Please read the attached JACS communication and answer the following questions about the paper. You have 2 hours for this closed book exam.

1. (10 pts) The term migratory insertion is often used to describe the general process of a neutral metal bound ligand reacting with a cisoidal anionic ligand to produce a new coupled anionic ligand. For example, the reaction of \( 3\text{a,b(mono)} \) to produce \( 4\text{a,b} \). There are separate, more specific descriptions for this general process called migration and insertion. An insertion specifically refers to the movement and insertion of the neutral ligand into the metal-anionic ligand bond. Sketch out the two structures formed from a migration and an insertion for the following complex.

   \[ \text{R}_2\text{P} \text{Ni} \text{CO} \text{CH}_3 \text{P} \text{R}_2 \]

   in an insertion, the neutral ligand, CO in this case, inserts into the anionic ligand to metal bond to form the new anionic ligand.

   \[ \text{in a migration, the anionic ligand, methyl in this case, does a nucleophillic like attack on the electron-deficent neutral ligand (CO) to produce the new anionic ligand.} \]

   \[ \text{R}_2\text{P} \text{Ni} \text{P} \text{R}_2 \]

Suggest one experiment that would allow you to differentiate between a migration and an insertion on this general type of complex. You can use a different phosphine ligand.

Use an unsymmetrical chelating phosphine ligand (different R groups on each phosphine) and a \(^{13}\text{C}\) labeled CO ligand. NMR will then allow you to unambiguously identify whether you are having a migration or an insertion based on the trans \(^{13}\text{CO}\) to \(^{31}\text{P}\) NMR coupling. You might be able to tell from the \(^{31}\text{P}\) NMR shifts due to changes in trans-effects without the \(^{13}\text{C}\) labeled CO ligand, but the data from the \(^{13}\text{C}\) label and the unsymmetrical chelating phosphine would be a lot easier. Fluxional scrambling, of course, would limit the data from NMR. The effect of the trans phosphine ligand on the CO stretching frequency in the IR could also give you useful data, especially if you use a unsymmetrical phosphine with considerably different donor strengths. There will be more p-backbonding to the acyl ligand when it is trans to the more electron-donating phosphine. You will probably need to have some reference acyl compounds with symmetrical electron-rich and deficient chelating phosphines to provide CO frequency benchmarks.

2. (5 pts) Brookhart mentions that the Pd(II) and Ni(II) complexes discussed are catalysts for alkene/CO copolymerizations. What is the product formed from the copolymerization of ethylene and CO? Sketch out at least three repeating units.

\[
\left[ \begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \end{array} \right]_n 
\]

Perfectly alternating CO-ethylene polymer. Ethylene units are colored red.
3. (15 pts) On the first page, the second column, first full paragraph, Brookhart states that “In contrast, the CO ligands in dppp-based 5a are not as labile, . . .” Which phosphine ligand (a or b) is the stronger electron donating ligand (discuss)? Describe why the CO ligands in 5b are more labile relative to 5a and whether steric or electronic factors dominate.

The methoxy-substituted phenyl rings on ligand b make the phosphines more electron-rich relative to the dppp ligand. The lone pairs on the OCH3 group are lower in energy compared to the phenyl ring π-system and there is a filled-filled orbital interaction between the MO’s that pushes up the energy of the phenyl π-system and lowers the energy of the methoxy oxygen lone pairs. The higher energy of the filled phenyl π-system makes the phenyl ring a better donor to the phosphorus atom, making it more electron-rich and a better donor in turn to the metal center.

But, the meta-substitution of the methoxy groups in the bisphosphine b puts them in the most sterically hindered position with respect to coordination to the metal center. Thus, b is the most sterically hindered ligand and the best donor. But it is the increased sterics that have the biggest labilizing effect on the coordinated CO ligands. Brookhart comments on this in the previous paragraph where he notes: “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).” So although the somewhat stronger donor ability of ligand b makes for a more electron-rich metal that should π-backbond more strongly to the CO ligands, the increased steric effects more than compensate for this.

4. (15 pts) On page 1, second column, bottom, Brookhart states that “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).” Explain how 3a gets to 4a. Use structural diagrams to clearly illustrate what is happening.

What Brookhart is saying is that 3a(mono) reacts with CO to produce the 5-coordinate complex 3a(bis) and that the migratory insertion of CO and methyl occurs from 3a(bis) to produce 4a. This is illustrated in the top line of the scheme above. This is different from the Pd chemistry which does the migratory insertion directly from the 4-coordinate complex 3a(mono) to directly produce 6a, which can then subsequently react with more CO to make 4a.
5. (20 pts) The reaction of ethylene with 6a (page 2, first column) to form 7a could proceed by two possible mechanisms. Starting with 6a sketch out the two most likely mechanistic possibilities (these are quite similar). Do not consider backtracking to 3b(mono) as a possibility (i.e., don’t include 8b). Label each step with a brief discussion of what is happening and briefly discuss the difference between the two reactions.

The first possibility is that ethylene binds to 7a to form a 5-coordinate complex without dissociation of the CO\text{Ni} interaction and that the migratory insertion proceeds directly from this 5-coordinate complex:

The second possibility is that 7a dissociates the weak CO\text{Ni} bond to form the 3-coordinate acyl. Ethylene then binds to the free square planar coordination site to form the 4-coordinate complex and migratory insertion occurs from this followed by recoordination of the carbonyl group to the metal.

Based on what you have read in the paper, which of these two mechanisms do you favor? Discuss.

I would favor the first mechanism as being simpler (fewer steps, less unsaturation) and proceeding through a 5-coordinate intermediate. Brookhart’s data indicates that for nickel the 5-coordinate migratory insertion seems to have a lower energy barrier than the migratory insertion from a 4-coordinate complex, as happens for palladium.

6. (20 pts) Complex 8b (page 2 second column) has a choice of two possible migratory insertions. Show what these are. Assuming the structure shown for 8b help rationalize the favored insertion to 11b.

The first possible migratory insertion is between CO and methyl to make the acyl complex, which can then do a migratory insertion with ethylene to make 7a,b.

The second, and one not observed, is to have the ethylene do a migratory insertion with the methyl to make a propylene chain.

If one assumes a square pyramidal structure as shown for 8b, then the ethylene ligand is in the more weakly coordinated apical coordination site. The CO and methyl groups will be closer to one another and more likely to do a migratory insertion compared to the ethylene and methyl that will be further apart and have less orbital overlap to do the migratory insertion.
7. (15 pts) Why is the analogous Pd(II) complex mentioned in the intro less likely to go through 5-coordinate complexes compared to the Ni(II) complexes. This is NOT discussed in the paper. You will have to use your knowledge of the periodic table, Ni(II) and Pd(II) complexes, hybridization energies, orbital extensions, electronegativities, d-, s-, and p-orbital energies, etc.

The first reason is that the Pd center has a larger d orbital extensions and the lone pair of electrons in the 4dz² orbital will “stick out” further, resulting in more filled-filled orbital repulsion with the incoming lone pair orbital of a fifth ligand that wants to bind in the axial coordination site via the empty 5pz orbital. The less extended 3d orbital in nickel will offer less overlap and repulsion.

The second reason is that the 5s-5p-4d orbital energy gap in Pd is larger than in Ni. This makes it less likely that you will get 5p-4d orbital hybridization that would favor a 5-coordinate complex. The empty 5pz orbital could potentially hybridize with the filled 4dz² orbital to give a new combination of MO's (one filled, one empty) that will point in opposite directions along the z axis. This allows a ligand to come in and coordinate with less filled-filled orbital repulsions with the 4z² orbital. The smaller 4s-4p-3d energy gap in nickel, due to nickel’s higher electronegativity, makes the 4pz and 3dz² orbital hybridization more likely than for Pd, although still not particularly favorable.
Four- and Five-Coordinate CO Insertion
Mechanisms in d8-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)CH₃⁺ complexes is not accelerated by external CO and, for L = 1,10-phenanthroline and 1,3-bis(diphenylphosphino)propane, is virtually the same in methylene chloride and the strong donor solvent, acetone. 1,2 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-methoxy-phenethyl)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)NiMe₂, 1a, or (o-MeO-dppe)-NiMe₂, 1b, with H(OEt₂)₂BAR₄ in halogenated solvents such as CH₂Cl₂ at −80 °C yields (dppp)NiMe(solv)⁺, 2a, and (o-MeO-dppe)NiMe(solv)⁺, 2b, (solv = OEt₂, OH₂) 3 which are highly reactive precursors to carbonylated species.

Exposure of 2a to CO at −130 °C (CDCl₃ F) results in immediate formation of the five-coordinate acyl 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, ΔG° > 10 kcal/mol. In contrast, exposure of 2b to CO at −130 °C resulted in the formation of the methyl dicarbonyl complex 3b(bis) 5 which undergoes insertion at −127 °C (k = 3.4 × 10⁻³ s⁻¹, ΔG° = 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 dppp complex 4a, in which a four-coordinate acyl monocationic complex is formed. 6b The five-coordinate structures are supported by low-temperature ¹³C(¹H), ³¹P(¹H), ¹H, and IR spectroscopic data. 4,5 The relative intensities of the v_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 (CD₂Cl₂, −80 °C) 5a,b are heavily favored. Purging a solution of the o-MeO-dppe-derived 5b with argon at −80 °C for 30 min liberates an equivalent of CO to generate the four-coordinate acyl monocationic 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 monocational 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–CH₂), 1H, 0.56 ppm). 4 The acetyl group is still present in the major complex, 6a (Ni–COCH₂), 1H, 2.14 ppm), 4 and we tentatively assign the structure as an η²-acyl complex as shown, on the basis of the following observations: 6

(1) A (dppp)Ni(CO)(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 CH₃ resonance in 6a and suggests that a β-agostic structure, (dppp)NiCOCH₂=CH₂, is unlikely. 7 (3) A reasonable analogue of 6a, a Ni(II) η²-iminocarbonyl complex has been structurally characterized by Carmona et al. 8

At higher temperatures, both 3a(mono) and 6a exhibit a pattern of H and ³¹P NMR line broadening, which establishes that they are rapidly interconverting. Applying the slow-exchange approximation to the broadening of the CH₃ signal of 3a(mono) at −25 °C yields a rate constant for migratory insertion of 50 s⁻¹, ΔG° = 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/b cannot occur via migratory insertion of 3a(mono). 6a


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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; ∆G^° ≈ 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(CO)Me(C_2H_4), must also be less than 11 kcal/mol since this species is unobserved.)

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.

![Informative kinetic results](chart)

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}, ∆G^°(−80 °C) = 14.0(1) kcal/mol.

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

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^η-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 8b 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(bis) 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 equilibrium (with K_{eq} such that 8b does not build up under reaction conditions). An alternative to eq 5 is concerted ethylene attack and insertion.

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-dppp 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-Pd(CH_2CH_2COCH_3)_x) to insert CO, the chelate must convert to the four-coordinate (P-Pd(CO)-CH_2CH_2COCH_3)_x, an energetically unfavorable process under moderate CO pressures. In contrast, the Ni(II) chelates, 7a,b, identified as the resting states of the copolymerization, 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.

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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.

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