Cationic Four- and Five-Coordinate Nickel(II) Complexes: Insights into the Nickel(II)-Catalyzed Copolymerization of Ethylene and Carbon Monoxide

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Summary: Using the dppp-derived Ni(II) catalyst system ***2****, several four- and five-coordinate intermediates relevant to the alternating copolymerization of ethylene and carbon monoxide have been characterized. In addition, the activation barriers for the migratory insertion steps corresponding to chain growth have been determined to be at or below ca. 10 kcal/mol, indicating that a strongly stabilized catalyst resting state is most likely responsible for the low activity of* ***2*** *for copolymerization.*

Cationic palladium(II) complexes containing bidentate phosphine and nitrogen ligands emerged nearly two decades ago as excellent catalysts for the alternating copolymerization of olefins and carbon monoxide, and extensive mechanistic and theoretical studies have been carried out on these systems.[1−8] Nickel(II) complexes for the copolymerization[9−15] have found little success, despite the expectation of lower insertion barriers for both CO and olefins.[4,16] SHOP-type catalysts have been examined for the copolymerization of ethylene and carbon monoxide,[10,11] as have a Ni(II) catalyst containing an S,O-chelate[12] and the well-defined catalyst Ni-(o-tolyl)(PPh$_3$)(Tp^{Ph}).[13] All of these systems exhibit only modest activity. Initial attempts of Drent et al. using simple aryl-substituted bidentate phosphorus ligands similarly suffered from low productivity;[14] however, the

Scheme 1
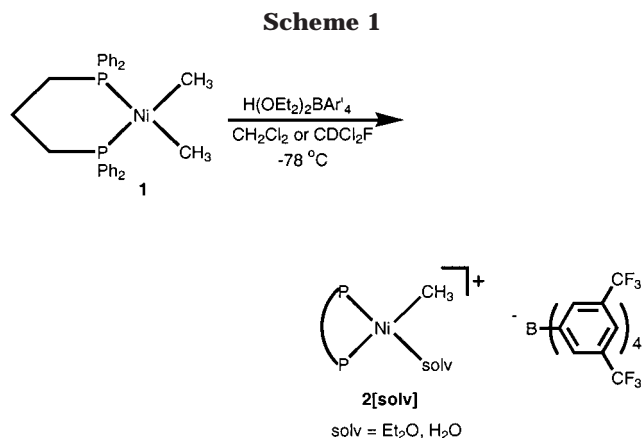
use of the modified ligand 1,2-bis(bis(2-methoxyphenyl)-phosphino)ethane effected a 10-fold increase in catalyst activity.[15]

In this communication we describe the synthesis and study of a series of nickel complexes containing the 1,3-bis(diphenylphosphino)propane (dppp) ligand which yield insight into the structures of intermediates and the migratory insertion processes in the alternating copolymerization of CO and ethylene using dppp-derived nickel catalysts. This work illustrates significant differences between the nickel system and the highly active dpppPd^{II} catalyst system as well as uncovering a number of mechanistic features characteristic of the nickel(II)-based catalyst systems.

Treatment of the dimethyl complex **1** with the oxonium acid H(OEt$_2$)$_2$BAr′$_4$ (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) in CD$_2$Cl$_2$ or CDCl$_2$F liberates 1 equiv of methane and generates the cationic methyl complex **2** in situ (Scheme 1). Complex **2** was too unstable to be isolated; however, it was completely characterized by ^{1}H, ^{31}P{^{1}H}, and ^{13}C-{^{1}H} NMR spectroscopy at low temperatures in CD$_2$-Cl$_2$.[17] The nickel-bound methyl group in **2[OEt$_2$]** was observed in the ^{1}H NMR spectrum at δ −0.08, and the coordinated ether resonances appear slightly upfield of free diethyl ether. Two ^{31}P{^{1}H} NMR signals were observed at δ 27.2 (d) and 0.95 (d) with J_{PP} = 30 Hz.

Upon treatment of **2** with CO at −140 °C (CDCl$_2$F) an acetyl complex is rapidly generated (Scheme 2); no intermediate methyl carbonyl complex is observed, indicating that the barrier to CO insertion in such a species must be less than ca. 10 kcal/mol. NMR and IR

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(8) For more recent references on olefin/CO copolymerization systems see: Milani, B.; Corso, G.; Mestroni, G.; Carfagna, C.; Formica, M.; Seraglia, R. *Organometallics* **2000**, *19*, 3435. Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779 and references therein.
(9) For a very early report of catalysis using a Ni(II) source and a Lewis acid see: Shryne, T. M.; Holler, H. V. U.S. Patent 3,984,388, 1976; *Chem. Abstr.* **1976**, *85*, 178219w.
(10) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123.
(11) Desjardins, S. Y.; Cavell, K. J.; Hoare, J. L.; Skelton, B. W.; Sobolev, A. N.; White, A. H.; Keim, W. *J. Organomet. Chem.* **1997**, *544*, 163.
(12) Driessen, B.; Green, J. J.; Keim, W. U.S. Patent 5,214,126, 1993; *Chem. Abstr.* **1992**, *116*, 152623g.
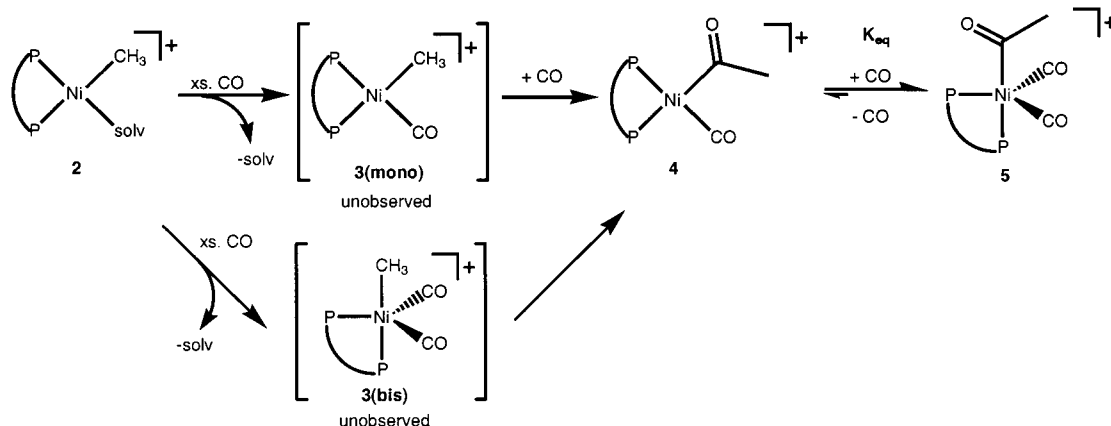(13) Domhöver, B.; Kläui, W.; Kremer-Aach, A.; Bell, R.; Mootz, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 3050.
(14) Drent, E. U.S. Patent 4,835,250, 1989.
(15) Drent, E.; Catharina, M.; De Kock, T. U.S. Patent 5,688,909, 1997.
(16) Bernardi, F.; Bottoni, A.; Nicastro, M.; Rossi, I.; Novoa, J.; Prat, X. *Organometallics* **2000**, *19*, 2170.

(17) See the Supporting Information for complete spectroscopic details.
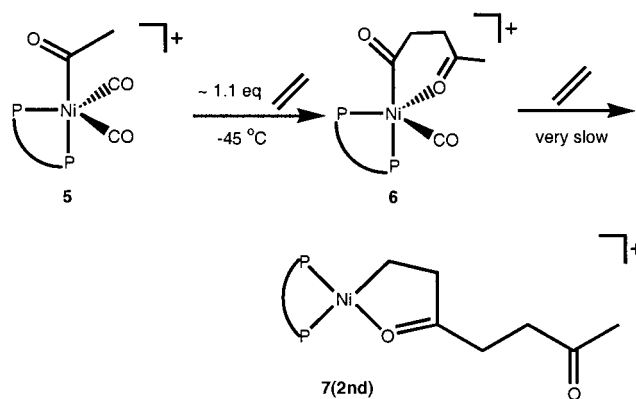
Scheme 2

Scheme 3

analysis reveals that the acetyl complex formed is a five-coordinate dicarbonyl complex, **5**, in marked contrast to the reaction of the analogous palladium complex, in which a four-coordinate acyl monocarbonyl complex is observed.[18] On the basis of spectral data the trigonal-bipyramidal structure **5**, shown in Scheme 2, is proposed.[17] The $^{13}C\{^1H\}$ NMR spectrum of **5** generated from ^{13}CO shows equivalent CO resonances at δ 184.5 (dd) coupled to two inequivalent ^{31}P nuclei ($J_{P-CO} = 24$, 22 Hz), while the acyl ^{13}CO appears at δ 221.3 as a broad doublet ($J_{P-CO} = 45$ Hz). Unlabeled **5** exhibits two $^{31}P\{^1H\}$ NMR signals at δ 11.65 and -0.19 ($J_{PP} = 85$ Hz) and a ^1H CH$_3$ resonance at δ 2.20. The low-temperature (-80 °C) IR spectrum of **5** exhibits two ν_{CO} bands at 2094 and 2059 cm^{-1}, and from the relative intensities the estimated angle between the CO ligands is 130°, consistent with the proposed structure.[17] Complex **5** is in equilibrium with its four-coordinate precursor **4**, but under 1 atm of CO in CD$_2$Cl$_2$ at -80 °C complex **5** is heavily favored. Purging this solution with argon at -20 °C liberates 1 equiv of carbon monoxide to generate the four-coordinate acyl monocarbonyl complex **4** (Scheme 2). The bound ^{13}CO ligand in **4** is now observed at δ 180.6 as a doublet of doublets ($J_{CP} = 52$, 15 Hz) and ν_{CO} 2082 cm^{-1}. In addition, the acetyl CH$_3$ group shifts to δ 1.87 and a new set of doublets is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 3.13 and -1.28 ($J_{PP} = 57$ Hz).[17]

Since no intermediate methyl carbonyl species can be detected in the conversion of **2** to **5**, we have been unable to determine whether migratory insertion occurs via the four-coordinate species, **3(mono)**, or the five-coordinate species, **3(bis)**. The extremely low insertion barrier is consistent with theoretical predictions. Bottoni et al. have calculated the insertion barriers for the neutral four- and five-coordinate complexes (CH$_3$)Ni(CO)$_2$Cl and (CH$_3$)Ni(CO)$_3$Cl to be 6.8 and 4.4 kcal/mol, respectively, suggesting possible insertion from a five-coordinate intermediate.[16] Morokuma et al. have calculated an insertion barrier of 9.8 kcal/mol for the four-coordinate diimine complex (NH=CH−CH=NH)Ni(CH$_3$)(CO)$^+$.[4] The measured barrier for the four-coordinate (dppp)-Pd(CH$_3$)(CO)$^+$ complex is 14.8 kcal/mol,[18] consistent with calculations.[2]

Treating the dicarbonyl complex **5** with ethylene gave a new acyl derivative identified as the six-membered

acyl chelate complex **6** (Scheme 3). If the stoichiometry is kept close to 1:1, quantitative formation of **6** is observed. Occasionally, a small amount of a second-generation five-membered chelate, **7(2nd)**, could be observed. The ν_{CO} absorption for **6** was observed at 2045 cm^{-1}. Under excess ethylene a mixture of five-membered chelates **7(2nd)**, **7(3rd)**, etc. is formed. The coordinated δ-keto moiety of **6** is observed as a singlet at δ 223.1 in the $^{13}C\{^1H\}$ NMR spectrum, approximately 15 ppm downfield from the expected resonance of a free keto group. The acyl carbon and the carbonyl carbon are observed at δ 241.2 (d) and 180.1 (dd), respectively, and the CH$_3$ group is observed at δ 2.35 in the ^1H NMR spectrum.[17]

Treating complex **6** with CO at -80 °C resulted in immediate formation of the second-generation acyl dicarbonyl complex **5(2nd)** (Scheme 4). Significantly, the first-generation five-membered chelate complex **7** could also be generated from complex **6** by purging a solution of **6** with argon and warming to ~-20 °C over 30 min (Scheme 4). The carbon of the coordinated keto moiety appears at δ 239.6 (d, $J_{CP} = 14$ Hz) in the ^{13}C-$\{^1H\}$ NMR spectrum, and the ^1H signal of the CH$_3$ group is at δ 2.24.[17] This experiment confirms that for this catalyst system CO insertion is a reversible process. Complex **7** was surprisingly stable (up to 40 °C) in CD$_2$Cl$_2$ solution.
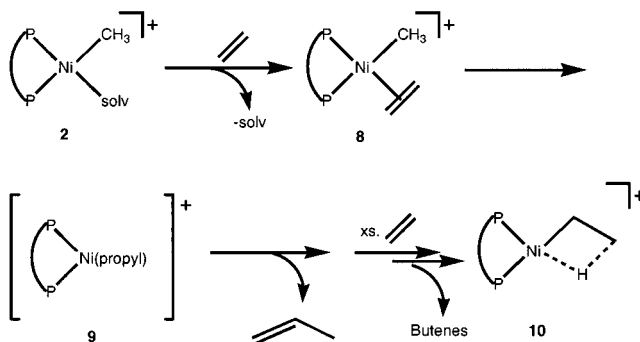
To assess the barrier to insertion of ethylene into the Ni−CH$_3$ bond, the methyl ethylene complex **8** was generated and studied (Scheme 5). The addition of 1−5 equiv of ethylene to **2** at -130 °C effected little displacement of diethyl ether; however, addition of a large excess

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Scheme 4
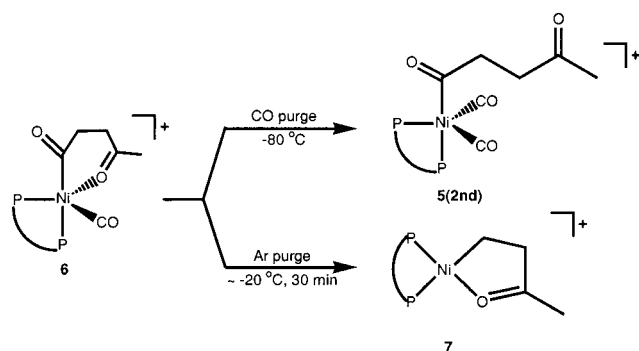
Scheme 5

of ethylene (ca. 25 equiv) resulted in complete displacement and formation of **8**. The ^{31}P{^{1}H} NMR spectrum of **8** exhibited resonances at δ 13.3 (d, $^2J_{PP}$ = 45) and 2.09 (d, $^2J_{PP}$ = 45), while the ^{1}H signal of the Ni–CH$_3$ group moved to −0.01 ppm. The bound ethylene in **8** rapidly exchanges with free ethylene, and only an average ^{1}H signal is observed.[19]

When the solution of **8** was warmed to −95.7 °C, the migratory insertion reaction of complex **8** was followed (Scheme 5). Propylene is released, and the β-agostic ethyl complex **10** is formed. A transient intermediate can be observed and is thought to be an agostic propyl complex, **9**.[20] In the presence of excess ethylene at −50 °C, complex **10** is the catalyst resting state of an ethylene dimerization cycle.[6,18] The −CH$_3$ group in complex **10** was observed at −1.0 ppm in the ^{1}H NMR spectrum. This resonance is indicative of an agostic −CH$_3$ group with an agostic hydrogen rapidly exchanging with two nonagostic hydrogens. Cooling the sample to −118 °C caused broadening of the resonance at −1.0

ppm; however, the low-temperature limiting spectrum could not be obtained. To better characterize complex **10**, the above experiment was repeated using doubly ^{13}C labeled ethylene. Upon loss of propylene (^{13}CH$_2$=^{13}CH$_2$-CH$_3$ and CH$_2$=^{13}CH$_2$13CH$_3$) the doubly ^{13}C labeled **10** was observed. The α-methylene ^{13}C resonance appears at 30.0 ppm (J_{CH} = 160 Hz), while the β-methyl resonance was observed at 3.17 ppm ($^1J_{CC}$ = 32 Hz, $^1J_{CH}$ = 124 Hz). The NMR spectral characteristics of **10** are completely consistent with other nickel(II) ethyl agostic complexes.[21] The migratory insertion of **8** follows clean first-order kinetics with k = 9.3 × 10^{-4} s^{-1} at −95.7 °C; $\Delta G^{\ddagger}$ = 12.7(1) kcal/mol. The barrier in the palladium analogue is 16.6(1) kcal/mol, while the barrier in a related nickel aryl diimine complex, (diimine)Ni(CH$_3$)-(C$_2$H$_4$)$^+$, is 13.3(1) kcal/mol, close to that of **8**.[22] We have not been able to access the acyl ethylene complex, (dppp)Ni(COCH$_3$)(C$_2$H$_4$)$^+$. We expect the migratory insertion barrier to be small (ca. 9 kcal/mol), as the barrier for the acyl ethylene migratory insertion reaction in the analogous series of palladium complexes ((dppp)Pd(R)(C$_2$H$_4$)$^+$, R = CH$_3$, COCH$_3$) is ca. 4 kcal/mol lower than the alkyl ethylene migratory insertion barrier.

In summary, we have characterized a number of potential intermediates in the nickel(II) dppp catalyzed copolymerization of C$_2$H$_4$ and CO as well as estimated key barriers to migratory insertions. The identification of several five-coordinate intermediates is in contrast to the palladium system, where four-coordinate species are the rule. Insertion barriers, as expected, fall well below those of the palladium analogues. That the Ni complex is a much less efficient catalyst is likely due to a strongly stabilized catalyst resting state relative to the transition state for the turnover-limiting step. In future work we will examine the working catalyst system by in situ spectroscopy in order to assess the role of the intermediates observed here, the catalyst resting state(s), and the kinetics of chain growth.

Supporting Information Available: Text giving experimental details for the synthesis and characterization of complexes **1**, **2**, **4**−**8**, and **10**, representative spectra, and kinetic data for the migratory insertion reaction of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

(19) Generation of **8** by reaction of **1** with (C$_6$F$_5$)$_3$B in the presence of ca. 5 equiv of C$_2$H$_4$ allows observation of the bound ethylene resonance at 5.2 ppm. That rapid exchange occurs with increasing ethylene concentration implies an associative exchange mechanism. See: Temple, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6626.

(20) When a solution containing complex **9** is cooled to ca. −110 °C, a broad resonance at ca. −5 ppm is observed, which we believe to be that of an agostic proton attributable to complex **9**.

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