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Synthesis, Properties, and Reactivity with Carbon Dioxide of $(allyl)_2Ni(L)$ Complexes

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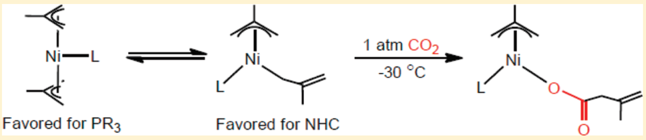
Supporting Information



ABSTRACT: A family of nickel allyl complexes of the type $(allyl)_2Ni(L)$ ($L = PMe_3$ (**1**), PEt_3 (**2**), PPh_3 (**3**), NHC (**4**); NHC = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-2*H*-imidazol-2-ylidene) and $(2\text{-methylallyl})_2Ni(L)$ ($L = PMe_3$ (**5**), PEt_3 (**6**), PPh_3 (**7**), NHC (**8**)) have been prepared using literature methods. Compounds **5**, **7**, and **8** were characterized by X-ray crystallography. Whereas compounds **5** and **7** are 18-electron species with two η^3-allyl ligands, the NHC-supported complexes are 16-electron species with one η^1- and one η^3-allyl ligand. Using DFT we have identified the key factors in predicting whether complexes of the type $(allyl)_2M(L)$ (M = Ni, Pd) are 16- or 18-electron species. Compounds **1**, **2**, and **5**−**8** readily decompose to give a mixture of products, while compound **4** decomposes to give the unusual Ni^0 species (η^4-1,5-hexadiene)Ni(NHC) (**9**), which was characterized by X-ray crystallography. The reactions of **1**−**8** with CO_2 were investigated. Compounds **5**−**8** react rapidly with CO_2 at low temperature to form well-defined unidentate nickel carboxylates of the type (η^3-2-methylallyl)$Ni(OC(O)C_4H_7)(L)$ ($L = PMe_3$ (**10**), PEt_3 (**11**), PPh_3 (**12**), NHC (**13**)). The structure of **13** was elucidated using X-ray crystallography. In contrast, compounds **1**−**4** do not react with CO_2. We believe that the difference in reactivity between the 2-methylallyl-supported complexes and the allyl-supported complexes is related to the mechanism of CO_2 insertion.

INTRODUCTION

The potential environmental consequences of continuing to utilize fossil fuels as an energy source and the decline in our petroleum reserves has led to considerable research into alternative carbon sources.[1] CO_2 is a particularly attractive feedstock for the synthesis of both commodity chemicals and complex organic molecules, due to its low toxicity and cost, high abundance, and relative ease of transport.[2−9] However, the catalytic conversion of CO_2 into value-added products is complicated by its high kinetic and thermodynamic stability. One approach for the functionalization of CO_2 is to utilize transition metals to weaken the strong C═O double bond, and several transition-metal complexes have been developed as catalysts for carboxylation reactions.[10−22] The key step in many of these cycles is proposed to involve the insertion of CO_2 into a metal−carbon bond, and one of the most well-studied and successful reactions involves the insertion of CO_2 into Pd−allyl bonds. A number of catalytic cycles are proposed to involve the formation of Pd carboxylates from the reactions of Pd allyl species with CO_2. These include systems for the coupling of CO_2 with butadiene to form lactones,[23−25] the carboxylation of allylstannanes[10,13] and -allenes,[15] and the carboxylative coupling of allylstannanes with allyl halides.[11]

In order to further understand the carboxylation of allylstannanes, both Wendt's and our group have recently reported studies describing the mechanism of CO_2 insertion into monomeric Pd η^1-allyls.[13,26,27] Our group initially prepared a family of thermally sensitive Pd allyl complexes of the type $(2\text{-methylallyl})_2Pd(L)$ ($L = PMe_3$ (**I**), PEt_3 (**II**), PPh_3 (**III**), NHC (**IV**); NHC = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-2*H*-imidazol-2-ylidene), which contain one η^1- and one η^3-2-methylallyl ligand. All of these species rapidly insert CO_2 at low temperature to form the unidentate carboxylate species **V**−**VIII**. Using a combination of computational and experimental techniques, we performed mechanistic studies on the carboxylation reaction. We proposed that the reaction of η^1-Pd allyls with CO_2 does not proceed via direct insertion of CO_2 into the Pd−C bond but through nucleophilic attack of the terminal olefin on electrophilic CO_2, followed by ligand substitution to give the O-bound product (Scheme 1). As a result only nucleophilic η^1-allyls will react with CO_2 and electrophilic η^3-allyls are inert. Wendt and co-workers reached a similar conclusion by performing mechanistic studies on a system in which a PCP pincer ligand supported an η^1-Pd allyl (Scheme 1).[26] We subsequently demonstrated that catalysts based on **VIII** were some of the most active for the carboxylation of allylstannanes with CO_2 and were also able to carboxylate allylboranes.[22]

Although Ni is significantly cheaper than Pd (the cost of pure Ni is approximately 1000 times cheaper than the cost for pure Pd on May 1, 2011, on the London Metal Exchange) and there is significant precedent for the reaction of Ni(0) with CO_2,[3] there has been little work investigating the reactions of Ni allyls with CO_2. In fact, studies of the insertion of CO_2 into Ni−R σ-bonds (R = H, alkyl) remain rare.[20,28,29] Early work by Jolly and co-workers in the late 1970s established that CO_2 could react with $(2\text{-methylallyl})_2Ni(L)$ ($L = PMe_3$, PCy_3) but the products of the

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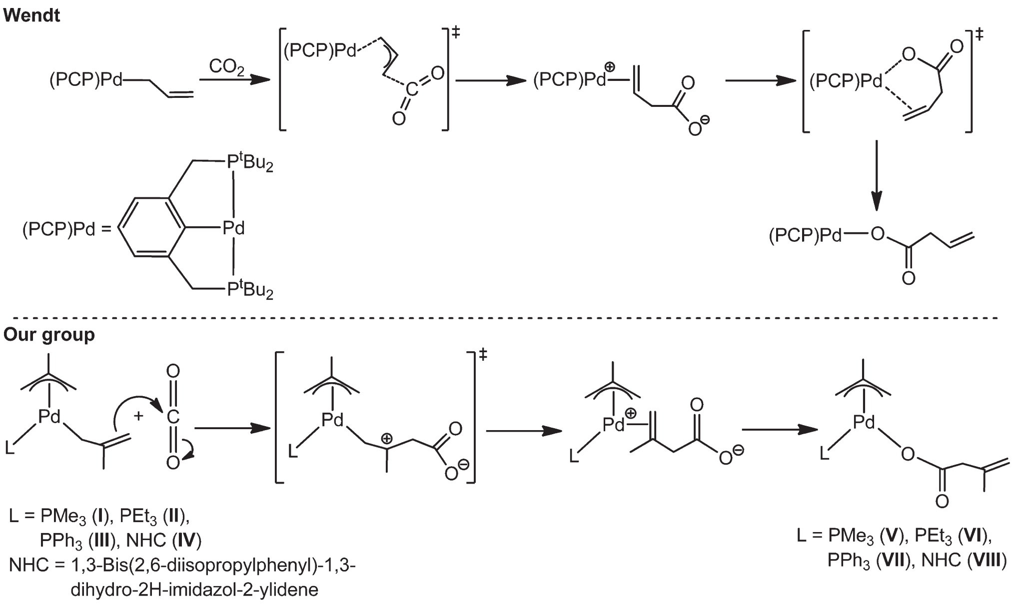
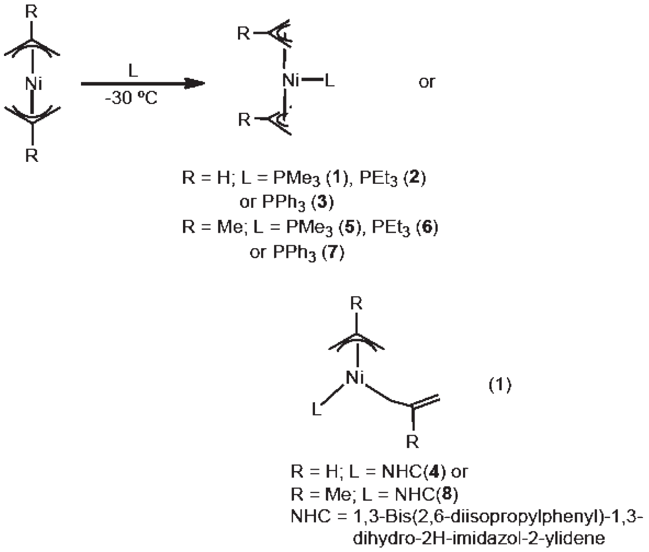
Scheme 1



reaction were not well characterized.[30] Subsequently, Tsuda and co-workers demonstrated that $(allyl)_2Ni$ could be reacted with CO_2 to form five-membered lactones in polar solvents.[31] Recently, we demonstrated that CO_2 could insert into a well-defined Ni PCP η^1-allyl to form an η^1-carboxylate and presented evidence that this reaction proceeds through a mechanism similar to that described for η^1-Pd allyls (Scheme 1).[32] Unfortunately, these Ni species were not active catalysts for the carboxylation of allylstannanes and allylboranes. In this work, we synthesize a series of complexes of the type $(2\text{-methylallyl})_2Ni(L)$, including those supported by NHC ligands, and explore their structures and decomposition pathways. We build on Jolly's preliminary results and demonstrate that these species react cleanly with CO_2 to form η^1-carboxylates. Furthermore, we use our new results to make comparisons about CO_2 insertion into related Pd and Ni systems and draw conclusions about the design of future Ni catalysts for CO_2 reduction.

RESULTS AND DISCUSSION

Synthesis and Structures of $(allyl)_2Ni(L)$ Complexes. Using the route first described by Jolly and co-workers,[33] a family of complexes of the type $(allyl)_2Ni(L)$ (L = PMe_3 (**1**), PEt_3 (**2**), PPh_3 (**3**), NHC (**4**); NHC = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-2*H*-imidazol-2-ylidene) and $(2\text{-methylallyl})_2Ni(L)$ (L = PMe_3 (**5**), PEt_3 (**6**), PPh_3 (**7**), NHC (**8**)) were prepared through the reaction of $(allyl)_2Ni$ or $(2\text{-methylallyl})_2Ni$ with the appropriate free ligand at low temperature (eq 1). Although the phosphine-supported complexes had previously been prepared by Jolly et al.,[33] to the best of our knowledge this is the first example of the preparation of NHC-supported complexes of this type. Complexes **1**−**7** were all unstable in solution at room temperature and displayed highly fluxional ^1H NMR spectra. The ^1H NMR spectrum of compound **8** was also highly fluxional, but **8** could be left at room temperature for days with minimal decomposition. Jolly et al. had previously crystallized $(allyl)_2Ni(PMe_3)$ (**1**) and demonstrated that it is an 18-electron species with two η^3-allyl ligands.[33] They also performed low-temperature ^1H NMR spectroscopy on **1** at −110 °C, which suggested that the solution-state structure was consistent with that observed in the solid state.[33] In contrast, even at −80 °C only two broad peaks were observed for the allyl or 2-methylallyl groups in the ^1H NMR spectra of **2**−**8** and the binding mode of the allyl or 2-methylallyl ligands was not clear. We recently prepared the Pd species $(2\text{-methylallyl})_2Pd(L)$ (L = PMe_3 (**I**), PEt_3 (**II**), PPh_3 (**III**), NHC (**IV**)), and in all cases the ^1H NMR spectra indicated that at low temperature (−80 °C) the η^1:η^3-isomer of the complex was present.[27] These results were supported by the solid-state structure of **III**, which unequivocally showed one η^1- and one η^3-2-methylallyl ligand.[27]



In order to properly compare the Pd and Ni systems, we were interested in gaining greater clarity about the structures of **1**−**8**. We were able to crystallize compounds **5**, **7**, and **8** from saturated

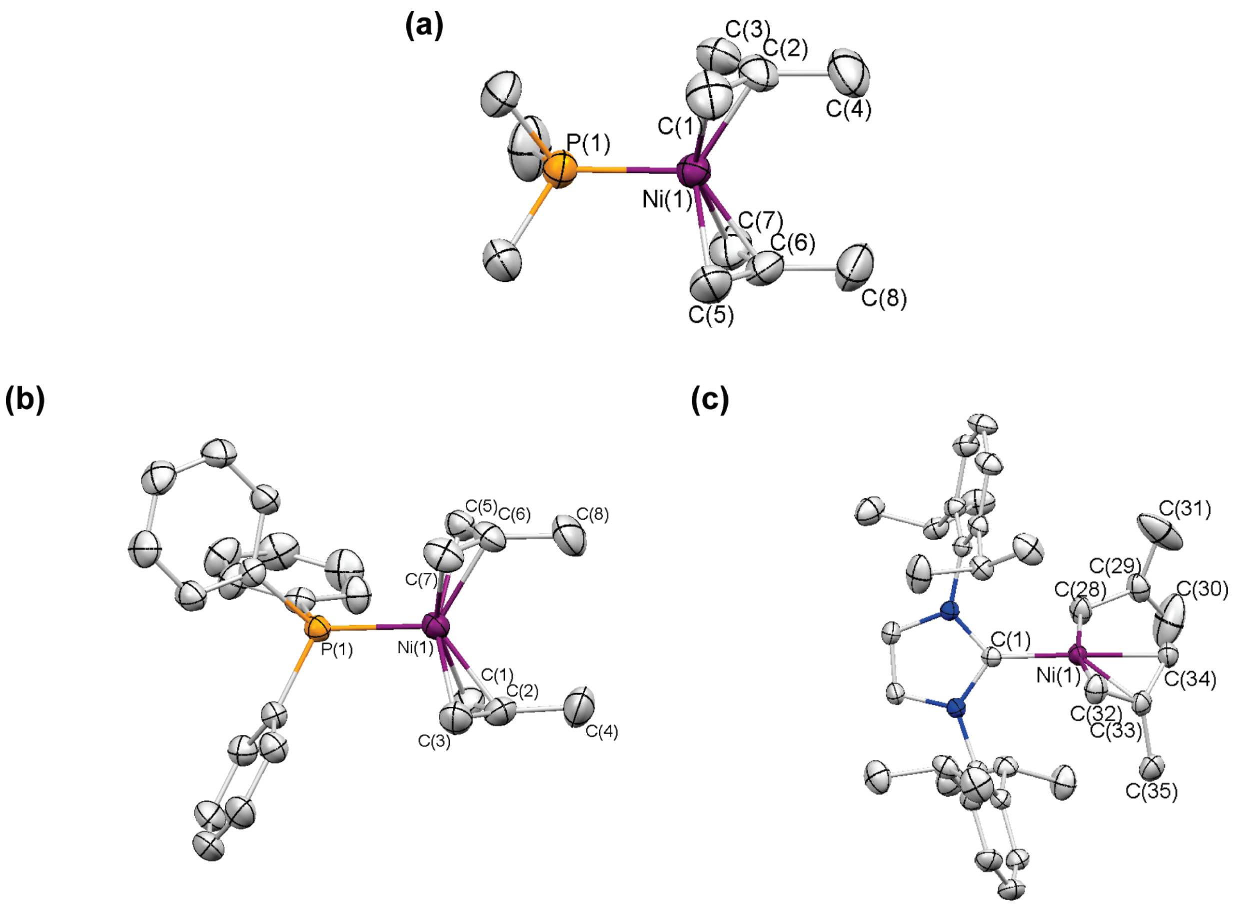


Figure 1. (a) X-ray structure of **5** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−P(1) 2.2517(7), Ni(1)−C(1) = 2.063(4), Ni(1)−C(2) = 2.015(3), Ni(1)−C(3) = 2.060(3), Ni(1)−C(5) = 2.057(3), Ni(1)−C(6) = 2.018(2), Ni(1)−C(7) = 2.057(3), C(1)−C(2) = 1.403(4), C(2)−C(3) = 1.407(5), C(2)−C(4) = 1.506(4), C(5)−C(6) = 1.405(4), C(6)−C(7) = 1.402(5), C(6)−C(8) = 1.507(4); Ni(1)−C(1)−C(2) = 68.08(19), Ni(1)−C(2)−C(3) = 71.52(17), Ni(1)−C(5)−C(6) = 68.36(16), Ni(1)−C(6)−C(7) = 72.08(17). (b) X-ray structure of **7** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−P(1) = 2.2925(9), Ni(1)−C(1) = 2.083(3), Ni(1)−C(2) = 2.024(3), Ni(1)−C(3) = 2.041(3), Ni(1)−C(5) = 2.091(3), Ni(1)−C(6) = 2.025(2), Ni(1)−C(7) = 2.043(3), C(1)−C(2) = 1.397(4), C(2)−C(3) = 1.399(5), C(2)−C(4) = 1.499(5), C(5)−C(6) = 1.389(4), C(6)−C(7) = 1.399(4), C(6)−C(8) = 1.515(5); Ni(1)−C(1)−C(2) = 67.83(19), Ni(1)−C(2)−C(3) = 70.5(2), Ni(1)−C(5)−C(6) = 67.73(14), Ni(1)−C(6)−C(7) = 70.56(15). (c) X-ray structure of **8** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) = 1.889(3), Ni(1)−C(28) = 1.966(3), Ni(1)−C(32) = 2.058(4), Ni(1)−C(33) = 2.003(3), Ni(1)−C(34) = 2.001(4), C(28)−C(29) = 1.467(5), C(29)−C(30) = 1.354(8), C(29)−C(31) = 1.388(7), C(32)−C(33) = 1.394(6), C(33)−C(34) = 1.400(5), C(33)−C(35) = 1.496(5); Ni(1)−C(28)−C(29) = 121.7(2), Ni(1)−C(32)−C(33) = 67.81(19), Ni(1)−C(33)−C(34) = 69.45(17).

solutions of pentane at low temperature (Figure 1). Whereas compounds **5** and **7** are both square-pyramidal 18-electron species with two η^3-2-methylallyl ligands, compound **8** is a square-planar 16-electron species with one η^1- and one η^3-2-methylallyl ligand. The structures of **5** and **7** are similar and feature a syn arrangement of the 2-methylallyl ligands. The bonds of the Ni to the two 2-methylallyl ligands are virtually identical, and each 2-methylallyl ligand is symmetrically bound to the metal center. For example, in the structure of **5**, the Ni(1)−C(1) distance of 2.063(4) Å is the same (within experimental error) as the Ni(1)−C(3) distance of 2.060(3) Å. Unsurprisingly, the Ni−phosphorus distance is longer in **7** (Ni(1)−P(1) = 2.2925(9) Å), which contains the less donating and more sterically bulky PPh_3 ligand, in comparison with the Ni−phosphorus distance in **5** (Ni(1)−P(1) = 2.2517(7) Å), which contains the PMe_3 ligand. The structures of **5** and **7** are analogous to that reported for **1** by Jolly,[33] but the 18-electron square-pyramidal structure for **7** stands in contrast to the 16-electron square-planar structure observed for its direct Pd analogue **III**.[27]

The structure of the NHC-supported complex **8** unambiguously shows that the molecule contains one η^1- and one η^3-2-methylallyl ligand. In fact, **8** is a rare example of a crystallographically characterized Ni η^1-allyl.[32,34] The Ni−η^1-allyl bond length is 1.966(3) Å, which is significantly shorter than the Ni−η^1-allyl bond length observed in a pincer-supported complex (in (PCP)Ni(η^1-allyl), which contains two independent molecules in the unit cell, the Ni−allyl bond lengths are 2.094(5) and 2.071(6) Å) presumably because of the strong *trans* influence of the anionic carbon in the pincer ligand.[32] However, the bond length is comparable with the only other example of a Ni complex which features two different coordination modes of an allyl ligand (the Ni−η^1-allyl bond lengths in $[Li(tmeda)]^+$-$[(\eta^3\text{-}C_3H_5)Ni(\eta^1\text{-}C_3H_5)_2]^-$ are 1.953(4) and 1.979(3) Å).[34] The Ni−η^3-allyl bond lengths are comparable to those observed in **5** and **7**, although the 2-methylallyl ligand is no longer symmetrically bound. The Ni(1)−C(32) bond length, 2.058(4) Å, is longer than the Ni(1)−C(34) bond length, 2.001(4) Å, seemingly because C(32) is *trans* to the η^1 2-methylallyl ligand, which exerts a stronger *trans* influence than the NHC ligand, which is *trans* to C(34). Overall, the structure of **8** is similar to that described for (η^1-2-methylallyl)(η^3-2-methylallyl)Pd-(PPh_3) (**III**).[27]

Our experimental results clearly indicate that, depending on the metal, ancillary ligand, and substitution of the allyl ligand, complexes of the type $(allyl)_2M(L)$ (M = Ni, Pd) can adopt either a 16-electron square-planar or 18-electron square-pyramidal geometry. In order to further probe the factors that cause these species to have either two η^3-allyl ligands or one η^1- and one η^3-allyl ligand, a series of DFT calculations were performed. The structures of the molecules that were calculated are shown in Figure 2, and the relative energies are given in Table 1. In the case of the bis η^3:η^3-allyl isomers, both anti and syn isomers were calculated. It should be noted that we have used a simplified NHC ligand to model **4** and **8**; however, we do not believe that steric factors cause large changes to our results.

In general, the calculated energies are in excellent agreement with our experimental results and good agreement was obtained between calculated and experimental geometries. The only case where the calculated energy suggests that an isomer which was not experimentally observed is the most stable isomer, is for $(2\text{-methylallyl})_2Ni(PMe_3)$ (**5**). For **5**, calculations suggest that the 16-electron complex is more stable than the syn 18-electron complex by 9.4 kJ mol^{-1}, even though the X-ray structure showed two syn η^3-2-methylallyl ligands. In this case the calculated difference in energy is small and can probably be attributed to either error associated with the calculation or crystal-packing effects. All complexes show a preference for the syn 18-electron configuration over the anti 18-electron configuration, which is also consistent with experimental results.

On the basis of both our experimental and computational trends we believe that the following conclusions can be made about the preferred geometry and properties of complexes of type $(allyl)_2M(L)$ (M = Ni, Pd). (i) Electron-donating ancillary ligands increase the electron richness of the metal center and promote the formation of 16-electron η^1:η^3-allyl complexes, rather than 18-electron η^3:η^3-allyl complexes. Thus, 16-electron complexes are favored for NHC-supported species compared with phosphine-supported species. (ii) The 2-methylallyl ligand inductively increases the donating power of the allyl ligand, and hence 16-electron compounds are more favorable for 2-methylallyl ligands than for allyl ligands. On this basis we suggest that if an even more strongly electron donating group were present at the 2-position (i.e. OMe), a 16-electron compound would become even more favorable. (iii) A 16-electron isomer is more favored for Pd than for Ni. We believe this is related to the fact that Pd forms stronger metal−ligand bonds and therefore the olefin of the second allyl group is less likely to coordinate. (iv) In the systems that we studied, the energy difference between the different isomers is generally significantly larger for Pd compared with Ni. This could explain why it is possible to freeze out the lowest energy conformation using ^{1}H NMR spectroscopy for Pd complexes,[27] but for Ni complexes even at low temperatures fluxional NMR spectra are observed.

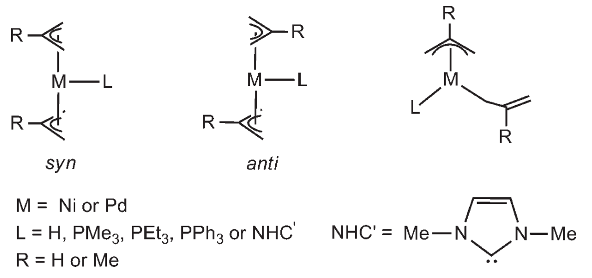


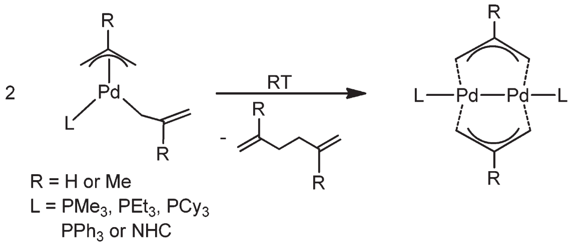
Figure 2. Model compounds used for computational calculations.

Table 1. Relative SCF Energies of Different Isomers of $(allyl)_2M(L)$ and $(2\text{-methylallyl})_2M(L)$ (M = Ni, Pd)[a]

compd					
ligand	metal	allyl	η^3-syn	η^3-anti	η^1
PH_3	Ni	C_3H_5	0	10.0	7.63
	Pd	C_3H_5	27.6	*b*	0
PMe_3	Ni	C_3H_5	0	14.2	2.10
	Pd	C_3H_5	43.5	56.5	0
PEt_3	Ni	C_3H_5	3.20	15.5	0
	Pd	C_3H_5	40.1	57.5	0
PPh_3	Ni	C_3H_5	0	10.2	1.31
	Pd	C_3H_5	36.5	*b*	0
NHC′	Ni	C_3H_5	29.1	49.6	0
	Pd	C_3H_5	67.2	84.2	0
PH_3	Ni	C_4H_7	1.63	5.10	0
	Pd	C_4H_7	33.7	*b*	0
PMe_3	Ni	C_4H_7	9.43	20.3	0
	Pd	C_4H_7	45.0	*b*	0
PEt_3	Ni	C_4H_7	11.6	22.9	0
	Pd	C_4H_7	42.4	*b*	0
PPh_3	Ni	C_4H_7	0	6.22	0.70
	Pd	C_4H_7	35.7	*b*	0
NHC′	Ni	C_4H_7	37.8	48.3	0
	Pd	C_4H_7	72.9	85.7	0

[a] Relative energies are given in kJ mol^{-1}, with the lowest energy structures assigned as being at 0 kJ mol^{-1}. [b] Convergence on an optimized structure was not achieved.

Decomposition of $(allyl)_2Ni(L)$ Complexes. It is relatively well-known that compounds of the type $(allyl)_2Pd(L)$ and $(2\text{-methylallyl})_2Pd(L)$ (L = PR_3, NHC) decompose readily in solution to give Pd^I bridging allyl dimers (eq 2).[33,35,36] In contrast, Jolly showed that **3** decomposes to give a Ni^0 species containing a bidentate 1,5-hexadiene ligand. We observed that at room temperature complexes **1**, **2**, and **5**−**7** all decomposed to give a mixture of products. Either 1,5-hexadiene or 2,6-dimethyl-1,5-hexadiene was detected by ^{1}H NMR spectroscopy in all cases, but the metal-containing products could not be identified. The NHC-supported complex **8** is significantly more stable than compounds **5**−**7** and decomposed very slowly at room temperature to give a complex mixture. On the other hand, the unsubstituted NHC-supported compound **4** decomposed cleanly to give a single product (eq 3). On the basis of ^{1}H and ^{13}C NMR spectroscopy we propose that this complex is the Ni^0 hexadiene species **9**. Unlike compound **4**, the room-temperature ^{1}H NMR spectrum of **9** was not fluxional and displayed three separate signals for the six protons corresponding to the coordinated olefins. The ^{1}H NMR spectrum showed that the resonance corresponding to the central allyl proton in **4** was shifted from δ 5.05 to 4.10 ppm when it became part of the coordinated olefin in **9**. The carbene resonance in the ^{13}C spectrum was observed at δ 206.1 ppm, which is considerably further downfield than the shift in **4** (δ 198.2 ppm), consistent with the decrease in oxidation state from **4** to **9**.



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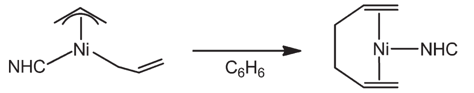


4 **9**

(3)

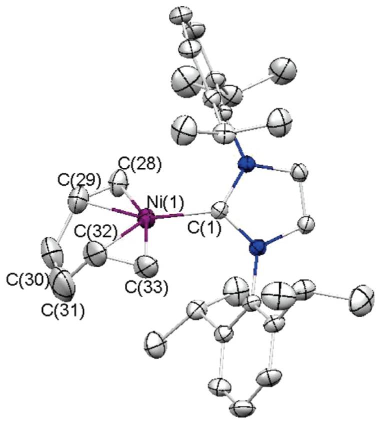
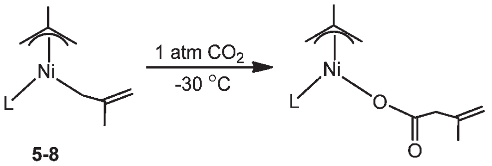


Figure 3. X-ray structure of **9** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) = 1.916(3), Ni(1)−C(28) = 2.045(4), Ni(1)−C(29) = 2.0022(5), Ni(1)−C(32) = 1.981(6), Ni(1)−C(33) = 2.022(5), C(28)−C(29) = 1.362(6), C(29)−C(30) = 1.543(8), C(30)−C(31) = 1.553(11), C(31)−C(32) = 1.477(10), C(32)−C(33) = 1.416(7); C(1)−Ni(1)−C(28) = 98.70(13), C(1)−Ni(1)−C(29) = 137.83(16), C(1)−Ni(1)−C(32) = 143.12(18), C(1)−Ni(1)−C(33) = 101.82(16), C(28)−Ni(1)−C(32) = 117.5(2), C(28)−Ni(1)−C(33) = 157.48(20).

Further confirmation of the structure of **9** was obtained through X-ray crystallography (Figure 3). In the solid state the geometry around the pseudo-three-coordinate Ni is approximately trigonal planar. The hexadiene ligand is clearly bound to Ni in an η^4 fashion, and the C−C bond lengths in the 1,5-hexadiene unit show that the olefins are in terminal positions with a saturated linker. The C−C bond lengths of the coordinated olefins (C(28)−C(29) = 1.362(6) Å and C(32)−C(33) = 1.416(7) Å) are consistent with moderate back-donation from the Ni to the olefins and indicate that the structure is unsymmetric.[37] Surprisingly, the Ni−NHC bond length in **9** (Ni(1)−C(1) = 1.916(3) Å) is similar to that observed in **8**, despite the change in formal oxidation state at the metal center. In general transition-metal complexes containing coordinated 1,5-hexadiene units are rare.[38−42] Two previous examples of structurally characterized Ni^0 species containing a coordinated η^4-1,5-hexadiene are known, but these complexes are both 18-electron species featuring two additional L type donors alongside the hexadiene.[43,44] However, a 16-electron Pt complex featuring one η^4-1,5-hexadiene ligand and a coordinated maleic anhydride group is known.[45] The structural parameters observed in that complex are similar to those observed in **9**.

At this stage it is unclear why the Ni species **4** decomposes to give the monomeric Ni^0 species **9**, whereas the analogous Pd complex $(allyl)_2Pd(NHC)$ decomposes to give a dimeric Pd^I species with bridging allyl ligands.[36] It should be noted that extended heating of the Pd^I bridging allyl dimers does eventually lead to the formation of Pd^0 but there is no evidence to suggest that a dimeric species is an intermediate in the formation of **9**.[46]

Reactions of $(allyl)_2Ni(L)$ Complexes with CO_2. Compounds **5**−**8** all reacted with CO_2 at low temperature (eq 4) to cleanly form the unidentate carboxylate species **10**−**13**, which were fully characterized. These reactions are similar to those described for analogous Pd systems (**I**−**IV**), and the rates of reaction are comparable.[27] IR spectroscopy indicated that in all cases the difference between the symmetric and asymmetric CO_2 stretch was greater than 200 cm^{-1}, which is consistent with the presence of a unidentate carboxylate.[47] The structure of **13** was elucidated by X-ray crystallography, which unequivocally confirmed the presence of both an η^3-allyl and a unidentate carboxylate (Figure 4). The coordination geometry around Ni is square planar, and the bond lengths and angles are unsurprising. The η^3-allyl ligand is again bound to Ni in an asymmetric fashion due to the differing *trans* influences of the NHC and carboxylate ligands, with the NHC being the stronger donor.



(4)

5-8

L = PMe_3 (**10**), PEt_3 (**11**), PPh_3 (**12**), NHC (**13**)

The resonances associated with the terminal hydrogens of the 2-methylallyl ligands in the ^1H NMR spectra of **10**−**13** are all fluxional. At low temperature (−70 °C) four distinct resonances are observed for the terminal protons in compounds **10**, **11**, and **13**, while for the PPh_3-supported complex **12** no resonances are visible. At room temperature one broad peak integrating to four protons is observed for **10**, two broad peaks each integrating to two protons each are observed for **11** and **12**, and none of the terminal protons of the 2-methylallyl ligand can be detected for **13**, as they have presumably broadened into the baseline. Unfortunately, the spectra were too complicated for line shape analysis to be used to accurately determine the rates of the fluxional processes and investigate the mechanism. However, it appears that two processes are occurring: an initial process which causes the four inequivalent protons to coalesce into two sets of two protons, followed by another process requiring more energy which results in all four protons becoming equivalent. Further support for this hypothesis is obtained by heating samples of **11** and **12** to 80 °C, which causes coalescence of the two sets of protons, so that only one broad peak integrating to four protons is observed. Presumably if the PPh_3-supported complex could be

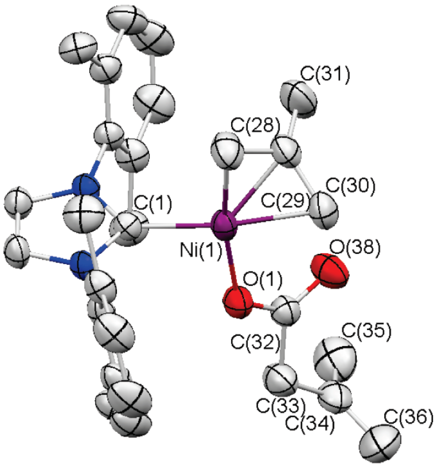
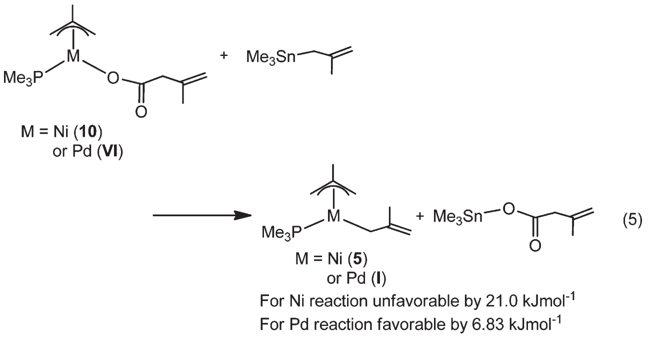


Figure 4. X-ray structure of **13** (hydrogen atoms and methyl groups of NHC ligand omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) = 1.921(2), Ni(1)−C(28) = 1.970(4), Ni(1)−C(29) = 1.985(3), Ni(1)−C(30) = 2.072(3), Ni(1)−O(1) = 1.9136(20), C(28)−C(29) = 1.406(4), C(29)−C(30) = 1.393(4), C(29)−C(31) = 1.504(4), O(1)−C(32) = 1.290(3), C(32)−O(38) = 1.227(3), C(32)−C(33) = 1.529(4), C(33)−C(34) = 1.504(4), C(34)−C(35) = 1.489(4), C(34)−C(36) = 1.317(5); Ni(1)−C(28)−C(29) = 69.75(19), Ni(1)−C(29)−C(30) = 73.32(18), Ni(1)−O(1)−C(32) = 127.71(16), C(1)−Ni(1)−C(28) = 94.30(11), C(30)−Ni(1)−O(1) = 97.79(11), O(1)−Ni(1)−C(1) = 96.07(8).

cooled past −70 °C, four separate resonances would eventually be observed.

The effect on rate of varying the ancillary ligand for CO_2 insertion into **5**−**8** is similar to that observed for Pd.[27] Thus, the rate of reaction increases as the ancillary ligand becomes more electron rich; therefore, $PPh_3 < PEt_3 < PMe_3 <$ NHC. Our previous studies on CO_2 insertion into Pd allyl complexes **I**−**IV** and a pincer-supported Ni η^1-allyl species suggest that CO_2 insertion occurs via nucleophilic attack of the terminal olefin of the η^1-allyl on electrophilic CO_2 (Scheme 1).[27,32] Our results with complexes **5**−**8** are consistent with this mechanism, and in all cases we believe that reaction occurs from the nucleophilic η^1:η^3-2-methylallyl isomer. Further support for this mechanism is provided by the observation that the unsubstituted allyl complexes **1**−**4** do not react with CO_2. At temperatures around −10 °C decomposition of **1**−**4** occurs before any insertion of CO_2. In our proposed mechanism the barrier for CO_2 insertion into an unsubstituted allyl is significantly higher than for the 2-methylallyl ligands because a secondary carbocation is formed in the transition state rather than a tertiary carbocation.[27]

In the case of the Pd carboxylate complexes **V**−**VIII**, treatment with allylstannanes or allylboranes results in transmetalation and the regeneration of the starting bis(allyl) complexes **I**−**IV** and a tin or boron carboxylate.[22] This reaction is a key component of our catalytic cycle for the carboxylation of allylstannanes and allylboranes with CO_2. In contrast, no reaction is observed between the Ni carboxylates **10**−**13** and either tri-*n*-butyl(2-methylallyl)stannane or (pincaol)(2-methylallyl)borane, even at elevated temperatures. Calculations using trimethyl(2-methylallyl)stannane and the Pd complex **V** and the Ni complex **10** show that, whereas transmetalation is favorable for Pd, it is unfavorable for Ni (eq 5). This suggests that achieving catalytic reactions with Ni will be significantly harder than with Pd and will require the use of transmetalating agents that form extremely strong metal−oxygen bonds.



For Ni reaction unfavorable by 21.0 $kJmol^{-1}$
For Pd reaction favorable by 6.83 $kJmol^{-1}$

CONCLUSIONS

We have prepared a series of complexes of the type $(allyl)_2Ni(L)$ and $(2\text{-methylallyl})_2Ni(L)$, including the first species supported by NHC ligands. NMR spectroscopy shows that these complexes are fluxional, while X-ray crystallography demonstrates that they can either be 18-electron species with two η^3-allyl ligands or 16-electron species with one η^1- and one η^3-allyl ligand. In general the 16-electron configuration is more likely to be preferred for complexes with strongly donating ancillary ligands, for complexes with methyl groups on the 2-position of the allyl ligand compared with an unsubstituted allyl ligand, and for Pd relative to Ni. In fact, to the best of our knowledge all known Pd species adopt the 16-electron conformation, while a mixture of 16- and 18-electron species is observed for Ni. Another difference between the properties of $(allyl)_2Ni(L)$ and $(2\text{-methylallyl})_2Ni(L)$ complexes in comparison with those of their Pd analogues is that Pd species decompose relatively cleanly to give Pd^I dimers, while Ni species decompose to give either monomeric Ni^0 hexadiene species or complex mixtures. This suggests that, at least in the cases where clean reactions occur, the Pd decomposition pathway is bimolecular, whereas the Ni pathway is unimolecular. At this stage further studies are required to fully understand the mechanistic pathway by which decomposition occurs.

The reactivity of complexes of the type $(2\text{-methylallyl})_2Ni(L)$ with CO_2 is similar to that previously reported for related Pd species.[27] The trend in the rate of reaction as the ancillary ligand is varied is identical, and we propose that the reaction follows the same mechanistic pathway. Unfortunately the unidentate carboxylate complexes formed from the insertion of CO_2 into $(2\text{-methylallyl})_2Ni(L)$ do not undergo transmetalation to regenerate $(2\text{-methylallyl})_2Ni(L)$ species. This prevents $(2\text{-methylallyl})_2Ni(L)$ species from being used as catalysts for the carboxylation of allylstananes and allylboranes using CO_2. If Ni catalysts for these reactions are to be developed, it appears that alternative methods for the liberation of the carboxylate fragment will need to be explored.

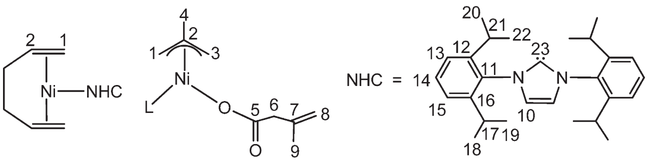
EXPERIMENTAL DETAILS

General Methods. Experiments were performed under a dinitrogen atmosphere in an M. Braun drybox or using standard Schlenk techniques. (Under standard glovebox conditions purging was not performed between uses of petroleum ether, diethyl ether, benzene, toluene, and tetrahydrofuran; 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. The solvents for air- and moisture-sensitive reactions 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. Anhydrous nickel chloride was purchased from Alfa Aesar, while PMe_3, PEt_3, and PPh_3 were purchased from Aldrich or Strem. Anhydrous CO_2 was obtained from Airgas, Inc. and was not dried prior to use. C_6D_6 and toluene-d_8 were dried over sodium metal. NMR spectra were recorded on Bruker AMX-400 and -500 spectrometers at ambient probe temperatures unless noted. Chemical shifts are reported with respect to residual internal protio solvent for ^{1}H and ^{13}C{^{1}H} NMR spectra and to an external standard for ^{31}P spectra (85% H_3PO_4 at 0.0 ppm). Atom numbering for the peak assignments is given below. All assignments are based on two-dimensional ^{1}H,^{13}C-HMQC and HMBC experiments. IR spectra were measured using a Diamond Smart Orbit ATR on a Nicolet 6700 FT-IR instrument. Robertson Microlit Laboratories, Inc. performed the elemental analyses (inert atmosphere). Literature procedures were followed to prepare the following compounds: 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-2*H*-imidazol-2-ylidene,[48] (allyl)$_2$Ni,[49] (2-methylallyl)$_2$Ni,[49] (allyl)$_2$Ni(PMe_3) (**1**),[33] (allyl)$_2$Ni(PEt_3) (**2**),[33] (allyl)$_2$Ni(PPh_3) (**3**),[33] (2-methylallyl)$_2$Ni(PMe_3) (**5**),[33] (2-methylallyl)$_2$Ni(PEt_3) (**6**),[33] and (2-methylallyl)$_2$(PPh_3)[33]. Compounds 5 and 7 were characterized by X-ray crystallography, and the single crystals were grown from a saturated pentane solution at −35 °C.

Computational Methods. Density functional calculations were carried out using Gaussian 09 Revision A.02.[50] Calculations were performed using the B3LYP functional. The LANL2DZ basis set and pseudopotential were used for Ni, Pd, and Sn, and the 6-31G++(d,p) basis set was used for all other atoms. Initial geometries were obtained using the coordinates from X-ray structures, and all optimized structures were verified using frequency calculations to check that they did not contain any imaginary frequencies. All energies given in the Results and Discussion are SCF energies. The coordinates for the optimized structures are given in the Supporting Information.

X-ray Crystallography. The diffraction experiments were carried out on a Rigaku Mercury275R CCD (SCX mini) diffractometer with a sealed tube at 23 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The software used was SMART for collecting frames of data, indexing reflections, and determination of lattice parameters, SAINT for integration of intensity of reflections and scaling, SADABS for empirical absorption correction, and SHELXTL for space group determination, structure solution, and least-squares refinements on $|F|^2$. The crystals were mounted at the end of glass fibers and used for the diffraction experiments. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed in their ideal positions. Details of the crystal and refinement data for complexes **5**, **7**−**9**, and **13** are given in the Supporting Information.

Synthesis and Characterization of New Compounds. The following numbering scheme is used for the purposes of assigning NMR data



*(η^1-allyl)(η^3-allyl)Ni(NHC) (**4**).* A solution of NHC (32 mg, 0.08 mmol) in toluene (0.5 mL) was added to a stirred solution of (allyl)$_2$Ni (12.5 mg, 0.08 mmol) in pentane (4 mL) at −40 °C. The mixture was stirred for 2 h. The resulting precipitate was collected by filtration and dried at −40 °C to give **4** as an orange solid. Yield: 38 mg (81%). This compound is thermally unstable and was stored at −30 °C (no elemental analysis was obtained due to the thermal instability). The ^{1}H NMR spectrum of **4** is provided in the Supporting Information.

^{1}H NMR (500 MHz, toluene-d_8, −70 °C): δ 7.14 (d, 4H, H13 and H15), 6.96 (m, 2H, H14, overlapping with solvent peak), 6.13 (s, 2H, H10), 5.05 (s, 2H, allyl-central H), 3.16 (br s, 4H, H17 and H21), 2.70 (br s, 8H, allyl-end H), 1.36 (br s, 12H, H18, H19, H20 or H22), 1.05 (br s, 12H, H18, H19, H20, or H22). ^{13}C{^{1}H} NMR (125.8 MHz, toluene-d_8, −70 °C): δ 198.2 (s, C23), 145.9 (s, C11), 137.0 (s, C12 and C16), 130.2 (s, C13 and C15), 125.3 (s, allyl-central C, overlapping with solvent peak), 124.4 (s, C14), 123.9 (s, C10), 57.4 (br s, allyl-end C), 29.1 (s, C17 and C21), 26.6 (s, C18, C19, C20, or C22), 23.0 (s, C18, C19, C20, or C22).

*(η^1-2-methylallyl)(η^3-2-methylallyl)Ni(NHC) (**8**).* A solution of NHC (64.5 mg, 0.17 mmol) in toluene (0.5 mL) was added to a stirred solution of (2-methylallyl)$_2$Ni (28 mg, 0.17 mmol) in pentane (4 mL) at −40 °C. The mixture was stirred for 2 h. The resulting precipitate was collected by filtration and dried at −40 °C to give **8** as an orange solid. Orange single crystals for X-ray analysis were grown from pentane at −35 °C. Yield: 78 mg (85%). Anal. Calcd (found) for $C_{35}H_{50}N_2Ni$: C, 75.41 (75.18); H, 9.04 (8.91); N, 5.02 (5.12).

^{1}H NMR (500 MHz, toluene-d_8, −70 °C): δ 7.14 (d, 4H, H13 and H15), 6.96 (m, 2H, H14, overlapping with solvent peak), 6.13 (s, 2H, H10), 5.05 (s, 2H, allyl-central H), 3.16 (br s, 4H, H17 and H21), 2.70 (br s, 8H, allyl-end H), 1.36 (br s, 12H, H18, H19, H20, or H22), 1.05 (br s, 12 H, H18, H19, H20, or H22). ^{13}C{^{1}H} NMR (125.8 MHz, toluene-d_8, −70 °C): δ 199.1 (s, C23), 146.3 (s, C12), 145.9 (s, C16), 139.0 (s, C11), 137.6 (s, C12), 130.2 (s, C13 and C15), 124.2 (s, C14), 124.0 (s, C10), 121.6 (s, allyl-central C), 36.1 (s, allyl-end C), 29.1 (s, C17), 29.0 (s, C21), 26.6 (s, C18, C19, C20, or C22), 25.6 (s, C18, C19, C20, or C22), 25.3 (s, Me from allyl), 23.6 (s, C18, C19, C20, or C22), 23.0 (s, C18, C19, C20, or C22).

*(1,5-hexadiene)Ni(NHC) (**9**).* NHC (26 mg, 0.07 mmol) was added to a stirred solution of (allyl)$_2$Ni (9.3 mg, 0.07 mmol) in toluene (2 mL) at −40 °C. The mixture was warmed to room temperature and heated to 40 °C for 3 h. The mixture was evaporated to dryness to give **9** as an orange powder. Orange single crystals for X-ray analysis were grown from pentane at −35 °C. Yield: 32 mg (91%). Anal. Calcd (found) for $C_{33}H_{46}N_2Ni$: C, 74.87 (72.65); H, 8.76 (8.84); N, 5.29 (5.28). The ^{1}H NMR spectrum of **9** is provided in the Supporting Information.

^{1}H NMR (500 MHz, C_6D_6): δ 7.18 (t, 8 Hz, 2H, C14), 7.62 (d, J = 8 Hz, 4H, C13 and C15), 6.64 (s, 2H, H10), 4.10 (m, 2H, H2), 3.23 (m, 4H, H17 and H21), 2.61 (m, 2H, CH_2), 2.58 (d, J = 9 Hz, 2H, H1), 2.20 (d, J = 13 Hz, 2H, H1′), 1.52 (m, 2H, CH_2), 1.32 (d, J = 7 Hz, 12H, 12H, H18, H19, H20, or H22), 1.08 (d, J = 7 Hz, 12H, H18, H19, H20, or H22). ^{13}C{^{1}H} NMR (125.8 MHz): δ 206.1 (s, C23), 146.6 (s, C11), 138.4 (s, C16), 129.7 (s, C14), 128.7 (s, C10), 124.1 (s, C13 and C15), 123.2 (s, C12 and C16), 76.7 (s, C2), 54.4 (s, C1), 36.5 (s, CH_2), 29.0 (s, C17 and C21), 26.2 (s, C18, C19, C20, or C22), 23.1 (s, C18, C19, C20 or C22).

*(η^3-2-methylallyl)(η^1-$CO_2C_4H_7$)Ni(PMe_3) (**10**).* To a solution of (2-methylallyl)$_2$Ni (235 mg, 1.4 mmol) in toluene (2 mL) at −78 °C was added PMe_3 (0.15 mL, 1.40 mmol). The mixture was then degassed using three freeze−pump−thaw cycles and warmed to −40 °C. Excess 1 atm CO_2 was then added via a dual-manifold Schlenk line at −40 °C. The mixture was slowly warmed to room temperature. After 3 h the mixture was evaporated to dryness to give **10** as a brown powder. Yield: 390 mg (97%). Anal. Calcd (found) for $C_{12}H_{23}O_2PNi$: C, 49.88 (49.21); H, 8.02 (7.98).

IR (cm^{-1}): 1581 (ν_{asym,CO_2}), 1282 ($\nu_{sym,CO}$). ^{1}H NMR (500 MHz, C_6D_6): δ 5.06 (m, 1H, H8), 4.96 (m, 1H, H8′), 3.39 (s, 2H, H6), 2.62 (br s, 4H, H1 and H3), 2.15 (s, 3H, H9), 1.64 (s, 3H, H4), 0.99 (d, J = 5 Hz, 9H, PMe_3). ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8, −15 °C): δ 176.4 (s, CO_2), 143.9 (s, C7), 124.0 (s, C2), 112.7 (s, C8), 69.4 (s, C3), 47.8 (s, C6), 42.6 (s, C1), 24.1 (s, C9), 23.8 (s, C4), 14.0 (d, J_{C-P} = 24 Hz, PCH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ −11.4 (s).

*(η^3-2-methylallyl)(η^1-$CO_2C_4H_7$)Ni(PEt_3) (**11**).* To a solution of (2-methylallyl)$_2$Ni (225 mg, 1.33 mmol) in toluene (2 mL) at −78 °C was added PEt_3 (0.20 mL, 1.33 mmol). The mixture was then degassed using three freeze−pump−thaw cycles and warmed to −40 °C. Excess 1 atm CO_2 was added via a dual-manifold Schlenk line at −40 °C. The mixture was slowly warmed to room temperature. After 3 h the mixture was evaporated to dryness to give **11** as a brown-orange oil. Yield: 430 mg (97.5%). Anal. Calcd (found) for $C_{15}H_{29}O_2PNi$: C, 54.42 (51.19); H, 8.83 (8.64). The ^{1}H NMR spectrum of **11** is provided in the Supporting Information.

IR (cm^{-1}): 1580 (ν_{asym,CO_2}), 1284 (ν_{sym,CO_2}). ^{1}H NMR (500 MHz, toluene-d_8): δ 4.93 (s, 1H, H8), 4.87 (s, 1H, H8′), 3.20 (s, 2H, H6), 2.70 (br s, 2H, H1 and H3), 2.15 (br s, 2H, H1′ and H3′, overlapping with solvent), 2.02 (s, 3H, H9), 1.98 (s, 3H, H4), 1.20 (m, 6H, P*CH*$_2$CH$_3$), 0.89 (m, 9H, PCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8): δ 175.5 (s, CO_2), 143.6 (s, C7), 123.3 (s, C2), 111.8 (s, C8), 47.7 (s, C6), 23.3 (s, C4), 23.1 (s, C9), 15.9 (d, PCH_2, J_{C-P} = 17 Hz), 8.14 (s, PCH_2CH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ −19.1 (s).

*(η^3-2-methylallyl)(η^1-$CO_2C_4H_7$)Ni(PPh_3) (**12**).* To a solution of (2-methylallyl)$_2$Ni (12.1 mg, 0.086 mmol) in toluene (4 mL) at −78 °C was added PPh_3 (23 mg, 0.086 mmol). The mixture was then degassed using three freeze−pump−thaw cycles and warmed to −40 °C. Excess 1 atm CO_2 was added via a dual-manifold Schlenk line at −40 °C. The mixture was slowly warmed to room temperature. After 10 h the mixture was evaporated to dryness. The resulting residue was extracted with pentane, and the extract was dried to give **12** as an orange powder. Yield: 10.1 mg (30.1%). Anal. Calcd (found) for $C_{27}H_{29}O_2PNi$: C, 68.25 (68.04); H, 6.15 (5.93).

IR (cm^{-1}): 1587 (ν_{asym,CO_2}), 1360 (ν_{sym,CO_2}). ^{1}H NMR (500 MHz, C_6D_6): δ 7.58 (br s) and 7.01 (br s) (15H, Ph), 4.86 (m, 2H, H8), 3.08 (s, 2H, H6), 2.62 (br s, 2H, H1 and H3) and 2.34 (br s, 4H, H1′ and H3′), 2.02 (s, 3H, H9), 1.85 (s, 3H, H4). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 176.6 (s, CO_2), 145.8 (s, C7), 143.6 (s, C2), 134.5, 134.4, 129.7, 129.1, and 126.0 (Ph), 110.8 (s, C8), 59.8 (s, C3), 51.5 (s, C1), 47.7 (s, C6), 24.7 (s, C9), 22.8 (s, C4). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 24.82 (s).

*(η^3-2-methylallyl)(η^1-$CO_2MeC_3H_4$)Ni(NHC) (**13**).* To a solution of (2-methylallyl)$_2$Ni (168 mg, 1.0 mmol) in toluene (2 mL) at −78 °C was added NHC (388 mg, 1.0 mmol), and the mixture was stirred for 2 h. The mixture was then degassed using three freeze−pump−thaw cycles and warmed to −40 °C. Excess 1 atm CO_2 was added via a dual-manifold Schlenk line at −40 °C. The mixture was slowly warmed to room temperature. After it was stirred for 1 h, the mixture was evaporated to dryness to give **13** as a yellow powder. Colorless single crystals for X-ray analysis were grown from toluene/pentane at −35 °C. Yield: 445 mg (74%). Anal. Calcd (found) for $C_{36}H_{50}N_2O_2Ni$: C, 71.89 (71.76); H, 8.38 (8.61).

IR (cm^{-1}): 1602 (ν_{asym,CO_2}), 1327 (ν_{sym,CO_2}). ^{1}H NMR (500 MHz, toluene-d_8, −35 °C): δ 7.23 (t, 2H, H14), 7.14 (m, 4H, H13 and H15, overlapping with solvent peak), 6.48 (s, 2H, H10), 5.03 (s, 2H, H8), 3.16 (m, 4H, H17 and H21), 2.91 (br s, 2H, H6), 3.69 (s, 1H), 2.53 (s, 1H), 1.61 (s, 1H) and 0.85 (s, 1H), 2.62 (H1 and H3), 2.05 (s, 3H, H9), 1.73 (s, 3H, H4), 1.45 (br s, 12H, H18, H19, H20, or H22), 1.03 (m, 12 H, H18, H19, H20, or H22). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 188.7 (s, C23), 176.2 (s, C5), 146.4 (s, C11), 144.6 (s, C7), 137.1 (s, C16), 130.4 (s, C14), 128.7 (s, C2), 124.9 (s, C10), 124.6 (s, C12 and C16), 111.5 (s, C8), 47.8 (s, C6), 29.1 (s, C21), 26.4 (s, C20 and C22), 23.8 (s, C9), 23.2 (s, C18 and C19), 22.3 (s, C4).

Reactions between CO_2 and (allyl)$_2$Ni(L) Complexes. In an typical reaction 8 mg of (allyl)$_2$Ni(PMe_3) (**1**), (allyl)$_2$Ni(PEt_3) (**2**), (allyl)$_2$Ni(PPh_3) (**3**), or (allyl)$_2$Ni(NHC) (**4**) was dissolved in 0.4 mL of toluene-d_8 in a J. Young NMR tube at −78 °C. The mixture was then degassed using three freeze−pump−thaw cycles, and excess 1 atm CO_2 was added via a dual-manifold Schlenk line at −78 °C. No reaction was observed with CO_2 before decomposition of the starting material occurred at approximately −10 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures giving NMR spectra of selected compounds, tables and CIF files giving details of the X-ray structures, and tables giving *xyz* coordinates for optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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