New Palladium Polymerisation Catalyst Systems

By D. T. Thompson
Consulting Chemist, Reading, England

There has been considerable interest in the use of early transition metal d^0 – and lanthanide d^0f^n – based catalysts for the polymerisation of ethylene and α-olefins. These systems act as mechanistic models for Ziegler-Natta stereo-orienting catalysts used in olefin polymerisation. Structural variations in these homogeneous catalysts allow the resulting polymer microstructures and molecular weights to be controlled.

However, catalyst systems based on the "late" transition metals usually dimerise or oligomerise olefins (rather than form high molar mass polymers) due to competing β-hydride elimination.

Now, researchers at the University of North Carolina at Chapel Hill have published two papers describing new catalyst systems based on palladium(II) or nickel(II) for olefin polymerisation, which polymerise ethylene and α-olefins (1), and new copolymerisation catalysts based on palladium(II) for copolymerising ethylene and propylene with alkyl acrylates (2).

These new highly active palladium(II) and nickel(II) catalyst systems, which are based on cationic initiators of general formula:

$[(ArN{=}C(R)\text{-}C(R){=}NAr)M(CH_3)(OEt_2)]^+[BAr'_4]^-$ (I)
where M = Pd or Ni; Ar = 2,6-C_6H_3(i-Pr)$_2$, etc;
R = H, Me, etc; Ar′ = 3,5-$C_6H_3(CF_3)_2$

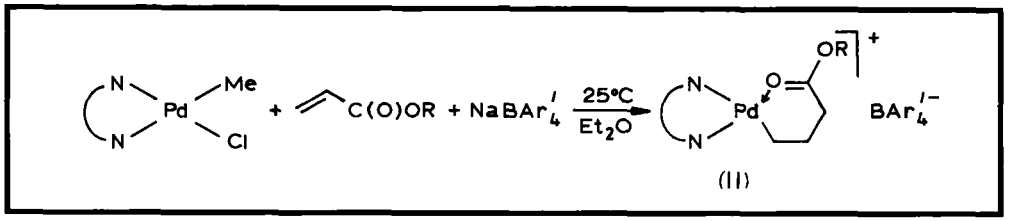
incorporate bulky diimine ligands which effectively retard chain transfer, and thus promote the conversion of ethylene and α-olefins to high molar mass polymers with varied and unique microstructures.

The new catalysts are the first reported that allow the production of ethylene homopolymers with structures varying from highly branched, completely amorphous materials, through to linear, semicrystalline, high-density materials, by a simple variation of pressure, temperature and ligand substituents. Once the palladium catalysts have been activated, exposure to ethylene, propylene or 1-hexene produces high molecular weight polymers. These polyolefins are amorphous materials and have extensive chain-branching along the backbone of the molecules, with the branches being randomly distributed and of variable length. The amorphous polyethylene produced by this process is claimed to constitute a new class of polyethylene far more highly branched than low density polyethylene.

Collaboration between Dupont and the researchers at the University of North Carolina is now leading towards a definition of applications for this new polyolefin technology (3).

Mechanistic studies have shown that the 'resting state' of the catalyst – the state that the catalyst exists in for most of the time – during the polymerisation of ethylene is an alkyl ethylene complex. Following the migratory insertion of this species, a new metal alkyl cation is formed that may be immediately trapped by the ethylene, and after insertion this leads to a linear chain segment. Alternatively, the metal alkyl cation may undergo chain migration before being trapped by ethylene, resulting in chain branching. The extent of the chain migration, and thus the extent of the branching, can be controlled via the parameters of the physical process. The steric hindrance caused by the bulky diimine ligands leads to higher rates of chain propagation than of chain transfer, giving rise to high molecular weight polymers.

The second paper reports on the first examples of metal-catalysed copolymerisations of non-polar olefins (ethylene and propylene) with alkyl acrylates resulting in high molar mass polymers via a co-ordination-type mechanism (2). These copolymerisation reactions were initiated by diethyl ether adducts (I), (when M is Pd), or by the more stable chelate complexes (II), which



are prepared as indicated in the above Equation.

The treatment of complexes (I) or (II) with ethylene or propylene in the presence of alkyl acrylates resulted in the formation of high molar mass random copolymers. These products are amorphous and highly branched polymeric materials. The ester groups are predominantly located at the ends of the branches, and the rates of polymerisation obtained are considerably less than those for the homopolymerisation of ethylene. It is claimed that these are the first transition-metal catalysts capable of polymerising ethylene and propylene with functionalised vinyl monomers to high molecular weight polymers by a co-ordination-type mechanism. Dupont has filed a broadly-based patent application on this technology.

References

1 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414

2 L. K. Johnson, S. Mecking and M. Brookhart, *ibid*, 1996, **118**, 267

3 J. Haggin, *Chem. Eng. News*, February 5, 1996, 6

Iridium Activation of Carbon-Hydrogen Bonds

The establishment of a straightforward method of activating the strong inert carbon-hydrogen bond in the alkyl groups of organic molecules and hydrocarbon fuels would increase the number of chemical reactions that can be performed and expand the usefulness of hydrocarbons. Several methods have been used to break the C-H bond, all use transition metal complexes. Among these is adding a "late" transition metal (on the right of the transition metals in the periodic table) to a C-H bond to form (hydrido)-(alkyl) metal complexes; also, σ-bond metathesis where the C-H bond is added across a bond to an electropositive metal, usually an "early" transition metal, lanthanide or actinide, giving a different hydrocarbon and a new metal alkyl complex. The latter reaction proceeds under milder conditions and shows greater selectivity. It can activate methane and terminal alkanes at temperatures as low as 45°C.

However, the preparation of a "late" iridium complex, with behaviour closer to "early" metal σ-bond metathesis processes has now been reported (B. A. Arndtsen and R. G. Bergman, *Science*, 1995, **270**, (5244), 1970–1973). This iridium complex:

$$Cp^*(P(CH_3)_3)Ir(CH_3)(ClCH_2Cl)^+BAr_f^-$$
$$Cp^* = \eta^5\text{-}C_5(CH_3)_5,\ BAr_f = B(3,5\text{-}C_6H_3(CF_3)_2)_4$$

shows unequalled C-H bond activation in organic compounds below room temperature and significant selectivity in the C-H bond that it activates. The complex contains two CH_2Cl_2 molecules per iridium complex, one of which is weakly bound to the metal centre. The high activity of the complex is thought to be due to these labile CH_2Cl_2 ligands. Their dissociation allows low-temperature access to the iridium cation. This complex is considered to be the first structurally characterised example of a η^1-bound CH_2Cl_2 unit to a transition metal.

Among C-H reactions that have been investigated was the addition of benzene to a CH_2Cl_2 solution of the Ir complex; methane was immediately lost, and a phenyl-substituted complex was generated at –30°C. The iridium complex also activates methane at 10°C, and activates terminal alkanes at room temperature to generate terminal olefin complexes.

Preliminary experiments with more complicated molecules show that even when other functionalities are present the complex reacts cleanly at ambient temperatures to break specific C-H bonds, followed rapidly by rearrangement or secondary co-ordination to the metal centre to form saturated 18-electron complexes.

The activation of hydrocarbons by this iridium complex is the simplest, general C-H activation by a metal complex observed to-date. As its exceptional reactivity is due to the labile CH_2Cl_2 unit, it it suggested that more weakly solvated forms of $[Cp^*(L)Ir(CH_3)]^+$, should demonstrate even higher reactivity toward organic compounds.