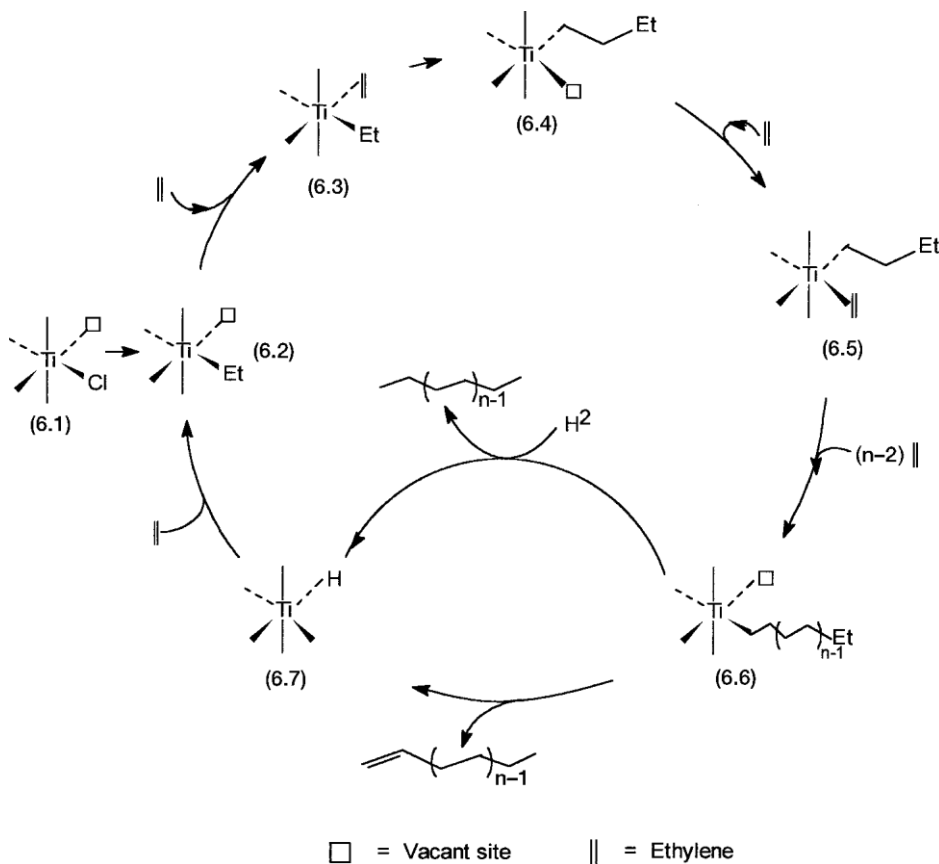


### **Cossee–Arlman Mechanism**

The Cossee–Arlman mechanism proposes direct insertion of alkene into the metal–alkyl bond (see Section 2.3.2) without the formation of any intermediate. In the solid catalyst anion vacancies at the crystal edges are formed by simple

cleavage of the bulk. Some of the  $Ti^{4+}$  ions located at these surfaces are thus coordinatively unsaturated (i.e., five rather than six coordinate). Moreover, steric constraints arising due to the presence of the surface anions make the coordination of an alkene such as propylene stereospecific. This gives rise to isotacticity in the product polypropylene. For the time being we defer any discussion on the tacticity aspect and confine our attention to the basic mechanism of polymer growth. A catalytic cycle for ethylene polymerization according to the Cossee–Arlman mechanism is shown in Fig. 6.3.

Coordinatively unsaturated 6.1 represents the surface  $Ti^{4+}$  responsible for catalyzing the polymerization reaction. By reaction with the  $Et_3Al$  (or  $Et_2AlCl$ ), a  $Ti-Et$  bond, as shown for 6.2, is formed. Ethylene coordination at the vacant



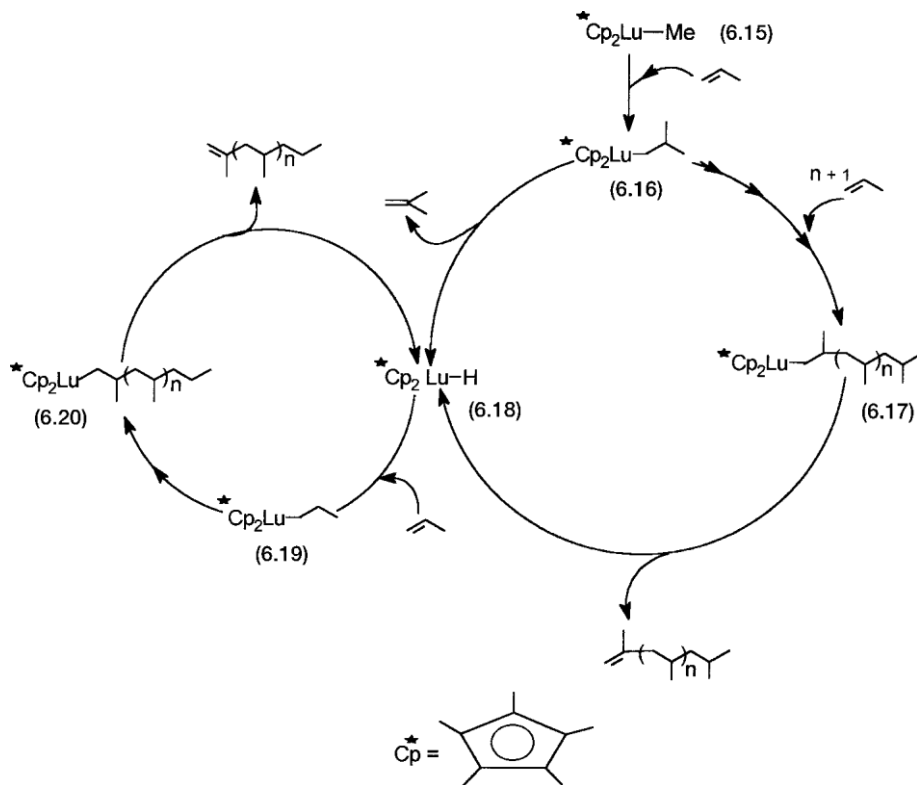
**Figure 6.3** Proposed catalytic cycle for ethylene polymerization by the Ziegler catalyst. From 6.5 to 6.6  $n - 2$  ethylene molecules undergo insertion. Note the alteration of coordination sites between the polymer chain and coordinated ethylene, that is, migratory insertion, is assumed.

site of 6.2 produces 6.3. The subsequent step, conversion of 6.3 to 6.4 is crucial. It is here that direct insertion of ethylene into the metal–alkyl bond takes place. As shown by 6.5 the vacant coordination site thus created is occupied again by another molecule of ethylene. Conversion of 6.5 to 6.6 is basically a repeat of the two preceding steps  $n - 2$  times. The polymer chain grows by continuous coordination followed by insertion or, more accurately, migratory insertion. Conversion of 6.6 to 6.7 may occur by two reactions. If hydrogen is deliberately added, then cleavage of the metal–alkyl bond, and formation of a metal–hydrogen bond, frees the saturated polymer. Alternatively, 6.6 undergoes  $\beta$ -hydride elimination, leading to the formation of a polymer chain with an unsaturated end group and the metal–hydrogen bond.

As far as the fate of 6.6 is concerned, there is a third possibility. The polymer chain may remain attached to the metal atom; that is, the metal–alkyl bond remains intact. The product of the overall reaction in this case is 6.6. Polymerization of this type is often called *living polymerization*. Note that in this case there is no polymer chain termination step, and the catalytic cycle is not completed. In other words, although a single  $\text{Ti}^{4+}$  ion may be responsible for the polymerization of thousands of ethylene molecules, in the strictest sense of the term it is not a true catalytic reaction. In the event 6.6 is converted to 6.7 either by reaction with  $\text{H}_2$  or by  $\beta$ -elimination, 6.7 further reacts with ethylene. Insertion of ethylene into the Ti–H bond regenerates 6.2 and completes the catalytic cycle.

## METALLOCENE CATALYSTS

The discovery of homogeneous metallocene catalysts in the 1980s was a very important milestone in polymer technology. With these catalysts the plastic industry is poised to move into an era of an entirely new range of polymeric materials with several specific advantages. From the initial discovery in the 1980s, close to five billion dollars is estimated to have been invested by several large chemical companies in research and development. In a relatively short time, this has resulted in approximately fifteen hundred patent applications! Close to 0.5 million tons of metallocene-catalyzed polypropylene is expected to be manufactured by the year 2003.

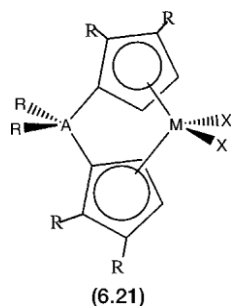


**Figure 6.5** Mechanism and catalytic cycle for propylene polymerization with a model metallocene catalyst. Conversion of 6.16 to 6.17 and 6.19 to 6.20 involve insertion of  $(n + 1)$  propylene molecules.

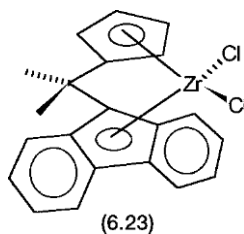
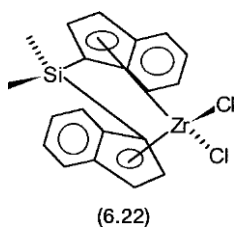
Sandwich or metallocene complexes have been known for almost 50 years. However, only in the 1970s was it discovered that when trimethylaluminum was used as a co-catalyst, small amounts of water greatly increased the polymerization activity of a metallocene catalyst. As we shall see in the following sections, this apparently simple observation has an interesting mechanistic explanation. We first discuss the general structures of the metallocene catalysts and the co-catalysts.

### Structures of Metallocene Catalysts and the Co-Catalysts

A general structure that describes all metallocene catalysts cannot be given since a variety of bicyclopentadienyl and monocyclopentadienyl complexes have been used as catalysts. A general structure for bicyclopentadienyl complexes used as catalysts is shown by 6.21.



The following points need to be made. First, the five-membered ring may also be a part of an indenyl ring structure, and the two five-membered rings may be indenyl ligands or one may be an indenyl while the other is a cyclopentadienyl ring. Second, the metal (M) is titanium or zirconium in the oxidation state of four. Third, A is an optional bridging atom, generally a carbon or silicon atom with R—CH<sub>3</sub>, H, alkyl, or other hydrocarbon groups. The Rs on A and on the five-membered rings need not necessarily be the same. Finally, X is usually Cl or an alkyl group. Two typical examples of this type of catalyst are shown by structures 6.22 and 6.23. As we shall see later, the structural difference in terms of symmetry between 6.22 and 6.23 has an important bearing on the tacticity of polypropylene produced by these catalysts.



Monocyclopentadienyl complexes have also been used as active polymerization catalysts. Indeed, titanium monocyclopentadienyl metallocenes—the so-called “constrained geometry catalysts”—have been focal points of Dow’s activity in this area. A typical example of such a catalyst is shown by the structure 6.24.

