

NIH Public Access

Author Manuscript

Organometallics. Author manuscript; available in PMC 2011 November 2.

Published in final edited form as:

Organometallics. 2010 November 2; 29(23): 6369-6376. doi:10.1021/om1007456.

The Reaction of Carbon Dioxide with Palladium Allyl Bonds

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Abstract

A family of palladium allyl complexes of the type bis(2-methylallyl)Pd(L) (L = PMe₃ (1), PEt₃ (2), PPh₃ (3) or NHC (4); NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2ylidene) have been prepared through the reaction of bis(2-methylallyl)Pd with the appropriate free ligand. Compounds 1–4 contain one η^1 and one η^3 -2-methylallyl ligand and 3 was characterized by X-ray crystallography. These complexes react rapidly with CO₂ at low temperature to form well defined unidentate palladium carboxylates of the type (η^3 -2-methylallyl)Pd(OC(O)C₄H₇)(L) (L = PMe₃ (6), PEt₃ (7), PPh₃ (8) or NHC (9). The structure of 9 was elucidated using X-ray crystallography. The mechanism of the reaction of 1–4 with CO₂ was probed using a combination of experimental and theoretical (density functional theory) studies. The coordination mode of the allyl ligand is crucial and whereas nucleophilic η^1 -allyls react rapidly with CO₂, η^3 -allyls do not react. We propose that the reaction of η^1 -palladium allyls with CO₂ does not proceed via direct insertion of CO₂ into the Pd-C bond but through nucleophilic attack of the terminal olefin on electrophilic CO₂, followed by an associative substitution at palladium.

Introduction

In recent years there has been significant interest in the catalytic functionalization of CO_2 due to the potential 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 already been developed as catalysts for carboxylation reactions and the key step is proposed to involve a reaction between the metal center and CO_2 .1a-d In particular the formation of palladium carboxylates from the reactions of palladium allyl species with CO_2 has been suggested as a crucial step in several catalytic cycles. These include systems for the coupling of CO_2 with butadiene to form lactones,² the carboxylation of allyl stannanes³ and allenes⁴ and the carboxylative coupling of allylstannanes and allyl halides.⁵ A pioneering example in this area was the report by Nicholas and Shi that Pd(PPh₃)₄ can catalyze the coupling of allylstannanes with CO_2 to form tin carboxylates at elevated pressure (33 atom of CO_2) and temperature (70 °C).^{3a} The mechanism of this reaction has not been thoroughly investigated but is proposed to involve the insertion of CO_2 into palladium(II) allyls formed *in situ* and recent work by Johansson and Wendt supports this hypothesis.^{3b}

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Supporting Information Available

X-ray information for 3, 9 and $(\eta^3$ -allyl)Pd(PMe₃)Cl and computational details are available free of charge via the Internet at http://pubs.acs.org.

Despite these intriguing results there has been little research investigating stoichiometric reactions of well defined palladium allyl complexes with CO₂ and the feasibility, scope and mechanism of this reaction remain unclear. Preliminary work almost thirty years ago suggested that palladium allyls react with CO₂, but well defined and characterized metal complexes were not isolated.⁶ In a review article in 1985 Jolly reported that the reaction of bis(2-methylallyl)Pd(PPh₃) with CO₂ led to the formation of a crystallographically characterized insertion product, but no details of the reaction were presented.⁷ More recently Wendt and Johansson demonstrated that mixtures of palladium allyl and palladium hydride species with pincer ligands react with CO₂ to give palladium carboxylate species and proposed a preliminary mechanism for this transformation.^{3b} However analysis of this reaction was complicated by the presence of two complexes in the starting material. In this work, we conclusively establish that the reaction of CO_2 with a variety of palladium allyl complexes is facile and demonstrate that the coordination mode of the allyl ligand is critical. Furthermore, through a combination of experimental and computational studies, we propose a mechanism for this reaction which does not involve direct coordination of CO₂ to the metal center.

Results and Discussion

Synthesis of Palladium Allyls and Reaction with CO₂

A family of palladium allyl complexes of the type bis(2-methylallyl)Pd(L) (L = PMe₃ (1), PEt₃ (2), PPh₃ (3) or NHC (4); NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2Himidazol-2-ylidene) were prepared through the reaction of bis(2-methylallyl)Pd with one equivalent of ligand, L, at low temperature (Eq 1). The ¹H NMR spectra of 1–4 are all highly fluxional and indicate rapid exchange between the 2-methylallyl ligands. At low temperature ($-60 \,^{\circ}$ C) the exchange is sufficiently slow on the NMR timescale to suggest the complex contains one η^1 and one η^3 -2-methylallyl ligand, and has an analogous structure to that proposed for bis(allyl)Pd(L) (L = PR₃).8 For example at room temperature the ¹H NMR spectrum of bis(2-methylallyl)Pd(PEt₃) (2) contains only two resonances for the 2methyallyl ligands in the ratio 8 (for the 4 CH₂ groups) to 6 (for the 2 CH₃ groups). In contrast at low temperature 10 resonances are observed for the 2-methylallyl ligands, as each of the 8 protons associated with CH₂ groups gives a unique resonance and the two methyl groups give distinct signals. Compounds 1, 3 and 4 display similar properties.



L = PMe₃ (**1**), PEt₃ (**2**), PPh₃ (**3**), NHC (**4**) NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3dihydro-2H-imidazol-2-ylidene

(1)

Crystals of **3** were grown from a toluene/pentane solution at -35 °C and the structure is shown in Figure 1. The bond lengths and angles are consistent with one η^1 and one η^3 -2-methylallyl ligand and the coordination geometry around Pd is square planar. To the best of our knowledge, **3** is the first structurally characterized palladium complex with two different coordination modes for the allyl ligands and is a rare example of a crystallographically characterized palladium η^1 -allyl (especially without pincer ligands).⁹ A similar η^1, η^3 -Pt

Compounds 1–4 are thermally unstable and decompose in solution at room temperature in the case of 2 and at temperatures above -20 °C for 1, 3 and 4. In most cases the products of decomposition are not clear, however, 3 decomposes relatively cleanly to give the dimeric bridging 2-methylallyl Pd^I species 5 and one equivalent of 2,5-dimethylhexa-1,5-diene (Eq 2). A similar process has previously been observed for complexes of the type bis(allyl)Pd(L) (L = PR₃),⁸ and [(η^3 -allyl)Pd(PPh_3)]₂ has been crystallographically characterized.¹¹



Reaction of excess CO₂ with 1-4 led to rapid and quantitative formation of the unidentate carboxylate complexes 6-9 (Eq 3). Compounds 1-3 react in approximately 1 hour at -20 $^{\circ}$ C, while compound 4 reacts in less than 5 minutes at -40 $^{\circ}$ C. As the ancillary ligand was changed the rate of reaction increased in the following order: $PPh_3 < PEt_3 \approx PMe_3 < NHC$. This demonstrates that more electron rich ligands lead to faster reactions. The difference between the symmetric and asymmetric CO₂ stretches in the IR spectra of 6-9 were significantly greater than 200 cm⁻¹, which is characteristic of the presence of a unidentate carboxylate ligand.¹² Furthermore, the magnitude of the difference between symmetric and asymmetric CO₂ stretch was related to the electron richness of the ligand, with the largest difference observed for the NHC complex 9 and the smallest for the PPh₃ complex 8. When 2 was reacted with 13 C-labeled CO₂, 7 with a 13 C-labeled carboxylate was formed. The CO₂ stretching frequencies shifted from 1601 and 1338 cm⁻¹ in the unlabeled complex to 1562 and 1315 cm^{-1} in the labeled complex (calculated 1565 and 1309 cm^{-1}). Further confirmation for the proposed structures of 6-9 was obtained through the solid state structure of **9** (Figure 2), which clearly shows a unidentate carboxylate and an η^3 -2methylallyl ligand. The overall coordination geometry around Pd is approximately square planar and the carboxylate group is oriented away from the allyl ligand. Compound 9 is the first structurally characterized product from the reaction of CO₂ with a palladium allyl.



(3)

For comparison the unsubstituted allyl compounds bis(allyl)Pd(PMe₃),¹⁰ bis(allyl)Pd(PEt₃) and bis(allyl)Pd(PPh₃)¹⁰ were prepared using literature methods. Interestingly no reaction

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(2)

was observed with CO_2 before decomposition of the starting material (predominantly to dimeric Pd^I species)⁸ occurred at approximately -10 °C. This suggests that the barrier for reaction with CO_2 is higher for the unsubstituted allyls compared with the 2-methylallyl compounds.¹³ Furthermore, no variation in the rate of CO_2 insertion into **1–4** was observed when excess ligand was added to the reaction mixture. These observations strongly suggest that the reaction does not follow a straightforward insertion mechanism involving initial coordination of CO_2 to the Pd center, followed by allyl migration, and the formation of a new C-C bond between the metal coordinated carbon of the allyl and CO_2 (Scheme 1). This type of insertion mechanism has been proposed in the reaction of CO_2 with octadienyl species, which is proposed as a key step in the coupling of butadiene with CO_2 to form lactones.²

Mechanism of Reaction between Palladium Allyls and CO₂

In order to probe the mechanism of reaction between CO_2 and palladium allyl species a density functional theory (DFT) study was performed. Calculations were carried out on model compounds with both allyl and 2-methylallyl groups on Pd and PH₃, PMe₃ and a simplified NHC as the supporting ligands (Figure 3). The ADF program suite was used to optimize geometries and search for transition states.¹⁴

Initially the key features of the reaction of **ii** with CO₂ will be discussed and then the effect of changing the supporting ligand and the 2-methylallyl group to an allyl group will be described. Binding of PH₃ to $(\eta^3-C_3H_4Me)_2Pd$ is energetically favorable and the isomer of $(C_3H_4Me)_2Pd(PH_3)$ with one η^1 and one η^3 -allyl ligand is lower in energy (22 kJ mol⁻¹) than the isomer with two η^3 -allyl ligands. This is consistent with our experimental results and suggests that an intermediate of the type $(\eta^3-C_3H_4Me)_2Pd(L)$ could be an easily accessible intermediate for exchange between the 2-methylallyl ligands in $(\eta^1-C_3H_4Me)(\eta^3-C_3H_4Me)Pd(L)$ (1–4).

The bis-allyl compounds of group 10 are unusual among transition metal organometallic complexes in possessing a HOMO that is largely ligand based.¹⁵ This is also the case with **ii**, $(\eta^1-C_3H_4Me)(\eta^3-C_3H_4Me)Pd(PH_3)$ (Figure 4). The electron density on the terminal carbon atoms of the 2-methylallyl groups suggests that they could be sites for electrophilic attack by the C of CO₂. Transition states were identified for CO₂ binding to all four terminal C atoms (Table 1). The electronic energy of activation was greatest for site a, 141 kJ mol⁻¹, and least for site b, 47 kJ mol⁻¹. Values for sites c and d were 103 and 134 kJ mol⁻¹, respectively. Thus the uncoordinated terminal carbon appears to be the most vulnerable to electrophilic attack. No transition states were identified in which CO_2 initially binds to the metal center. The calculations suggest that after initial nucleophilic attack by the terminal carbon of the η^1 -allyl on CO₂, the overall reaction proceeds via a number of steps as illustrated in Figure 5 and Scheme 2 and is energetically favored. The initial electrophilic attack of CO_2 leads to a zwitterionic transition state containing a carbocation on the 2-position of the terminal allyl and a negative charge on the carboxylate. This transition state collapses to a zwitterionic intermediate with a formal negative charge on the carboxylate group and a positive charge on the Pd. The C₃H₄MeCO₂ group is coordinated in a slipped manner to Pd by both Ca and Ce and the Ca-Ce bond acquires multiple bond character. This step has the highest activation energy of the sequence. The zwitterionic intermediate undergoes ligand substitution of Ca-Ce by a carboxylate oxygen. The barrier for this reaction is small in this case and leads to a higher energy conformer of the product, which can undergo ligand rotation to give the final product. Szabo has proposed a similar mechanism for the reaction of electrophilic aldehydes with η^1 -allyl Pd complexes with pincer ligands.¹⁶

The four modes of attack at the four terminal allyl carbons were also compared for i (Table 1). Attack at the uncoordinated terminal carbon of the σ -allyl group was again significantly

favoured. In comparing the effect of the ligand L only this pathway was explored. The energies of the identified stationary points for the reaction of i-vi are given in Table 2. In all cases TS1 is the highest point on the energy surface and all complexes show a similar intermediate, INT1. The methylation of the allyl group lowers the activation energy by approximately 10% because the resultant tertiary carbocation is more stable than a secondary carbocation. These energies are consistent with the experimental observation that the barrier for reaction of 2-methylallyl substituted complexes with CO₂ is lower than the barrier for unsubstituted species. When $L = PMe_3$ or NHC' the activation energies are similar and significantly lower than for the model PH₃ system, which agrees with the experimental observation that electron donating ligands increase the rate of reaction. The lowering of the barrier presumably occurs because the more electron donating ligands allow Pd to assist in stabilizing the carbocation in TS1 through inductive effects. The calculations suggest that the activation energy for NHC' is slightly higher than for PMe₃, whereas experimentally the NHC complex 4 reacts faster than the PMe₃ species 1. However there is one significant difference between the two systems. The formation of \mathbf{v} and \mathbf{vi} from the bisallylpalladium precursors is energetically much more favorable than iii and iv. Given that binding of a ligand is not favoured entropically the pre-equilibrium may well have a significant effect on the relative rates of the reactions, a larger ligand binding constant being expected for v and vi than for iii and iv.

Only minor differences were observed between the complexes for the conversion of INT1 into the final products. In cases **iii**, **iv** and **v** one carboxylate oxygen lay closer to Pd in INT1 than was found for **i**, **ii** and **vi**.¹⁷ In all cases the transition states found for the associative substitution of Ca and Ce by the carboxylate O (TS2) were barely distinguished in energy from INT1, although significantly different in structure.¹⁷ In the case of L = PMe₃ the substitution proceeded to the stable product isomer whereas with NHC' as with PH₃ a less stable conformer was detected on the reaction pathway. The conformers formed on the NHC and PH₃ pathways could undergo ligand rotation to give the final product.

Overall, the results of the calculations suggest that only nucleophilic η^1 -allyls will react with CO₂ and electrophilic η^3 -allyls will be unreactive. We prepared the η^3 -allyls (allyl)PdCl(PMe_3),18 (allyl)PdCl(NHC),¹⁹ (2-methylallyl)PdCl(PPh_3),²⁰ (2-methylallyl)PdCl(PMe_3),21 and (2-methylallyl)PdCl(NHC)²² using literature methods (the binding mode of the allyl ligand has either previously been confirmed using X-ray diffraction or was confirmed in this work).14 None of these species reacted with CO₂ even at elevated temperatures providing further support for our proposed mechanism.

Conclusions

In this work we have conclusively demonstrated that reactions between palladium η^1 -allyls and CO₂ are facile and structurally characterized the product. Mechanistic investigations strongly suggest that the reactions of η^1 -palladium allyls with CO₂ do not proceed via insertion of CO₂ into the Pd-C bond but through nucleophilic attack of the terminal olefin on electrophilic CO₂ followed by an associative ligand substitution. Our results suggests that in current systems for the catalytic carboxylation of allylstannanes the difficult steps are either formation of the active catalyst or transmetallation, as once a palladium allyl is formed reaction with CO₂ will be facile.³ More importantly they suggest that the proposed mechanism for the conversion of CO₂ and butadiene into lactones, which involves the direct insertion of CO₂ into a palladium octadienyl species and an unusual reductive elimination may not be correct.² Instead this reaction probably involves nucleophilic attack by the octadienyl ligand on CO₂. In further work, we will utilize our results to both improve current catalysts for the direct incorporation of CO₂ into organic compounds and design new catalysts.

Note added after Submission

After the submission of this work, a paper by Wendt and co-workers describing the mechanism of CO₂ insertion into (PCP)Pd(η^1 -allyl) species (PCP = 2,6-C₆H₃(CH₂PtBu₂)₂) was published.²³ In this elegant study the substituted allyl complex (PCP)Pd(1-methylallyl) was prepared. Reaction of this species with CO₂ resulted in the formation of the new C-C bond exclusively between the terminal carbon of the allyl and CO₂ (Eq 4), which is consistent with our mechanism. Furthermore DFT studies performed on the reaction between (PCP)Pd(allyl) and CO₂ proposed a two step mechanism (Scheme 3). In the first step the nucleophilic terminal olefin of the η^1 -allyl attacks CO₂ to generate a zwitterionic transition state, with a positive charge on the allyl and a negative charge on the carboxylate. This transition state collapses to a zwitterionic intermediate with a formal negative charge on the carboxylate group and a positive charge on the Pd. In the second step ligand substitution generates the observed final product. This mechanism is identical to our proposed mechanism, although in Wendt's system the transition state for ligand substitution is the highest point on the surface. This is presumably because the conformationally rigid PCP ligand makes it energetically more costly for the Pd species to adopt a *pseudo*-five coordinate geometry. The results of both Wendt and our studies strongly suggest that regardless of the supporting ligand framework, nucleophilic attack on CO₂ is the preferred pathway by which η^1 -allyl Pd species react with CO₂.

Experimental Section

General Methods

Experiments were performed under a dinitrogen atmosphere in an M-Braun dry box 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 airsensitive liquids were transferred by stainless steel cannula on a Schlenk line or in a dry box. 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. Palladium chloride was purchased from Pressure Chemical Co, while 2-methylallylchloride, PMe₃, PEt₃, PPh₃ and 1,3-Bis(2,6diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene were purchased from Aldrich or Strem. Anhydrous CO₂ was obtained from Airgas, Inc and was not dried prior to use. Deuterated solvents and ¹³C-labelled CO₂ were obtained from Cambridge Isotope Laboratories. C₆D₆ and toluene-d₈ were dried over sodium metal. NMR spectra were recorded on Bruker AMX-400, -500 spectrometers at ambient probe temperatures unless noted. Chemical shifts are reported with respect to residual internal protio solvent for 1 H and ¹³C{¹H} NMR spectra and to an external standard for ³¹P spectra (85% H₃PO₄ at 0.0 ppm). Atom numbering for the peak assignments is given below. All assignments are based on two dimensional ¹H,¹³C-HMQC and HMBC experiments. IR spectra were measured using 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: bis(2-methylallyl)Pd,24 bis(allyl)Pd,24 bis(allyl)Pd(PMe₃),¹⁰ bis(allyl)Pd(PEt₃), bis(allyl)Pd(PPh₃),¹⁰ (allyl)PdCl(PMe₃),18 (allyl)PdCl(NHC),¹⁹ (2-methylallyl)PdCl(PPh₃),²⁰ (2methylallyl)PdCl(PMe₃)²¹ and (2-methylallyl)PdCl(NHC).²²

DFT Calculations

Quantum chemical calculations were performed using density functional methods of the Amsterdam Density Functional (Version ADF2007.01) package.^{9b,25} TZP basis sets were used with triple- ζ accuracy sets of Slater-type orbitals, with polarization functions added to all atoms. Relativistic corrections were made using the ZORA (zero-order relativistic approximation) formalism²⁶ and the core electrons were frozen up to 1s for C, and O 2p for P and 3d for Pd. The local density approximation of Vosko, Wilk, and Nusair27 was utilized together with the nonlocal exchange correction by Becke28 and nonlocal correlation corrections by Perdew.29 All quoted electronic structure data from optimized structures use an integration grid of 6.0 for the minima and 5.0 for the transition states and were verified as minima using frequency calculations. The transitions states all showed one imaginary frequency with a motion connecting the reactant and product. The coordinates for the optimized structures are given in the supporting information.

X-Ray Crystallography

The diffraction experiments were carried out on a Bruker AXS SMART CCD three-circle diffractometer with a sealed tube at 23 °C using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The software used were 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. The hydrogen atoms were placed in their ideal positions. Details of the crystal and refinement data for complexes **3** and **9** are given in Table 1.

Synthesis and Characterization of New Compounds

The following numbering scheme is used for the purposes of assigning NMR Data:



(η¹-2-MeC₃H₄)(η³-2-MeC₃H₄)Pd(PMe₃) (1)

PMe₃ (7.8 μ L, 0.08 mmol) was added to a stirred solution of bis(2-methylallyl)palladium (16.3 mg, 0.08 mmol) in 1 mL of toluene at -40 °C. The mixture was stirred for 0.5 hr at -40 °C and was then warmed to room temperature. The volatiles were removed by vacuum to give **1** as yellow oil. Yield: 20.2 mg (92%). This compound is thermally unstable and was stored at -30 °C (no elemental analysis was obtained due to the thermal instability).

¹H NMR (500 MHz, toluene-d₈, -86 °C): 5.09 (s, 1H, H7), 4.84 (s, 1H, H7'), 3.38 (br s, 1H, H3), 3.00 (s, 2H, H1 and H5), 2.89 (s, 1H, H3'), 2.68 (m, 1H, H1'), 2.26 (s, 1H, H5'), 2.21 (s, 3H, H8), 1.59 (s, 3H, H4), 0.73 (m, 9H, CH₃P). ¹³C{¹H} NMR (125.8 MHz, toluene-d₈, -90 °C): 157.2 (s, C6), 131.9 (s, C2), 100.5 (s, C7), 63.1 (d, C3, J_{P-C} = 36.5 Hz), 58.1 (s, C5), 28.0 (s, C8), 25.4 (4, C4), 17.7 (s, C1), 16.0 (d, <u>C</u>H₃P, J_{P-C} = 25.2 Hz). ³¹P{¹H} NMR (135 MHz, C₆D₆): -17.3 (s).

(η¹-2-MeC₃H₄)(η³-2-MeC₃H₄)Pd(PEt₃) (2)

PEt₃ (65 μ L, 0.44 mmol) was added to a stirred solution of bis(2-methylallyl)palladium (96 mg, 0.44 mmol) in 1 mL of toluene at -40 °C. The mixture was stirred for 0.5 hr at -40 °C

and was then warmed to room temperature. The volatiles were removed by vacuum to give **2** as a yellow oil. Yield: 141 mg (95%). This compound is thermally unstable and was stored at -30 °C (no elemental analysis was obtained due to the thermal instability)

¹H NMR (400 MHz, toluene-d₈, -70 °C): 5.06 (s, 1H, H7), 4.80 (s, 1H, H7'), 3.36 (br s, 1H, H3), 3.06 (m, 1H, H1), 3.00 (s, 1H, H5), 2.97 (s, 1H, H3'), 2.54 (m, 1H, H1'), 2.29 (s, 1H, H5'), 2.17 (s, 3H, H8), 1.58 (s, 3H, H4), 1.26 (m, 6H, PCH₂), 0.71 (m, 9H, CH₃CH₂P). ¹³C{¹H} NMR (101 MHz, toluene-d₈, -70 °C): 157.3 (s, C6), 131.4 (s, C2), 100.4 (s, C7), 65.0 (d, C3, $J_{P-C} = 35.2$ Hz), 57.5 (s, C1), 27.9 (s, C8), 25.2 (s, C4), 17.7 (d, C5, $J_{P-C} = 10.1$ Hz), 16.5 (d, $\underline{C}H_2P$, $J_{P-C} = 22.1$ Hz), 8.8 (s, $\underline{C}H_3CH_2P$). ³¹P{¹H} NMR (135 MHz, C₆D₆): 21.9 (s).

$(\eta^{1}-2-MeC_{3}H_{4})(\eta^{3}-2-MeC_{3}H_{4})Pd(PPh_{3})$ (3)

A solution of PPh₃ (141 mg, 0.54 mmol) in 4 mL of a toluene and pentane mixture (v/v = 1:7) at -40 °C was added to a stirred solution of bis(2-methylallyl)palladium (117 mg, 0.54 mmol) in 2 mL of pentane at -78 °C. The mixture was warmed to -40 °C and stirred for another 2 hr. The resulting precipitate was collected by filtration, washed with pentane and dried in vacuo to give **3** as a yellow solid. Yellow single crystals for X-ray analysis were grown from toluene/pentane at -35 °C. Yield: 214.1 mg (83%). Anal. calcd (found) for $C_{26}H_{29}PPd$: C, 65.21 (65.31); H, 6.10 (6.00). This compound is thermally unstable in solution but was sufficiently stable as a solid to gather satisfactory elemental data.

¹H NMR (500 MHz, toluene-d₈, -95 °C): 7.45 (br s), 7.22 (s) & 6.94 (br s) (15H, Ph), 4.84 (br s, 2H, H7), 2.43 (br s, 1H, H1), 3.36 (br s, 2H, H3), 2.87 (br s, 1H, H5), 2.70 (br s, 1H, H5'), 2.57 (br s, 1H, H1'), 2.11 (br s, 3H, H8), 1.67 (br s, 3H, H4). ¹³C{¹H} NMR (125.8 MHz, toluene-d₈, -70 °C): 134.1, 134.0, 133.6, 128.9 (Ph), 112.5 (s, C6), 111.7 (s, C2), 100.0 (s, C7), 69.3 (s, C3), 63.0 (s, C1), 26.7 (s, C8), 24.6 (s, C4), 24.4 (s, C5). ³¹P{¹H} NMR (135 MHz, toluene-d₈, -75 °C): 34.6 (s).

(η¹-2-MeC₃H₄)(η³-2-MeC₃H₄)Pd(NHC) (4)

NHC (23.2 mg, 0.06 mmol) was added to a stirred solution of bis(2-methylallyl)palladium (12.1 mg, 0.06 mmol) in 0.5 mL of toluene- d_8 at -78 °C in a J. Young NMR tube. The mixture was warmed to -50 °C and the NMR data was collected at -50 °C. No attempts were made to isolate this extremely unstable compound and it was only characterized spectroscopically.

¹H NMR (500 MHz, toluene-d₈, -50 °C): 7.14 (m, 2H, H14, overlapping with solvent peak), 6.97 (m, 4H, H13 and H15, overlapping with solvent peak), 6.44 (s, 2H, H10), 4.83 (s, 1H, H7), 4.64 (s, 1H, H7'), 3.36 (br s, 2H, H21), 2.95 (br s, 2H, H17), 2.82 (s, 1H, H1), 2.76 (s, 1H, H3), 2.54 (s, 1H, H1'), 2.19 (d, J = 10Hz, 1H, H5), 2.10 (d, J = 10Hz, 1H, H5', overlapping with solvent peak), 1.88 (s, 1H, H3'), 1.66 (s, 3H, H8), 1.38 (s, 6H, H20), 1.34 (s, 6H, H22), 1.29 (s, 3H, H4), 1.04 (s, 6H, H18), 1.01 (s, 6H, H19). ¹³C{¹H} NMR (125.8 MHz, toluene-d₈, -50 °C): 194.1 (s, C23), 158.7 (s, C6), 145.6 (s, C12), 145.2 (s, C16), 137.0 (s, C11), 130.0 (s, C12), 129.5 (s, C13 and C15), 123.9 (s, C14), 123.2 (s, C10), 100.1 (s, C7), 65.4 (s, C3), 53.2 (s, C3), 50.3 (s, C1), 28.6 (s, C17), 28.4 (s, C21), 26.2 (s, C4), 25.9 (s, C20 or C22), 25.6 (s, C8), 24.8 (s, C22 or C20), 22.8 (s, C18), 22.5 (s, C19).

${(\eta^{3}-2-MeC_{3}H_{4})Pd(PPh_{3})}_{2}$ (5)

PPh₃ (121.8 mg, 0.46 mmol) was added to a stirred solution of bis(2-methylallyl)palladium (100.4 mg, 0.46 mmol) in 8 mL toluene at -30 °C. The mixture was slowly warmed to room temperature and stirred for 1 hr. The volatiles were then removed under reduced pressure. The resulting residue was washed with cold pentane and dried in vacuo to give **5** as an

orange-yellow powder. Yield: 165.2 mg (84%). Anal. calcd (found) for $C_{44}H_{44}P_2Pd_2$: C, 64.55 (62.50); H, 5.71 (5.10).

¹H NMR (500 MHz, C_6D_6): 7.73 (br s), 7.62 (d), 7.28 (s), 7.08 (m) & 7.01 (m) (30H, Ph), 2.96 (m, 4H, allyl), 2.32 (br s, 4H, allyl), 1.58 (m, 6H, CH₃). ¹³C{¹H} NMR (125.8 MHz): 140.2 (s), 136.6 (t), 134.7 (s), 134.6 (s), 134.5 (s) & 129.7 (Ph), 115.4 (s, allyl-center C), 38.9 (s, allyl-end C), 38.9 (s, CH₃). ³¹P{¹H} NMR (135 MHz, C_6D_6): 29.3 (s).

(η³-2-MeC₃H₄)(η¹-CO₂C₄H₇)Pd(PMe₃) (6)

To a solution of bis(2-methylallyl)palladium (13.3 mg, 0.06 mmol) in 0.5 mL toluene-d₈ at -78 °C, PMe₃ (6.4 µL, 0.06 mmol) was added. The mixture was allowed to warm to room temperature with stirring. Excess 1 atm CO₂ was added via a dual manifold Schlenk line to the above solution at room temperature. After 0.5 hr the mixture was evaporated to dryness. The residue was dissolved in a minimum amount of pentane and was then cooled at -35 °C for 6 hr. A white precipitate formed, which was isolated by filtration. The solid was dried in vacuo to give 6 as a white powder. Yield: 19.1 mg (92%). Anal. calcd (found) for C₁₂H₂₃O₂PPd: C, 42.81 (42.53); H, 6.89 (6.78).

(η³-2-MeC₃H₄)(η¹-CO₂C₄H₇)Pd(PEt₃) (7)

Excess 1 atm CO₂ was added via a dual manifold Schlenk line to an agitated solution of 2 (20.7 mg, 0.06 mmol) in 0.5 mL of toluene-d₈ at room temperature. After 0.5 hr the mixture was evaporated to dryness to give **7** as a pale yellow solid. Yield: 21.1 mg (90%). Anal. calcd (found) for C₁₅H₂₉O₂PPd: C, 47.56 (47.29); H, 7.72 (7.57). Pd(PEt₃)(η^3 -2-MeC₃H₄) (η^{1-13} CO₂C₄H₇) (**7**-¹³CO₂) was prepared by performing the same procedure under an atmosphere of ¹³C-labelled CO₂.

 $\begin{array}{l} IR(cm^{-1}) \ 1601 \ (v_{asymCO2}), \ 1338 \ (v_{symCO2}). \ ^{1}H \ NMR \ (400 \ MHz, \ C_6D_6): \ 5.09 \ (s, \ 1H, \ H8), \\ 4.98 \ (s, \ 1H, \ H8'), \ 4.44 \ (d, \ J = 4Hz, \ 1H, \ H3), \ 3.55 \ (d, \ J = 4Hz, \ 1H, \ H3'), \ 3.48 \ (s, \ 2H, \ H6), \\ 2.18 \ (s, \ 2H, \ H1), \ 2.16 \ (s, \ 3H, \ H9), \ 1.63 \ (s, \ 3H, \ H4), \ 1.36 \ (m, \ 6H, \ PCH_2), \ 0.86 \ (m, \ 9H, \\ CH_3CH_2P). \ ^{13}C\{^{1}H\} \ NMR \ (101 \ MHz, \ C_6D_6): \ 175.9 \ (s, \ CO_2), \ 144.5 \ (s, \ C8), \ 131.0 \ (s, \ C2), \\ 112.0 \ (s, \ C7), \ 77.0 \ (d, \ J_{C-P} = 30.3 \ Hz, \ C3), \ 48.1 \ (s, \ C6), \ 45.3 \ (s, \ C1), \ 23.9 \ (s, \ C9), \ 23.6 \ (s, \ C4). \ 17.4 \ (d, \ \underline{CH}_2P, \ J_{C-P} = 22.2 \ Hz), \ 8.8 \ (s, \ \underline{CH}_3CH_2P). \ ^{31}P\{^{1}H\} \ NMR \ (135 \ MHz, \ C_6D_6): \\ 24.1 \ (s). \end{array}$

Spectroscopic Data for 7-¹³CO₂. IR(cm⁻¹) 1562 ($v_{asymCO2}$), 1315 (v_{symCO2}). ¹H NMR (400 MHz, toluene-d₈): 4.99 (s, 1H, H8), 4.90 (s, 1H, H8'), 4.36 (d, J = 12Hz, 1H, H3), 3.46 (d, J = 12Hz, 1H, H3'), 3.34 (d, J = 8Hz, 2H, H6), 2.19 (s, 2H, H1), 2.09 (s, 3H, H9), 1.64 (s, 3H, H4), 1.37 (m, 6H, PCH₂), 0.87 (m, 9H, CH₃CH₂P). ¹³C{¹H} NMR (101 MHz, toluene-d₈): 175.5 (CO₂). ³¹P{¹H} NMR (135 MHz, toluene-d₈): 24.2 (s).

(η³-2-MeC₃H₄)(η¹-CO₂C₄H₇)Pd(PPh₃) (8)

Excess 1 atm CO₂ was added via a dual manifold Schlenk line to a stirred solution of **3** (60 mg, 0.13 mmol) in 0.6 mL of toluene at -40 °C. The reaction was stirred at -78 °C overnight and excess CO₂ was removed under vacuum. Cold pentane (12 mL) was then added. The resulting precipitate was collected by filtration at -78 °C, washed with cold

pentane and dried in vacuo to give **8** as a pale yellow solid. Yield: 45.2 (69%). Anal. calcd (found) for $C_{27}H_{29}O_2PPd$: C, 62.02 (63.73); H, 5.59 (4.31).

 $\begin{array}{l} IR(cm^{-1}) \ 1600 \ (v_{asymCO2}), \ 1339 \ (v_{symCO2}). \ ^{1}H \ NMR \ (400 \ MHz, \ toluene-d_8, -70 \ ^{\circ}C): \ 7.67 \\ (m), \ 7.47 \ (br \ s) \ \& \ 7.17 \ (br \ s) \ (15H, \ Ph), \ 5.02 \ (s, \ 2H, \ H8), \ 4.92 \ (s, \ 1H, \ H3'), \ 3.51 \ (s, \ 1H, \ H3), \ 3.50 \ (s, \ 2H, \ H6), \ 2.24 \ (s, \ 1H, \ H1), \ 1.98 \ (1H, \ H1'), \ 1.85 \ (s, \ 3H, \ H9), \ 1.66 \ (s, \ 3H, \ H4). \ ^{13}C \ obtained \ from \ ^{1}H^{-13}C \ HMBC \ \& \ HMQC \ (toluene-d_8, \ -70 \ ^{\circ}C): \ 134.3, \ 134.1 \ \& \ 128.2 \ (Ph), \ 175.9 \ (s, \ CO_2), \ 143.9 \ (s, \ C7), \ 133.6 \ (s, \ C2), \ 112.4 \ (s, \ C8), \ 75.4 \ (s, \ C3), \ 54.7 \ (s, \ C1), \ 47.2 \ (s, \ C6), \ 22.9 \ (s, \ C9 \ \& \ C4). \ ^{31}P\{^{1}H\} \ NMR \ (135 \ MHz, \ toluene-d_8, \ -70 \ ^{\circ}C): \ 23.2 \ (s). \end{array}$

$(\eta^{3}-2-MeC_{3}H_{4})(\eta^{1}-CO_{2}MeC_{3}H_{4})Pd(NHC)$ (9)

To a stirred solution of bis(2-methylallyl)palladium (300 mg, 1.4 mmol) in 20 mL of toluene at -78 °C, a solution of NHC (NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) (539 mg, 1.4 mmol) in 20 mL toluene at -78 °C was added via cannula. The mixture was allowed to stir for 2 hr and was then degassed using 3 freeze-pump-thaw cycles and allowed to warm to -40 °C. Excess 1 atm CO₂ was added via a dual manifold Schlenk line at -40 °C. After stirring for 1 hr the mixture was evaporated to dryness. The yellow-brown solid was washed with 2×10 mL pentane revealing **9** as a white powder. Colorless single crystals for X-ray analysis were grown from CH₂Cl₂/pentane at -70 °C. Yield: 355 mg (40%). Anal. calcd (found) for C₃₆H₅₀N₂O₂Pd: C, 66.60 (66.38); H, 7.76 (7.74); N, 4.32 (4.24).

IR(cm⁻¹) 1611 ($v_{asymCO2}$), 1330 (v_{symCO2}). ¹H NMR (400 MHz, CD₂Cl₂): 7.47 (t, J = 8Hz, 2H, H14), 7.31 (d, J = 8Hz, 4H, H13 and H15), 7.17 (s, 2H, H10), 4.61 (s, 1H, H8), 4.55 (s, 1H, H8'), 3.90 (s, 1H, H3), 2.90 (br m, 4H, H10), 2.79 (s, 1H, H3'), 2.65 (s, 2H, H6), 2.03 (br, 2H, H1), 1.66 (s, 3H, H9), 1.35 (s, 6H, H20), 1.33 (s, 6H, H22), 1.27 (s, 3H, H4), 1.13 (s, 6H, H18 or H19), 1.11 (s, 6H, H19 or H18). ¹³C NMR (500MHz, CD₂Cl₂): 186.8 (s, C23), 175.5 (s, C5), 146.5 (s, C11), 144.8 (s, C7), 136.9 (s, C16), 130.2 (s, C14), 129.1 (s, C2), 124.8 (s, C10), 124.4 (s, C12 and C16), 111.1 (s, C8), 71.2 (s, C3), 47.0 (s, C6), 44.9 (s, C1), 29.0 (s, C21), 26.1 (s, C20 and C22), 23.2 (s, C9), 23.1 (s, C18 and C19), 22.5 (s, C4).

Reactions between CO₂ and bis(allyl)Pd complexes

In a typical reaction 10 mg of bis(allyl)Pd(PMe₃), bis(allyl)Pd(PEt₃) or bis(allyl)Pd(PPh₃) was dissolved in 0.4 mL of toluene-d₈ in a J. Young NMR tube at -78 °C. The mixture was then degassed using 3 freeze-pump-thaw cycles and excess 1 atm CO₂ was added via a dual manifold Schlenk line at -78 °C. No reaction was observed with CO₂ before decomposition of the starting material occurred at approximately -10 °C.

Reactions between CO₂ and η³-allyl and η³-2-methylallyl Pd complexes

In an typical reaction 10 mg of (allyl)PdCl(NHC), (2-methylallyl)PdCl(PPh₃), (2-methylallyl)PdCl(PMe₃) or (2-methylallyl)PdCl(NHC) was dissolved in 0.4 mL of C_6D_6 in a J. Young NMR tube. The mixture was then degassed using 3 freeze-pump-thaw cycles and excess 1 atm CO₂ was added via a dual manifold Schlenk line. The reaction was monitored using ¹H NMR spectroscopy and heated for extended periods of time at 80 °C. No reaction was observed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Dr. Nathan West for insightful discussions and the NIH for a Chemical Biology Training Grant (TJS).

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Figure 1.

X-ray structure of **3** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)-P(1) 2.2822(9), Pd(1)-C(7) 2.240(3), Pd(1)-C(5) 2.154(4), Pd(1)-C(6) 2.186(3), Pd(1)-C(1) 2.111(2), C(1)-C(2) 1.480(5), C(2)-C(3) 1.343(6), C(2)-C(4) 1.465(5), C(5)-C(6) 1.409(5), C(6)-C(7) 1.384(6), C(6)-C(8) 1.500(6), Pd(1)-C(1)-C(2) 115.6(2), Pd(1)-C(5)-C(6) 72.3(2), Pd(1)-C(6)-C(7) 73.9(2).



Figure 2.

X-ray structure of **9** (Hydrogen atoms, methyl groups of NHC ligand and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)-C(1) 2.036(3), Pd(1)-C(33) 2.205(4), Pd(1)-C(34) 2.147(4), Pd(1)-C(35) 2.069(6), Pd(1)-O(1) 2.112(3), C(33)-C(34) 1.378(7), C(34)-C(35) 1.405(7), C(34)-C(36) 1.505(7), O(1)-C(28) 1.265(5), C(28)-O(2) 1.222(5), C(28)-C(29) 1.531(6), C(29)-C(30) 1.495(8), C(30)-C(31) 1.487(9), C(30)-C(32) 1.311(9), Pd(1)-C(33)-C(34) 69.2(2), Pd(1)-C(35) 67.6(2), Pd(1)-O(1)-C(28) 122.0(2), C(1)-Pd(1)-C(35) 100.20(18), C(33)-Pd(1)-O(1) 103.61(18), O(1)-Pd(1)-C(1) 89.02(13).

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Figure 4. HOMO of $(\eta^1-C_3H_4Me)(\eta^3-C_3H_4Me)Pd(PH_3)$ (ii) and labeling scheme for terminal C atoms.

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Figure 5.

Energy profile for formation of $(\eta^3-C_3H_4Me)(\eta^1-O_2CC_3H_4Me)Pd(PH_3)$ from $(\eta^3-C_3H_4Me)Pd_2$ (Cf is the CO₂ carbon). C-C distances in the intermediates and transition states are given at the bottom of the Figure.



Scheme 1.



Scheme 2.

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Scheme 3.

Table 1

SCF energies of the possible transition states, TS1, representing attack at the four terminal allyl carbons for i and ii. Energies (kJmol⁻¹) are given relative to (η^1 -allyl)(η^3 -allyl)PdPH₃.

Allyl	Ca	Cb (TS1)	Cc	Cd
C ₃ H ₅ , i	171	52	76	108
C ₄ H ₈ , ii	141	47	103	134

Table 2

SCF energies of the identified stationary points for the reaction of i-vi with CO_2 . Energies (kJ mol⁻¹) are given relative to $(\eta^1$ -ally1)(η^3 -ally1)PdL.

Compound	Pd(allyl) ₂	$(\eta^1-allyl)(\eta^3-allyl)Pd(L)$	TS1	INTI	TS2	INT2	Pd(allyl) (allylCO ₂)L
i	15	0	52	42	44	16	-34
ij	15	0	47	41	45	16	-35
iii	41	0	36	18	20	-38	-40
iv	39	0	33	23	23	-40	-41
v	85	0	40	25	25	0	-38
vi	79	0	35	25	25	6-	-43

Table 1

Crystal and Refinement Data for Complexes 3 and 9.

	3	9
Empirical formula	PdPC ₂₆ H ₂₉	$PdO_2N_2C_{38}H_{54}Cl_4$
Formula weight	478.89	819.07
Temperature (K)	223	223
a (Å)	9.3455(4)	18.6604(18)
b (Å)	9.9853(5)	12.5634(12)
c (Å)	13.9430(7)	17.8121(17)
α (deg)	72.6291(12)	90
β(deg)	83.6782(13)	98.961(2)
γ(deg)	70.4556(12)	90
Volume (Å ³)	1170.17(10)	4124.9(7)
Z	2	4
Crystal system	Triclinic	Monoclinic
Space group	P-1 (#2)	P2 ₁ /c (#14)
$d_{\text{calc}} (\text{mg/m}^3)$	1.359	1.319
θrange (deg)	3.1 to 27.5	3.1 to 27.5
$\mu(mm^{-1})$	0.870	0.741
Abs. correction	Semi-empirical from equivalents	Semi-empirical from equivalents
GOF	1.051	1.043
R_{I} , ^a $WR_{2}^{b} [I > 2\sigma(I)]$	0.0412, 0.0869	0.0648, 0.1435

 ${}^{a}R1 = \Sigma ||FO| - |FC|| / \Sigma |FO|.$

 ${}^{b}wR_{2} = [\Sigma[W(F_{O}^{2} - F_{C}^{2})^{2}]/\Sigma[w(F_{O}^{2})^{2}]^{1/2}.$