



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 tran-

sition-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
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## 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,  $\sigma$ -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  $\sigma$ -bond metathesis processes has now been reported (B. A. Arndtsen and R. G. Bergman, *Science*, 1995, **270**, (5244), 1970-1973). This iridium complex:

$$\text{Cp}^+(\text{P}(\text{CH}_3)_3)\text{Ir}(\text{CH}_3)(\text{ClCH}_2\text{Cl})^+\text{BAR}_4^-$$

$\text{Cp}^+ = \eta^1\text{-C}_5(\text{CH}_3)_5$ ,  $\text{BAR}_4 = \text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4$ , 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  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  ligands. Their dissociation allows low-temperature access to the iridium cation. This complex is considered to be the first structurally characterised example of a  $\eta^1$ -bound  $\text{CH}_2\text{Cl}_2$  unit to a transition metal.

Among C-H reactions that have been investigated was the addition of benzene to a  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  unit, it is suggested that more weakly solvated forms of  $[\text{Cp}^+(\text{L})\text{Ir}(\text{CH}_3)]^+$ , should demonstrate even higher reactivity toward organic compounds.