

Comparative Study of CO₂ Insertion into Pincer Supported Palladium Alkyl and Aryl Complexes

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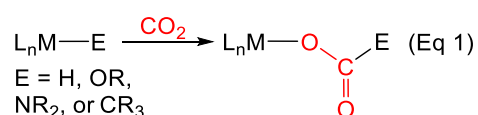
Abstract

The insertion of CO₂ into metal alkyl bonds is a crucial elementary step in transition metal-catalyzed processes for CO₂ utilization. Here, we synthesize pincer-supported palladium complexes of the type (^tBuPBP)Pd(alkyl) (^tBuPBP = B(NCH₂P^tBu₂)₂C₆H₄[−]; alkyl = CH₂CH₃, CH₂CH₂CH₃, CH₂C₆H₅, and CH₂-4-OMe-C₆H₄) and (^tBuPBP)Pd(C₆H₅) and compare the rates of CO₂ insertion into the palladium alkyl bonds to form metal carboxylate complexes. Although, the rate constant for CO₂ insertion into (^tBuPBP)Pd(CH₂CH₃) is more than double the rate constant we previously measured for insertion into the palladium methyl complex (^tBuPBP)Pd(CH₃), insertion into (^tBuPBP)Pd(CH₂CH₂CH₃) occurs approximately one order of magnitude slower than (^tBuPBP)Pd(CH₃). CO₂ insertion into the benzyl complexes, (^tBuPBP)Pd(CH₂C₆H₅) and (^tBuPBP)Pd(CH₂-4-OMe-C₆H₄), is significantly slower than any of n-alkyl complexes and CO₂ does not insert into the palladium phenyl bond of (^tBuPBP)Pd(C₆H₅). While (^tBuPBP)Pd(CH₂CH₃) and (^tBuPBP)Pd(CH₂CH₂CH₃) are resistant to β-hydride elimination, we were unable to synthesize complexes with n-butyl, iso-propyl, and tert-butyl ligands due to β-hydride elimination and an unusual reductive coupling, which involves the formation of new C–B bonds. This reductive process also occurred for (^tBuPBP)Pd(CH₂C₆H₅) at elevated temperature and a related process involving the formation of a new H–B bond prevented the isolation of (^tBuPBP)PdH. DFT calculations provide insight into the relative rates of CO₂ insertion and indicate that steric factors are critical. Overall, this work is one of the first comparative studies of the rates of CO₂ insertion into different metal alkyl bonds and provides fundamental information that may be important for the development of new catalysts for CO₂ utilization.

Introduction

There is considerable interest in the use of carbon dioxide (CO₂) as a carbon containing chemical feedstock due to its low cost, non-toxic nature, and abundance.¹ However, only a small number of chemicals are currently industrially produced from CO₂.^{1g} This is in part because the kinetic barriers associated with bond forming processes involving CO₂ are often prohibitively high. Transition metal catalysts represent a promising method to increase the range of products generated from CO₂ because they can create lower energy pathways for activating and functionalizing CO₂.¹ To date, most transition metal catalysts for CO₂ utilization have converted CO₂ into other C₁ products such as methane, CO, formic acid, and methanol and there are limited examples of catalysts that can form products containing C–C bonds, such as fuels, from CO₂.^{1g} As a result, the formation of products containing a C–C bond from CO₂ has been identified as a high priority research area by the United States National Academies of Science.²

In many transition metal catalyzed processes for CO₂ utilization, the insertion of CO₂ into a metal–E σ-bond (for example E = H, OR, NR₂, or CR₃) is a crucial elementary



step (Eq 1).³ This is especially the case for late transition metals, where the relative weakness of the M–O bonds makes subsequent cleavage of the M–O bond more facile.³ The insertion of CO₂ into a metal alkyl bond is a particularly important reaction because it can ultimately result in the generation of products containing a C–C bond. For example, Group 10 catalysts have been used for the formation of carboxylic acids through the carboxylation of a variety of alkyl halides and pseudo halides.⁴ In these reactions, C–C bonds are proposed to form between CO₂ and the alkyl electrophile via the insertion of CO₂ into a metal alkyl bond. However, at this stage there is limited experimental information on the pathways for CO₂ insertion into metal alkyl bonds, as most studies have primarily involved isolated examples with a single metal complex,^{5,6,7,8,9,10,11,12,13,14} and thus, it is unclear how changing the nature of the alkyl group or ancillary ligand impacts the reaction. Further, kinetic studies are relatively rare,^{6,8a,8b,9d,11c,13g,14b} which means that computational results cannot be benchmarked against experimental data.

Previous kinetic studies exploring CO₂ insertion into well-defined metal alkyl complexes have almost exclusively focused on metal methyl species.^{6,8a,8b,9d,11c,13g,14b} This is because of the stability of metal methyl complexes, which in contrast to longer chain alkyl containing complexes, such as

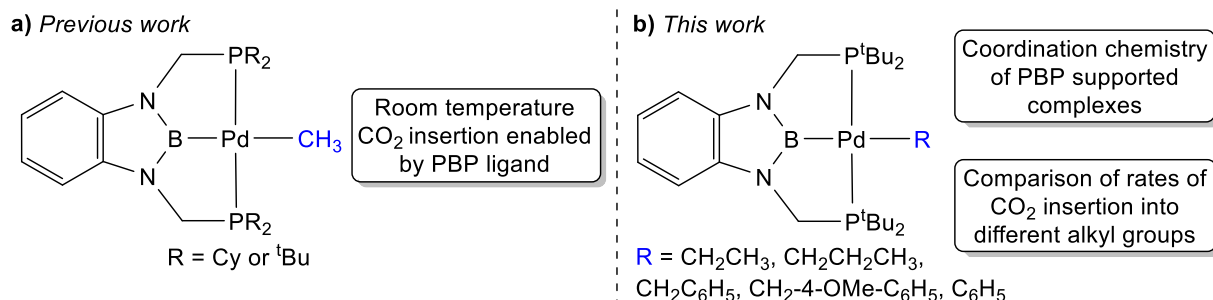


Figure 1: **a)** Previous example of CO_2 insertion into $^{\text{R}}\text{PBP}$ supported palladium methyl complexes at room temperature. **b)** $^t\text{BuPBP}$ supported palladium complexes studied in this work, which reveal fundamental information about the coordination chemistry of the $^t\text{BuPBP}$ ligand and enable a comparison between the rates of CO_2 insertion as a function of the alkyl ligand.

metal ethyl complexes, do not undergo β -hydride elimination. A major limitation in studying CO_2 insertion into metal methyl bonds, and in particular the types of Group 10 metal alkyl complexes that are relevant to catalysis, is the paucity of systems that are stable and react under mild reaction conditions. Most systems require high temperatures and do not give quantitative yields of products, which prevents kinetic studies. We recently described the insertion of CO_2 into palladium and nickel methyl complexes supported by $^{\text{R}}\text{PBP}$ ($^{\text{R}}\text{PBP} = \text{B}(\text{NCH}_2\text{PR}_2)_2\text{C}_6\text{H}_4$; $\text{R} = \text{Cy or } ^t\text{Bu}$) pincer ligands (Figure 1a).^{13g} The strong *trans*-influence of the boryl donor in the pincer ligand destabilizes the methyl group and as a consequence these complexes insert CO_2 at room temperature, which enabled us to perform detailed kinetic studies on CO_2 insertion into a metal methyl bond.

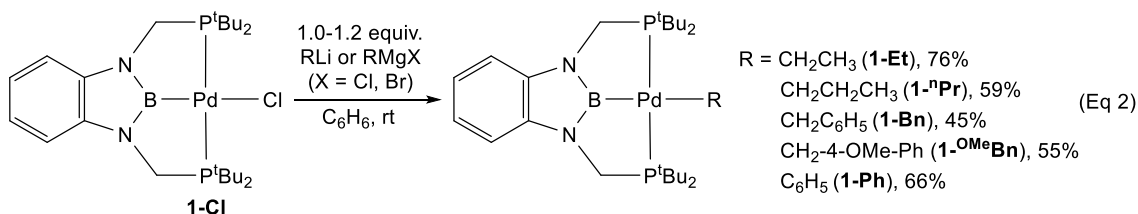
We hypothesized that the $^{\text{R}}\text{PBP}$ framework may stabilize palladium complexes with other alkyl ligands, as pincer ligands are known to inhibit β -hydride elimination from square planar palladium(II) complexes.¹⁵ Further, given that the $^{\text{R}}\text{PBP}$ ligand can facilitate CO_2 insertion reactions under mild conditions,^{13g} we postulated that the synthesis of a family of $^{\text{R}}\text{PBP}$ supported palladium alkyl complexes would enable us to perform a rare experimental comparison of the rates of CO_2 insertion as the alkyl ligand is varied. In this work, we describe the synthesis of a series of $^t\text{BuPBP}$ supported palladium complexes with ethyl, n-propyl, benzyl, and phenyl ligands. Although $(^t\text{BuPBP})\text{Pd}(\text{CH}_2\text{CH}_3)$ (**1-Et**), $(^t\text{BuPBP})\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_3)$ (**1-ⁿPr**), $(^t\text{BuPBP})\text{PdCH}_2\text{C}_6\text{H}_5$ (**1-Bn**), and $(^t\text{BuPBP})\text{PdCH}_2\text{-4-OMe-C}_6\text{H}_4$ (**1-^{OMe}Bn**), are sufficiently stable in solution to be isolated, attempts to synthesize complexes with n-butyl, iso-propyl, and tert-butyl ligands were unsuccessful due to rapid decomposition via either β -hydride elimination or an unusual reductive pathway that generates a new C–B bond. A similar reductive process to form a new H–B bond occurs in the

putative hydride complex (^tBuPBP)PdH. The stability of **1-Et**, **1-ⁿPr**, **1-Bn**, and **1-OMeBn** allowed us to determine the rates of CO₂ insertion into the palladium alkyl bonds. The rate constant for CO₂ insertion into **1-Et** is *over double* the rate constant previously measured for CO₂ insertion into (^tBuPBP)Pd(CH₃) (**1-Me**),^{13g} while insertion into **1-ⁿPr** occurs at *approximately one-tenth* the rate of **1-Me**. This is a remarkable difference given the relatively minor changes in the alkyl ligand. The insertion of CO₂ into the benzyl complexes, **1-Bn** and **1-OMeBn**, is significantly slower than any of n-alkyl complexes and CO₂ does not insert into the palladium phenyl bond of the related complex (^tBuPBP)Pd(C₆H₅) (**1-Ph**). DFT calculations enabled the rationalization of the relative rates of CO₂ insertion and suggest that steric factors are the predominant reason for the differences in the rates of insertion between **1-Me**, **1-Et**, and **1-ⁿPr**. Overall, the fundamental insight on CO₂ insertion provided in this work will likely assist in the development of improved and new catalysts for CO₂ utilization.

Results and Discussion

Synthesis of ^tBuPBP Supported Palladium Alkyl and Aryl Complexes

Previous studies have demonstrated that reactions of complexes of the form (^RPBP)PdCl (R = ⁱPr or ^tBu) with MeLi generate stable palladium methyl complexes.^{13g} In an analogous fashion, treatment of (^tBuPBP)PdCl (**1-Cl**) with EtLi or ⁿPrMgCl in benzene results in the formation of (^tBuPBP)Pd(CH₂CH₃) (**1-Et**) and (^tBuPBP)Pd(CH₂CH₂CH₃) (**1-ⁿPr**), which were isolated in yields of 76 and 59%, respectively, after recrystallization (Eq 2).¹⁶ **1-Et** is a rare example of an isolated pincer supported palladium ethyl complex,^{15,17} while **1-ⁿPr** is to the best of our knowledge only the second example of an isolated palladium propyl complex.¹⁸ **1-Et** and **1-ⁿPr** are indefinitely stable at room temperature in benzene and β-hydride elimination to generate ethylene or propene and a putative palladium hydride (*vide infra*) only occurs at temperatures greater than 60 °C. Recrystallization from pentane generated crystals of **1-Et** and **1-ⁿPr** suitable for X-ray diffraction (Figures 2a & 2b). In both cases, the geometry around Pd is distorted square planar and the P(1)-Pd(1)-P(2) bond angles are 153.99(6) and 154.23(2)° in **1-Et** and **1-ⁿPr**, respectively, indicating



that the phosphorus donors of the pincer ligand deviate significantly from linearity. The Pd–B bond distances are 2.029(7) Å in **1-Et** and 2.020(3) Å in **1-ⁿPr**, which are significantly longer than the Pd–B bond distance in (^tBuPBP)PdCl (Pd–B is 1.972(4) Å in **1-Cl**).¹⁹ This is consistent with the ethyl or propyl ligand exerting a stronger *trans*-influence than a chloride ligand. Although, crystallographically characterized examples of palladium ethyl complexes are rare,^{15,17,20} the Pd–C bond distance in **1-Et** is longer than those typically reported (Pd(1)–C(1) is 2.226(6) Å in **1-Et**) and is most comparable to a PSiP-supported palladium ethyl complex, which also contains a strong *trans*-influence donor (silyl) opposite the palladium.¹⁵ In **1-ⁿPr** the Pd(1)–C(1) is 2.209(2) Å, which is within error of the Pd–C bond distance in **1-Et**. The carbon atom bound to palladium (C(1)) is distorted from tetrahedral in both **1-Et** and **1-ⁿPr** and Pd(1)–C(1)–C(2) angles of 115.8(4)° and 114.49(15)°, respectively, are observed. Analysis of the literature reveals that this is a general trend for Group 10 alkyl complexes.²¹ Overall, the geometrical parameters around palladium are similar in **1-Me**,^{13g} **1-Et**, and **1-ⁿPr**, with the exception that the Pd–C bond distance in **1-Me** is slightly shorter than in **1-Et** or **1-ⁿPr** (Pd(1)–C(1) is 2.185(4) Å in **1-Me**), which is qualitatively consistent

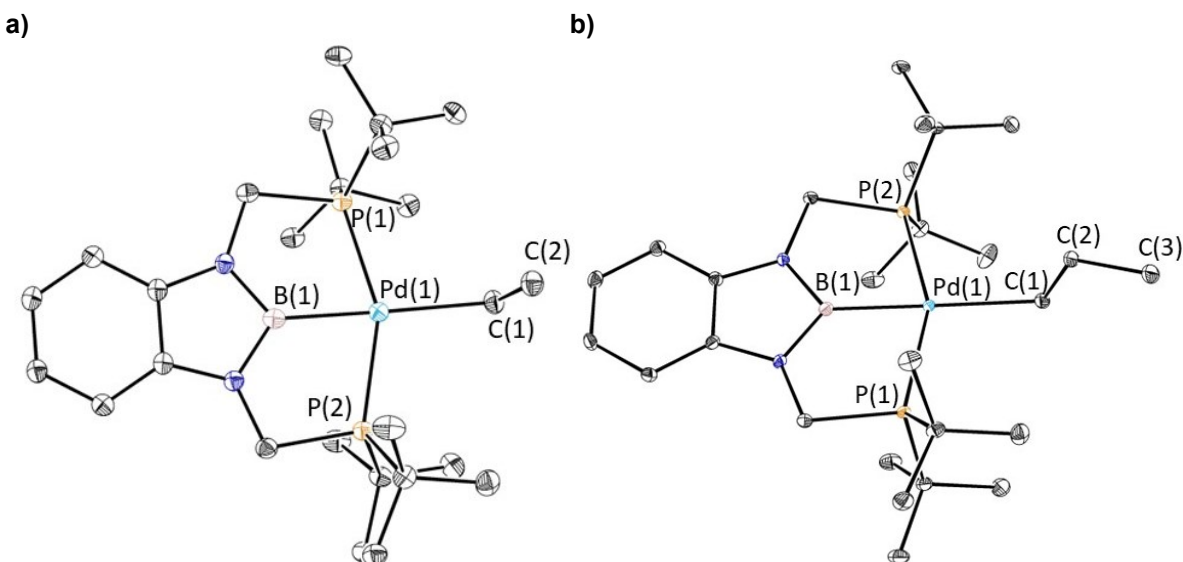


Figure 2: **a)** Solid-state structure of **1-Et** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)–B(1) 2.029(7), Pd(1)–C(1) 2.226(6), Pd(1)–P(1) 2.3184(15), Pd(1)–P(2) 2.3189(14), C(1)–C(2) 1.506(9), B(1)–Pd(1)–C(1) 175.3(2), B(1)–Pd(1)–P(1) 76.39(19), B(1)–Pd(1)–P(2) 78.23(19), C(1)–Pd(1)–P(1) 103.15(18), C(1)–Pd(1)–P(2) 102.61(18), P(1)–Pd(1)–P(2) 153.99(6), Pd(1)–C(1)–C(2) 115.8(4). **b)** Solid-state structure of **1-ⁿPr** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)–B(1) 2.020(3), Pd(1)–C(1) 2.209(2), Pd(1)–P(1) 2.3143(5), Pd(1)–P(2) 2.3135(5), C(1)–C(2) 1.531(3), C(2)–C(3) 1.528(3), P(1)–Pd(1)–P(2) 154.23(2), C(1)–Pd(1)–P(1) 101.54(6), C(1)–Pd(1)–P(2) 103.95(6), B(1)–Pd(1)–P(1) 77.67(7), B(1)–Pd(1)–P(2) 77.07(7), B(1)–Pd(1)–C(1) 177.01(9), Pd(1)–C(1)–C(2) 114.49(15).

with DFT calculations (*vide infra*). This suggests that as expected the change from methyl to ethyl to n-propyl has little impact on the geometry around palladium.

The reaction of **1-Cl** with (CH₂C₆H₅)MgCl or (4-OMe-CH₂C₆H₄)MgCl resulted in the isolation of **1-Bn** or **1-OMeBn**, which are rare examples of pincer supported benzyl complexes,²² in yields of 45% or 55%, respectively (Eq 2). In both cases, it is important to remove the MgCl₂ by-product from the Grignard reagent or the benzyl complexes slowly convert back to **1-Cl** in solution. In fact, the relatively low yields of **1-Bn** and **1-OMeBn** are in part due to the successive recrystallizations that are required to ensure MgCl₂ impurities are not present. Both **1-Bn** and **1-OMeBn** were characterized by X-ray crystallography (Figures 3a & 3b). The solid-state structures indicate that the geometry around palladium is distorted square planar and the geometrical parameters associated with the binding of the ^tBuPBP ligand in **1-Bn** and **1-OMeBn** are analogous to those in **1-Et** and **1-ⁿPr**. The long Pd–B bond distances (2.032(4) Å in **1-Bn** and 2.025(3) Å in **1-OMeBn**) are consistent with the high *trans*-influence of the benzyl ligand. The benzyl ligand binds in an η¹-fashion with Pd–C bond distances of 2.260(3) Å in **1-Bn** and 2.249(3) Å in **1-OMeBn**, which are longer than almost all other palladium complexes that feature an η¹-benzyl ligand.²² Further, the carbon atom bound to palladium (C(1)) is significantly distorted from tetrahedral, with

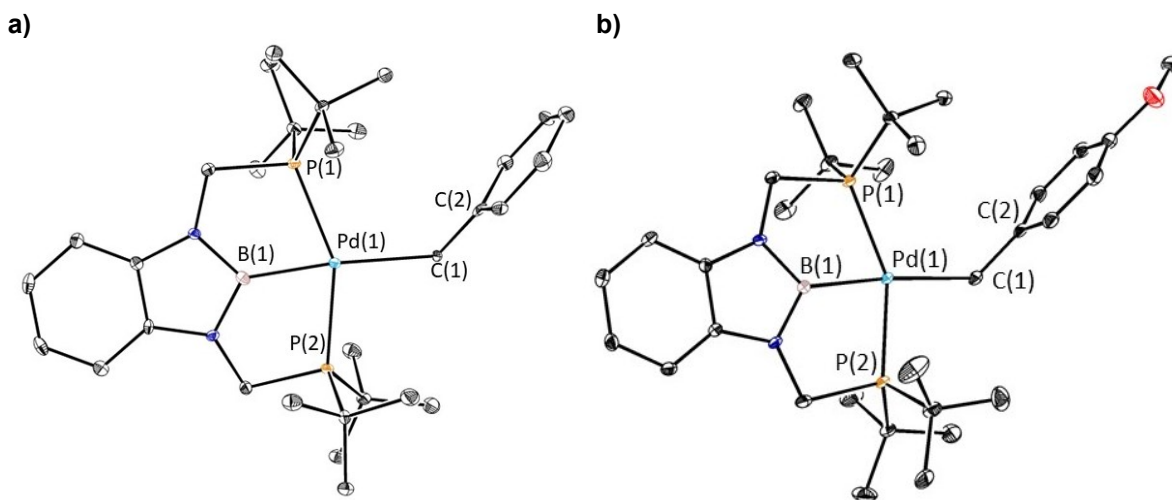
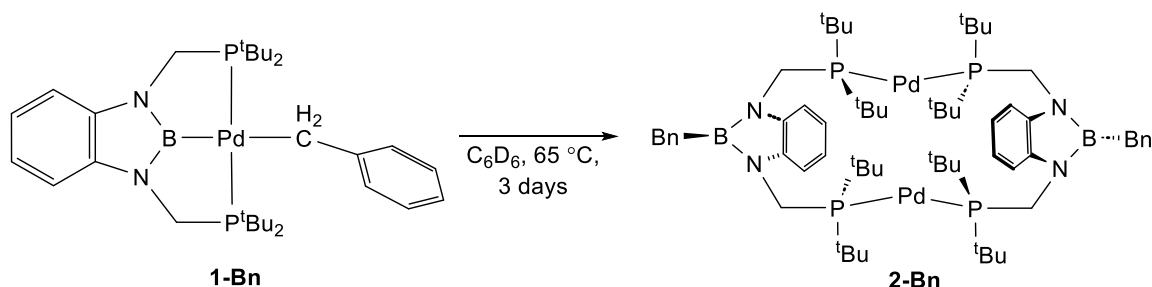


Figure 3: **a)** Solid-state structure of **1-Bn** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)–B(1) 2.032(4), Pd(1)–C(1) 2.260(3), Pd(1)–P(1) 2.3429(10), Pd(1)–P(2) 2.3407(10), C(1)–C(2) 1.477(5), B(1)–Pd(1)–C(1) 174.32(15), B(1)–Pd(1)–P(1) 76.60(12), B(1)–Pd(1)–P(2) 77.27(12), C(1)–Pd(1)–P(1) 108.72(9), C(1)–Pd(1)–P(2) 97.33(9), P(1)–Pd(1)–P(2) 153.77(3), Pd(1)–C(1)–C(2) 127.7(2). **b)** Solid-state structure of **1-OMeBn** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)–B(1) 2.025(3), Pd(1)–C(1) 2.249(3), Pd(1)–P(1) 2.3360(7), Pd(1)–P(2) 2.3402(8), C(1)–C(2) 1.486(4), P(1)–Pd(1)–P(2) 154.50(3), C(1)–Pd(1)–P(1) 107.42(8), C(1)–Pd(1)–P(2) 97.83(7), B(1)–Pd(1)–P(1) 77.05(9), B(1)–Pd(1)–P(2) 77.53(9), B(1)–Pd(1)–C(1) 174.21(11), Pd(1)–C(1)–C(2) 123.44(18).

Pd(1)-C(1)-C(2) angles of 127.7(2)° and 123.44(18)° observed for **1-Bn** and **1-OMeBn**, respectively. Although this deviation from tetrahedral is typical for Group 10 benzyl complexes,^{21a,21c,23} these are some of the largest angles reported perhaps due to the steric congestion around the palladium.

1-Bn is stable when left in C₆D₆ at room temperature, but complete decomposition is observed when it is heated for 3 days at 65 °C, with the major product being a new dimeric complex, (t^{Bu}PB^{Bn}P)₂Pd₂ (**2-Bn**, Bn = benzyl) (Figure 4a). Based on NMR spectroscopy we propose that **1-OMeBn** decomposes via a similar pathway (see SI). **2-Bn** was characterized by X-ray crystallography (Figure 4b). In **2-Bn**, two new C–B bonds have formed presumably due to a reductive coupling reaction between the benzyl ligands and the boron atom of the t^{Bu}PBP ligands. This causes a reduction in the palladium center from palladium(II) in **1-Bn** to palladium(0) in **2-Bn**. The boron atom of the pincer ligand no longer coordinates to the palladium center and the two

a)



b)

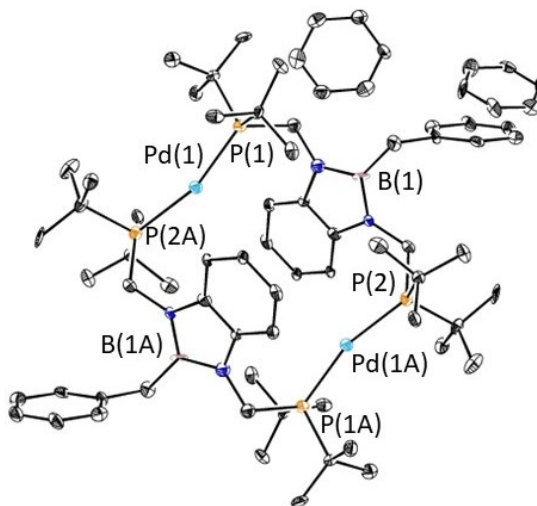
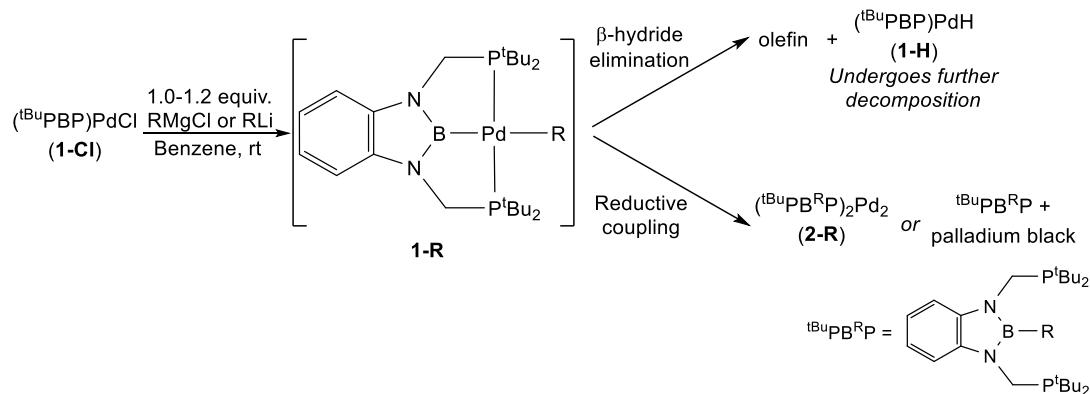


Figure 4: a) Reaction scheme for decomposition of (t^{Bu}PBP)Pd(CH₂C₆H₅) (**1-Bn**) to (t^{Bu}PB^{Bn}P)₂Pd₂ (**2-Bn**) and b) Solid-state structure of **2-Bn** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)-P(1) 2.277(2), Pd(1)-P(2A) 2.273(2), P(1)-Pd(1)-P(2A) 163.34(9).



Entry	Reagent	1-R isolable	Stability of 1-R at rt	Decomposition Pathway
1	<i>MeLi</i>	Yes ^a	Stable ^a	Slow reductive coupling (at 65 °C) to give 2-Me (see SI)
2	<i>EtLi</i>	Yes	Stable	β -Hydride Elimination (at 65 °C)
3	<i>nPrMgCl</i>	Yes	Stable	β -Hydride Elimination (at 60 °C)
4	<i>nBuLi</i>	No	Unstable	Reductive Coupling to give $t\text{BuPB}^{\text{nBu}}\text{P}$ and palladium black
5	<i>iPrLi</i>	No	Not Observed	Reductive Coupling to give $t\text{BuPB}^{\text{iPr}}\text{P}$ and palladium black
6	<i>tBuMgCl</i>	No	Not Observed	β -Hydride Elimination
7	<i>BenzylMgCl</i>	Yes	Stable	Reductive Coupling (at 65 °C) to give 2-Bn
8	<i>4-OMe-BenzylMgCl</i>	Yes	Stable	Reductive Coupling (at 65 °C) to give 2-OMeBn^b

Table 1: Summary of the reactions of RMgCl or RLi with $(t\text{BuPBP})\text{PdCl}$ (**1-Cl**). ^aSee reference 13g, ^b**2-OMeBn** was characterized by analogy to **2-Bn** and was not isolated.

phosphorus donors of the new bidentate $t\text{BuPB}^{\text{Bn}}\text{P}$ ligands do not coordinate to the same palladium center but instead coordinate to two different palladium atoms. The pathway for this ligand rearrangement is unclear. Consistent with the reduction in oxidation state, the geometry around the palladium centers in **2-Bn** are distorted linear. We have previously observed a similar decomposition pathway for $(t\text{BuPBP})\text{Ni}(\text{CH}_3)$, which results in the formation of a nickel(0) dinitrogen complex,^{13g} but this is the first time the reductive decomposition pathway has been observed for palladium. We hypothesize that reductive coupling occurs more readily in **1-Bn** compared to **1-Et** or **1-Me** (where it is not observed to any significant extent spectroscopically) because there is greater steric congestion in the case of the palladium benzyl complex. This is also in agreement with the observation of reductive coupling in the case $(t\text{BuPBP})\text{Ni}(\text{CH}_3)$ but not **1-Me**, as the smaller nickel center presumably results in a more congested metal center.^{13g} Our results

suggest that C–B bond formation is potentially a general decomposition pathway for ^RPBP supported complexes, rather than a curiosity that is only relevant to a single complex.

Although the reaction between **1-Cl** and EtLi results in clean formation of **1-Et**, the corresponding reactions between **1-Cl** and $^n\text{BuLi}$, $^i\text{PrLi}$, and $^t\text{BuMgCl}$ did not result in the generation of isolable palladium alkyl complexes and instead various decomposition products are observed (Table 1).^{24,25} In the case of $^t\text{BuMgCl}$, the initial metathesis reaction is slow and even after three days at room temperature some **1-Cl** is still present, along with three new peaks in the ^{31}P NMR spectra. Although we do not observe $(^t\text{BuPBP})\text{Pd}(^t\text{Bu})$ (**1- ^tBu**) directly, the peaks observed are consistent with the formation and decomposition of $(^t\text{BuPBP})\text{PdH}$ (**1-H**) (*vide infra* and see SI). **1-H** presumably forms via β -hydride elimination from **1- ^tBu** and in agreement with this proposal isobutene is observed by ^1H NMR spectroscopy. This suggests that **1- ^tBu** is unstable at room temperature and performing the reaction at low temperature is not possible due to the slow rate of the initial metathesis reaction.

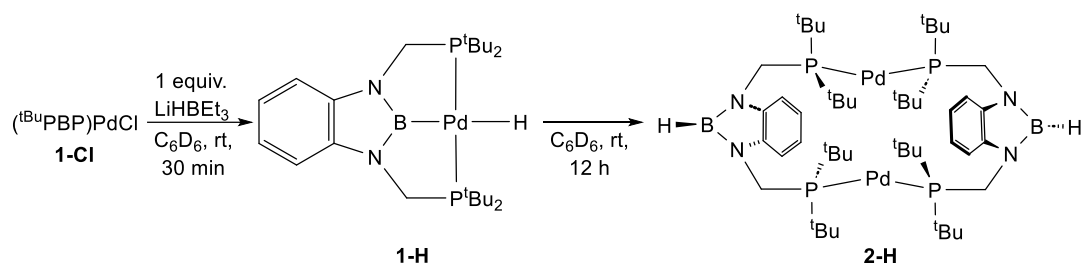
The reaction between **1-Cl** and $^i\text{PrLi}$ is rapid and after 10 minutes at room temperature there is no **1-Cl** left in the reaction mixture. At this time, one major peak is observed in the ^{31}P NMR spectrum at 15.6 ppm, which based on its downfield chemical shift is unlikely to be $(^t\text{BuPBP})\text{Pd}(^i\text{Pr})$ (**1- ^iPr**). Typically, palladium(II) complexes containing a $^t\text{BuPBP}$ ligand have chemical shifts between 60–120 ppm, whereas the chemical shift of the free $^t\text{BuPB}^{\text{HP}}$ ligand is 17.0 ppm.²⁶ There is also no evidence for the generation of products associated with β -hydride elimination from **1- ^iPr** , as no signals corresponding to $(^t\text{BuPBP})\text{PdH}$ (**1-H**) (or related decomposition products, *vide infra*) are observed in the ^1H or ^{31}P NMR spectra, and there are no resonances associated with propene in the ^1H NMR spectrum. Instead, we propose that the major species in the ^{31}P NMR spectrum is the organic compound $^t\text{BuPB}^{i\text{Pr}}\text{P}$, which was confirmed by mass spectrometry (see SI). We propose that $^t\text{BuPB}^{i\text{Pr}}\text{P}$ forms from the rapid reductive decomposition of **1- ^iPr** , which is generated but not observed in the reaction. The reductive process that **1- ^iPr** is postulated to undergo is akin to what we observed in the decomposition of **1-Bn** (*vide supra*) in that a new C–B bond is formed. However, in the case of **1- ^iPr** , we only see the free organic product $^t\text{BuPB}^{i\text{Pr}}\text{P}$ and there is no evidence that $^t\text{BuPB}^{i\text{Pr}}\text{P}$ coordinates to palladium to form a dimer analogous to **2-Bn**. Instead, palladium black precipitates out of solution. At this stage, it is unclear why $^t\text{BuPB}^{i\text{Pr}}\text{P}$ does not

coordinate to palladium in a similar fashion to $^t\text{BuPB}^{\text{Bn}}\text{P}$, and it is possible although unlikely that $^t\text{BuPB}^{\text{iPr}}\text{P}$ is formed through a pathway that does not even involve the formation of **1-ⁱPr**.

The reaction between **1-Cl** and $^n\text{BuLi}$ proceeds in an analogous fashion to the reaction between **1-Cl** and $^i\text{PrLi}$ and ultimately gives palladium black and $^t\text{BuPB}^{\text{nBu}}\text{P}$. However, the proposed intermediate alkyl complex, $(^t\text{BuPBP})\text{Pd}(^n\text{Bu})$ (**1-ⁿBu**), is more stable and at $-35\text{ }^\circ\text{C}$ the reaction mixture contained primarily **1-ⁿBu** ($\sim 97\%$), with only a small amount of the organic decomposition product $^t\text{BuPB}^{\text{nBu}}\text{P}$ ($\sim 3\%$) (see SI). Heating the sample to room temperature resulted in an increase in the amount of decomposition product and it was not possible to isolate **1-ⁿBu**. In contrast, as described above, it is possible to cleanly isolate **1-ⁿPr** from the reaction between **1-Cl** and $^n\text{PrMgCl}$ and decomposition of **1-ⁿPr** only occurs at $60\text{ }^\circ\text{C}$ (Eq 2). In this case, propene is observed in the ^1H NMR spectra along with products consistent with the formation and decomposition of **1-H** (*vide infra*), suggesting that decomposition primarily occurs via β -hydride elimination. Similar decomposition via β -hydride elimination is observed at $65\text{ }^\circ\text{C}$ for **1-Et**, with ethylene observed as a by-product. We also examined the stability of previously reported **1-Me**^{13g} and demonstrated that at $65\text{ }^\circ\text{C}$ it undergoes very slow C–B reductive coupling to form $(^t\text{BuPB}^{\text{Me}}\text{P})_2\text{Pd}_2$ (**2-Me**) (see SI). Our results indicate that the stability of $^t\text{BuPBP}$ ligated Pd alkyl complexes is related to the steric bulk of the alkyl group, so the order of stability is **1-^tBu** $\sim$ **1-ⁱPr** $<$ **1-ⁿBu** $<$ **1-ⁿPr** $\sim$ **1-Et** $<$ **1-Me**. Interestingly, the least and most sterically bulky complexes decompose via β -hydride elimination, while those with intermediate steric properties decompose through reductive coupling. **1-Me** is an exception as it lacks any β -hydrogens and therefore despite its small size decomposes via reductive coupling.

To verify our hypothesis that the rapid decomposition of **1-^tBu** results in the formation of the palladium hydride complex **1-H**, we attempted to independently prepare **1-H**. Reaction of **1-Cl** with 1 equivalent of LiHBEt_3 in C_6D_6 generated two major products in an approximately 55:45 ratio by ^1H and ^{31}P NMR spectroscopy (Figure 5). We propose that one of these is **1-H** because the ^{31}P NMR chemical shift (115 ppm, 55%) is very close to the shift for the corresponding $(^t\text{BuPBP})\text{PtH}$ complex (114.5 ppm).²⁷ The other resonance in the ^{31}P NMR spectra is observed at 96.4 ppm, but even though it is present in both the decomposition of **1-^tBu**, **1-Et**, and **1-ⁿPr**, as well as the attempted direct synthesis of **1-H**, we are unsure of the identity of the complex giving rise to this signal. Further, although the complex giving rise to the signal at 96.4 ppm is relatively

a)



b)

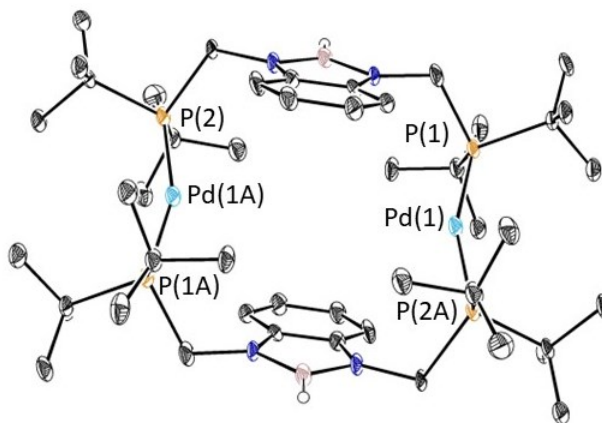


Figure 5: a) Synthesis and decomposition of $t\text{BuPBP}$ supported palladium hydride, **1-H**, to form $(t\text{BuPBP})_2\text{Pd}_2$ (**2-H**). The decomposition at room temperature in solution prevented the isolated of **1-H**. b) Solid-state structure of **2-H** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)-P(1) 2.2821(15), Pd(1)-P(2A) 2.2850(15), P(1)-Pd(1)-P(2A) 159.99(5).

stable over 12 hours, the complex giving rise to the signal at 115 ppm decomposes at room temperature in C_6D_6 to give a dimeric palladium(0) complex, **2-H**, in which the hydride has reductively coupled with the boron atom of the $t\text{BuPBP}$ ligand to give a new H–B bond (Figure 5). This is an analogous process to the decomposition of **1-Bn**, except an H–B bond is formed instead of a C–B bond. **2-H** was characterized by single crystal X-ray diffraction (Figure 5b) and contains two distorted linear palladium(0) centers. The phosphorous atoms of the pincer ligands have rearranged so they bind to two different palladium centers rather than a single palladium center. In this case, it is presumably not steric factors that drive the decomposition of the palladium hydride but the formation of a strong H–B bond. Given the large number of stable pincer-supported palladium hydrides,²⁸ we hypothesize that **1-H** is unstable because of the *trans*-influence of the boryl ligand, which significantly destabilizes the hydride relative to other species which have weaker *trans*-influence ligands opposite the hydride.

To compare the reactivity of $t\text{BuPBP}$ supported palladium alkyl complexes with a $t\text{BuPBP}$ supported

palladium aryl species, we prepared (^tBuPBP)Pd(C₆H₅) (**1-Ph**) (Eq 2). Although, the synthesis of **1-Ph** followed the same route as the palladium alkyl species described above,²⁹ the reaction of **1-Cl** with PhMgBr was significantly slower than the corresponding reactions with alkyl lithium or Grignard reagents. Specifically, the reaction with PhMgBr took two days to reach completion at room temperature, whereas the reactions with alkyl lithium or Grignard reagents were typically complete in less than one hour at room temperature (except for ^tBuMgCl). This is likely related to the lower nucleophilicity of aryl Grignard reagents compared with alkyl Grignard reagents. After recrystallization to remove Mg salt impurities, we were able to isolate **1-Ph** in 66% yield. **1-Ph** was characterized by X-ray crystallography (see SI). The Pd–C bond distance in is 2.162(3) Å, which is significantly shorter than the Pd–C bond length in all of our palladium alkyl complexes. This is likely due to the fact that the carbon atom bound to palladium in **1-Ph** is sp²-hybridized and is consistent with the trend observed for PCP-supported pincer complexes.¹⁴

Reactivity of ^tBuPBP Supported Palladium Alkyl and Aryl Complexes with CO₂

The reaction of **1-Et** with 1 atm of CO₂ in C₆D₆ at room temperature quantitatively generated the palladium carboxylate complex (^tBuPBP)Pd{OC(O)CH₂CH₃} (**3-Et**) in approximately 2 hours (Figure 6). This is the fastest rate of CO₂ insertion observed for a pincer supported palladium alkyl species. **3-Et** was isolated and characterized using single crystal X-ray diffraction (Figure 7). The solid-state structure confirms κ¹-binding of the carboxylate. The Pd–O bond distance is 2.1803(14) Å, which is relatively long for a palladium(II) carboxylate complex.^{13g,14a,30} This suggests that it will be easier to cleave the Pd–O bond in **3-Et** compared to related palladium carboxylate complexes, which have been generated via CO₂ insertion reactions.^{6,14a} The Pd–B bond distance is significantly shorter in **3-Et** (1.973(2) Å) compared with **1-Et** (2.029(7) Å), which is consistent with the carboxylate ligand exerting a significantly weaker *trans*-influence than the ethyl ligand.

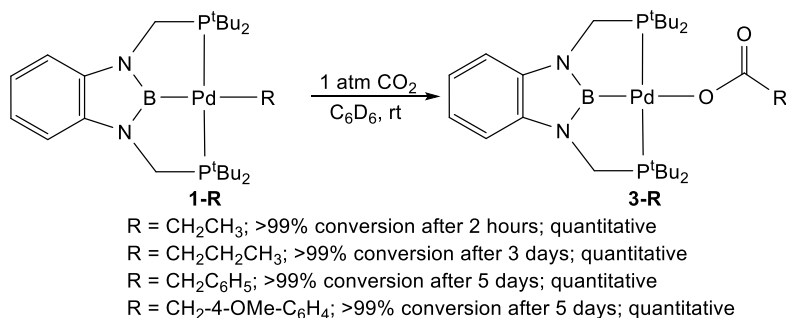


Figure 6: Relative rates of CO₂ insertion into ^tBuPBP supported palladium alkyl complexes to form palladium carboxylate complexes.

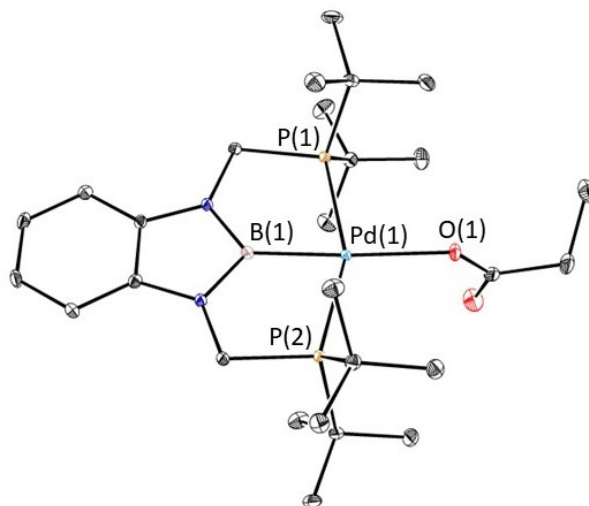


Figure 7: Solid-state structure of **3-Et** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pd(1)-B(1) 1.973(2), Pd(1)-O(1) 2.1803(14), Pd(1)-P(1) 2.3449(5), Pd(1)-P(2) 2.3450(5), B(1)-Pd(1)-O(1) 173.80(7), B(1)-Pd(1)-P(1) 78.20(7), B(1)-Pd(1)-P(2) 78.45(7), O(1)-Pd(1)-P(1) 101.78(4), O(1)-Pd(1)-P(2) 101.30(4), P(1)-Pd(1)-P(2) 156.617(19), Pd(1)-O(1)-C(1) 123.46(14).

The rapid insertion of CO₂ into **1-Et** at room temperature enabled us to use NMR spectroscopy to measure the kinetics of the reaction. We performed kinetics experiments under pseudo-first order conditions with an excess of CO₂ and measured both the disappearance of **1-Et** and the appearance of **3-Et** (Figure 8a). The reaction is first order in both **1-Et** and [CO₂], so the overall rate law is $k_1[(^t\text{BuPBP})\text{Pd}(\text{CH}_2\text{CH}_3)][\text{CO}_2]$ (Figure 8b and SI). We were able to obtain values of k_1 at different temperatures by dividing the k_{obs} values obtained from a plot of $\ln[(^t\text{BuPBP})\text{Pd}(\text{CH}_2\text{CH}_3)]$ versus time by the concentration of CO₂ (Table 2 and SI). The most striking feature of our k_1 values is

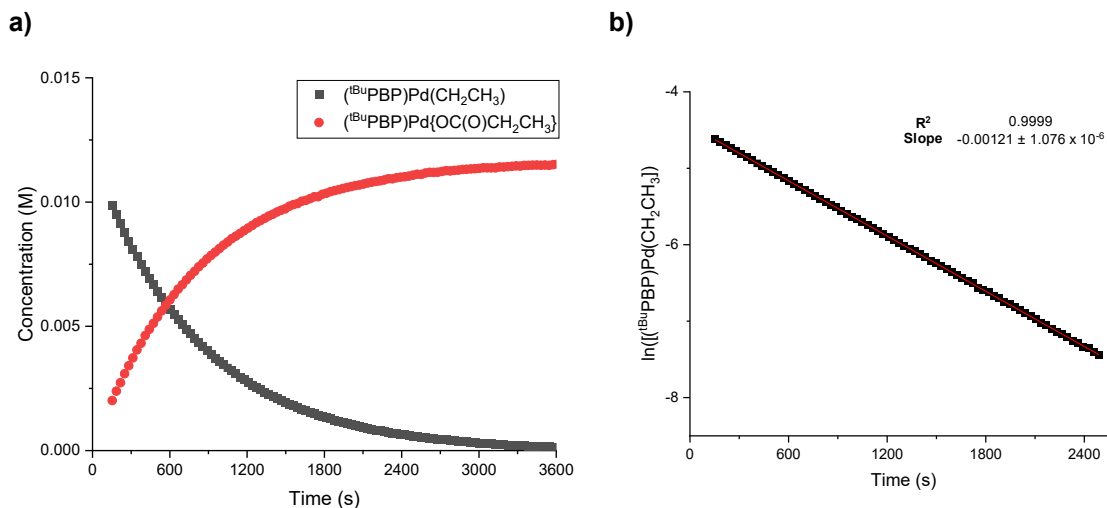


Figure 8: Representative traces for the insertion of CO₂ into (^tBuPBP)Pd(CH₂CH₃) (**1-Et**) at 30 °C in C₆D₆ with 1 atm of CO₂ showing **a)** the concentrations of (^tBuPBP)Pd(CH₂CH₃) (**1-Et**) and (^tBuPBP)Pd{OC(O)CH₂CH₃} (**3-Et**) as a function of time and **b)** the ln of the concentration of (^tBuPBP)Pd(CH₂CH₃) (**1-Et**) as a function of time.

that at 40 °C, the rate constant for CO₂ insertion into **1-Et** is *more than double* the rate constant for insertion into **1-Me** that we measured previously.^{13g} In the only other comparative study of the rates of CO₂ insertion into metal methyl and ethyl species, Darensbourg and co-workers observed that CO₂ insertion into [RW(CO)₅]⁻ (R = CH₃ or CH₂CH₃) is 1.5 times faster for methyl than for ethyl, the opposite trend to our system.^{8b} At this stage, given the paucity of other comparative studies on the rates of CO₂ insertion into different metal alkyls, it is unclear if either result is an outlier or the nature of the underlying factors that cause the variation in trends.

Entry	Complex	Temperature (°C)	Solvent	k ₁ (M ⁻¹ s ⁻¹ x 10 ⁻²) ^a
1	1-Et	25	C ₆ D ₆	1.2
2	1-Et	30	C ₆ D ₆	2.1
3	1-Et	35	C ₆ D ₆	2.9
4	1-Et	40	C ₆ D ₆	3.4
5	1-Et	45	C ₆ D ₆	4.7
6	1-Me	40	C ₆ D ₆	1.3
7	1-Me	45	C ₆ D ₆	2.3
8	1-Bn	30	Pyridine- <i>d</i> ₅	0.48
9	1-OMeBn	30	Pyridine- <i>d</i> ₅	0.43

Table 2: Comparison of the rate constants for CO₂ insertion into (^tBuPBP)Pd(alkyl) at various temperatures, solvents, and 1 atm of CO₂. ^aThese values are the average of two trials and the errors are ±10%.

Using the values of k₁ at different temperatures we determined the activation parameters for CO₂ insertion into **1-Et** through Eyring analysis. The enthalpy of activation, ΔH[‡], is 11.3 ± 1.1 kcal mol⁻¹, the entropy of activation, ΔS[‡], is -29.0 ± 2.9 cal mol⁻¹ K⁻¹, and ΔG[‡]₂₉₈ is 20.0 ± 2.0 kcal mol⁻¹ (see SI). All of these values are within error to those previously measured for **1-Me**,^{13g} suggesting that the reactions proceed via similar pathways. The enthalpy for CO₂ insertion into **1-Et** is lower than that observed for insertion into palladium methyl complexes with pincer ligands that contain a lower *trans*-influence donor in the central position. For example, ΔH[‡] for CO₂ insertion into (^tBuPCP)Pd(CH₃) (^tBuPCP = 2,6-C₆H₃(CH₂P^tBu)₂) is 17.4 ± 1.7 kcal/mol.^{14b} This is consistent with the ^tBuPBP ligand destabilizing **1-Et** by weakening the Pd–C bond of the palladium ethyl ligand. The negative entropy of activation is similar to those observed in other systems for CO₂ insertion^{13g,14b} and is in agreement with a rate-limiting transition state in which two molecules are combining to form one compound in the transition state.

The reaction of **1-ⁿPr** with 1 atm of CO₂ in C₆D₆ at room temperature also cleanly generated the palladium carboxylate complex (^tBuPBP)Pd{OC(O)CH₂CH₂CH₃} (**3-ⁿPr**) (Figure 6). Surprisingly, CO₂ insertion into **1-ⁿPr** is significantly slower than the corresponding insertion reactions with **1-Me** and **1-Et**. In the case of **1-ⁿPr**, the reaction required 3 days to reach completion at room

temperature.³¹ This slow rate of insertion precluded the measurement of a rate constant using our NMR method, but based on the reaction half-life of approximately 11 hours we estimate that insertion into **1-ⁿPr** occurs approximately *one order of magnitude slower than* the rate of insertion into **1-Me**. Further, we were unable to heat the reaction of **1-ⁿPr** with CO₂ to sufficiently speed up the reaction, as this resulted in decomposition of **1-ⁿPr**. Overall, our results show that the simple change in alkyl group from **1-Me** to **1-Et** to **1-ⁱPr** results in significant and non-intuitive changes in the rates of CO₂ insertion. This is potentially important in catalysis as it implies the rate of CO₂ insertion into palladium alkyl complexes (and potentially other metal alkyl complexes) will be heavily substrate dependent.

The reactions of the benzyl complexes **1-Bn** and **1-^{OMe}Bn** with 1 atm of CO₂ at room temperature formed the carboxylate complexes (^tBuPBP)Pd{OC(O)CH₂C₆H₅} (**3-Bn**) and (^tBuPBP)Pd{OC(O)CH₂-4-OMe-C₆H₄} (**3-^{OMe}Bn**), respectively (Figure 6). These reactions were significantly slower than the corresponding insertion reactions with **1-Me**, **1-Et**, or even **1-ⁿPr**. For example, in C₆D₆ at room temperature the reactions took approximately 5 days to reach completion. The slower rate of insertion into palladium benzyl complexes compared with palladium n-alkyl complexes is unsurprising as the benzylic carbon bound to palladium is expected to be a worse nucleophile due to the electron-withdrawing nature of the aromatic group, which makes it less energetically favorable to attack electrophilic CO₂. In order to measure the kinetics of insertion into **1-Bn** and **1-^{OMe}Bn** we needed to increase the rate of the reaction. Unfortunately, it is not possible to raise the temperature to promote CO₂ insertion into **1-Bn** in C₆D₆ as this leads to decomposition to form the palladium(0) complex, **2-Bn**, as well as the CO₂ inserted product. However, we have previously demonstrated that the rates of CO₂ insertion reactions can be increased by performing the reaction in solvents with a higher Dimroth-Reichardt *E*_T(30) parameter,^{13g,32} which is an empirical measure of the polarity of a solvent.^{33,34} When CO₂ insertion reactions were performed in pyridine-*d*₅, the reactions with **1-Bn** and **1-^{OMe}Bn** were complete in approximately 5 hours at room temperature, with no evidence for the formation of palladium(0) complexes. This again highlights the dramatic effect of solvent on CO₂ insertion reactions.^{13g,32,35} At 30 °C, the rate constants for CO₂ insertion into **1-Bn** and **1-^{OMe}Bn** in pyridine-*d*₅ were 0.0048 ± 0.0005 and 0.0043 ± 0.0004 M⁻¹s⁻¹, respectively. The fact that these values are the same within error indicates that the substitution on the phenyl ring surprisingly does not significantly affect the nucleophilicity of the carbon bound to palladium and means that in the catalytic carboxylation of

benzylic substrates³⁶ the electronic effect of the substituents on the rate of CO₂ insertion is likely minimal. Unfortunately, we are unable to measure the rate constants for CO₂ insertion into **1-Me** or **1-Et** in pyridine-*d*₅ because the reaction occurs too fast to obtain an accurate rate constant using NMR spectroscopy. However, we estimate a minimum rate constant of 0.2 M⁻¹s⁻¹, which is significantly faster than for the benzyl compounds.

In contrast to our results with palladium alkyl complexes, no reaction was observed when **1-Ph** was treated with 1 atm of CO₂, even after prolonged heating at elevated temperature. Although at this stage it is unclear whether kinetic or thermodynamic factors are responsible for the lack of reactivity, our result is consistent with observations for other pincer supported Group 10 phenyl complexes, which also do not react with CO₂.^{13b,13e} Hence, although the PBP ligand promotes CO₂ insertion into palladium alkyl complexes, it does not facilitate insertion reactions into palladium aryl complexes.

Computational Studies of CO₂ Insertion into Palladium Alkyl and Aryl Complexes

We performed DFT calculations (PBE0-D3BJ,[IEFPCM]) to further understand the mechanism of CO₂ insertion into **1-Me**, **1-Et**, **1-ⁿPr**, **1-Bn**, and **1-OMeBn**. Previously, we have demonstrated that

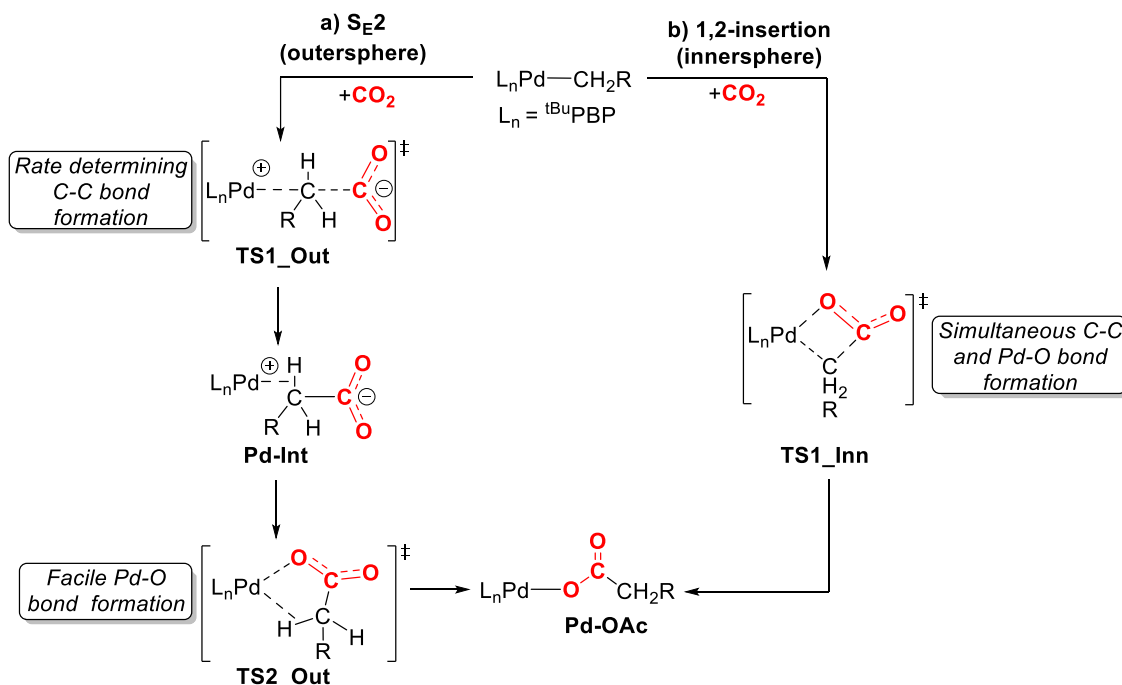


Figure 9: Two plausible mechanisms for CO₂ insertion into pincer-supported palladium alkyl complexes: **a)** S_E2 (outersphere) and **b)** 1,2-insertion (insphere). For **1-Me** we previously demonstrated that the S_E2 pathway is lower energy and the initial nucleophilic attack of the carbon atom of the methyl group on CO₂ is rate-determining.^{13g}

CO₂ insertion into **1-Me** follows an S_E2 (or outersphere) pathway (Figure 9a),^{13g} in which the first and rate-limiting step is nucleophilic attack of the carbon atom of the palladium methyl on the electrophilic carbon atom of CO₂ to form the C–C bond. Notably, there is no interaction between CO₂ and the palladium center in this transition step. The second step in CO₂ insertion into **1-Me** via an S_E2 pathway has a significantly lower barrier and involves the rearrangement of an carboxylate-palladium ion pair bound through a C–H σ-bond to the neutral Pd–O containing product.^{13g} An alternative pathway involving 1,2-insertion (innersphere, Figure 9b) in which both the Pd–O and C–C bonds are formed at the same transition state was calculated to be energetically unfavorable for **1-Me**.

Here, we calculated that for CO₂ insertion into **1-Et**, the barrier for the first step in the S_E2 pathway is 17.7 kcal mol⁻¹ at 298 K (Figure 10, Table 3).³⁷ This is in good agreement with the experimentally determined barrier of 20.0 ± 2.0 kcal mol⁻¹ (*vide supra*). The barrier for the innersphere 1,2-insertion pathway is calculated to be 26.0 kcal mol⁻¹, unambiguously indicating that the S_E2 pathway is preferred. A surprising feature of **1-Et** is that it does not undergo facile β-hydride elimination. We calculated that the barrier for β-hydride elimination is relatively high (32.3 kcal mol⁻¹), consistent with the stability of the complex towards β-hydride elimination. β-

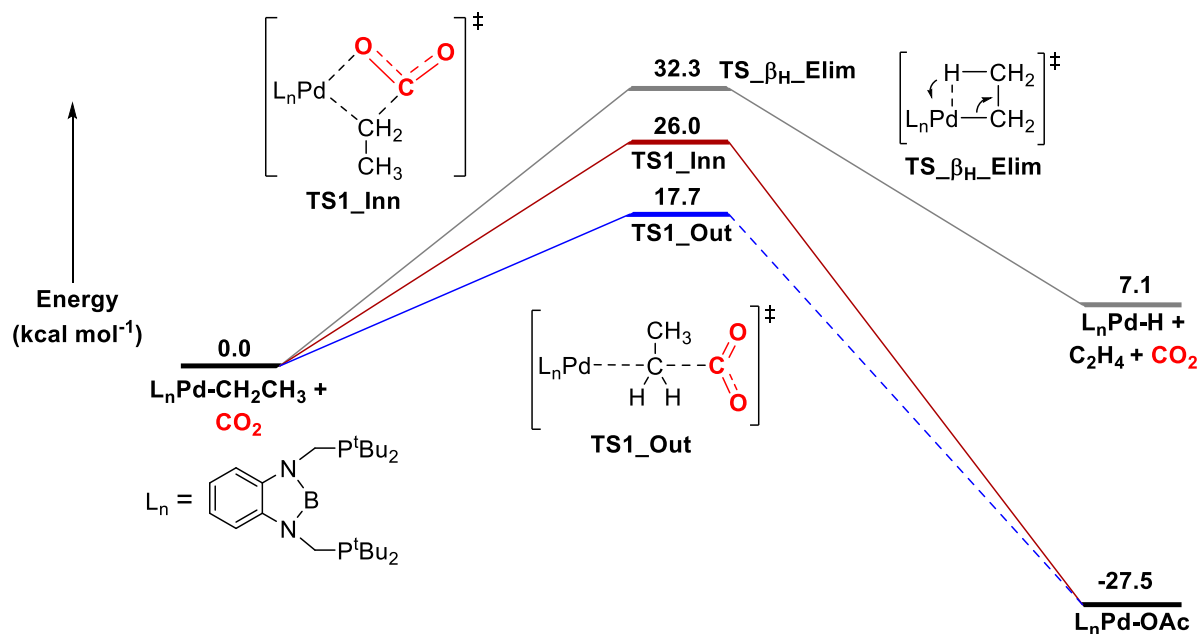


Figure 10: Relative energies of CO₂ insertion into **1-Et** via an S_E2 (outersphere) and 1,2-addition (innersphere) pathway, as well as the energy for β-hydride elimination. In the S_E2 pathway, we were unable to find the intermediate and barrier for the second rearrangement step to form the palladium carboxylate product, as the rearrangement occurs spontaneously during geometry optimization. However, this process has previously been demonstrated to be low energy in related systems.^{13g}

hydride elimination is presumably disfavored because of the rigidity of the pincer ligand, which makes it energetically difficult for the complex to distort to form the syn co-planar arrangement of the palladium, C α , C β , and H required for β -hydride elimination.

DFT calculations predict that the barriers for CO₂ insertion into **1-Me** and **1-ⁿPr** are 19.4 kcal mol⁻¹ and 21.8 kcal mol⁻¹, respectively, which means that the calculations are in line with the experimental trends in rate (**1-Et** > **1-Me** > **1-ⁿPr**) (Table 3).³⁸ The rate-determining transition states for CO₂ insertion into **1-Me**, **1-Et**, and **1-ⁿPr** are analogous (the 1st step in the S_E2 mechanism), so the differences in rate are not related to a change in mechanism. Instead, we propose that the difference in rates is due primarily to steric factors, which affect the relative stability of both the reactant complexes and the transition states. **1-Et** and **1-ⁿPr** are likely slightly destabilized relative to **1-Me** because of steric interactions between the ethyl or propyl ligand and the tert-butyl substituents of the ^tBuPBP ligand. This is reflected by the increased thermodynamic favorability of CO₂ insertion into **1-Et** and **1-ⁿPr** compared to **1-Me** ($\Delta G^\circ = -27.5$ and -26.2 kcal/mol, respectively, versus -22.9 kcal mol⁻¹). Presumably, in the carboxylate complexes, the steric pressure is relieved because of the absence of hydrogens on the oxygen bound to palladium.

Table 3: Calculated barriers for CO₂ insertion into (^RPBP)Pd(alkyl) complexes.

Complex	$\Delta G^\ddagger$ (kcal mol ⁻¹)
(^t BuPBP)Pd(CH ₃) (1-Me)	19.4
(^t BuPBP)Pd(CH ₂ CH ₃) (1-Et)	17.7
(^t BuPBP)Pd(CH ₂ CH ₂ CH ₃) (1-ⁿPr)	21.8
(^t BuPBP)Pd{CH(CH ₃) ₂ } (1-ⁱPr)	28.2
(^t BuPBP)Pd(CH ₂ C ₆ H ₅) (1-Bn)	20.3
(^t BuPBP)Pd(CH ₂ -4-OMeC ₆ H ₄) (1-^{OMe}Bn)	20.5
(^t BuPBP)Pd(CH ₂ -4-CF ₃ C ₆ H ₄) (1-^{CF3}Bn)	20.6
(^t BuPBP)Pd(C ₆ H ₅) (1-Ph)	34.6 ^a
(ⁱ PrPBP)Pd(CH ₃)	16.8 ^a
(ⁱ PrPBP)Pd(CH ₂ CH ₃)	18.7
(ⁱ PrPBP)Pd(CH ₂ CH ₂ CH ₃)	20.3
(^{Me} PBP)Pd(CH ₃)	17.5 ^a
(^{Me} PBP)Pd(CH ₂ CH ₃)	17.3 ^a
(^{Me} PBP)Pd(CH ₂ CH ₂ CH ₃)	17.5 ^a

^aThe lowest energy pathway for CO₂ insertion is the 1,2-insertion (or innersphere) mechanism rather than the S_E2 (or outersphere) mechanism.

The steric properties of **1-Me**, **1-Et**, and **1-ⁿPr** were quantitatively evaluated by calculating the percent buried volume (%V_{Bur}) of these complexes based on their crystal structures using the Salerno molecular buried volume program (SambVca 2.1) (Figure 11).³⁹ Although there is only a small difference in %V_{Bur} between the three complexes (86.9% for **1-Me**, 87.7% for **1-Et**, and

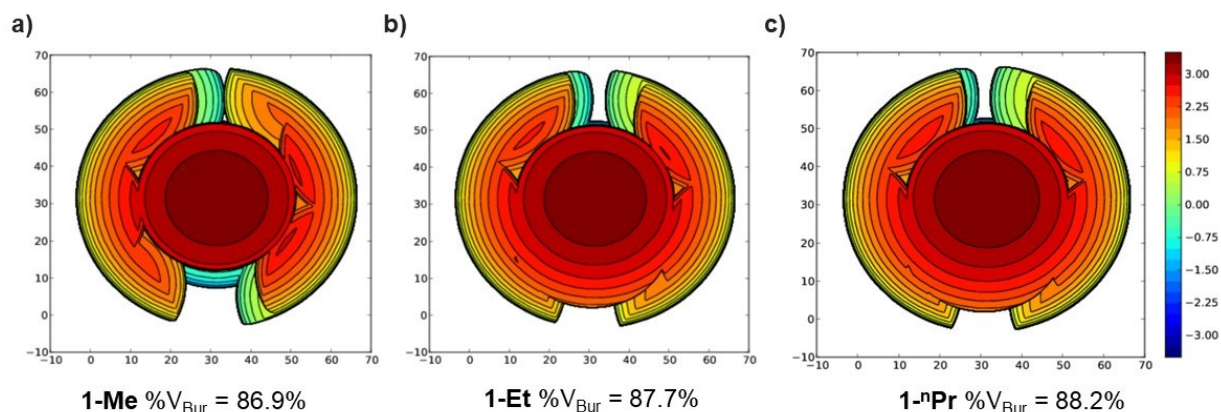


Figure 11: Topographic steric maps of **a) 1-Me**, **b) 1-Et**, and **c) 1-ⁿPr** as viewed down the C-Pd bond towards the plane defined by P-Pd-P.³⁹

88.2% for **1-ⁿPr**) the absolute magnitude of these numbers indicates the high degree of steric crowding around the palladium centers and suggests that small changes could have a significant impact on the rate of CO₂ insertion. Our proposal is that **1-Et** is sufficiently sterically crowded to destabilize the ethyl ligand, but still open enough for CO₂ to easily approach the ethyl group. This increases the rate of insertion in comparison to **1-Me**. In contrast, even though **1-ⁿPr** is sufficiently sterically crowded to destabilize the n-propyl ligand, the complex is so congested that it is unfavorable for CO₂ to approach, which increases the barrier for insertion. Consistent with this proposal, the computed barrier for CO₂ insertion into the even more sterically congested (^tBuPBP)Pd{CH(CH₃)₂} (**1-ⁱPr**) increases to 28.2 kcal mol⁻¹ (Table 3). Finally, the trajectory of electrophilic attack of CO₂ is quite different for **1-Me** compared to **1-Et** and **1-ⁿPr**. In **1-Me** the CO₂ is nearly orthogonal to the palladium methyl bond, whereas in **1-Et** and **1-ⁿPr** it is essentially co-planar (Figure 12). In **1-Et** and **1-ⁿPr** this geometry leads to close contacts between three C–H bonds and the incipient carboxylate group, which may help stabilize the emerging charge on the

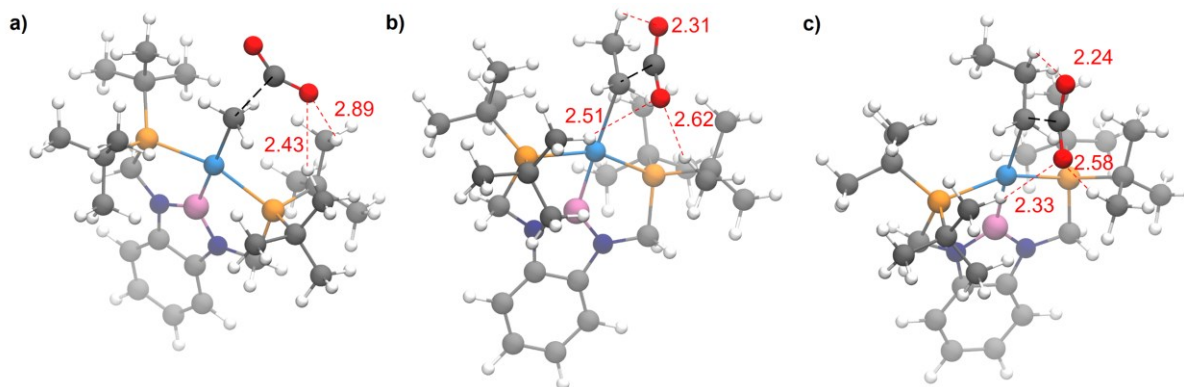


Figure 12: Rate determining transition states for CO₂ insertion into **a) 1-Me**, **b) 1-Et**, and **c) 1-ⁿPr**. Close contacts between ligand C–H bonds and the incipient carboxylate group are highlighted in red. The bond forming atoms are connected by a dotted black line.

carboxylate group. We were unable to locate a similar TS for insertion into **1-Me**, and in the calculated TS there are only interactions between two C–H bonds and the incipient carboxylate group. In the case of **1-Pr**, destabilization due to steric strain is likely a larger force than stabilization due to an extra non-covalent interaction and therefore the overall barrier is higher.

To further probe the role of steric factors on the rates of CO₂ insertion, we performed calculations on the smaller model complexes (^RPBP)Pd(alkyl) (R = Me or ⁱPr; alkyl = CH₃, CH₂CH₃, or CH₂CH₂CH₃). Interestingly, in the case of ^{Me}PBP, DFT predicts that the preferred CO₂ insertion pathway changes from S_E2 to 1,2-insertion for all tested alkyls (see SI), suggesting that the size of the ligand is crucial in determining the reaction pathway. We propose that complexes with a smaller steric profile are more likely to react via a 1,2-insertion pathway compared with complexes that are more congested, because in this case it is easier for CO₂ to interact with the metal center. Further, in the case of ^{Me}PBP supported complexes the calculated rates of insertion are the same for the methyl, ethyl, and n-propyl species, suggesting that the nature of the alkyl group is less important for systems that react through a 1,2-insertion pathway. This is unsurprising as in the 1,2-insertion pathway the metal center is directly involved, which likely lessens the impact of the alkyl group. For the ⁱPrPBP supported palladium complexes, the 1,2-insertion pathway is preferred for (ⁱPrPBP)Pd(CH₃), whereas the S_E2 is preferred for the ethyl and propyl complexes, with the later showing higher barriers than (ⁱPrPBP)Pd(CH₃). The barrier for insertion into (ⁱPrPBP)Pd(CH₂CH₃) is lower than for (ⁱPrPBP)Pd(CH₂CH₂CH₃), indicating that there is a likely still a steric effect with the ⁱPrPBP pincer ligand. Our results with smaller ancillary ligands suggest that the observation that CO₂ insertion is faster for **1-Et** than for **1-Me** or **1-Pr** is unlikely to be general to all systems. The ^tBuPBP ligand creates an environment where the sterics are sufficiently crowded that a minor change results in non-intuitive changes in rate, whereas for other supporting ligands this will not be the case, as evidenced by our calculated results with ⁱPrPBP and ^{Me}PBP.

We next investigated the barriers for CO₂ insertion into the palladium benzyl complexes **1-Bn**, **1-OMeBn**, as well as the hypothetical complex (^tBuPBP)Pd(CH₂-4-CF₃-C₆H₄) (**1-CF₃Bn**) (Table 3). The calculated barrier for CO₂ insertion into **1-Bn** (20.3 kcal mol⁻¹) is higher than for **1-Me** and **1-Et**, in agreement with our experimental observations. In contrast, we computationally predict that insertion into **1-Pr** is more challenging than insertion into **1-Bn**, which contradicts our experimental results, but likely reflects some computational error (Figure 6). Consistent with

computational error playing a role in this discrepancy when calculations were performed with different functionals (see SI) there were cases where the barrier for insertion into **1-Bn** was higher than for **1-ⁿPr**. The lowest energy pathway for insertion into **1-Bn** involves an S_E2 mechanism and the geometric parameters at the transition state for insertion are similar to those observed in **1-Me**, **1-Et**, and **1-ⁿPr**. Previous calculations on CO₂ insertion into palladium benzyl species have also invoked an S_E2 pathway.⁴⁰ Calculations on CO₂ insertion into **1-OMeBn** or **1-CF₃Bn** indicate that the barriers for insertion into these species are approximately the same as for the unsubstituted palladium benzyl species. This is unexpected as it suggests that the impact of the para-substituent on the nucleophilicity of the benzylic carbon is negligible even though this substituent should impact the energy of the π*-orbital which stabilizes or destabilizes the carbon. Nevertheless, our calculations are in agreement with the experimental rate constants of **1-Bn** and **1-OMeBn** being within error (*vide supra*).

In contrast to the facile insertion of CO₂ into palladium alkyl complexes supported by ^tBuPBP ligands, we did not observe CO₂ insertion into **1-Ph**. To understand this reactivity, we calculated the kinetic and thermodynamic parameters associated with CO₂ insertion into **1-Ph**. Although the reaction is considerably thermodynamically downhill (by -19.2 kcal mol⁻¹), the kinetic barrier is 34.6 kcal mol⁻¹, which explains why no reaction is observed experimentally. Consistent with our previous results for CO₂ insertion into palladium-C(sp²) bonds,⁴⁰ the transition state is classified as innersphere, with a Pd-C_{CO2} interaction of 3.03 Å. To understand the influence of the ^tBuPBP ligand on CO₂ insertion into **1-Ph**, we calculated the energy of the transition state for CO₂ insertion into (^tBuPCP)Pd(C₆H₅) (^tBuPCP = 2,6-C₆H₃(CH₂P^tBu₂)₂), which features a pincer ligand with a lower *trans*-influence donor opposite the phenyl group. In this case, the activation energy associated with an innersphere transition state is 46.3 kcal mol⁻¹, indicating that influence of the ^tBuPBP ligand is significant. However, in order for CO₂ insertion to become kinetically viable experimentally, a different approach needs to be adopted than introducing a stronger *trans*-influence ligand opposite the phenyl ligand, as the ^tBuPBP ligand is one of the strongest *trans*-influence ligands available and it does not lower the activation energy for CO₂ insertion enough for the reaction to proceed under mild conditions.

Conclusions

In this work, we prepared and crystallographically characterized an unusual series of ^tBuPBP

supported palladium alkyl and aryl complexes including species with ethyl, n-propyl, benzyl, and phenyl ligands. In contrast, ^tBuPBP supported palladium complexes with n-butyl, iso-propyl, and tert-butyl ligands were either unstable or could not be observed. The rates of decomposition of the alkyl complexes are related to the steric bulk of the alkyl ligand with a putative tert-butyl complex decomposing faster than the ethyl species. The palladium alkyl complexes decompose via two different routes. The least and most sterically bulky complexes containing ethyl or tert-butyl ligands decompose via β -hydride elimination. In contrast, complexes containing n-butyl and iso-propyl ligands are stable towards β -hydride elimination and along with benzyl complexes decompose via an uncommon reductive coupling reaction, which involves the formation of a new C–B bond and either well-defined palladium(0) dimers or palladium black. Attempts to synthesize a ^tBuPBP supported palladium hydride were unsuccessful because a similar reductive coupling occurred to generate a dimeric palladium(0) complex with two new H–B bonds. The observation of decomposition via reductive coupling across a series of complexes confirms that this is a general reaction for ^RPBP supported complexes.

^tBuPBP ligated palladium complexes with ethyl, n-propyl, and benzyl ligands all cleanly insert CO₂ to form the corresponding carboxylate complexes, allowing for a rare study of the rates of CO₂ insertion across an analogous series of metal alkyl complexes. Kinetic studies demonstrate that the rate of CO₂ insertion into **1-Et** is more than double the rate for insertion into **1-Me**, which in turn is ten times faster than the rate of insertion into **1-ⁿPr**. CO₂ insertion into ^tBuPBP supported palladium benzyl complexes is much slower than insertion into n-alkyl complexes, likely because the carbon atom of the benzyl group is less nucleophilic. DFT calculations indicate that insertion reactions into **1-Me**, **1-Et**, **1-ⁿPr**, and **1-Bn** proceed via an outersphere S_E2 pathway and steric factors are responsible for the observed differences in rate between the n-alkyl complexes. They also suggest that the counterintuitive trends in the rates of CO₂ insertion observed in the present work will not occur for all metal alkyl systems but are related to the specific steric factors present in this group of complexes. Although the strong *trans*-influence of the boryl ligand in ^tBuPBP promotes CO₂ insertion into palladium alkyl complexes, no reaction is observed between **1-Ph** and CO₂, which is calculated to proceed via an innersphere, 1,2-addition mechanism. Overall, our results highlight how the rates of CO₂ vary across an analogous series of palladium alkyl and aryl complexes and DFT calculations provide explanations for the observed trends. This information

will be valuable for the development of catalytic reactions that involve CO₂ insertion into metal alkyl bonds as an elementary step.

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Supporting information

Supporting information about selected experiments, NMR spectra, DFT-optimized geometries and other details are available via the Internet.

Competing Financial Interests

The authors declare no competing financial interests.

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24. We used $^t\text{BuMgCl}$ instead of $^t\text{BuLi}$ for safety reasons.

25. In the supporting information we also describe attempts to prepare $(^t\text{BuPBP})\text{Pd}(\text{allyl})$.

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31. A reviewer suggested that the presence of different halide salt impurities in variable concentrations may be causing the large changes in the rates of CO_2 insertion into **1-Me**, **1-Et**, and **1- n Pr**. In the supporting information, we have described experiments that were performed to discount this possibility.

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37. In the $\text{S}_{\text{E}}2$ pathway, we were unable to find the intermediate and barrier for the second rearrangement step to form the palladium carboxylate product, as the rearrangement occurs spontaneously during geometry optimization. However, this process has previously been demonstrated to be low energy in related systems.

38. The calculated increase in barrier from **1-Et** (17.7 kcal mol $^{-1}$) to **1-Me** (19.4 kcal mol $^{-1}$) is around 1 kcal mol $^{-1}$ larger than would be expected for a two-fold difference in rate. Nevertheless, this is good agreement when computational error is considered.

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TOC Graphic

