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Synthesis, Properties, and Reactivity of Palladium and Nickel NHC Complexes Supported by Combinations of Allyl, Cyclopentadienyl, and Indenyl Ligands

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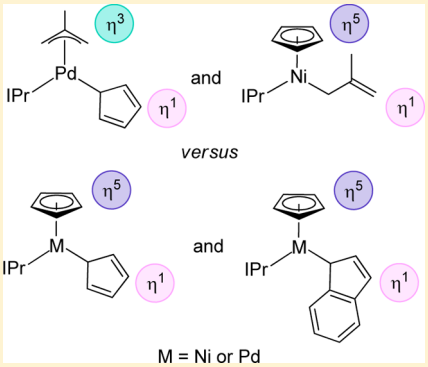
Supporting Information

ABSTRACT: The synthesis of a series of Pd and Ni complexes containing combinations of 2-methylallyl (C_4H_7), cyclopentadienyl (C_5H_5, Cp), and indenyl (C_7H_9, Ind) ligands is reported. In all cases these complexes are supported by the electron-donating N-heterocyclic carbene ligand 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IPr). The mixed Cp/2-methylallyl complexes (η^1-Cp)(η^3-2-methylallyl)Pd(IPr) (^{CpAll}**Pd**) and (η^5-Cp)(η^1-2-methylallyl)Ni(IPr) (^{CpAll}**Ni**) were synthesized through the reaction of IPr with (Cp)(2-methylallyl)M (M = Ni, Pd). The binding mode of the ligands is different in the two complexes, and as a result the total valence electron count around the metal is 18 for the Ni complex and only 16 for the Pd species. In the case of Pd, an analogue of ^{CpAll}**Pd** containing an indenyl ligand, (η^1-Ind)(η^3-2-methylallyl)Pd(IPr) (^{IndAll}**Pd**), was synthesized through the reaction of (η^3-Ind)Pd(IPr)Cl (^{IndCl}**Pd**) with (2-methylallyl)magnesium chloride. The corresponding Ni complex (η^5-Ind)(η^1-2-methylallyl)Ni(IPr) (^{IndAll}**Ni**) could not be isolated. The binding modes of the ligands in the mixed indenyl/Cp complexes (η^1-Ind)(η^5-Cp)M(IPr) (M = Ni (^{IndCp}**Ni**), Pd (^{IndCp}**Pd**)) were the same for both Ni and Pd. ^{IndCp}**Pd** was prepared through the reaction of ^{IndCl}**Pd** with NaCp, while ^{IndCp}**Ni** was synthesized through the reaction of (η^5-Cp)Ni(IPr)Cl (^{CpCl}**Ni**) with lithium indenyl. Similarly, the structures of the bis(Cp) complexes (η^5-Cp)(η^1-Cp)Ni(IPr) (^{CpCp}**Ni**) and (η^5-Cp)(η^1-Cp)Pd(IPr) (^{CpCp}**Pd**) were identical for the two different metals. In contrast to ^{CpCp}**Pd**, which is an 18-electron complex, the related bis(indenyl) Pd complex (η^3-Ind)(η^1-Ind)Pd(IPr) (^{IndInd}**Pd**) is a 16-electron species, while no Ni analogue of ^{IndInd}**Pd** was characterized. Preliminary reactivity studies with electrophiles indicate that, in all systems with mixed ligands, the η^1-ligand is nucleophilic and reacts selectively. The complexes ^{CpAll}**Pd**, ^{CpAll}**Ni**, ^{CpCp}**Pd**, ^{CpCp}**Ni**, ^{IndCl}**Pd**, ^{IndAll}**Pd**, and ^{IndInd}**Pd** were characterized by X-ray crystallography.



INTRODUCTION

Group 10 metal complexes containing allyl ligands play an important role in metal-mediated organic synthesis as catalysts[1] and precursors[2] for a variety of bond-forming reactions. Additionally, they are interesting on a fundamental level, as the bonding and subsequent reactivity of complexes with allyl ligands is heavily dependent on the identity of the metal center and the nature of the ancillary ligands.[3] In general, allyl ligands bind to transition metals in one of two different coordination modes; η^1-allyls (Figure 1a) are nucleophilic and have been invoked as a key intermediates in many reactions with electrophiles[4] such as CO_2,[5] aldehydes,[6] and imines.[6b,7] Conversely, η^3-allyls (Figure 1b) are electrophilic and are crucial intermediates in the Tsuji–Trost reaction,[8] as well as several other catalytic reactions involving attack at the η^3-allyl ligand by a nucleophile.[9]

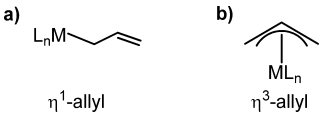
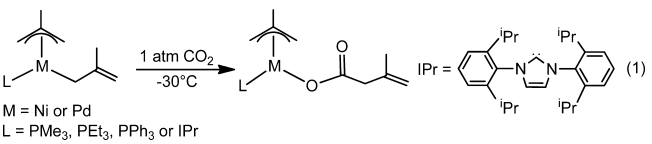


Figure 1. Depictions of the two most common binding modes of allyl ligands: (a) η^1-allyl; (b) η^3-allyl.

We have previously synthesized highly unstable complexes of the type (η^3-allyl)(η^1-allyl)M(L) (M = Ni, Pd; L = PR_3, IPr; IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene).[5a,b] These complexes react readily with CO_2 to give carboxylated products in which one molecule of CO_2 inserts into the nucleophilic M–η^1-allyl bond (eq 1). In the case of Pd



the bis(allyl) species are highly active catalysts for the carboxylation of allylstannanes[5a,10] and allylboranes;[10a] however, we believe their poor thermal stability limits the substrate scope. Mechanistic studies suggest that the η^3-allyl ligand is

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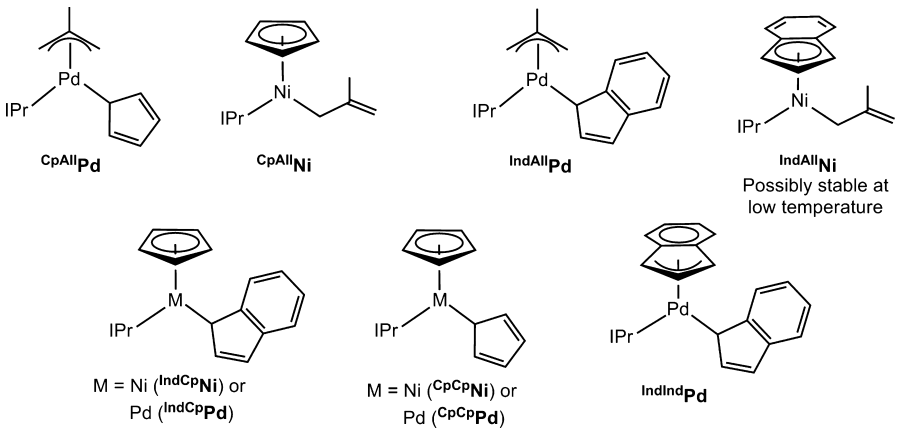
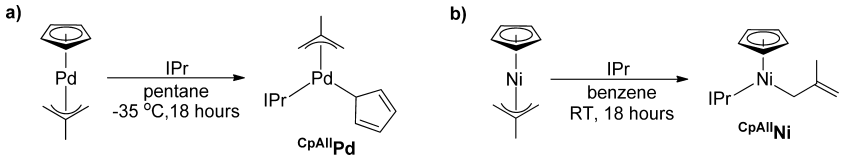


Figure 2. Ni and Pd complexes with combinations of allyl, Cp, and indenyl ligands prepared as part of this work.

Scheme 1



simply a spectator and only the η^1-allyl ligand is required to facilitate catalysis.[5a,b] Related work by Wendt and co-workers using Pd–η^1-allyl complexes supported by tridentate pincer ligands is consistent with this proposal.[5c] However, our attempts to use thermally stable Ni–η^1-allyl complexes supported by pincer ligands[11] or Pd^I dimers with bridging allyl ligands[12] for catalytic carboxylation did not improve catalyst efficiency. Therefore, we wished to explore alternative ligand frameworks to support thermally stable Pd and Ni complexes containing η^1-allyl ligands.

It is widely accepted that the allyl ligand is closely related to both the cyclopentadienyl (Cp) and indenyl ligands.[13] However, despite the close similarities between Cp and indenyl ligands, they do not always bind in the same mode to a transition metal.[14] This is primarily due to the "indenyl effect", which stabilizes η^3-binding of indenyl ligands, and as a consequence they are far more likely to bind in an η^3-fashion than Cp ligands, which generally bind in an η^1- or η^5-manner. Currently, a limited number of Pd and Ni complexes containing combinations of allyl and Cp ligands have been prepared.[15] For example, as part of their studies toward the synthesis of Pd^I dimers with bridging Cp and allyl ligands,[16] Werner and co-workers prepared the monomeric complex (η^5-Cp)(η^1-2-chloroallyl)Pd{P(O-*o*-tolyl)$_3$}, as well as related species with different phosphine and allyl ligands.[15e] In particular, they noted that (η^5-Cp)(η^1-2-chloroallyl)Pd{P(O-*o*-tolyl)$_3$} was stable at temperatures up to 50 °C. Furthermore, Werner found that the related complexes (η^5-Cp)(η^1-2-methylallyl)Pd-(PR_3) (R = P^iPr_3, PCy_3, P^tBuPh_2)[15a] showed unusual fluxional behavior in solution and at −60 °C the (η^5-Cp)(η^1-2-methylallyl)Pd(PR_3) isomer could also be observed. This species is a relatively rare example of a Pd complex with an η^1-Cp ligand.[15b,17] At this stage there is only one example of a Pd complex containing both an indenyl and allyl ligand,[18] while to the best of our knowledge Ni species containing mixed Cp and allyl or indenyl and allyl ligand sets are unknown.

Given the stability of (η^5-Cp)(η^1-2-chloroallyl)Pd{P(O-*o*-tolyl)$_3$} and our desire to prepare complexes containing thermally stable η^1-allyl ligands, we were interested in further exploring the synthesis and reactivity of Ni and Pd complexes with both Cp and allyl ligands. Ideally these complexes would be supported by a strongly donating ligand such as IPr,[19] as this was the ancillary ligand for our most active bis(allyl)Pd systems for catalytic carboxylation.[5a] In addition, given the close relationship between Cp and indenyl ligands,[15] we wanted to prepare Pd and Ni complexes with indenyl and allyl ligands supported by IPr. Here, we report the synthesis, characterization, and preliminary reactivity of the series of IPr-supported Ni and Pd complexes shown in Figure 2, which have combinations of allyl, Cp, and indenyl ligands. The structures and reactivity of these systems have been compared to those of complexes of the type (η^3-allyl)(η^1-allyl)M(IPr) (M = Ni, Pd) that we recently studied.[5a,b]

RESULTS AND DISCUSSION

Synthesis and Structure of Ni and Pd Complexes Supported by both Cyclopentadienyl and 2-Methylallyl Ligands. Previously, we have demonstrated that the reaction of IPr with the homoleptic Ni and Pd complexes $(allyl)_2M$ (M = Ni, Pd) generates $(allyl)_2M(IPr)$ in high yield.[5a] Through the reaction of the previously prepared mixed-ligand species (Cp)(2-methylallyl)Pd[5b] with IPr at −35 °C, we were able to synthesize (η^1-Cp)(η^3-2-methylallyl)Pd(IPr) (^{CpAll}**Pd**) in moderate yield (Scheme 1a). Synthetic attempts at temperatures greater than −35 °C gave mixtures of products, and significant decomposition was observed if a toluene solution of ^{CpAll}**Pd** was left at room temperature for longer than 48 h. In addition, ^{CpAll}**Pd** was unstable when stored in the solid state at room temperature; however, it could be stored indefinitely at −35 °C in a nitrogen-filled drybox. When the unsubstituted allyl complex (Cp)(allyl)Pd was mixed with IPr, only the dimeric product (μ-Cp)(μ-allyl)$Pd_2(IPr)_2$ was isolated.[20] Similar dimers supported by phosphines have been studied by Werner and are proposed to form through the monomeric compound (η^1-Cp)(η^3-allyl)$Pd(PR_3)$.[16] However, all attempts to spectroscopi-

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cally characterize the related IPr-supported monomeric intermediate were unsuccessful.

The solution-state hapticities of the Cp and 2-methylallyl ligands in ^{CpAll}**Pd** were determined using NMR spectroscopy. Sergeyev has demonstrated that the ^{1}H and ^{13}C NMR chemical shifts of the Cp ligand can be used as a diagnostic tool to determine the coordination mode of Cp ligands in transition-metal complexes.[21] Typically, the ^{1}H NMR chemical shift for the Cp resonance in complexes where the Cp ring forms a σ bond (η^1) to the metal ranges from 5.6 to 6.2 ppm, while in complexes where the Cp ring forms both σ and π bonds (η^5), the shift of the Cp resonance ranges from 4.0 to 4.8 ppm. In the case of ^{13}C NMR spectroscopy, chemical shifts for the Cp resonance ranging from 113 to 118 ppm are proposed to be indicative of η^1-binding, while shifts ranging from 70 to 93 ppm are consistent with η^5-binding.[21] The ^{1}H NMR spectrum of ^{CpAll}**Pd** at −35 °C showed a single peak for all five Cp protons at 6.13 ppm, which is consistent with η^1-binding. This is further substantiated by the ^{13}C NMR shift of the Cp ligand at 108.9 ppm, which is also in the range proposed by Sergeyev for η^1-binding. It should be noted that Sergeyev's ranges for the chemical shift of the Cp ligand are based only on data from η^1- and η^5-coordinated Cp ligands and at this stage no general trends have been determined for η^3-bound Cp ligands, which are significantly less common.[22] As such, it is not possible to completely rule out the unlikely possibility of η^3-binding of the Cp ligand in ^{CpAll}**Pd** on the basis of NMR spectroscopy; however, X-ray crystallography (vide infra) is also consistent with an η^1-bound Cp. The resonances for the 2-methylallyl ligand in the ^{1}H NMR spectrum of ^{CpAll}**Pd** are typical of those expected for η^3-binding of an allyl ligand in a C_1-symmetric complex.[23] Four distinct resonances are observed for the terminal protons, with each below 3.5 ppm.

Even at very low temperature, −60 °C, only one sharp resonance was observed for the Cp ligand in the ^{1}H NMR spectrum of ^{CpAll}**Pd**, suggesting that there is a low barrier for metallotropic rearrangement (a 1,2-shift) which makes the Cp protons equivalent. Werner and co-workers have previously reported analogous NMR properties for compounds of the type (η^1-Cp)(η^3-2-*tert*-butylallyl)Pd(PR_3) (R = P^iPr_3, PCy_3, P^tBuPh_2).[15a] In contrast, low-temperature ^{1}H NMR spectroscopy on complexes of the type (η^1-Cp)(η^3-2-methylallyl)Pd(PR_3) (R = P^iPr_3, PCy_3, P^tBuPh_2) suggested that both the 16-electron species (η^1-Cp)(η^3-2-methylallyl)Pd(PR_3) and the 18-electron species (η^5-Cp)(η^1-2-methylallyl)Pd(PR_3) were present at low temperature,[15b] although the 16-electron species was the major isomer. It may be that the more electron donating NHC ligand in ^{CpAll}**Pd** exclusively favors the 16-electron isomer. Alternatively, the 16- and 18-electron isomers may be in rapid equilibrium even at low temperature and therefore would be indistinguishable by NMR spectroscopy.

The solid-state structure of ^{CpAll}**Pd** was elucidated using X-ray crystallography and clearly contains an η^1-Cp ligand and an η^3-2-methylallyl ligand (Figure 3). The Pd(1)−C(1) distance for the η^1-Cp ligand is 2.186(4) Å, which is consistent with the bond lengths observed in the few other examples of Pd^{II} species containing η^1-Cp ligands.[17b] The Pd−C distances to all other carbon atoms of the η^1-Cp ligand are greater than 2.85 Å. The C−C bond distances within the Cp ligand are also indicative of η^1-coordination. Two short bond distances of 1.363(6) and 1.381(8) Å are observed for C(2)−C(3) and C(4)−C(5), while three longer bond distances of 1.446(7), 1.416(9), and 1.439(7) Å are observed for C(1)−C(2), C(3)−C(4), and C(1)−C(5), respectively. The 2-methylallyl ligand is clearly bound in an η^3-fashion, although somewhat surprisingly the binding of the ligand is symmetric and the Pd(1)−C(6), Pd(1)−C(7), and Pd(1)−C(8) bond distances of 2.171(4), 2.178(5), and 2.173(5) Å, respectively, are equivalent. This suggests that both the IPr ligand and the η^1-Cp ligand exert comparable *trans* influences. Overall, the solid-state structure of ^{CpAll}**Pd** is similar to that observed in the closely related (η^1-Cp)(η^3-2-*tert*-butylallyl)Pd(P^iPr)$_3$.[15b]

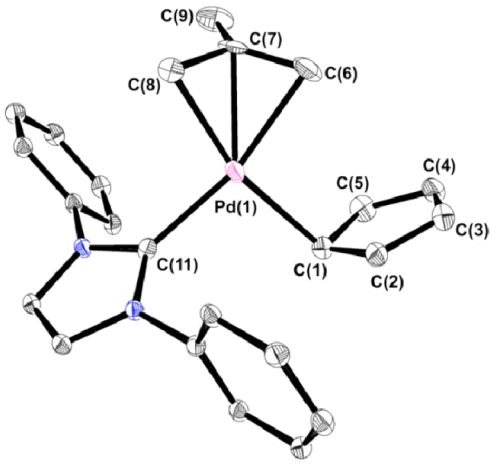

Figure 3. ORTEP drawing of ^{CpAll}**Pd** at the 30% probability level (hydrogen atoms, solvent in crystal lattice, and the isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.186(4), Pd(1)−C(6) = 2.174(5), Pd(1)−C(7) = 2.171(5), Pd(1)−C(8) = 2.171(5), Pd(1)−C(11) = 2.043(4), C(1)−C(2) = 1.446(7), C(2)−C(3) = 1.363(6), C(3)−C(4) = 1.416(9), C(4)−C(5) = 1.381(8), C(1)−C(5) = 1.439(7), C(6)−C(7) = 1.382(8), C(7)−C(8) = 1.420(7), C(7)−C(9) = 1.506(9); C(1)−Pd(1)−C(6) = 197.9(2), C(1)−Pd(1)−C(11) = 198.0(2), C(8)−Pd(1)−C(11) = 197.5(2), C(6)−Pd(1)−C(11) = 1163.0(2), C(1)−Pd(1)−C(6) = 197.5(2).

The Ni analogue of ^{CpAll}**Pd**, (η^5-Cp)(η^1-2-methylallyl)Ni(IPr) (^{CpAll}**Ni**), was prepared using a synthetic route similar to that for the Pd complex (Scheme 1b). Initially, the precursor (Cp)(2-methylallyl)Ni was synthesized through the reaction of $(Cp)_2Ni$ with (2-methylallyl)magnesium chloride in THF.[24] Subsequently, treatment of (Cp)(2-methylallyl)Ni with 1 equiv of IPr in benzene at room temperature gave ^{CpAll}**Ni** in good yield. In contrast to the case for ^{CpAll}**Pd**, the ^{1}H and ^{13}C NMR chemical shifts for the resonances associated with the Cp ligand in ^{CpAll}**Ni**, 4.64 and 91.6 ppm, respectively, are consistent with an η^5-bound Cp. Furthermore, in the ^{1}H NMR spectrum the resonances associated with the 2-methylallyl ligand are consistent with an η^1-binding mode for the allyl ligand. Two signals, both integrating to one proton, at 4.55 and 4.59 ppm, are assigned as the terminal protons of the noncoordinated olefin, while a resonance at 1.24 ppm, integrating to two protons, is assigned as the protons of the metal-bound CH_2 group. Their NMR shifts are similar to those that we observed for the η^1-2-methylallyl ligand in Pd complexes of the type (η^3-2-methylallyl)(η^1-2-methylallyl)Pd(L) (L = PR_3, IPr)[5a] and those that Werner noted for (η^5-Cp)(η^1-2-methylallyl)Pd(P^iPr)$_3$.[15b] At room temperature the resonances associated with the 2-methylallyl ligand are not fluxional, which indicates that no exchange processes involving an η^3-2-methylallyl ligand are occurring. This stands in contrast to the previously reported compound (η^3-2-methylallyl)(η^1-2-methylallyl)Ni(IPr), where

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rapid interconversion between η^1- and η^3-2-methylallyl ligands is observed at −80 °C by ^{1}H NMR spectroscopy.[5b]

The η^5-binding of the Cp ligand in ^{CpAll}**Ni** means that the total valence electron count around the Ni is 18 electrons, whereas in ^{CpAll}**Pd**, there are only 16 electrons around Pd. This is in agreement with our results for $(allyl)_2M(L)$ complexes (M = Ni, Pd, L = PR_3, NHC), where Ni systems are more likely to adopt an 18-electron structure with two η^3-allyl ligands, whereas Pd systems prefer 16-electron structures with one η^1-allyl and one η^3-allyl ligand.[5a,b] In the bis(allyl) systems the preference for Pd complexes to have a lower total valence electron count is proposed to be related to the fact that Pd forms stronger metal−ligand bonds and therefore an extra π-type bond from the ligand is not required.[13] This explanation is also plausible for explaining the difference between ^{CpAll}**Ni** and ^{CpAll}**Pd**, although in mixed-ligand systems alternative explanations are also possible. Presumably, due to the difficulty of full ring slippage from η^5-Cp to η^3-Cp,[14b] ^{CpAll}**Ni** forms the 18-electron structure through η^5-binding of the Cp ligand and η^1-binding of the 2-methylallyl ligand, rather than η^3-binding of both ligands. Most likely due to its stable 18-electron configuration, ^{CpAll}**Ni** is stable both as a solid and in solution at room temperature, although it does decompose to Ni^0 when heated at 40 °C for longer than 24 h.

The solid-state structure of ^{CpAll}**Ni** clearly contains an η^5-bound Cp ligand (Figure 4). The Ni−C bond lengths for the Cp ligand range from 2.075(6) to 2.217(6) Å, with the longest Ni−C bond length being observed for the carbon atom opposite the 2-methylallyl ligand. The C−C bond lengths within the Cp ligand are quite similar, ranging from 1.382(5) to 1.418(6) Å. It does not appear that a diene distortion of the Cp ligand, which was observed by Crabtree[25] in complexes of the type (η^5-Cp)Ni(NHC)Cl, is present in ^{CpAll}**Ni**. However, in complexes of the type (η^5-Cp)Ni(PR_3)Cl, Bergman[26] has previously described an ene−allyl distortion of the Cp ligand, in which there is slight ring slippage.[14a] In ^{CpAll}**Ni** there is some evidence for an ene−allyl distortion of the Cp ligand, as the shortest C−C bond distance inside the Cp ring (C(1)−C(5) = 1.383(8) Å) involves the same carbon atoms, which form the longest Ni−C bonds (Ni(1)−C(1) = 2.203(5) Å and Ni(1)−C(5) = 2.217(6) Å). However, the magnitude of the distortion is small, and it is reasonable to describe ^{CpAll}**Ni** as an 18-electron complex. The 2-methylallyl ligand is bound in an η^1-fashion, with the C(6)−C(7) bond length of 1.474(3) Å being significantly longer than the C(7)−C(8) bond length of 1.336(3) Å. The Ni−C bond length for the η^1-bound 2-methylallyl ligand (Ni(1)−C(6) = 1.971(2) Å) is similar to that observed in (η^3-2-methylallyl)(η^1-2-methylallyl)Ni(IPr),[5b] while the Ni−NHC bond distance is also consistent with those previously reported in the literature.[27] Overall, ^{CpAll}**Ni** exhibits a classic piano-stool geometry with a pseudo-five-coordinate arrangement around Ni.

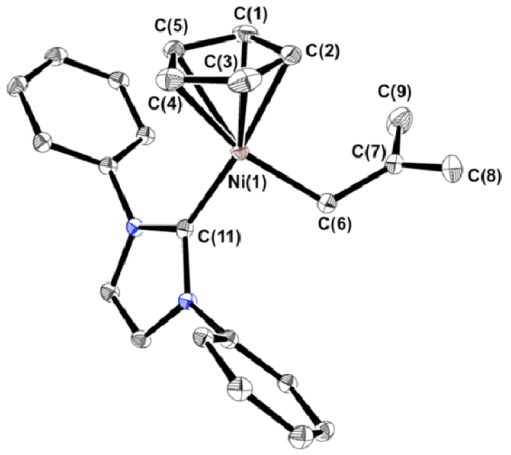
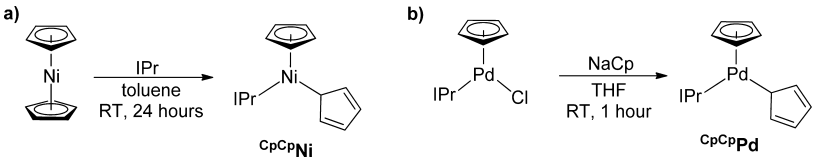


Figure 4. ORTEP drawing of ^{CpAll}**Ni** at the 30% probability level (hydrogen atoms and the isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) = 2.203(5), Ni(1)−C(2) = 2.075(6), Ni(1)−C(3) = 2.111(7), Ni(1)−C(4) = 2.158(9), Ni(1)−C(5) = 2.217(6), Ni(1)−C(6) = 1.971(2), Ni(1)−C(11) = 1.870(2), C(1)−C(2) = 1.42(1), C(2)−C(3) = 1.40(1), C(3)−C(4) = 1.405(9), C(4)−C(5) = 1.42(1), C(1)−C(5) = 1.383(8), C(6)−C(7) = 1.474(3), C(7)−C(9) = 1.496(4), C(7)−C(8) = 1.336(3); C(2)−Ni(1)−C(6) = 97.7(2), C(4)−Ni(1)−C(11) = 108.2(2), C(6)−Ni(1)−C(11) = 110.2(2), C(2)−Ni(1)−C(11) = 172.6(2), C(4)−Ni(1)−C(6) = 156.1(2).

Synthesis and Structure of Ni and Pd Complexes Supported by Two Cyclopentadienyl Ligands. For the purpose of comparison with ^{CpAll}**Ni**, the 18-electron complex (η^5-Cp)(η^1-Cp)Ni(IPr) (^{CpCp}**Ni**), which was stable at room temperature both as a solid and in solution, was prepared through the reaction of $(Cp)_2Ni$ and IPr in toluene (Scheme 2a). Two different resonances, at 5.65 and 4.11 ppm, were observed for the Cp ligands in the ^{1}H NMR spectrum of ^{CpCp}**Ni**. This suggests the presence of both η^1- and η^5-bound Cp ligands and also indicates that there is a relatively high barrier for interconversion between the Cp ligands. Upon warming to 60 °C, the resonances associated with the two Cp ligands began to broaden and at 80 °C no Cp resonances were observed, presumably because they had broadened into the baseline. At temperatures above 80 °C, the compound decomposed. The room-temperature ^{1}H NMR spectrum did not change upon cooling to −60 °C, indicating that the barrier for metallotropic rearrangement in the η^1-Cp ligand is low. At temperatures below −60 °C the compound lacked sufficient solubility to obtain NMR spectra. In the room-temperature $^{13}C\{^1H\}$ NMR spectrum, two sharp peaks at 108.8 and 92.8 ppm were observed for the Cp ligands, consistent with both η^1- and η^5-binding of the two Cp ligands. X-ray crystallography confirmed this assignment (Figure 5a). To the best of our knowledge, there is only one other example of a Ni complex containing both η^1- and η^5-bound Cp ligands and it displays NMR properties similar to those of ^{CpCp}**Ni**.[27]

Scheme 2



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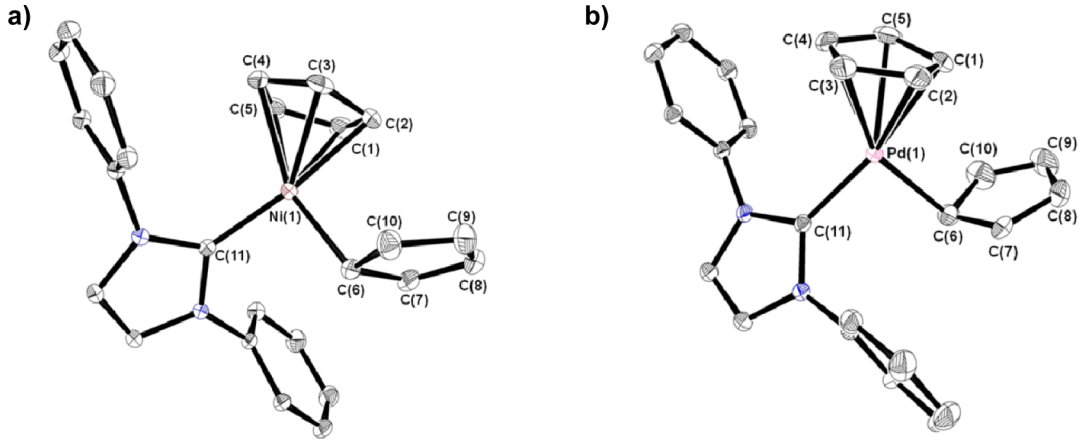

Figure 5. (a) ORTEP drawing of $^{Cp^{Cp}}$**Ni** at the 30% probability level (hydrogen atoms, solvent in the crystal lattice, and the isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) = 2.152(2), Ni(1)−C(2) = 2.077(2), Ni(1)−C(3) = 2.175(2), Ni(1)−C(4) = 2.179(2), Ni(1)−C(5) = 2.142(2), Ni(1)−C(6) = 2.026(2), Ni(1)−C(11) = 1.887(1), C(1)−C(2) = 1.406(3), C(2)−C(3) = 1.426(3), C(3)−C(4) = 1.389(2), C(4)−C(5) = 1.426(3). C(1)−C(5) = 1.397(2), C(6)−C(7) = 1.457(2), C(7)−C(8) = 1.336(2), C(8)−C(9) = 1.434(3), C(9)−C(10) = 1.335(2), C(6)−C(10) = 1.457(2); C(2)−Ni(1)−C(11) = 172.04(6), C(5)−Ni(1)−C(6) = 152.70(6), C(6)−Ni(1)−C(2) = 93.96(6), C(6)−Ni(1)−C(11) = 93.91(5), C(11)−Ni(1)−C(4) = 109.26(6). (b) ORTEP drawing of $^{Cp^{Cp}}$**Pd** at the 30% probability level (hydrogen atoms, solvent in the crystal lattice, and isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.233(2), Pd(1)−C(2) = 2.348(3), Pd(1)−C(3) = 2.364(3), Pd(1)−C(4) = 2.380(3), Pd(1)−C(5) = 2.373(3), Pd(1)−C(6) = 2.115(2), C(1)−C(2) = 1.402(4), C(2)−C(3) = 1.381(4), C(3)−C(4) = 1.423(5), C(4)−C(5) = 1.391(4), C(1)−C(5) = 1.425(4), C(6)−C(7) = 1.458(4), C(7)−C(8) = 1.363(4), C(8)−C(9) = 1.426(6), C(9)−C(10) = 1.359(5), C(6)−C(10) = 1.468(4); C(1)−Pd(1)−C(11) = 170.38(9), C(3)−Pd(1)−C(6) = 148.4(1), C(6)−Pd(1)−C(2) = 114.45(9), C(6)−Pd(1)−C(11) = 92.18(8), C(11)−Pd(1)−C(4) = 112.18(9).

The Pd complex (η^5-Cp)(η^1-Cp)Pd(IPr) ($^{Cp^{Cp}}$**Pd**) was synthesized from the reaction of (Cp)Pd(IPr)Cl[28] and sodium cyclopentadienyl in THF (Scheme 2b). It is unstable in solution at room temperature and decomposes to give the dimeric product (μ-Cp)$_2$Pd$_2$(IPr)$_2$.[20] Furthermore, unlike $^{Cp^{Cp}}$**Ni**, the room-temperature ^{1}H NMR spectrum of $^{Cp^{Cp}}$**Pd** showed one broad resonance at approximately 5.24 ppm for the Cp ligands. When the spectrum was recorded at −40 °C, the single broad resonance split into one sharp resonance at 4.69 ppm and one broad resonance at 5.90 ppm, which suggests the presence of both η^1- and η^5-bound Cp ligands. This was confirmed by X-ray crystallography (Figure 5b). Cooling the sample further resulted in significant loss of solubility, and as a result it was not possible to record spectra at lower temperatures. In the ^{1}H NMR spectrum at 60 °C both Cp signals had broadened and decreased in intensity, similar to what was seen with $^{Cp^{Cp}}$**Ni**. However, formation of the dimeric product (μ-Cp)$_2$Pd$_2$(IPr)$_2$ was accelerated at higher temperatures and precluded us from obtaining spectra above 60 °C, where two Cp peaks would coalesce. Overall, the ^{1}H NMR data for $^{Cp^{Cp}}$**Pd** suggests that two fluxional processes are occurring: (i) an η^5/η^1-exchange of the two Cp ligands, most likely through an intermediate structure which contains either two η^1-Cp ligands or one η^3- and one η^1-Cp ligand, and (ii) a lower energy metallotropic rearrangement, which makes the protons of the η^1-Cp ligand equivalent. Process (i) appears to be more facile for $^{Cp^{Cp}}$**Pd** than for $^{Cp^{Cp}}$**Ni**, probably because it is more favorable for Pd to form a structure with a lower total valence electron count around the metal. Similar fluxional behavior has been observed by Werner in compounds of the type (η^5-Cp)(η^1-Cp)Pd(PR$_3$).[17b] The ^{13}C{^{1}H} NMR spectrum at room temperature of $^{Cp^{Cp}}$**Pd** showed two broad resonances at 98.7 and 107.6 ppm for the Cp ligands, which become sharper at lower temperature.

The solid-state structures of $^{Cp^{Cp}}$**Ni** and $^{Cp^{Cp}}$**Pd** are isomorphous. In both structures, the presence of both an η^5- and η^1-Cp ligand is confirmed by comparison of the M−C and C−C bond lengths associated with the Cp ligands. In the η^5-bound Cp ligand, all the C−C bond lengths are similar (between 1.381(4) and 1.426(3) Å), whereas in the η^1-bound Cp ligand there are three long C−C bonds (between 1.426(4) and 1.448(4) Å) and two short C−C bonds (between 1.335(2) and 1.363(4) Å). The M−C bond lengths for the η^5-bound Cp ligand range from 2.077(2) to 2.179(2) Å for Ni and from 2.233(2) to 2.380(2) Å for Pd, with the shorter bond lengths for Ni reflecting its smaller size. The η^5-Cp ligands in both complexes display a small ene−allyl distortion, with the shortest C−C bond in the ring corresponding to the atoms which form the longest Pd−C or Ni−C bonds. In $^{Cp^{Cp}}$**Pd**, the bond lengths between the Pd and the η^5-Cp ligand are considerably longer than those observed between the Pd and the η^3-2-methylallyl ligand in $^{Cp^{All}}$**Pd**. This implies that the Pd−C interactions in the η^5-Cp ligand are weaker than those for Pd−C in the η^3-2-methylallyl ligand. The M−C bond length for the η^1-bound Cp ligands is 2.115(2) Å for Pd and 2.026(1) Å for Ni. Although examples of crystallographically characterized Ni and Pd complexes containing η^1-Cp ligands are rare, these bond distances are comparable to those previously reported.[17b,27,29] The overall "piano stool" geometry for both molecules is analogous to that observed for $^{Cp^{All}}$**Ni**.

Synthesis and Structure of Ni and Pd Complexes Supported by both Indenyl and 2-Methylallyl Ligands. Indenyl and Cp ligands are often compared because of their ability to bind to metal centers in η^1-, η^3-, and η^5-fashions, although their reactivity can differ significantly due to the "indenyl effect".[14b] We were interested in exploring the consequences of replacing the Cp ligand of $^{Cp^{All}}$**Ni** and $^{Cp^{All}}$**Pd** with an indenyl ligand. Unfortunately, the Pd and Ni complexes (Ind)(2-methylallyl)M (M = Ni, Pd) have not been reported, and attempts to prepare them as part of this work resulted in extremely unstable products, which could not be used as precursors for direct reaction with IPr. We postulated that

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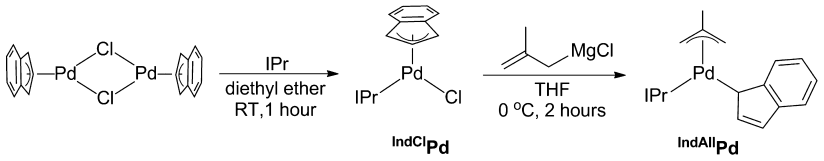
Scheme 3



treatment of the unknown Pd complex (η^3-Ind)Pd(IPr)Cl (**^{IndCl}Pd**) and the known Ni species (η^3-Ind)Ni(IPr)Cl (**^{IndCl}Ni**)[30] with (2-methylallyl)magnesium chloride could generate the desired **^{CpAll}Ni** and **^{CpAll}Pd** complexes. Previously, Zargarian[31] and co-workers reported the syntheses of (η^3-Ind)Pd(PR_3)Cl (R = Ph, Cy, Me) through the reaction of $\{(\eta^3\text{-Ind})Pd(\mu\text{-Cl})\}_2$ with the appropriate free phosphine. The reaction of 2 equiv of IPr with $\{(\eta^3\text{-Ind})Pd(\mu\text{-Cl})\}_2$ in diethyl ether generated **^{IndCl}Pd** as a bench-stable orange solid, which served as the starting material for our further studies with indenyl-supported Pd complexes (Scheme 3).

Analysis of the $^{13}C\{^1H\}$ NMR spectrum of **^{IndCl}Pd** allowed for the coordination mode of the indenyl ligand to be determined. While η^1-indenyl ligands have their own characteristic ^1H NMR pattern, more sophisticated analysis is required to differentiate between η^3- and η^5-indenyl ligands. Baker[32] and Marder[33] have shown that whether an indenyl ligand binds in an η^3- or η^5-mode can be determined by comparing the average ^{13}C NMR chemical shifts of the hinge carbons (labeled 3a and 7a in Figure 6) of the indenyl ligand with those of sodium

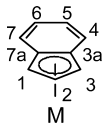


Figure 6. Numbering scheme of the indenyl ligand.

indenyl. The magnitude of this difference, defined as $\Delta\delta_{av}$ ($\Delta\delta_{av}$ = δ_{av}(C(3a),C(7a) of M-Ind) − δ_{av}(C(3a),C(7a) of Na^+Ind^-)) is related to the solution hapticity of the indenyl ligand. A value of $\Delta\delta_{av} \ll 0$ is indicative of η^5-coordination and a value of $\Delta\delta_{av} \gg 0$ is indicative of η^3-coordination. Values of $\Delta\delta_{av}$ close to zero indicate intermediate hapticity between η^3- and η^5-coordination. For **^{IndCl}Pd**, $\Delta\delta_{av}$ was equal to 8.7, a value consistent with η^3-coordination.[14b]

In the solid state **^{IndCl}Pd** also contains an η^3-bound indenyl ligand (Figure 7). The bond distances between Pd and C(1), C(2), and C(3) are 2.270(2), 2.167(2), and 2.173(2) Å, respectively. All of these values are comparable with those observed in similar complexes.[14b,34] The Pd−C distances to the hinge carbons of the indenyl ligand are significantly longer: 2.608(2) and 2.643(2) Å. As a result, the ΔM−C value, which is defined as ΔM−C = (average M−C(3a),C(7a) distance) − (average M−C(1),C(3) distance), is 0.40(2) Å.[32,33] The disparity in the Pd(1)−C(1) and Pd(1)−C(3) bond distances is likely due to the difference in *trans* influence between the Cl and IPr ligands, with the shorter Pd−C bond distance observed for the carbon opposite the Cl ligand. This asymmetry has also been observed in related phosphine-supported indenyl Ni complexes.[31,35] The coordination of indenyl ligands to transition metals can be further described by the hinge and fold angles, which quantify the degree to which the indenyl ring has slipped from the idealized η^5-coordination. The hinge angle is defined as the angle between the planes formed by C(1),

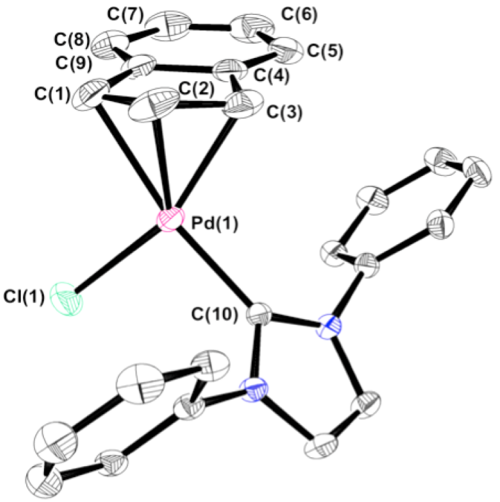


Figure 7. ORTEP drawing of **^{IndCl}Pd** at the 30% probability level (hydrogen atoms and the isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.3265(7), Pd(1)−C(1) = 2.270(2), Pd(1)−C(2) = 2.167(2), Pd(1)−C(3) = 2.173(2), Pd(1)−C(4) = 2.608(2), Pd(1)−C(9) = 2.643(2), Pd(1)−C(10) = 2.007(2), C(1)−C(2) = 1.468(8), C(2)−C(3) = 1.34(1), C(3)−C(4) = 1.415(9), C(4)−C(5) = 1.406(1), C(5)−C(6) = 1.36(1), C(6)−C(7) = 1.38(1), C(7)−C(8) = 1.41(1), C(8)−C(9) = 1.391(9), C(1)−C(9) = 1.451(8), C(4)−C(9) = 1.411(8); Cl(1)−Pd(1)−C(1) = 100.64(7), Cl(1)−Pd(1)−C(3) = 160.12(6), C(1)−Pd(1)−C(10) = 166.95(8), Cl(1)−Pd(1)−C(10) = 92.05(5), C(3)−Pd(1)−C(10) = 106.66(8).

C(2), and C(3) and C(1), C(3), C(3a), and C(7a), while the fold angle defines the angle between the planes formed by C(1), C(2), and C(3) and C(3a), C(4), C(5), C(6), C(7), and C(7a), with numbering consistent with Figure 6.[31] **^{IndCl}Pd** has a hinge angle of 14.83° and a fold angle of 12.53°. These values along with the ΔM−C value are consistent with other examples of η^3-indenyl compounds.[14b,31] A similar solid-state structure has been described for the analogous compound **^{IndCl}Ni**, although in this case the hapticity of the indenyl ligand is more ambiguous and is proposed to be between η^3- and η^5-binding.[36]

The reaction of 1 equiv of 2-methylallyl magnesium chloride with **^{IndCl}Pd** in THF generated **^{IndAll}Pd** in good yield. **^{IndAll}Pd** is stable at room temperature in the solid state for up to 3 weeks and is stable in solution at room temperature overnight. Significant formation of Pd^0 was observed when a benzene solution of **^{IndAll}Pd** was heated above 50 °C overnight. The ^1H NMR spectrum of **^{IndAll}Pd** shows 2-methylallyl resonances similar to those of **^{CpAll}Pd**, with four signals below 3.5 ppm integrating to one proton each. This is consistent with an η^3-2-methylallyl ligand.[23] The ^1H NMR spectrum indicates that the indenyl ligand is coordinated in an η^1-fashion. The aromatic region shows four resonances above 7.0 ppm, which correspond to the protons of the benzene ring of the indenyl ligand. An apparent triplet at 6.57 ppm and two broad resonances at 5.97 and 5.90 ppm are associated with the five-

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membered ring of the indenyl ligand. These resonances are consistent with literature examples of η^1-indenyl complexes.[14b,34a] When the sample is cooled to −40 °C in toluene, the broad resonances separate into two unique signals at 6.00 and 5.64 ppm, each integrating to one proton. The apparent triplet at 6.57 ppm does not change upon cooling. Loss of solubility below −40 °C prevented analysis at lower temperatures. X-ray crystallography confirmed the presence of both an η^1-indenyl and an η^3-2-methylallyl ligand (Figure 8). The Pd−C bond

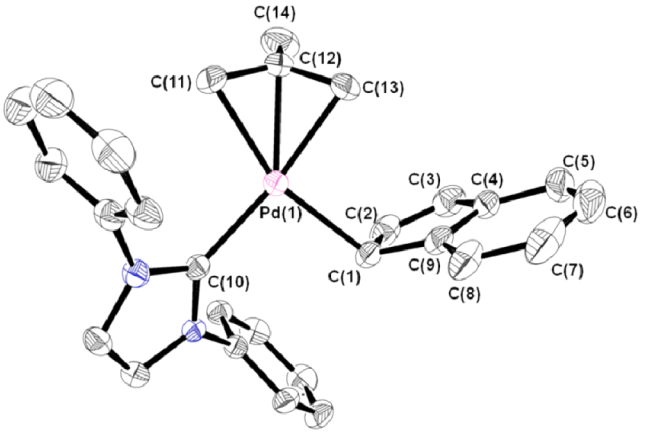


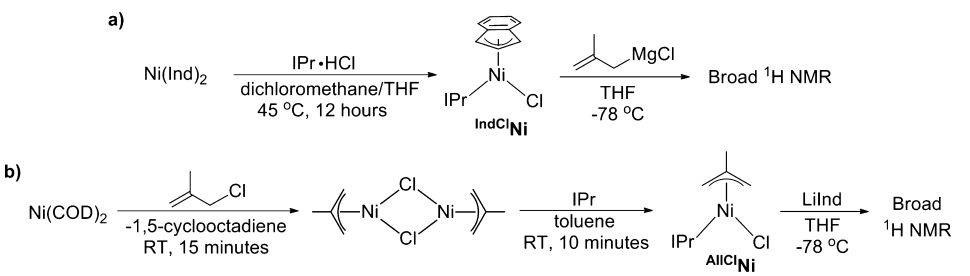
Figure 8. ORTEP drawing of ^{IndAll}**Pd** at the 30% probability level (hydrogen atoms and the isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.162(6), Pd(1)−C(10) = 2.073(5), Pd(1)−C(11) = 2.188(5), Pd(1)−C(12) = 2.171(5), Pd(1)−C(13) = 2.132(5), C(1)−C(2) = 1.468(8), C(2)−C(3) = 1.34(1), C(3)−C(4) = 1.415(9), C(4)−C(5) = 1.40(1), C(5)−C(6) = 1.36(1), C(6)−C(7) = 1.38(1), C(7)−C(8) = 1.41(1), C(8)−C(9) = 1.391(9), C(1)−C(9) = 1.451(8), C(4)−C(9) = 1.411(8), C(11)−C(12) = 1.400(8), C(12)−C(13) = 1.400(8), C(12)−C(14) = 1.495(9); C(1)−Pd(1)−C(13) = 93.0(2), C(1)−Pd(1)−C(10) = 95.7(2), C(10)−Pd(1)−C(11) = 104.6(2), C(1)−Pd(1)−C(11) = 159.7(2), C(10)−Pd(1)−C(13) = 167.3(2).

distances for the 2-methylallyl ligand are 2.188(5), 2.171(5), and 2.132(5) Å, respectively. The longest Pd−C bond is *trans* to the η^1-indenyl ligand. This bond is slightly longer than the Pd−C bond to the 2-methylallyl ligand for the carbon atom *trans* to the η^1-Cp ligand in ^{CpAll}**Pd**, suggesting that the η^1-indenyl ligand is a stronger donor than the η^1-Cp ligand. The Pd only interacts with one carbon of the indenyl ligand, and the Pd(1)−C(1) bond length is 2.162(6) Å. This is longer than the Pd−C bond length in other reported η^1-indenyl complexes, presumably due to the increased *trans* influence of the allyl ligand as compared to Cl, the most common *trans* ligand in reported structures.[34a] The C−C bond distances within the five-membered ring of the indenyl ligand are also suggestive of η^1-coordination. The C(2)−C(3) bond distance of 1.34(1) Å is consistent with a double bond, while the C(1)−C(9) distance of 1.451(8) Å is significantly longer.

Unfortunately, the Ni compound ^{IndAll}**Ni** was not successfully isolated. Two different routes were attempted, as summarized in Scheme 4. The reaction of (2-methylallyl)magnesium chloride with ^{IndCl}**Ni** (synthesized using a literature route)[36,37] at low temperature (−78 °C) gave a product which displayed broad signals in the ^{1}H NMR spectrum (Scheme 4a). We were unable to characterize this product, as when the solution was raised above −78 °C rapid decomposition to Ni^0 occurred. An alternative route using ^{AllCl}**Ni** as the starting material was attempted. Initially, the dimeric compound $\{(\eta^3\text{-2-methylallyl})\text{Ni}(\mu\text{-Cl})\}_2$ was synthesized in situ from the reaction of Ni(COD)$_2$ and 2-methylallyl chloride (Scheme 4b).[38] Subsequent addition of IPr generated ^{AllCl}**Ni**. The addition of lithium indenyl to ^{AllCl}**Ni** at both room temperature and −35 °C gave a mixture of products. Performing the reaction at −78 °C gave a deep red solution that showed broad ^{1}H NMR signals. These signals were the same as those observed in the reaction between (2-methylallyl) magnesium chloride and ^{IndCl}**Ni**. The sample quickly decomposed to Ni^0 when the solution was raised even slightly above −78 °C. Although both routes resulted in the same species, we cannot say with certainty that this is our desired ^{IndAll}**Ni** product, due to the extreme thermal instability of the complex, which prevented further characterization.

Synthesis and Structure of Ni and Pd Complexes Supported by both Indenyl and Cyclopentadienyl Ligands. The mixed Cp/indenyl complex ^{IndCp}**Pd** was synthesized through the reaction of ^{IndCl}**Pd** with NaCp in THF at 0 °C (Scheme 5a). While low temperature was required during the synthesis to avoid the formation of multiple products, ^{IndCp}**Pd** is stable for up to 1 week in solution at room temperature under a nitrogen atmosphere and indefinitely stable as a solid. ^{1}H NMR spectroscopy indicates ^{IndCp}**Pd** has an η^1-indenyl ligand and an η^5-Cp ligand. In a fashion similar to that for ^{IndAll}**Pd**, ^{IndCp}**Pd** shows four aromatic resonances above 6.8 ppm associated with the benzene ring of the indenyl ligand. Of these four resonances, two are coincident with the aryl protons of the IPr ligand. The remaining resonances appear as a doublet at 7.54 ppm and a doublet at 6.88 ppm. The proton bound to the η^1-carbon of the five-membered indenyl ring appears as a singlet at 4.54 ppm. The two olefinic protons of this ring appear as an apparent triplet at 6.40 ppm and a broad resonance at 6.74 ppm. These shifts are consistent with what has been reported for η^1-indenyl complexes of Pt and Pd.[14b,39] Furthermore, the ^{1}H NMR spectrum shows a single resonance at 4.63 ppm for the five Cp

Scheme 4



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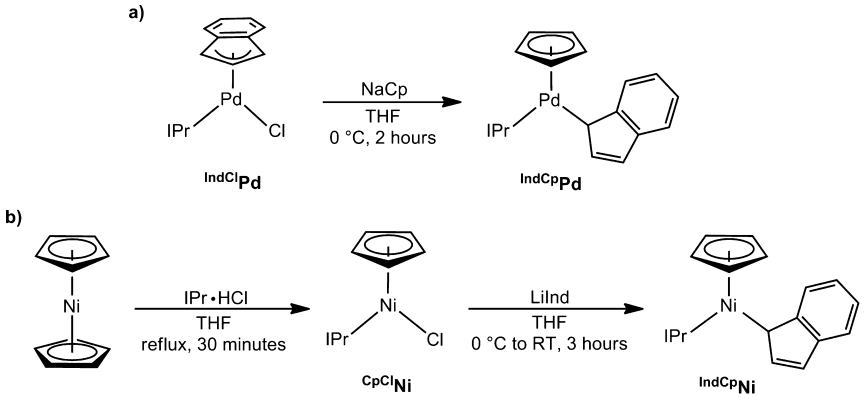
Scheme 5

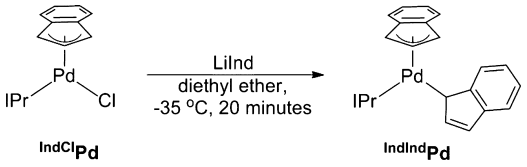


protons, well within the range cited by Sergeyev for η^5-bound Cp rings.[21]

For unknown reasons we were unable to synthesize a pure sample of the analogous Ni complex ^{IndCp}**Ni** through the reaction of ^{IndCl}**Ni** with sodium cyclopentadienyl. However, ^{IndCp}**Ni** was synthesized through the reaction of (η^5-Cp)Ni(IPr)Cl[40] (^{CpCl}**Ni**) with lithium indenyl in THF at −40 °C (Scheme 5b). ^{IndCp}**Ni** is stable as a solid at room temperature under a nitrogen atmosphere and slowly decomposes to Ni^0 in solution over the course of 3 days at room temperature. The ^{1}H and $^{13}C\{^1H\}$ NMR shifts for the Cp ring, 4.17 and 92.5 ppm, respectively, confirm that the Cp is η^5-bound. ^{1}H NMR spectroscopy suggests that as in ^{IndAll}**Pd** and ^{IndCp}**Pd**, the indenyl ligand is η^1-bound. A singlet at 3.82 ppm corresponds to the proton on the η^1-bound carbon of the indenyl ring. The two olefinic protons for the five-membered ring appear at 6.56 ppm as an apparent triplet and as a complex multiplet coincident with an indenyl aryl peak at 6.79 ppm.

Synthesis and Structure of Ni and Pd Complexes Supported by Two Indenyl Ligands. The Pd species with two indenyl ligands ^{IndInd}**Pd** was synthesized through the reaction of ^{IndCl}**Pd** with lithium indenyl at −35 °C in diethyl ether (Scheme 6). The dark pink solid is not stable at room

Scheme 6



temperature and decomposes to give $(\mu\text{-Ind})_2Pd_2(IPr)_2$ as the major product with a minor amount of $Pd(IPr)_2$.[20] The ^{1}H NMR spectrum at −40 °C displays 14 unique indenyl resonances. The eight aromatic resonances appear above 6.31 ppm, and the remaining six protons on the five-membered rings appear below 6.25 ppm. Attempts to prepare the Ni analogue of ^{IndInd}**Pd** either through the reaction of $(Ind)_2Ni$ with IPr or the treatment of ^{IndCl}**Ni** with lithium indenyl were unsuccessful and resulted in complex mixtures of products.

X-ray-quality crystals of ^{IndInd}**Pd** were grown from a concentrated solution of diethyl ether at −35 °C (Figure 9). The solid-state structure clearly shows two different coordination modes for the two indenyl ligands. One indenyl ligand is bound in a η^1-fashion, with a Pd(1)−C(1) bond distance of

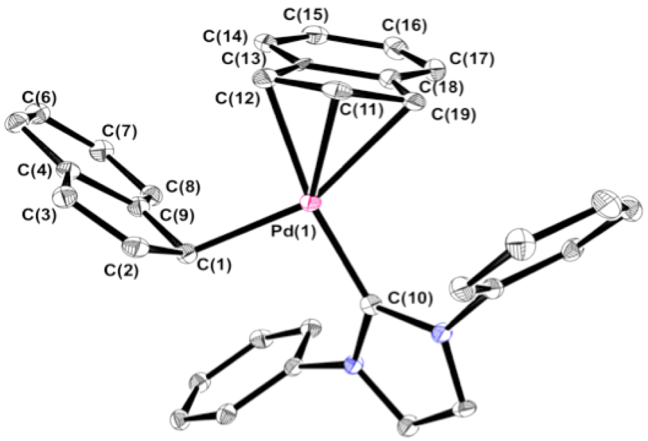


Figure 9. ORTEP drawing of ^{IndInd}**Pd** at the 30% probability level (hydrogen atoms and the isopropyl groups of IPr have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.115(4), Pd(1)−C(10) = 2.017(4), Pd(1)−C(11) = 2.217(5), Pd(1)−C(12) = 2.220(5), Pd(1)−C(13) = 2.610(4), Pd(1)−C(19) = 2.345(4), C(1)−C(2) = 1.468(8), C(2)−C(3) = 1.348(7), C(3)−C(4) = 1.453(6), C(4)−C(5) = 1.396(6), C(5)−C(6) = 1.391(7), C(6)−C(7) = 1.397(8), C(7)−C(8) = 1.381(6), C(8)−C(9) = 1.383(7), C(1)−C(9) = 1.480(6), C(4)−C(9) = 1.417(8), C(11)−C(12) = 1.406(5), C(12)−C(13) = 1.450(7), C(13)−C(14) = 1.403(6), C(14)−C(15) = 1.391(8), C(15)−C(16) = 1.399(7), C(16)−C(17) = 1.390(6), C(17)−C(18) = 1.394(8), C(13)−C(18) = 1.435(6), C(18)−C(19) = 1.443(6), C(11)−C(19) = 1.420(8); C(10)−Pd(1)−C(12) = 169.7(2), C(1)−Pd(1)−C(12) = 97.3(2), C(1)−Pd(1)−C(10) = 92.8(2), C(10)−Pd(1)−C(19) = 109.6(2), C(1)−Pd(1)−C(19) = 157.3(2), C(12)−Pd(1)−C(19) = 60.2(2).

2.115(4) Å. All other Pd−C distances to this indenyl ligand are greater than 2.9 Å. The other indenyl ring is coordinated in an η^3-fashion, similar to that seen in ^{IndCl}**Pd**. The Pd(1)−C(11) and Pd(1)−C(12) bond lengths are similar at 2.217(5) and 2.220(5) Å, respectively, while the Pd(1)−C(19) distance is considerably longer at 2.345(4) Å, indicating the increased *trans* influence of the η^1-indenyl ligand compared to IPr. The Pd−C distances to the hinge carbons are 2.610(4) and 2.674(5) Å, resulting in a ΔM−C value of 0.36(4) Å.[32,33] As with ^{IndCl}**Pd**, the hinge and fold angles of 12.53 and 13.53° for the η^3-indenyl ligand of ^{IndInd}**Pd** are consistent with previous examples for η^3-indenyl complexes.[34a,41] The Pd(1)−C(1) bond distance to the η^1-indenyl ligand is shorter than that in ^{IndAll}**Pd**, presumably because the η^3-allyl ligand exerts a stronger *trans* influence than the η^3-indenyl ligand. It is noteworthy that

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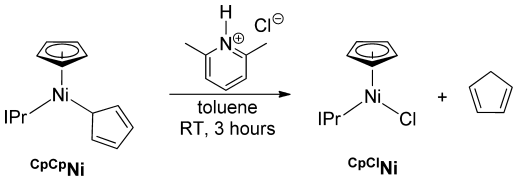
^{IndInd}**Pd** is a 16-electron species, with one η^1-indenyl ligand and one η^3-indenyl ligand, whereas the related species ^{CpCp}**Pd** is an 18-electron species with one η^1-Cp ligand and one η^5-Cp ligand. This highlights the "indenyl effect"[14b] with the indenyl ligand adopting an η^3-binding mode, while the Cp ligand prefers an η^5-binding mode.

Reactivity of Ni and Pd Compounds with Electrophiles. Previously, it has been proposed that in complexes of the type (η^3-allyl)(η^1-allyl)M(L) (M = Ni, Pd; L = PR_3, IPr), electrophiles such as Brønsted acids, aldehydes, and CO_2 react with the nucleophilic η^1-allyl ligand.[1a,2c,4,6a,42] In comparison, relatively little is known about the reactivity of η^1-Cp and η^1-indenyl ligands bound to Pd and Ni with these substrates.[43] As a result, we were interested in probing the reactivity of the mixed compounds prepared as part of this work with simple electrophiles. Table 1 summarizes our results for the reactions

Table 1. Summary of Reactivity of Species Prepared in This Work with Acid (2,6-Lutidinium Chloride)[a]



^{CpCp}**Ni** ^{CpCl}**Ni**

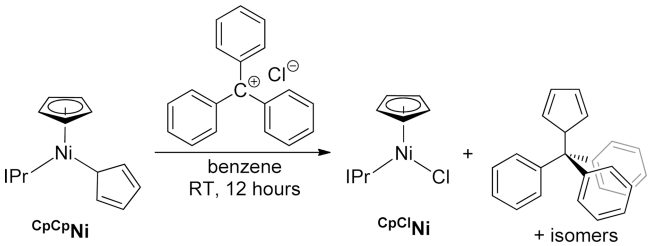
compd	conditions	metal product[b]	organic product[b]
^{CpAll}**Pd**	toluene, −35 °C, 4 h	^{AllCl}**Pd**	cyclopentadiene
^{CpAll}**Ni**	toluene, room temp, 4 h	^{CpCl}**Ni**	2-methylpropene
^{IndAll}**Pd**	toluene, 0 °C to room temp, 2 h	^{AllCl}**Pd**	indene
^{IndCp}**Pd**	toluene, 0 °C to room temp, 2 h	^{CpCl}**Pd**	indene
^{IndCp}**Ni**	toluene, 0 °C to room temp, 2 h	^{CpCl}**Ni**	indene
^{CpCp}**Pd**	benzene, room temp, 1 h	^{CpCl}**Pd**	cyclopentadiene
^{CpCp}**Ni**	toluene, room temp, 3 h	^{CpCl}**Ni**	cyclopentadiene

[a]A representative reaction is shown above the body of the table. [b]Products determined using ^{1}H NMR spectroscopy. See the Experimental Section for more information.

of ^{CpAll}**Pd**, ^{CpAll}**Ni**, ^{IndAll}**Pd**, ^{IndCp}**Pd**, and ^{IndCp}**Ni** with the solid source of HCl, 2,6-lutidinium chloride. Although different reaction conditions needed to be employed depending on the specific reaction to obtain clean conversion, in all cases with mixed ligands selective protonation at the η^1-ligand was observed and high yields of the organic product were detected by ^{1}H NMR spectroscopy. For example, in the case of ^{CpAll}**Pd**, which contains an η^1-Cp ligand and an η^3-2-methylallyl ligand, the sole product of protonation was (η^3-2-methylallyl)Pd(IPr)-Cl (^{AllCl}**Pd**), whereas for ^{CpAll}**Ni**, which contains an η^5-Cp ligand and an η^1-2-methylallyl ligand, the only product was (η^5-Cp)Ni(IPr)Cl (^{CpCl}**Ni**). From the results of these reactions we believe that two conclusions can be drawn: (i) in the case of acid, where the reaction is proposed to proceed directly with the carbon bound to the metal center, η^1-allyl, η^1-Cp, and η^1-indenyl ligands all display similar reactivity and (ii) protonation with acid can almost certainly be used as a general technique to confirm the identity of the ligand bound in an η^1-fashion in mixed-ligand complexes of the type described here.

The above reactions with a Brønsted acid led us to investigate reactivity with nonacidic electrophiles. In 2009, Legzdins and co-workers reported the reaction of tungsten compounds supported by both η^5-pentamethycyclopentadienyl and η^3-allyl ligands with triphenylcarbenium tetafluoroborate to give allylated triphenylmethyl products.[44] The first step in these reactions was proposed to be the isomerization of the allyl ligand from an η^3- to an η^1-binding mode, followed by nucleophilic attack of the terminal carbon of the η^1-allyl ligand (as opposed to the metal-bound carbon) on triphenylcarbenium tetafluoroborate to form a new C−C bond. In our systems, the reaction of ^{CpAll}**Ni** with 1 equiv of triphenylcarbenium chloride gave quantitative conversion to the new organic compound (2-methylallyl)triphenylmethane and ^{CpCl}**Ni**. The organic compound was isolated using column chromatography. The reaction with ^{CpAll}**Pd** showed orthogonal reactivity, giving ^{AllCl}**Pd** and several isomers of the organic product, cyclopentadienyltriphenylmethane, which have previously been characterized by Werner.[45] Similar reactions were performed on the remaining compounds of the series, as shown in Table 2.

Table 2. Summary of Reactivity of Species Prepared in This Work with Triphenylcarbenium Chloride[a]



^{CpCp}**Ni** ^{CpCl}**Ni**

compd	conditions	metal product[b]	organic product[b]
^{CpAll}**Pd**	toluene, −35 °C to room temp, 24 h	^{AllCl}**Pd**	cyclopentadienyltriphenylmethane[c]
^{CpAll}**Ni**	benzene, room temp, 12 h	^{CpCl}**Ni**	2-methylallyltriphenylmethane
^{IndAll}**Pd**	toluene, 0 °C to room temp, 24 h	^{AllCl}**Pd**	indenyltriphenylmethane[c]
^{IndCp}**Pd**	toluene, 0 °C to room temp, 24 h	^{CpCl}**Pd**	indenyltriphenylmethane[c]
^{IndCp}**Ni**	toluene, 0 °C to room temp, 24 h	^{CpCl}**Ni**	indenyltriphenylmethane[c]
^{CpCp}**Pd**	benzene, room temp, 12 h	^{CpCl}**Pd**	cyclopentadienyltriphenylmethane[c]
^{CpCp}**Ni**	benzene, room temp, 12 h	^{CpCl}**Ni**	cyclopentadienyltriphenylmethane[c]

[a]A representative reaction is shown above the body of the table. [b]Products determined using ^{1}H NMR spectroscopy. See the Experimental Section for more information. [c]Several different isomers were formed.

In contrast to the reactions with ^{CpAll}**Pd** and ^{CpAll}**Ni**, the reactions with indenyl ligands did not give quantitative conversion. Multiple organic and metal-containing products were seen by ^{1}H NMR spectroscopy; however, the metal-containing product reported in Table 2 was the major product. Similarly, the major organic product was indenyltriphenylmethane.[46] It is noteworthy that, although these reactions were not clean, there was no evidence to support a reaction taking place at either the η^3-2-methylallyl ligand in the case of ^{IndAll}**Pd** or the η^5-Cp ligand in the case of ^{IndCp}**Pd** or ^{IndCp}**Ni**. Overall, the reactions described in Table 2 suggest that in an analogous

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fashion to η^1-allyl ligands, η^1-Cp and η^1-indenyl ligands can also act as nucleophiles with substrates where the initial point of attack of the electrophile is not proposed to be the metal-bound carbon. However, the exact pathway for the reaction of triphenylcarbenium chloride with the η^1-Cp and η^1-indenyl species studied in this work still needs to be determined.

CONCLUSIONS

A family of Pd and Ni complexes containing combinations of 2-methylallyl, Cp, and indenyl ligands, as well as an ancillary IPr ligand, has been synthesized. Unfortunately, a single general synthetic route cannot be used to access the family of complexes, due to differences in the stability of the precursors. For example, ^{CpAll}**Pd** and ^{CpAll}**Ni** can be prepared through the reaction of IPr with (Cp)(2-methylallyl)Pd and (Cp)(2-methylallyl)Ni, respectively. However, because $(Cp)_2$Pd does not exist, an alternative strategy was used to synthesize ^{CpCp}**Pd**.

In general, the hapticities of the 2-methylallyl, Cp, and indenyl ligands in the complexes synthesized in this work can be explained by the following two observations: (i) Cp ligands prefer to adopt either an η^5- or an η^1-binding mode as opposed to an η^3-binding mode and (ii) Ni complexes prefer to be 18-electron species, whereas Pd complexes prefer to be 16-electron complexes.[47] As a result, in ^{CpAll}**Pd**, the Cp ligand binds in an η^1-fashion and the 2-methylallyl ligand in an η^3-fashion to give a complex with 16 electrons around Pd. In the corresponding Ni complex ^{CpAll}**Ni**, the Cp ligand binds in an η^5-fashion and the 2-methylallyl ligand in an η^1-fashion so that Ni has 18 electrons. Normally, observation (i) takes priority over (ii). Therefore, ^{CpCp}**Pd** is an 18-electron species with one η^1- and one η^5-bound Cp ligand. An exception to our observations is ^{IndCp}**Pd**, an 18-electron species with one η^1-bound indenyl ligand and one η^5-bound Cp ligand, whereas we would predict a 16-electron species with one η^1-bound Cp ligand and one η^3-bound indenyl ligand. In contrast to the Cp ligand, due to the indenyl effect, the indenyl ligand can bind in an η^1-, η^3-, or η^5-fashion to satisfy observation (ii), although the structure of ^{IndCp}**Pd** suggests that even for the indenyl ligand η^3-binding is not favored. In this work, the only compound isolated with both indenyl and allyl ligands was ^{IndAll}**Pd**; therefore, at this stage there are not enough data to evaluate the preferred hapticity of the allyl ligand in comparison to the indenyl ligand. Overall, we believe that the trends observed here will be general for related Pd and Ni complexes with combinations of allyl, Cp, and indenyl ligands.

Preliminary reactivity studies of our new complexes with electrophiles indicate that the η^1-ligand reacts selectively, regardless of whether it is an allyl, Cp, or indenyl ligand. Therefore, whereas acid protonates the Cp ligand in ^{CpAll}**Pd**, it protonates the 2-methylallyl ligand in ^{CpAll}**Ni**. Similar reactivity is observed using the nonacidic electrophile triphenylcarbenium chloride. Although it is well-known that Pd and Ni complexes with η^1-allyl ligands will act as nucleophiles, comparable reactions with η^1-Cp and η^1-indenyl ligands are significantly less common. Further work will look to explore the reactivity of these species with less activated electrophiles such as aldehydes and CO_2.

EXPERIMENTAL SECTION

General Methods. Experiments were performed under a dinitrogen atmosphere in an M. Braun drybox or using standard Schlenk techniques, unless otherwise noted. (Under standard glovebox conditions, purging was not performed between uses of pentane, diethyl ether, benzene, toluene and THF; thus, when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles.) Moisture- and air-sensitive liquids were transferred by stainless steel cannula on a Schlenk line or in a drybox. Solvents were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received, except where noted. $(Cp)_2$Ni was purchased from Alfa Aesar and triphenylcarbenium chloride from Fisher Scientific Co. Deuterated solvents were obtained from Cambridge Isotope Laboratories. C_6D_6 and d_8-toluene were dried over sodium metal and vacuum-transferred prior to use. NMR spectra were recorded on Bruker AMX-400 and -500 spectrometers at ambient probe temperatures, unless otherwise noted. Chemical shifts are reported in ppm with respect to residual internal protio solvent for ^{1}H and ^{13}C{^{1}H} NMR spectra; J values are given in Hz. Robertson Microlit Laboratories, Inc., performed the elemental analyses. Literature procedures were used to prepare the following compounds: (Cp)(2-methylallyl)Pd,[48] 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IPr),[49] (2-methylallyl)magnesium chloride,[50] (η^5-Cp)Pd(IPr)Cl,[28] sodium cyclopentadienyl,[51] {(η^3-Ind)Pd(μ-Cl)}$_2$,[52] (η^5-Cp)Ni(IPr)Cl,[40] ^{AllCl}**Ni**,[38] lithium indenyl,[53] and 2,6-lutidinium chloride.[54]

X-ray Crystallography. Low-temperature diffraction data (ω scans) were collected on either a Rigaku SCXmini diffractometer coupled to a Mercury275R CCD detector with Mo Kα radiation (λ = 0.71073 Å), a Rigaku R-AXIS RAPID diffractometer coupled to a R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) or a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å). All structures were solved by direct methods using SHELXS[55] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[56] using established refinement techniques.[57] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). All disorders were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Further details of the crystal and refinement data are given in the Supporting Information.

Synthesis and Characterization of Compounds. *(η^1-Cp)(η^3-2-methylallyl)Pd(IPr) (^{CpAll}Pd).* A solution of (Cp)(2-methylallyl)Pd (0.025 g, 0.110 mmol) in 5 mL of pentane was added to a solution of IPr (0.042 g, 0.110 mmol) in 5 mL of pentane at −35 °C. The solution was stirred at −35 °C for 14 h. The volatiles were removed under reduced pressure at −35 °C to give a pale yellow solid. The solid was washed three times with 5 mL portions of cold pentane and dried under vacuum at −35 °C to give ^{CpAll}**Pd** as a pale yellow solid. Yield: 0.040 g, 53%. Due to the thermal instability of this compound elemental analysis was not performed. X-ray-quality crystals were grown by slow diffusion of pentane into a saturated toluene solution at −35 °C.

^{1}H NMR (d_8-toluene, −35 °C, 400 MHz): 7.19 (t, J = 6.6 Hz, 2H, *p*-H Ar$_{IPr}$), 7.12 (d, J = 6.6 Hz, 4H, *m*-H Ar$_{IPr}$), 6.55 (s, 2H, *HCCH*), 6.13 (s, 5H, *Cp*), 3.36 (sept, J = 6.3 Hz, 2H, $(CH_3)_2CH$), 3.03 (s, 1H, CH_2 allyl), 2.91 (sept, J = 6.3 Hz, 2H, $(CH_3)_2CH$), 2.30 (s, 1H, CH_2 allyl), 1.51 (s, 1H, CH_2 allyl), 1.28 (d, J = 6.3 Hz, 12H, $(CH_3)_2CH$), 1.22 (s, 3H, CH_3 allyl), 1.04 (d, J = 6.3 Hz, 12H, $(CH_3)_2CH$), 0.77 (s, 1H, CH_2 allyl). ^{13}C{^{1}H} NMR (d_8-toluene, −35 °C, 126 MHz): 191.7, 145.8, 145.4, 109.1, 87.6, 47.2, 28.7, 26.2, 25.5, 25.0, 23.5, 23.4, 22.7, 22.4.

(Cp)(2-methylallyl)Ni. There is a literature procedure for the synthesis of (Cp)(2-methylallyl)Ni,[58] however we believe that the procedure described below represents an improved protocol.

A solution of $(Cp)_2$Ni (0.250 g, 1.32 mmol) in 10 mL THF was cooled to 0 °C and 2-methylallyl magnesium chloride (2.09 mL of a 0.657 M solution in diethyl ether, 1.32 mmol) was added dropwise with stirring. The resulting solution was allowed to warm to room temperature and stirred for twelve hours to give a dark purple solution.

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The solvent was removed at 30 Torr and the resulting residue extracted three times with 10 mL portions of pentane. The filtrate was concentrated at 30 Torr to give **(Cp)(2-methylallyl)Ni** as a dark purple oil. Yield: 0.200 g, 84.7%. The ^{1}H NMR data was consistent with that previously reported in the literature.[58]

(η^5-Cp)(η^1-2-methylallyl)Ni(IPr) (**^{CpAll}Ni**). A solution of (Cp)(2-methylallyl)Ni (0.183 g, 1.02 mmol) was dissolved in 5 mL benzene and added to a solution of IPr (0.397 g, 1.02 mmol) in 5 mL benzene. The solution was stirred at room temperature for twelve hours and the solvent removed under reduced pressure. The residue was washed three times with 10 mL portions of cold pentane and dried under vacuum to give **^{CpAll}Ni** as a pale green solid. Yield: 0.350 g, 60%. X-ray quality crystals were grown from a concentrated pentane solution at −35 °C.

^{1}H NMR(d_8-toluene, 400 MHz): 7.25 (t, J = 7.3 Hz, 2H, p-H Ar$_{IPr}$), 7.16 (d, J = 7.6 Hz, 4H, m-H Ar$_{IPr}$), 6.50 (s, 2H, *HCCH*), 4.64 (s, 5H, *Cp*), 4.59 (d, J = 2.6 Hz, 1H, CH$_2$ allyl), 4.55 (d, J = 1.9 Hz, 1H, CH$_2$ allyl), 3.06 (sept, J = 6.8 Hz, 4H, (CH$_3$)$_2$*CH*), 1.45 (s, 3H, CH$_3$ allyl), 1.40 (d, J = 6.8 Hz, 12H, (C*H*$_3$)$_2$CH), 1.24 (s, 2H, CH$_2$ allyl), 0.98 (d, J = 6.8 Hz, 12H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (d_8-toluene, 126 MHz): 188.0, 158.7, 146.1, 138.0, 129.8, 124.1, 101.6, 91.6, 28.9, 25.8, 24.0, 22.4, 1.0. Anal. Calcd (found) for $C_{36}H_{48}N_2Ni$: C, 76.06 (76.23); H, 8.69 (8.41); N, 4.93 (4.83).

(η^5-Cp)(η^1-Cp)Ni(IPr) (**^{CpCp}Ni**). (Cp)$_2$Ni (0.010 g, 0.052 mmol) was dissolved in 2 mL of benzene at room temperature. A 3 mL benzene solution of IPr (0.020 g, 0.052 mmol) was added and the resulting suspension stirred at room temperature for 10 h to give a dark red solution. The solvent was removed under reduced pressure. The residue was extracted in 5 mL of pentane and dried under vacuum to give **^{CpCp}Ni** as a dark red solid. Yield: 0.025 g, 82%. X-ray-quality crystals were grown by layering pentane on top of a saturated toluene solution at −35 °C.

^{1}H NMR (d_8-toluene, 400 MHz): 7.26 (t, J = 7.6 Hz, 2H, p-H Ar$_{IPr}$), 7.15 (d, J = 7.6 Hz, 4H, m-H Ar$_{IPr}$), 6.48 (s, 2H, *HCCH*), 5.65 (s, 5H, *Cp*), 4.11 (s, 5H, *Cp*), 3.20 (s, br, 4H, (CH$_3$)$_2$*CH*), 1.31 (d, J = 6.6 Hz, 12H, (C*H*$_3$)$_2$CH), 0.98 (d, J = 6.5 Hz, 12H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (d_8-toluene, 126 MHz): 182.6, 145.8, 137.4, 130.0, 124.1, 108.8, 92.3, 28.8, 28.4, 25.6, 24.5. Anal. Calcd (found) for $C_{37}H_{46}N_2Ni$: C, 76.82 (76.92); H, 8.19 (7.92); N, 4.84 (4.58).

(η^5-Cp)(η^1-Cp)Pd(IPr) (**^{CpCp}Pd**). (Cp)Pd(IPr)Cl[28] (0.019 g, 0.032 mmol) was dissolved in 2 mL of THF at room temperature. A 2.0 M THF solution of sodium cyclopentadienyl (0.016 mL, 0.032 mmol) was added and the resulting solution stirred at room temperature for 1 h to give a dark green solution. The solvent was removed under reduced pressure, and the residue was extracted twice in 5 mL of pentane. The combined extracts were dried under vacuum to give **^{CpCp}Pd** as a dark green solid. Yield: 0.014 g, 71%. X-ray-quality crystals were grown by layering pentane on a saturated solution of diethyl ether at −35 °C.

^{1}H NMR (C$_6$D$_6$, 400 MHz): 7.25 (m, J = 7.5 Hz, 2H, p-H Ar$_{IPr}$), 7.13 (d, J = 7.6 Hz, 4H, m-H Ar$_{IPr}$), 6.56 (s, 2H, *HCCH*), 5.51 (br s, 5H, *Cp*), 5.07 (br s, 5H, *Cp*), 3.08 (sept, J = 6.5 Hz, 4H, (CH$_3$)$_2$*CH*), 1.30 (d, J = 6.8 Hz, 12H, (C*H*$_3$)$_2$CH), 0.98 (d, J = 6.9 Hz, 12H, (C*H*$_3$)$_2$CH). ^{1}H NMR (d_8-toluene, 400 MHz, −30 °C): 7.23 (t, J = 7.5 Hz, 2H, p-H Ar$_{IPr}$), 6.47 (s, 2H, *HCCH*), 5.86 (s, 5H, *Cp*), 4.64 (s, 5H, *Cp*), 3.04 (m, 4H, (CH$_3$)$_2$*CH*), 1.28 (d, J = 6.4 Hz, 12H, (C*H*$_3$)$_2$CH), 0.97 (d, J = 6.8 Hz, 12H, (C*H*$_3$)$_2$CH). The m-H Ar$_{IPr}$ protons are under the solvent resonances. ^{13}C{^{1}H} NMR (d_8-toluene, 100 MHz): 181.1, 146.4, 137.6, 130.5, 124.6, 124.4, 109.7 (br), 100.2 (br), 29.5, 26.1, 22.9. Anal. Calcd (found) for $C_{37}H_{46}N_2Pd$: C, 71.08 (71.15); H, 7.42 (7.66); N, 4.48 (4.26).

(η^3-Ind)Pd(IPr)Cl (**^{IndCl}Pd**). {(η^3-Ind)Pd(μ-Cl)}$_2$ (0.060 g, 0.116 mmol) and IPr (0.090 g, 0.232 mmol) were suspended in 15 mL of diethyl ether and stirred at room temperature for 1 h. The resulting orange suspension was filtered and the filtrate concentrated to approximately 5 mL under reduced pressure. A 20 mL portion of cold pentane was added to the concentrated filtrate, and an orange solid precipitated out of solution. The solid was isolated via filtration, washed three times with 5 mL portions of cold pentane, and dried under vacuum to give **^{IndCl}Pd** as a dark orange solid. Yield: 0.113 g, 75%. X-ray-quality crystals were grown by slow diffusion of pentane into a saturated toluene solution at room temperature. ^{1}H and ^{13}C{^{1}H} NMR spectra of **^{IndCl}Pd** are provided in the Supporting Information.

^{1}H NMR (C$_6$D$_6$, 400 MHz): 7.37 (t, J = 7.7 Hz, 2H, p-H Ar$_{IPr}$), 7.26 (d, J = 7.7 Hz, 2H, m-H Ar$_{IPr}$), 7.08 (d, J = 7.7 Hz, 2H, m-H Ar$_{IPr}$), 6.97 (s, 2H, *HCCH*), 6.78 (d, J = 7.4 Hz, 1H, Ar$_{Ind}$), 6.60 (t, J = 7.4 Hz, 1H, Ar$_{Ind}$), 6.21 (m, 2H, Ar$_{Ind}$), 5.66 (d, J = 7.4 Hz, 1H, Cp$_{Ind}$), 5.48 (t, J = 2 Hz, 1H, Cp$_{Ind}$), 5.22 (t, J = 2 Hz, 1H, Cp$_{Ind}$), 3.03 (sept, J = 6.8 Hz, 2H, (CH$_3$)$_2$*CH*), 2.57 (sept, J = 6.8 Hz, 2H, (CH$_3$)$_2$*CH*), 1.36 (d, J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 1.10 (d, J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 0.97 (d, J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 0.85 (d, J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz): 177.9, 146.3, 138.6, 137.7, 136.8, 130.2, 124.8, 118.4, 116.3, 110.2, 86.1, 69.5, 28.8, 28.7, 26.4, 25.7, 23.7, 22.4. Anal. Calcd (found) for $C_{36}H_{43}N_2PdCl$: C, 66.87 (65.09); H, 6.86 (5.69); N, 4.33 (4.12).

(η^1-Ind)(η^3-2-methylallyl)Pd(IPr) (**^{IndAll}Pd**). **^{IndCl}Pd** (0.050 g, 0.077 mmol) was dissolved in 3 mL of THF, and the solution was cooled to 0 °C. (2-Methylallyl)magnesium chloride (0.117 mL of a 0.657 M THF solution, 0.077 mmol) was added dropwise with stirring, and the resulting solution was stirred at 0 °C for 90 min to give a bright yellow solution. The solvent was removed under reduced pressure and the resulting residue extracted twice with 5 mL portions of pentane. The combined extracts were dried under vacuum to give **^{IndAll}Pd** as a bright yellow solid. Yield: 0.037 g, 68%. X-ray-quality crystals were grown from a saturated pentane solution at −35 °C. ^{1}H and ^{13}C{^{1}H} NMR spectra of **^{IndAll}Pd** are provided in the Supporting Information.

^{1}H NMR (C$_6$D$_6$, 500 MHz): 7.46 (d, J = 6.5 Hz, 1H, Ar$_{Ind}$), 7.24 (t, J = 7.7 Hz, 2H, p-H Ar$_{IPr}$), 7.21 (d, J = 1.3 Hz, 1H, Ar$_{Ind}$), 7.19 (d, J = 1.6 Hz, 1H, Ar$_{Ind}$), 7.14 (d, J = 7.7 Hz, 2H, m-H Ar$_{IPr}$), 7.10 (d, J = 7.7 Hz, 2H, m-H Ar$_{IPr}$), 6.64 (s, 2H, *HCCH*), 6.56 (t, J = 3.2 Hz, 1H, Cp$_{Ind}$), 5.97 (br, 1H, Cp$_{Ind}$), 5.90 (br, 1H, Cp$_{Ind}$), 3.38 (sept, J = 6.8 Hz, 2H, (CH$_3$)$_2$*CH*), 3.01 (sept, J = 6.8 Hz, 2H, (CH$_3$)$_2$*CH*), 2.31 (d, J = 3.2 Hz, 1H, CH$_2$ allyl), 2.13 (s, 1H, CH$_2$ allyl), 1.50 (s, 1H, CH$_2$ allyl), 1.30 (d, J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 1.21 (d, J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 1.05 (d, J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 1.01 (d, J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 1.00 (s, 3H, CH$_3$ allyl), 0.95 (d, J = 2.8 Hz, 1H, CH$_2$ allyl), one Ar$_{Ind}$ peak is coincidental with solvent. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): 191.8, 146.4, 146.2, 138.6, 137.8, 130.5, 124.8, 124.6, 124.5, 121.2, 120.1, 119.9, 78.5, 51.3, 29.3, 29.2, 26.7, 25.9, 23.8, 23.2, 23.1, 1.77. Anal. Calcd (found) for $C_{40}H_{51}N_2Pd$: C, 72.11 (70.89); H, 7.72 (7.66); N, 4.20 (4.20).

(η^1-Ind)(η^5-Cp)Pd(IPr) (**^{IndCp}Pd**). **^{IndCl}Pd** (0.050 g, 0.077 mmol) was dissolved in 3 mL of THF, and the solution was cooled to 0 °C. A solution of sodium cyclopentadienyl (0.038 mL of a 2 M THF solution, 0.077 mmol) was added dropwise with stirring and the resulting solution stirred at 0 °C for 90 min. The solvent was removed under reduced pressure and the residue extracted twice with 5 mL portions of pentane. The solvent from the combined extracts was removed under vacuum to give **^{IndCp}Pd** as an orange solid. Yield: 0.040 g, 71%.

^{1}H NMR (C$_6$D$_6$, 400 MHz): 7.53 (d, J = 7.1 Hz, 1H, Ar$_{Ind}$), 7.26 (t, J = 7.7 Hz, 2H, p-H Ar$_{IPr}$), 7.20−7.11 (m, 6H, Ar$_{Ind}$ and Ar$_{IPr}$), 6.89 (d, J = 7.2 Hz, 1H, Ar$_{Ind}$), 6.74 (br, 1H, Cp$_{Ind}$), 6.56 (s, 2H, *HCCH*), 6.40 (m, 1H, Cp$_{Ind}$), 4.63 (s, 5H, *Cp*), 4.54 (br, 1H, Cp$_{Ind}$), 3.19 (sept, J = 6.8 Hz, 2H, (CH$_3$)$_2$*CH*), 3.06 (sept, J = 6.8 Hz, 2H, (CH$_3$)$_2$*CH*), 1.32 (d, J = 7.0 Hz, 6H, (C*H*$_3$)$_2$CH), 1.25 (J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 1.01 (d, J = 7.0 Hz, 6H, (C*H*$_3$)$_2$CH), 0.99 (d, J = 7.0 Hz, 6H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): 181.5, 146.5, 146.3, 141.8, 137.8, 130.6, 124.9, 124.8, 124.6, 124.2, 122.9, 121.9, 121.1, 118.1, 99.2, 34.9, 29.4, 26.3, 22.8, 23.0, 14.6. Anal. Calcd (found) for $C_{41}H_{49}N_2Pd$: C, 72.82 (73.09); H, 7.30 (7.11); N, 4.14 (4.13).

(η^1-Ind)(η^5-Cp)Ni(IPr) (**^{IndCp}Ni**). (η^5-Cp)Ni(IPr)Cl (0.050 g, 0.091 mmol) was dissolved in 2 mL of THF and cooled to −40 °C. Lithium indenyl (0.0012 g, 0.100 mmol) in 1 mL of THF was added dropwise with stirring. The solution was warmed to room temperature over 1 h and stirred for an additional 2 h at room temperature. The solvent was removed under vacuum and the residue extracted twice with 5 mL portions of pentane to give a red solution. The solvent was removed

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from the combined extracts to give ^{IndCp}**Ni** as a red solid. Yield: 0.045 g, 75%.

^{1}H NMR (C_6D_6, 500 MHz): 7.51 (d, J = 7.2 Hz, 1H, Ar_{Ind}), 7.30 (t, J = 7.7 Hz, 3H, Ar_{Ind} and *p-H* Ar_{IPr}), 7.21−7.19 (m, 5H, Ar_{Ind} and *m-H* Ar_{IPr}), 6.79 (m, 2H, Ar_{Ind} and Cp_{Ind}), 6.56 (t, J = 3.3 Hz, 1H, Cp_{Ind}), 6.55 (m, 1H, Cp_{Ind}), 6.52 (s, 2H, *HCCH*), 4.17 (s, 5H, *Cp*), 3.82 (br, 1H, Cp_{Ind}), 3.43 (br, 2H, $(CH_3)_2CH$), 3.08 (br, 2H, $(CH_3)_2CH$), 1.38 (d, J = 6.5 Hz, 6H, $(CH_3)_2CH$), 1.20 (d, J = 6.5 Hz, 6H, $(CH_3)_2CH$), 0.98 (d, J = 6.8 Hz, 12H, $(CH_3)_2CH$). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz): 184.0, 158.9, 146.5, 146.4, 146.2, 146.0, 142.3, 138.3, 138.1, 130.6, 130.5, 125.4, 124.7, 124.1, 122.2, 121.6, 120.9, 120.0, 117.1, 97.5, 34.7, 29.4, 26.3, 26.1, 22.8, 19.8. Anal. Calcd (found) for $C_{41}H_{49}N_2Ni$: C, 78.35 (78.07); H, 7.86 (8.01); N, 4.46 (4.47).

(η^3-Ind)(η^1-Ind)Pd(IPr) (^{IndInd}***Pd***). ^{IndCl}**Pd** (0.018 g, 0.028 mmol) was dissolved in 5 mL of diethyl ether at −35 °C. The solution was added to lithium indenyl (0.003 g, 0.028 mmol) in 5 mL of diethyl ether at −35 °C and stirred at this temperature for 20 min to give a cloudy, dark pink solution. The precipitate was removed by quickly filtering the mixture through a Celite plug. The solvent was removed from the filtrate under reduced pressure to give ^{IndInd}**Pd** as dark pink solid. Due to the thermal instability of this compound, elemental analysis was not performed, nor was a ^{13}C NMR spectrum recorded. X-ray-quality crystals were grown in a concentrated solution of diethyl ether at −35 °C. Yield: 0.016 g, 80%.

^{1}H NMR (d_8-toluene, −40 °C, 500 MHz): 7.78 (d, J = 6.8 Hz, 1H, Ar_{Ind}), 7.47 (t, J = 7.7 Hz, 1H, Ar_{Ind}), 7.34 (t, J = 7.7 Hz, 1H, Ar_{Ind}), 6.86 (d, J = 4.8 Hz, 1H, Ar_{Ind}), 6.71 (t, J = 7.4 Hz, 1H, Ar_{Ind}), 6.61 (m, 2H, Ar_{Ind}), 6.35 (d, J = 6.61 Hz, 1 H, Ar_{Ind}), 6.30 (s, 1H, *HCCH*), 6.22 (t, J = 3 Hz, 1H, Cp_{Ind}), 6.13 (t, J = 3 Hz, 1H, Cp_{Ind}), 6.06 (br, 1 H, Cp_{Ind}), 5.69 (d, J = 7.6 Hz, 1H, Cp_{Ind}), 4.94 (br, 1H, Cp_{Ind}), 4.54 (br, 1H, Cp_{Ind}), 3.01 (br, 4H, $(CH_3)_2CH$), 0.94 (br, 24H, $(CH_3)_2CH$).

Reactivity Studies. *General Procedure for the Reaction of Pd and Ni Compounds with 2,6-Lutidinium Chloride.* A solution of 2,6-lutidinium hydrochloride (0.010g, 0.006 mmol) in 0.25 mL d_8-toluene was added to a solution of the metal complex (0.006 mmol) in 0.25 mL of d_8-toluene at the desired temperature in an NMR tube. The solution was allowed to stand at the desired temperature for the specified time (see Table 1 for specific temperatures and reaction times). Quantitative formation of the known complexes (η^3-2-methylallyl)Pd(IPr)Cl[1b] and (η^5-Cp)Pd(IPr)Cl[59] was observed by ^{1}H NMR spectroscopy. (η^5-Cp)Ni(IPr)Cl[40] precipitated out of solution and was isolated by filtration and then identified using ^{1}H NMR spectroscopy.

Reaction between ^{CpAll}***Pd*** *and Triphenylcarbenium Chloride.* Triphenylcarbenium chloride (0.002 g, 0.008 mmol) was added to a solution of ^{CpAll}**Pd** (0.005 g, 0.008 mmol) in toluene at −35 °C in an NMR tube. The solution was slowly warmed to room temperature over 3 h and left at room temperature for 24 h. Quantitative conversion to (η^3-2-methylallyl)Pd(IPr)Cl[60] and three nonisolable isomers of cyclopentadienyltriphenylmethane was observed by ^{1}H NMR spectroscopy.[45] Independent synthesis of cyclopentadienyltriphenylmethane through the reaction of sodium cyclopentadienyl with triphenylcarbenium chloride provided a confirmation of the product identity.

Reaction between ^{CpAll}***Ni*** *and Triphenylcarbenium Chloride.* Triphenylcarbenium chloride (0.002 g, 0.008 mmol) was added to a solution of ^{CpAll}**Ni** (0.005 g, 0.008 mmol) in 0.5 mL of C_6D_6 in an NMR tube. The mixture was allowed to stand at room temperature for 12 h. The solvent was removed under reduced pressure and the residue dissolved in a minimal amount of chloroform and loaded onto a silica gel plug. ^{CpAll}**Ni** was isolated as a bright pink solid (0.003g, 0.005 mol) and identified by ^{1}H NMR spectroscopy.[40] (2-methylallyl)-triphenylmethane was isolated as a white solid (0.002 g, 0.006 mol) and characterized by ^{1}H and ^{13}C NMR spectroscopy. Yield: 0.002 g, 75%.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.29−7.15 (m, 15H, phenyl), 4.66 (s, 1H, terminal allyl CH_2), 4.26 (s, 1H, terminal allyl CH_2), 3.37 (s, 2H, allyl CH_2), 1.42 (s, 3H, allyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): 147.3, 142.2, 130.6, 129.7, 127.7, 125.9, 115.9, 48.6, 25.6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and tables giving X-ray information for ^{CpAll}**Pd**, ^{CpAll}**Ni**, ^{CpCp}**Pd**, ^{CpCp}**Ni**, ^{IndCl}**Pd**, ^{IndAll}**Pd** and ^{IndInd}**Pd** and figures giving ^{1}H and ^{13}C{^{1}H} NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(47) This observation assumes that the Cp and indenyl ligands do not have intermediate hapticities between η^3 and η^5. Although as a first-order approximation this is reasonable on the basis of the structures described in this work, some η^5-Cp ligands do display an ene−allyl distortion, suggesting some ring slippage away from η^5-Cp and donation of between three and five electrons (using the covalent bonding model). However, our proposal is that even if these slight distortions are taken into account, the total electron count around the metal will always be higher in Ni complexes in comparison to analogous Pd species, when all other factors are equal.
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