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Palladium(I)-Bridging Allyl Dimers for the Catalytic Functionalization of CO_2

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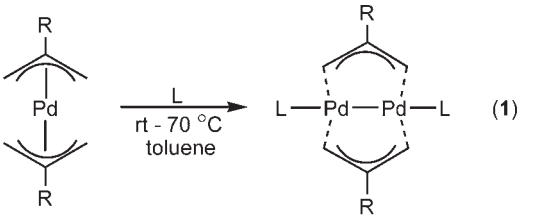
Supporting Information

ABSTRACT: In general, the chemistry of both η^1-allyl and η^3-allyl Pd complexes is extremely well understood; η^1-allyls are nucleophilic and react with electrophiles, whereas η^3-allyls are electrophilic and react with nucleophiles. In contrast, relatively little is known about the chemistry of metal complexes with bridging allyl ligands. In this work, we describe a more efficient synthetic methodology for the preparation of Pd^I-bridging allyl dimers and report the first studies of their stoichiometric reactivity. Furthermore, we show that these compounds can activate CO_2 and that an N-heterocyclic carbene-supported dimer is one of the most active and stable catalysts reported to date for the carboxylation of allylstannanes and allylboranes with CO_2.

In recent years, there has been significant interest in the catalytic functionalization of CO_2 because of the potential for use of this greenhouse gas as a readily available and inexpensive source of carbon in the synthesis of both commodity chemicals and complex organic molecules.[1] Several transition-metal complexes have been developed as catalysts for carboxylation reactions, and the key step is proposed to involve a reaction between the metal complex and CO_2.[2] Recently, both Wendt and our group have reported studies of the mechanism of CO_2 insertion into monomeric η^1-allyl Pd complexes and shown that these species are catalytically active for the carboxylation of allylstannanes and allylboranes.[3] During our studies of η^1-allyl Pd systems, we discovered that Pd(I)-bridging allyl dimers also undergo insertion of CO_2 to form a bridging carboxylate, and we report our findings here.

In general, the chemistry of both η^1-allyl and η^3-allyl Pd complexes is well-understood; η^1-allyls are nucleophilic and react with electrophiles, whereas η^3-allyls are electrophilic and react with nucleophiles.[4] In contrast, relatively little is known about the chemistry of metal complexes with bridging allyl ligands.[5] Only a handful of species of this type have been prepared, and their reactivity has not been probed in detail.[6] A particularly interesting class of bridging allyl Pd species consists of Pd^I dimers, which contain a metal−metal bond, two bridging allyl ligands, and a terminal phosphine ligand.[6b,7] Three examples of these complexes have been described, and generally they are generated by reductive dimerization from isolated complexes of the type (η^1-allyl)(η^3-allyl)Pd(L) with concomitant elimination of hexadiene.[6b,7a,7c] Unfortunately, (η^1-allyl)(η^3-allyl)Pd(L) complexes are air-, moisture-, and thermally sensitive, which makes working with these compounds difficult. Here we describe a more efficient synthetic methodology for the preparation of Pd^I-bridging allyl dimers and report the first studies of their stoichiometric reactivity. Our preliminary studies suggest that bridging allyl ligands are nucleophilic like η^1-allyl ligands rather than electrophilic like η^3-allyl ligands. Furthermore, we show that these compounds can activate CO_2 and that an N-heterocyclic carbene (NHC)-supported dimer is one of the most active and stable catalysts reported to date for the carboxylation of allylstannanes and allylboranes with CO_2.

Initially, the bridging allyl dimers **1**−**8** were prepared through the direct reaction of Pd(allyl)$_2$ or Pd(2-methylallyl)$_2$ with the appropriate free ligand (eq 1). This was a high-yielding and efficient route that allowed us to isolate a family of bridging allyl dimers, including those supported by NHC ligands. Our synthesis is an improvement on the literature route and avoids the isolation of compounds of the type (η^1-allyl)(η^3-allyl)Pd(L). However, Pd(allyl)$_2$ species are also thermally unstable and difficult to synthesize. A far superior synthesis of **1**−**8** involves treatment of the commercially available compounds [(η^3-allyl)Pd(μ-Cl)]$_2$ or [(η^3-2-methylallyl)Pd(μ-Cl)]$_2$ with the free ligand followed by reaction of the (η^3-allyl)Pd(L) or (η^3-2-methylallyl)Pd(L) intermediate with the appropriate allyl Grignard reagent (Scheme 1). The monomeric η^3-allyl Pd intermediates can be isolated, or the reaction can be performed in two sequential steps in one pot. In general, the yields of **1**−**8** are excellent, with only **4** and **8** being formed in less than 50% yield.



R = H; L = PMe_3 (**1**), PEt_3 (**2**), PPh_3 (**3**) or NHC (**4**)
R = Me; L = PMe_3 (**5**), PEt_3 (**6**), PPh_3 (**7**) or NHC (**8**)
NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene

Compounds **1**−**8** were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis (**1** and **3** have been previously reported[3c,7a]). In addition, crystals of **2**, **4**, and **6** were grown from saturated solutions at temperatures from −35 °C to room temperature. Compounds **2**, **4**, and **6** have similar geometries, and their structures are shown in Figure 1, Figure S1 in the Supporting Information, and Figure 2, respectively. Each allyl ligand is bound through the central carbon to both Pd atoms,

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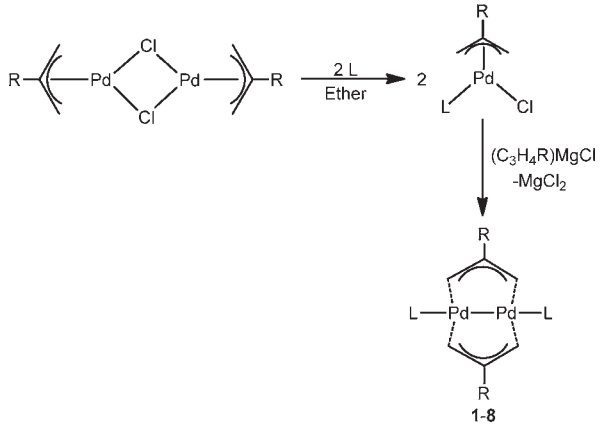
Scheme 1



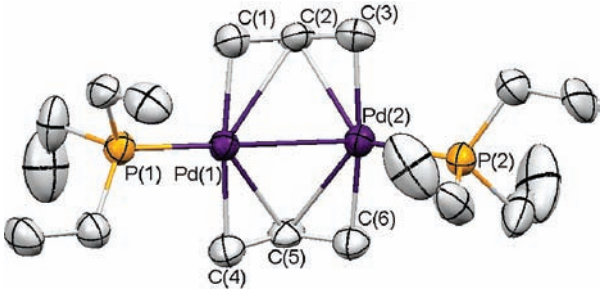


Figure 1. X-ray structure of **2** (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2), 2.7112(4); Pd(1)−P(1), 2.2591(12); Pd(2)−P(2), 2.2512(12); Pd(1)−C(1), 2.106(5); Pd(1)−C(2), 2.611(2); Pd(1)−C(4), 2.151(5); Pd(1)−C(5), 2.437(4); Pd(2)−C(3), 2.158(5); Pd(2)−C(2), 2.429(4); Pd(2)−C(6), 2.120(5); Pd(2)−C(5), 2.613(5); P(1)−Pd(1)−Pd(2), 157.47(5); P(2)−Pd(2)−Pd(1), 153.66(4).

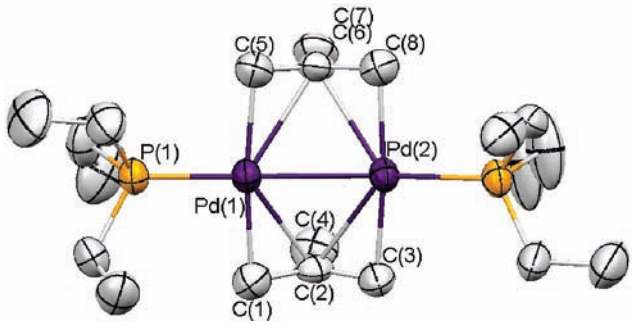
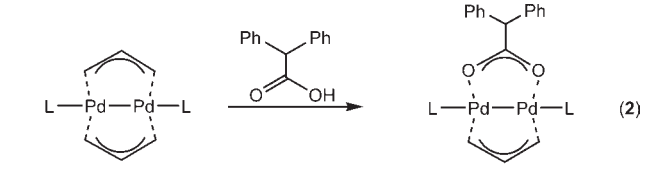
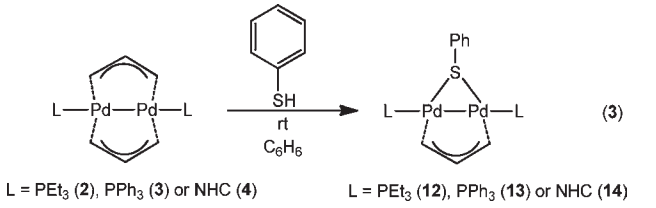


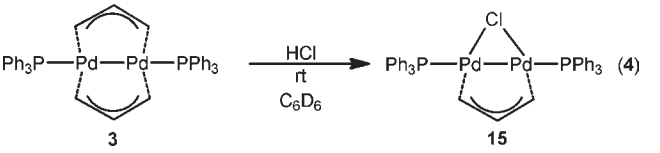
Figure 2. X-ray structure of **6** (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2), 2.6920(5); Pd(1)−P(1), 2.22457(16); Pd(2)−P(2), 2.2246(15); Pd(1)−C(1), 2.118(7); Pd(1)−C(2), 2.510(2); Pd(1)−C(5), 2.112(7); Pd(1)−C(6), 2.549(4); Pd(2)−C(3), 2.108(6); Pd(2)−C(2), 2.553(4); Pd(2)−C(8), 2.122(7); Pd(2)−C(6), 2.511(5); P(1)−Pd(1)−Pd(2), 157.47(5); P(2)−Pd(2)−Pd(1), 153.66(4).

while the terminal carbons bind only to the Pd atom in closest proximity. Interestingly, although in the 2-methylallyl compound **6** the central carbon of the 2-methylallyl groups is approximately equidistant from the two Pd atoms, there is a significant distortion in both **2** and **4** (the Pd−central carbon distance varies by ∼0.2 Å in **2** and **4**). In all of the compounds, the two allyl (or 2-methylallyl ligands) are oriented in a syn geometry, so the central hydrogen atoms (or methyl groups) are eclipsed and on the same face of the molecule. The phosphine or NHC ligands are bent away from the central hydrogen atom (or methyl group) of the allyl ligands, and the P−Pd−Pd or C−Pd−Pd (C of NHC) bond angles are significantly less than 180°. The short Pd−Pd distances [e.g., Pd(1)−Pd(2) = 2.7112(4) Å for **2**] are consistent with a single bond between the two metal centers and an oxidation state of Pd^{I}. Compounds **2** and **6** are only the second and third examples of structurally characterized Pd complexes with two bridging allyl ligands,[7b] while **4** is just the second example of a well-characterized NHC-supported Pd(I) species.[8]

In order to probe the reactivity of bridging allyl dimers, compounds **2**−**4** were used as models. Treatment with 1 equiv of diphenylacetic acid led to protonation of one of the bridging allyl ligands and the formation of dimers **9**−**11** containing both a bridging carboxylate ligand and a bridging allyl ligand (eq 2). These products were spectroscopically characterized. Although the reactions with **2** and **3** gave quantitative conversion, a second unidentified product was formed in ∼30% yield in the case of the NHC-supported complex **4**. Surprisingly, treatment with further equivalents of acid did not lead to protonation of the second bridging allyl ligand. Phenylthiol also reacted with **2**−**4** to give species **12**−**14** containing one bridging thiolate ligand and one bridging allyl ligand (eq 3), which were characterized spectroscopically. These protonation reactions with thiols are similar to the protonation reactions that Pd^{I} species with one bridging allyl ligand and one bridging cyclopentadienyl ligand have been shown to undergo.[9] Reaction of **3** with 1 equiv of HCl gave the mixed allyl−chloride species **15** (eq 4). Control experiments showed that whereas (η^1-allyl)(η^3-allyl)Pd(PPh_3) reacts with HCl to form (η^3-allyl)PdCl(PPh_3), no further reaction of the electrophilic η^3-allyl product with excess HCl is observed. Overall, these protonation reactions suggest that our bridging allyl is nucleophilic like an η^1-allyl.







Reaction of excess H_2 with **2**−**4** resulted in the generation of propene and propane and the formation of Pd black. In the case

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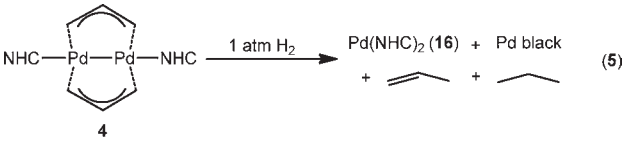
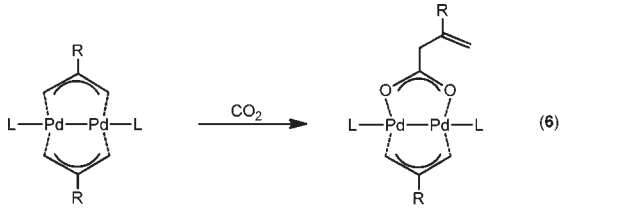
of **4**, a 50% yield of the Pd^0 species $Pd(NHC)_2$ (which was crystallographically characterized; see Figure S2) was obtained along with the Pd black (eq 5). In these reactions, H_2 presumably reacts with the bridging allyl to form propene and generate a species containing a Pd−H bond. The Pd−H bond then decomposes to form Pd black or, in the case of the NHC complex, a stable Pd^0 species.



The most interesting reactions of the bridging allyl dimers were observed with CO_2. Compounds **1**, **2**, and **4**−**8** all react with CO_2 to form the corresponding bridging carboxylates **17**−**23** (eq 6); these are the first examples of a reaction between CO_2 and a bridging allyl on any metal. All of the reactions gave quantitative conversion except for insertion into **8**, which gave the expected product **23** and an unidentified product in a 4:1 ratio. As a result, **23** was characterized only spectroscopically and not studied further. Compounds **17**−**23** are stable at room temperature in solution, and further exposure to CO_2 does not lead to the insertion of a second molecule of CO_2. The insertion of CO_2 is irreversible, and exposure of **19** to $^{13}CO_2$ did not lead to the incorporation of the label into the product. The IR spectra of **17**−**23** are consistent with a bridging carboxylate ligand, with the difference between the CO_2 stretches being less than 200 cm^{-1} in all cases.[10] For example, two CO_2 stretches were observed at 1558 and 1392 cm^{-1} for **22**. These bands shifted to 1517 and 1366 cm^{-1} when $^{13}CO_2$ was used to synthesize **22** (calcd 1523 and 1360 cm^{-1}).



Complexes **20** and **22** were crystallographically characterized, and the structures are shown in Figures 3 and 4. The single bridging 2-methyallyl ligand is bound to each Pd through two carbons, in an analogous fashion to **2** and **6**, while the bridging carboxylate binds only through the oxygen atoms. The alkyl group of the carboxylate is on the opposite face of the molecule from the methyl group of the allyl, and the P−Pd−Pd bond angles are much closer to 180 °C than in **2** and **6**. The Pd−Pd distances [Pd(1)−Pd(2) = 2.6267(3) Å for **20**] are shorter than those observed in **2** and **6** but still consistent with a single bond.

The rates of reaction with CO_2 vary depending on the substituent on the allyl group and the ancillary ligand, with reactions observed from room temperature to 70 °C. For the allyl ligand, the rate is NHC > PEt_3 > PMe_3, with no reaction observed for the PPh_3-supported ligand, while for the 2-methylallyl ligand, the rate is NHC > PPh_3 > PEt_3 > PMe_3. The reactions are faster for 2-methyallyl than for allyl. In all cases, the reactions of the dimeric species are significantly slower than for the monomeric species (η^1-2-methylallyl)(η^3-2-methyallyl)Pd(L) (L = PR_3, NHC), which react with CO_2 at approximately −30 °C.[3c] The

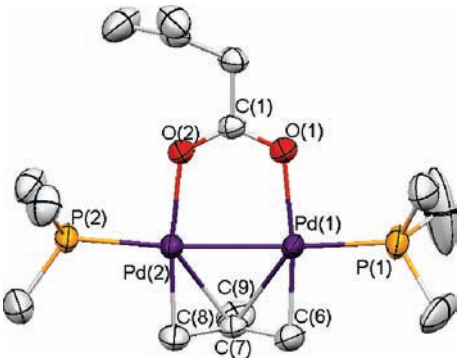


Figure 3. X-ray structure of **20** (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2), 2.6386(5); Pd(1)−P(1), 2.3018(10); Pd(2)−P(2), 2.3086(10); Pd(1)−O(1), 2.175(3); Pd(2)−O(2), 2.164(3); Pd(1)−C(6), 2.041(5); Pd(1)−C(7), 2.464(1); Pd(2)−C(7), 2.456(4); Pd(2)−C(8), 2.046(5); P(1)−Pd(1)−Pd(2), 172.92(3); P(2)−Pd(2)−Pd(1), 169.83(2).

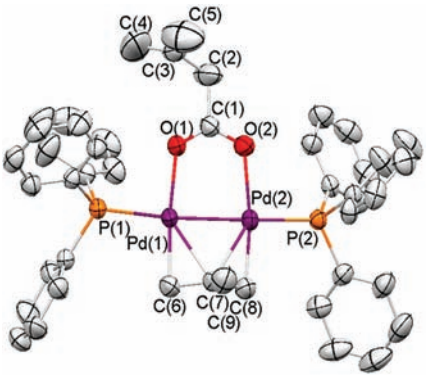


Figure 4. X-ray structure of **22** (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2), 2.6267(3); Pd(1)−P(1), 2.3044(9); Pd(2)−P(2), 2.3069(10); Pd(1)−O(1), 2.133(3); Pd(2)−O(2), 2.186(3); Pd(1)−C(6), 2.044(6); Pd(1)−C(7), 2.397(3); Pd(2)−C(7), 2.494(3); Pd(2)−C(8), 2.035(6); P(1)−Pd(1)−Pd(2), 161.16(2); P(2)−Pd(2)−Pd(1), 172.98(2).

mechanism of CO_2 insertion is unclear, but it is interesting to note that whereas nucleophilic terminal η^1-allyl ligands react with CO_2, electrophilic terminal η^3-allyl ligands do not. This again suggests that the bridging allyl ligand has reactivity similar to that of an η^1-allyl ligand.

We have recently demonstrated that complexes of the type (η^1-2-methylallyl)(η^3-2-methylallyl)Pd(L) (L = PR_3, NHC) are extremely effective catalysts for the carboxylation of allylstannanes and allylboranes.[3d] The proposed mechanism involves two steps: insertion of CO_2 followed by transmetalation. No reaction was observed in transmetalation reactions between the phosphine-supported carboxylates (**17**, **18**, and **20**−**22**) and tributylallylstannane. However, reaction of **19** with tributylallylstannane resulted in the generation of **4** and a tin carboxylate, suggesting that catalysis may be possible. In fact, **4** is a highly active catalyst for the carboxylation of allylstannanes with CO_2 (eq 7 and Table 1) and is comparable in reactivity with the best systems that have been reported.[3a,d] Compound **4** is also able to catalyze the carboxylation of allylboranes with an efficiency similar to that of our previously reported system.[3d] The major advantage of the

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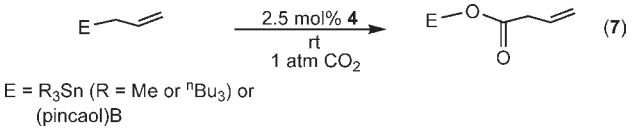
Table 1. Carboxylation of Different Allylstannanes and Allylboranes with CO_2 in C_6D_6 Using Complex 4 as the Catalyst[a]

substrate	time (h)	conversion (%)
Me_3Sn(2-methylallyl)	20	79
$^nBu_3Sn$(2-methylallyl)	24	80
Me_3Sn(allyl)	26	70
$^nBu_3Sn$(allyl)	24	82
(pinacol)B(allyl)	26	60
(pinacol)B(2-methylallyl)	55	81

[a] Reaction conditions: substrate (0.118 mmol), catalyst **4** (3.8 mg, 0.0059 mmol), and CO_2 (1 atm) in 0.25 mL of C_6D_6 at room temperature (unless otherwise stated).

dimeric system is that it is significantly easier to synthesize than monomeric systems and is more stable; thus, there is less catalyst decomposition, and the catalyst is capable of higher turnover numbers.



(7)

In conclusion, we have developed a facile synthesis for the preparation of allyl-bridged Pd^I dimers and performed the first reactivity studies with these molecules. An NHC-supported dimer is one of the most active catalysts reported to date for the catalytic carboxylation of allylstannanes and allylboranes with CO_2. From our results, it appears that bridging allyls react more like terminal η^1-allyls than η^3-allyls, and future work will look to further compare the reactivity of bridging allyls with terminal η^1-allyls and understand the mechanism of CO_2 insertion into bridging allyls.

■ ASSOCIATED CONTENT

Supporting Information. Experimental protocols, characterization data for all new compounds, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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