Cationic Organo-Nickel Complexes Involved in the Catalytic Oligomerization of Ethylene
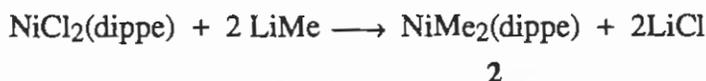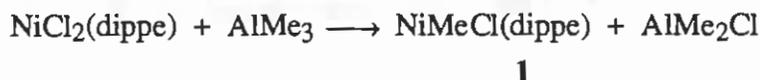
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The conversion of ethylene to oligomers with well defined and controllable chain lengths has enormous industrial applications. The Shell Higher Olefin Process (SHOP) uses neutral nickel(II) catalysts prepared from $Ni(COD)_2$ and various organic chelates to oligomerize ethylene to low molecular weight products and many similar catalysts have been investigated [1-4]. Recently, it has become increasingly evident that cationic transition metal alkyls are often more effective catalysts for the polymerization of ethylene [5-9]. Most of these cationic catalysts are based on early transition metals; we have now prepared a series of cationic nickel(II) alkyls from nickel(0) and nickel(II) precursors. Several of these cationic nickel(II) complexes catalyze the oligomerization of ethylene. The mechanism of the catalytic process has been investigated by NMR techniques; the structures of catalyst resting state, the deactivated catalyst, and the organic products have been established.

Several neutral nickel(II) alkyls and nickel(0) alkene complexes have been prepared as starting materials for the cationic organonickel catalysts. Alkylation of the nickel(II) complex, $NiCl_2$(dippe) (dippe = 1,2-bis(diisopropylphos-phino)ethane) with $AlMe_3$ or LiMe yields the mono-alkyl NiMeCl(dippe), **1**, and the dialkyl $NiMe_2$(dippe), **2**, respectively. These compounds are diamagnetic and they adopt cis square-planar configurations. The nickel(II) ethyl complex $NiEt_2$(dippe) can be prepared similarly.

$$NiCl_2(\text{dippe}) \ + \ AlMe_3 \longrightarrow NiMeCl(\text{dippe}) \ + \ AlMe_2Cl$$
1

$$NiCl_2(\text{dippe}) \ + \ 2 \, LiMe \longrightarrow NiMe_2(\text{dippe}) \ + \ 2LiCl$$
2

The known allylnickel dimer, $Ni_2(\eta^3\text{-}C_3H_5)_2Br_2$, reacts with two equivalents of dippe to yield the mononuclear five-coordinate nickel allyl, $Ni(\eta^3\text{-}C_3H_5)Br(\text{dippe})$, **3**. The low temperature ^{1}H NMR spectra (-60 °C) are consistent with a square-pyramidal structure with the bromine ligand occupying the axial postion. At higher temperatures, the molecule undergoes a rapid $\eta^3\text{-}\eta^1$ shift of the allyl ligand accompanied by rotation about the allyl C-C single bond. The corresponding four-coordinate cation $[Ni(\eta^3\text{-}C_3H_5)(\text{dippe})][FPB]$ (FPB = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), is not fluxional [10].

3

In addition, the nickel(0) alkene complexes, $Ni(C_2H_4)(\text{dcype})$ [11] and $Ni(C_3H_6)$-(dcype) (dcype = 1,2-bis(dicyclohexylphosphino)ethane) have been prepared by reduction of $NiCl_2$(dcype) under an atmosphere of the appropriate alkene. The methylmethacrylate complex, $Ni(C_5H_8O_2)(\text{dcype})$, **4**, is made by ligand exchange with $Ni(C_2H_4)(\text{dcype})$ and has been structurally characterized (Figure 1).

NiMeCl(dippe), **1**, reacts with [Na(thf)₂][FPB] to yield the chloride-bridged dinuclear cation [Ni₂Me₂(μ-Cl)(dippe)₂][FPB], **5**, which has been structurally chatacterized (Figure 2) [10]. The bridging chloride ligand cannot be displaced by [Na(thf)₂][FPB] or coordinating
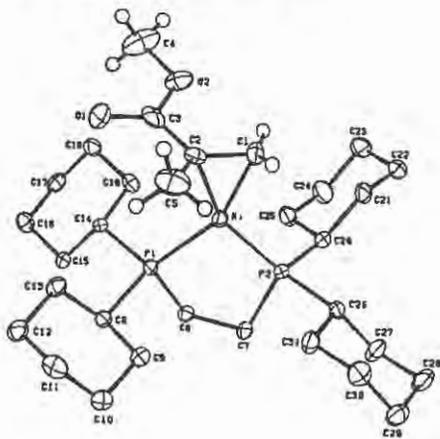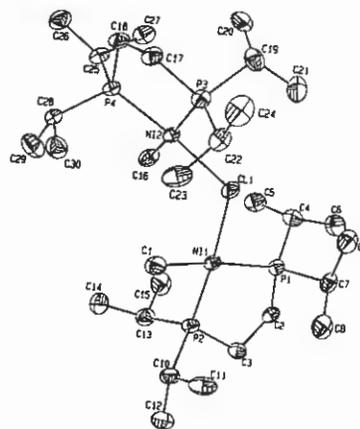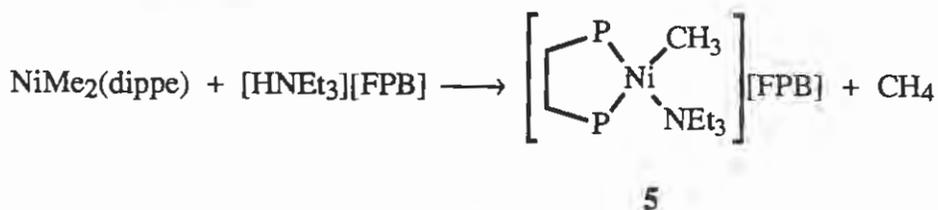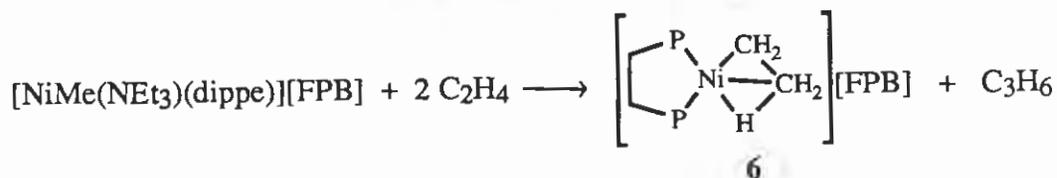

Figure 1

Figure 2

solvents and is unreactive toward alkenes. Protonation of the dimethyl compound, NiMe₂(dippe) with [HNEt₃][FPB], however, affords the mononuclear cation, [NiMe(NEt₃)(dippe)]⁺, **5**. Variable temperature NMR studies have shown the the triethylamine ligand is labile above -50 °C.

$$\text{NiMe}_2\text{(dippe)} + \text{[HNEt}_3\text{][FPB]} \longrightarrow \left[\begin{array}{c} P \diagdown \; \diagup CH_3 \\ \quad Ni \\ P \diagup \; \diagdown NEt_3 \end{array} \right] \text{[FPB]} + CH_4$$

5

Addition of ethylene to diethyl ether or thf solutions of **5** results in the conversion of to ethylene to oligomeric products. At low ethylene pressures (1 atm) the products consist of a mixture of 1-butene and cis- and trans-2-butene, but at high pressures (10 - 100 atm), longer chain oligomers are produced.

The catalytic reaction begins by insertion of one molecule of ethylene into the Ni-Me bond to form a nickel propyl cation, which immediately β-eliminates to give propene and a nickel hydride. The latter reacts with a second molecule of ethylene to form the nickel-ethyl cation, **6**. Variable temperature NMR studies show that **6** contains a β-agostic interaction similar to that in the known complex, [NiEt(dtbpe)]⁺ (dtbpe = 1,2-bis(di(tertbutyl)phosphino)-

$$\text{[NiMe(NEt}_3\text{)(dippe)][FPB]} + 2\,C_2H_4 \longrightarrow \left[\begin{array}{c} P \diagdown \; \diagup CH_2 \\ \quad Ni—CH_2 \\ P \diagup \; \diagdown H \end{array} \right] \text{[FPB]} + C_3H_6$$

6

ethane) [12]. This cation is the catalyst 'resting state'; no other nickel-containing species are observed in solution, but the ethylene is rapidly converted to a mixture of butenes. Proton-ation of Ni(C₂H₄)(dcype) affords an ethyl cation analogous to **6** and similar catalytic activity is observed.

Deactivation of the catalyst proceeds by phosphine transfer to form the five-coordinate nickel hydride $[NiH(dippe)_2]^+$, followed by dehydrogenation of butene and formation of the η^3-crotyl cation, $[Ni(\eta^3\text{-}C_4H_7)(dippe)]^+$.

The oligomer made with these catalysts at high pressures (70 atm) has been identified as a mixture of long-chain linear α-olefins ($M_n \approx 1000$). It has a melting point of approximately 115 °C, which is significantly lower than the 135 °C expected for high density (linear) polyethylene. From a detailed ^{13}C NMR study (Figure 3), it has been shown that the linear α-olefins have approximately one ethyl branch per 100 methylene carbons [13].
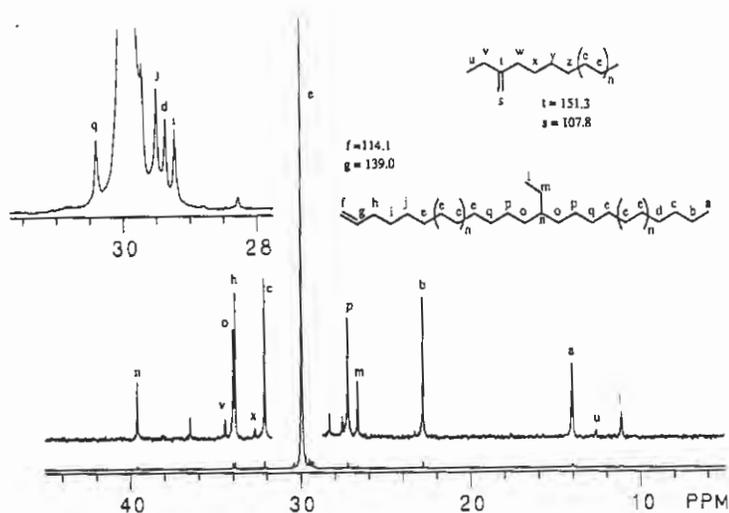

Figure 3

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