contained in the melt acted not only as a component of the ionic solvent but also for the formation of a nickel-carbon bond. The results are given in Table 1. The presence of sterically demanding phosphine (P/-Pr$_3$) led to high selectivity in 2,3-dimethylbutenes, thus demonstrating the effectiveness, in molten salts, of the "phosphine effect", already observed in organic media (4,5).

EtAlCl$_2$:BMIC (1.2:1) melts. In these molten salts, deactivation of the catalyst was observed, and the amount of dimers produced before the catalyst was deactivated was 45 kg/g Ni. This catalyst deactivation can be ascribed to the fact that, when contacted with a hydrocarbon phase, the Et$_2$Al$_2$Cl$_5^-$ polynuclear anions, present in the initial melt (6), disproportionate (Raman spectroscopy) (7), (Et$_2$AlCl)$_2$ being soluble in the hydrocarbon phase:

\[ \text{Et}_2\text{Al}_2\text{Cl}_5^- \rightleftharpoons \text{AlCl}_4^- + 0.5 (\text{Et}_2\text{AlCl})_2 \quad [1] \]
Thus, after extensive extraction, the melt was essentially composed of the AlCl$_4^-$ anions.

AlCl$_3$:EtAlCl$_2$:BMIC (1.2:0.1:1) melts. As shown by Raman spectroscopy (7), such melts contained the mixture of the Al$_2$Cl$_7^-$, EtAl$_2$Cl$_6^-$ and Et$_2$Al$_2$Cl$_5^-$ polynuclear anions and the AlCl$_4^-$ anions. However, extensive extraction of this melt by a hydrocarbon phase, led to a new melt which contained only the Al$_2$Cl$_7^-$ and the AlCl$_4^-$ anions. The AlCl$_4^-$ anions, already present in the initial melt, were also formed by the disproportionation reaction of the EtAl$_2$Cl$_6^-$ anions, (EtAlCl$_2$)$_2$ being soluble in the hydrocarbon phase:

$$\text{EtAl}_2\text{Cl}_6^- \rightleftharpoons \text{AlCl}_4^- + 0.5 (\text{EtAlCl}_2)_2 \quad [2]$$

In such melts, the 2,3-dimethylbutene content and catalyst activities were enhanced (entries 1 and 2, Table 1). Such an enhancement can be ascribed to the change in the anion associated with the active cationic nickel catalyst.

By using NiCl$_2$.2PBu$_3$ complexes as catalyst precursor, a constant dimer distribution was obtained throughout the reaction time (entry 4, Table 1). On the contrary, with NiCl$_2$.2Pi-Pr$_3$ complexes, the high yield in 2,3-dimethylbutenes found at the beginning, decreased rapidly (entry 2) suggesting that the "phosphine effect" gradually disappeared. It could be assumed that there is competition, for the phosphine, between "soft" nickel active catalyst and "hard" aluminum chloride:

$$\text{RMPR}_3^+ + \text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{RNi}^+ + \text{AlCl}_3, \text{PR}_3 + \text{AlCl}_4^- \quad [3]$$

The formation of a phosphine-aluminum chloride complex was also supported by the $^{31}$P NMR spectrum of the NiCl$_2$.2PCy$_3$ (Cy=cyclohexyl) complex in AlCl$_3$:BMIC (1.2:1) molten salts which showed the presence of a species with a $^{31}$P-$^{27}$Al coupling. On the other hand, no $^{31}$P-$^{27}$Al coupling was observed when the NiCl$_2$.2PBu$_3$ complex was dissolved in AlCl$_3$:BMIC (1.2:1) molten salts suggesting that, in that case, the equilibrium [3] was strongly displaced to the left.

We have anticipated that the best way to prevent such an interaction was to add a "soft" competitive base which does not interfere with the cationic nickel active species. It is known that aromatic hydrocarbons (ArH) interact with acidic melts (8) to give colored species:

$$\text{Al}_2\text{Cl}_7^- + \text{ArH} \rightleftharpoons \text{ArH}, \text{AlCl}_3 + \text{AlCl}_4^- \quad [4]$$

Thus, we have performed the reaction with NiCl$_2$.2Pi-Pr$_3$ complex in molten salts in which different aromatic hydrocarbons were added (1 molar equivalent per Al$_2$Cl$_7^-$ anion present in the melt). As shown in Figure 1, in the presence of tetramethylbenzene or pentamethylbenzene, the 2,3-dimethylbutene content decreased very slowly thus indicating that the interaction between the aromatic hydrocarbon and AlCl$_3$ can be strong enough to prevent the decoordination of the phosphine from the nickel. On the contrary, the 2,3-dimethylbutene content decreased much more rapidly when methylnaphtalene or toluene...
were added to the melt suggesting that the interaction is all the weaker as the aromatic hydrocarbon is less basic. The effect of hexamethylbenzene, the most basic of the hydrocarbons studied, is limited due to its insolubility in the melt. However, aromatic hydrocarbons tend to be extracted by the reaction products. Thus, toluene (0.5 equivalent per Al₂Cl₇⁻ anion present in the melt) was added to the melt after each withdrawal of the reaction product phase. In that way, the 2,3-dimethylbutene content remained constant as long as toluene was added but decreased when the addition was suppressed.

**OLEFIN METATHESIS**

The reaction is usually described by the following equilibrated disproportionation of olefins:

\[
2 \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \rightleftharpoons \text{CH}_3\text{CH} = \text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_2\text{CH}_3
\]

| 2-pentene 50% | 2-butene 25% | 3-hexene 25% |

In an organic solution, tungsten hexachloride (WCl₆) and tungsten oxytetrachloride (WOCl₄) associated with an organometallic compound, such as (EtAlCl₂), are the classical olefin metathesis catalysts.

In room-temperature chloroaluminate molten salts, these complexes proved to be inactive, which could be ascribed to their well-known reduction to tungsten V and IV by the chloride anions (9). However, it has been demonstrated by cyclic voltammetric measurements (10) that the W(OAr)ₓCl₆₋ₓ complexes, in which some chloride were replaced by aryloxide ligand were harder to reduce. Thus, we have investigated the efficiency of these complexes in AlCl₃/EtAlCl₂ based molten salts for 2-pentene metathesis. As shown in Table 2, the most efficient catalyst are the W(OAr)₂Cl₄ complexes (ArOH=2,6-diphenylphenol or 2,4,6-triphenylphenol). These results differ from those described for the catalysis in organic hydrocarbon solvents in which the most active catalysts are formed when aryloxide is substituted in ortho, ortho’ by a chlorine atom (11). The activity of the W(OAr)₂Cl₄ (ArOH=diphenylphenol or triphenylphenol) complexes, in molten salts could be ascribed to the steric and electronic influence of the diphenylphenoxide ligand on the metal (12).

**CONCLUDING REMARKS**

Room-temperature acidic haloaluminate molten salts containing ethylaluminum dichloride proved to be good solvents for coordination catalysts, mainly to perform dimerization and metathesis of olefins. They make possible the extension of two-phase catalysis to noncoordinating and nonproton active solvents.

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Table 1. Dimerization of Propylene Catalyzed by NiCl₂,2L Complexes in Molten Salts<sup>a</sup>.

| Entry | Molten Salt                  | Nature of L | Additive | Temp (°C) | Reaction Time (hours) | Yield (kg/gNi) | Dimer distribution (weight %) |
|-------|------------------------------|-------------|----------|-----------|-----------------------|----------------|-------------------------------|
| 1     | EtAlCl₂:BMIC 1.2:1          | Pi-Pr₃      | no       | -15       | 18                    | 45             | 70 27 3                        |
| 2     | AlCl₃:EtAlCl₂:BMIC 1.2:0.1:1| Pi-Pr₃      | no       | -15       | 8                     | 100            | 83 to 11 14 to 50 2 to 16     |
| 3     | AlCl₃:EtAlCl₂:BMIC 1.2:0.1:1| Pi-Pr₃      | yes<sup>c</sup> | -15 | 8 | 73 | 84 to 80 15 to 18 1 |
| 4     | AlCl₃:EtAlCl₂:BMIC 1.2:0.1:1| PBu₃        | no       | 5         | 12                    | 100            | 34 63 3                        |

<sup>a</sup>NiCl₂, 2PR₃ (R=Pi-Pr₃ or PBu₃) gave red solutions in heptane; when acidic molten salts were added, the heptane phase turned colorless and the molten salt turned yellow.

<sup>b</sup>DMB=2,3-dimethylbutenes, <sup>c</sup>MP=2-methylpentenes, <sup>d</sup>n-H=n-hexenes, <sup>e</sup>tetramethylbenzene (aromatic hydrocarbon:Al₂Cl₇⁻ molar ratio=1).
Table 2. Metathesis of 2-Pentene Catalyzed by Tungsten Complexes in Acidic 
AlCl₃:EtAlCl₂:BMIC (0.9:0.2:1) Molten Saltsa.

| Entry | Type            | Tungsten complex                        | Reaction time (hours) | 2-Pentene conversion (molar %) |
|-------|-----------------|-----------------------------------------|-----------------------|--------------------------------|
| 1     | W(OAr)₂Cl₄      | 2, 6-diphenylphenoxide                  | 4                     | 50b                            |
| 2     | W(OAr)₂Cl₄      | 2, 6-dichlorophenoxide                  | >4                    | 7                              |
| 3     | W(OAr)₂Cl₄      | 2, 4, 6-triphenylphenoxide              | 4                     | 50b                            |
| 4     | W(OAr)₂Cl₄      | 2, 6-di-tert-butyl 4-methylphenoxide    | >4                    | 40                             |
| 5     | W(OAr)₂Cl₄      | 2-phenylphenoxide                       | >4                    | <1                             |
| 6     | W(OAr)Cl₅       | 2, 6-diphenylphenoxide                  | >4                    | 33                             |
| 7     | W(OAr)₄Cl₂      | phenoxide                               | >4                    | no activity                    |
| 8     | W(OAr)₃Cl₃      | 2, 4, 6-trimethylphenoxide              | >4                    | no activity                    |

a Tungsten complexes dissolved in basic AlCl₃ based salts giving black solutions which turned brown upon addition of a heptane solution of (EtAlCl₂)
bMaximum of 2-pentene conversion (50% mole) was obtained when the reaction equilibrium was reached (25% 2-butene, 25% 3-hexene). The upper hydrocarbon phase was withdrawn, and 10 mL 2-pentene were again added in the melt containing the used catalyst.
Figure 1. Dimerization of Propylene Catalyzed by NiCl₂,₂PiPr₃ Complexes (0.1 mmole). Effect of the Addition of Aromatic Hydrocarbons on the 2,3-Dimethylbutene Selectivity.