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Four- and Five-Coordinate CO Insertion Mechanisms in d^8-Nickel(II) Complexes

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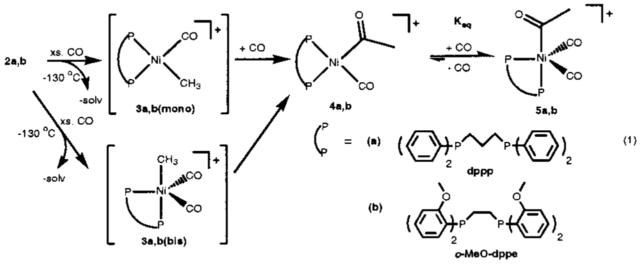
Monocationic Pd(II) complexes containing bidentate ligands have been exploited extensively as catalysts for olefin/CO copolymerizations. Mechanistic work employing well-defined systems has established that the carbonylation step occurs via migratory insertion of four-coordinate (L−L)Pd(alkyl)(CO)$^+$ species.[1] The migratory insertion rate of (L−L)Pd(CO)CH$_3$$^+$ complexes is not accelerated by external CO and, for L−L = 1,10-phenanthroline and 1,3-bis(diphenylphosphino)propane, is virtually the same in methylene chloride and the strong donor solvent, acetone.[1a,2] In short, all available evidence suggests that five-coordinate species are not involved either as transition states or as intermediates in the carbonylation step. We have been investigating ethylene/CO copolymerizations by Ni(II) analogues and report here that, in contrast to Pd analogues, carbonylation can occur via a four- or five-coordinate species but the five-coordinate pathway is preferred.

Investigations have focused on Ni(II) complexes of 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(bis(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe). Both systems are known to be active for copolymerization, but the latter is far more productive.[3] Protonation of (dppp)NiMe$_2$, **1a**, or (*o*-MeO-dppe)NiMe$_2$, **1b**, with H(OEt$_2$)$_2$BAr′$_4$ in halogenated solvents such as CH$_2$Cl$_2$ at −80 °C yields (dppp)NiMe(solv)$^+$, **2a**, and (*o*-MeO-dppe)NiMe(solv)$^+$, **2b**, (solv = OEt$_2$, OH$_2$),[4] which are highly reactive precursors to carbonylated species.



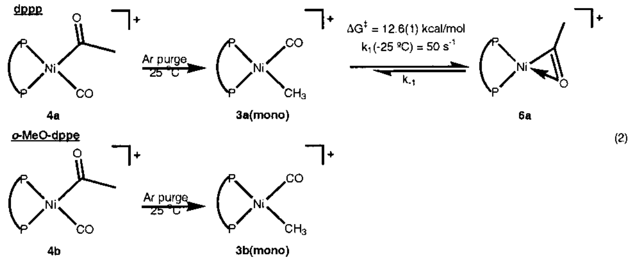
(1)

Exposure of **2a** to CO at −130 °C (CDCl$_2$F) results in immediate formation of the five-coordinate acetyl dicarbonyl complex **5a** (eq 1).[5] No intermediate methyl carbonyl complexes, **3a(mono)** or **3a(bis)**, were observed during this transformation. Assuming a generous half-life of 15 min at −130 °C indicates a maximum barrier for insertion, $\Delta G^‡ < 10$ kcal/mol. In contrast, exposure of **2b** to CO at −130 °C resulted in the formation of the methyl dicarbonyl complex **3b(bis)**[4] which undergoes insertion at −127 °C ($k = 3.4 \times 10^{-4}$ s^{-1}, $\Delta G^‡ = 10.6(2)$ kcal/mol) to give **5b**.

The five-coordinate acetyl complexes formed in these reactions are in marked contrast to reaction of the dpppPd(II) analogue in which a four-coordinate acyl monocarbonyl complex is formed.[1b] The five-coordinate structures are supported by low-temperature ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{1}H, and IR spectroscopic data.[4,5] The relative intensities of the ν_{CO} bands for **5a,b** (2094 and 2059 cm^{-1} for **5a**, 2096 and 2061 cm^{-1} for **5b**), indicate OC−Ni−CO bond angles of 130° and 106°, respectively. The reduction in bond angle suggests more steric crowding in **5b** which is likely responsible for the higher lability of the CO ligands in this complex (vide infra).

Complexes **5a,b** are in equilibrium with their four-coordinate precursors **4a,b**, but under 1 atm CO (CD$_2$Cl$_2$, −80 °C) **5a,b** are heavily favored. Purging a solution of the *o*-MeO-dppe-derived **5b** with argon at −80 °C for ca. 30 min liberates an equivalent of CO to generate the four-coordinate acyl monocarbonyl complex **4b**.[4] In contrast, the CO ligands in dppp-based **5a** are not as labile, and the argon purge must be carried out at −20 °C to drive the reaction to **4a**.[4]

Both monocarbonyl complexes **4a,b** can be further decarbonylated by warming to 25 °C under an argon purge (eq 2). Unexpectedly, in the case of the dppp complex **4a**, liberation of 1 equiv CO yields an equilibrium mixture (40:60) of two complexes. The minor one is readily assigned to the methyl carbonyl complex **3a(mono)** (Ni−C*H*$_3$, ^{1}H, 0.56 ppm).[4] The acetyl group is still present in the major complex, **6a** (Ni−COC*H*$_3$, ^{1}H, 2.14 ppm),[4] and we tentatively assign the structure as an η^2-acyl complex as shown, on the basis of the following observations:[6] (1) A (dppp)Ni(COCH$_3$)(solv)$^+$ structure is ruled out by the fact that the ratio of **3a(mono)** to **6a** is unchanged on addition of excess ether or water. (2) Cooling the solution to −130 °C results in no significant line broadening of the CH$_3$ resonance in **6a** and suggests that a β-agostic structure, (dppp)NiCOCH$_2$-μ-H$^+$, is unlikely.[7] (3) A reasonable analogue of **6a**, a Ni(II) η^2-iminoacyl complex has been structurally characterized by Carmona et al.[8]



(2)

At higher temperatures, both **3a(mono)** and **6a** exhibit a pattern of ^{1}H and ^{31}P NMR line broadening, which establishes that they are rapidly interconverting. Applying the slow-exchange approximation to the broadening of the CH$_3$ signal of **3a(mono)** at −25 °C yields a rate constant for migratory insertion of 50 s^{-1}, $\Delta G^‡ = 12.6(1)$ kcal/mol.[9] This barrier is at least 2.6 kcal/mol greater than that observed for carbonylation of **2a** and thus indicates conversion of **2a** to **5a**/**4a** *cannot* occur via migratory insertion of **3a(mono)**.

Treating the methyl carbonyl complex **3b(mono)** and the mixture of **3a(mono)** and **6a** with ethylene yields the alkyl chelate complexes **7a,b**[4] that must arise via formation of an acyl complex

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[1] (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Shultz, C. S.; Ledford, J.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6351. (c) Ledford, J. S.; Shultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. S.; Brookhart, M. *Organometallics* **2001**, in press.

[2] Ledford, J. S., Brookhart, M. Unpublished results.

[3] Drent, E.; Catharina, M.; De Kock, T. WO 9700127, 1997.

[4] See Supporting Information for complete spectroscopic details.

[5] For a preliminary report of formation of **5a** from **2a** see: Shultz, C. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 16.

[6] Theoretical analysis suggests L$_2$M(acyl)$^+$ (M = Pd, Ni) complexes are stabilized by an η^2 interaction, see: Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. Svensson, M.; Matsubara, T.; Morokuma, K. *Organometallics* **1996**, *15*, 5568.

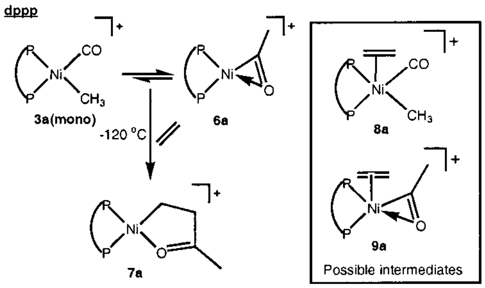
[7] For an example of a β-agosic acyl complex of molybdenum see: Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214.

[8] Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Sernau, V.; Carmona, E.; Gutiérrez, E.; Monge, A. *Polyhedron* **1995**, *14*, 323.

[9] Calculated using the standard equation for slow-exchange: $k_1 = \pi(\Delta\omega)$ where $\Delta\omega = 15$ Hz. $k_1 = 50$ s^{-1}.

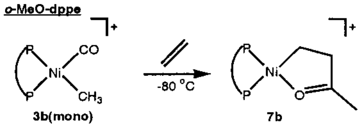
10.1021/ja0160896 CCC: $20.00

followed by insertion of ethylene and coordination of the carbonyl group (eq 3). For the dppp-derived complexes **3a(mono)** and **6a**, the chelate, **7a**, is formed immediately at −120 °C ($t_{1/2}$ < 15 min, $\Delta G^{\ddagger}$ < 11 kcal/mol), and no intermediates are detected. Since this rate is significantly greater than the rate of interconversion of **3a(mono)** and **6a**, kinetic trapping of the equilibrium mixture has occurred, and product formation via migratory insertion of **3a(mono)** can be ruled out. A likely scenario is that ethylene binds to both **3a(mono)** and **6a** to give different intermediates. (The barrier for subsequent insertion of the acyl ethylene complex, (dppp)Ni(COMe)(C_2H_4)$^+$, must also be less than 11 kcal/mol since this species is unobserved.)



(3)

Informative kinetic results came from examination of the trapping of **3b(mono)** (eq 4). Formation of **7b** was monitored at −80 °C in the presence of varying concentrations of excess ethylene.



(4)

A plot of the observed first-order rate constants versus ethylene concentration is shown in Figure 1. This plot shows a classical case of competing first- and second-order processes where $k_{obs} = k + k'[C_2H_4]$ The second-order rate constant, k', determined from the slope is 4.7(3) × 10^{-3} M^{-1} s^{-1}, while the first-order rate constant obtained from the intercept is 6.4(6) × 10^{-4} s^{-1}, $\Delta G^{\ddagger}(-80\ °C) = 14.0(1)$ kcal/mol.

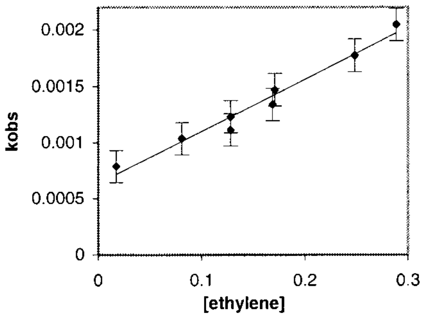
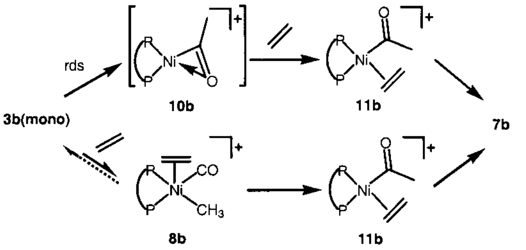


Figure 1. k_{obs} vs [ethylene] in the conversion of **3b(mono)** to **7b**.

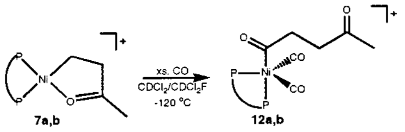
The first-order process is ascribed to rate-determining migratory insertion of **3b(mono)** to give **10b**, followed by rapid trapping of the acyl intermediate (eq 5). (**10b** is assumed to be an η^2-acyl complex based on **6a**.) The barrier of 14.0 kcal/mol for the migratory insertion of **3b(mono)** rules out the possibility that formation of **5b** from **3b(bis)** (eq 1) occurs via **3b(mono)**. The 14.0 kcal/mol barrier is consistent with the 12.6 kcal/mol barrier determined for **3a(mono)** via line broadening. The second-order process must involve coordination of ethylene in the transition state for CO insertion. Several mechanistic possibilities are consistent with these kinetics (eq 5). A five-coordinate intermediate **8b** is likely formed. Its formation could be rate-determining or **3b(mono)** and **8b** could be in rapid preequilibrium (with K_{eq} such that **8b** does not build up under reaction conditions). An alternative to eq 5 is concerted ethylene attack and insertion.



(5)

Regardless of the precise mechanistic scenario, CO insertion occurs via both four-and five-coordinate pathways for conversion of **3b(mono)** to **7b**, with the five-coordinate pathway dominating at high [C_2H_4]. As indicated before for the dppp system, conversion of **3a(mono)** to the chelate **7a** must also have access to a five-coordinate pathway since the rate exceeds the rate for migratory insertion of **3a(mono)**. This is clearly reasonable since the dppp system is less hindered than the *o*-MeO-dppe system and should react more rapidly with ethylene to form a five-coordinate species. These findings are consistent with the earlier results in the carbonylation of **2b** to **4b**/**5b**, where the reaction proceeds through the intermediate **3b(bis)**. The dppp-derived complex **2a** is also expected to proceed through the analogous dicarbonyl intermediate **3a(bis)** which is supported by the fact that the rate of carbonylation exceeds the migratory insertion rate of **3a(mono)**.

These results have a direct bearing on the propagation step involving carbonylation in olefin/CO copolymerization. For a Pd(II) chelate complex (P−P)Pd($CH_2CH_2COCH_3$)$^+$ to insert CO, the chelate must convert to the four-coordinate (P−P)Pd(CO)-$CH_2CH_2COCH_3^+$, an energetically unfavorable process under moderate CO pressures.[1b,10] In contrast, the Ni(II) chelates, **7a,b**, identified as the resting states of the copolymerization,[11] are very rapidly carbonylated at −120 °C to yield acyl derivatives **12a,b** (eq 6). The availability of low-energy five-coordinate insertion pathways for migratory insertion in Ni(II) complexes could have broad implications with respect to energetics of polymer chain growth in Ni(II)-based catalyst systems.[12]



(6)

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Supporting Information Available: Synthesis and characterization of complexes **1**−**7** and kinetic data for the insertion reactions of **3a,b(mono)**, and **3b(bis)** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0160896

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(11) Shultz, C. S., Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 2001.

(12) In the copolymerization system where CO is in excess, insertion of ethylene into the acyl bond may occur via a five-coordinate (P−P)Ni(acyl)-(C_2H_4)(CO)$^+$ complex rather than a four-coordinate acyl ethylene complex.