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Reaction of carbon dioxide with a palladium–alkyl complex supported by a bis–NHC framework†

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Abstract

The reactivity of a dimethyl palladium complex supported by a dicarbene chelate ($\text{MDC}^{\text{Mes}}\text{PdMe}_2$) towards CO_2 has been investigated. In the presence of trace H_2O , this reaction yields the corresponding methyl bicarbonate complex ($\text{MDC}^{\text{Mes}}\text{PdMe}(\text{O}_2\text{COH})$), which goes on to give the corresponding κ^2 -carbonato complex upon crystallization ($\text{MDC}^{\text{Mes}}\text{Pd}(\text{CO}_3)$). This chemistry, as well as related protonolysis by acetic acid was monitored by a combination of techniques including React-IR spectroscopy.

Introduction

Carbon dioxide is an inexpensive and abundant C1 feedstock,^{1,2} making it an attractive reagent for the synthesis of organic compounds and value added products.³ Moreover, CO_2 activation and reduction by transition metal complexes is an important goal toward the development of new catalysts for conversion of CO_2 to liquid fuels^{4,5} and synthetic petroleum.^{6,7} Determination of the molecular design principles required for catalysts that promote the incorporation of CO_2 into reduced organic species containing new C–C bonds is an important and active area of current research.^{8–10} Recent work has shown that insertion of CO_2 into late transition metal–carbon bonds can be accomplished given judicious choice of ligand.¹¹ Study of the reactivity of CO_2 at palladium centers has been an especially active area, as recent work has demonstrated an insertion chemistry for phosphine supported palladium allyls.^{12–15} Insertion of CO_2 into a $\text{Pd}(\text{II})\text{—Me}$ complex supported by a cyclometallated pincer ligand has also been described.¹⁶

The reactivity of CO_2 with dimethylpalladium complexes has also been probed. Complexes of this type supported by chelating diamines or bisphosphines are relatively unreactive toward dry carbon dioxide, but do display a pronounced acidolysis chemistry in the presence of CO_2 and trace water.¹⁷ The lack of observed reactivity in the absence of water can be attributed to the poor nucleophilicity of the Pd—Me bonds of these systems. By contrast, it has been demonstrated that transition metal complexes supported by *N*-heterocyclic carbene (NHC) ligands exhibit notable reactivity with CO_2 .^{18–23} Moreover, NHCs are robust ligands that combine superior thermal and oxidative stability with strong σ -donating and weak π -accepting properties.^{24,25} Accordingly, we became interested to see whether the reactivity profile exhibited by previously studied bisphosphine and diamine bound PdMe_2

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complexes¹⁷ could be attenuated by using a more strongly donating NHC based ligand scaffold.

Herein we report the improved synthesis, and structural characterization of a *cis*-dimethylpalladium complex supported by a methylene bridged *bis*-NHC ligand. Furthermore, the reactivity of this platform with carbon dioxide has been probed. Accordingly, this work extends the current understanding of the reactivity of CO₂ with PdMe₂ complexes to include those supported by carbene ligands.

Results and Discussion

In targeting a suitable system to investigate the reactivity described above, we focused our attention on a *cis*-dimethylpalladium complex supported by a Methylene-bridged DiCarbene ligand sporting ancillary mesityl groups (MDC^{Mes}). Homologous compounds of this type containing phosphine²⁶ and amine²⁷ based ligands are well known. Scheme 1 displays the synthetic route employed for preparation of this palladium complex. The bulky aryl groups appended to the ligand scaffold offer enhanced steric protection to the metal center and help to solubilize the metal complex. The synthesis of this ligand has been reported previously²⁸ and relies on the synthesis of 1-(2,4,6-trimethylphenyl)-1*H*-imidazole^{29,30} followed by condensation with dibromomethane to generate bisimidazolium **1**. Reaction of this NHC precursor with Pd(OAc)₂ in DMSO at 130 °C generates the corresponding dibromide complex (MDC^{Mes})Pd(Br)₂ in excellent yield.²⁸

Direct conversion of the dibromide to the corresponding palladium dimethyl complex (MDC^{Mes})PdMe₂ using methyllithium did not generate analytically pure material. By contrast, ligand replacement has proven to be a viable method to prepare palladium dimethyl complexes.^{7,31,32} Treatment of the bis-imidazolium salt with base in THF at -78 °C, followed by addition to (tmeda)PdMe₂ has been shown to generate (MDC^{Mes})PdMe₂ in modest yield.³³ We have found that amending this synthetic procedure, by carrying out the deprotonation at -40 °C and warming to room temperature over the course of several hours, the yield of (MDC^{Mes})PdMe₂ can be made nearly quantitative.

The improved synthetic route to (MDC^{Mes})PdMe₂ also facilitates isolation of crystals of the dicarbene complex that are suitable for X-ray diffraction. The solid state structure of (MDC^{Mes})PdMe₂ is shown in Figure 1 and relevant crystallographic data are summarized in Table 1. This complex is only the second structurally characterized PdMe₂ complex supported by a chelating bis-NHC ligand.³⁴ Consistent with other (MDC)Pd complexes,³⁰ the six-membered ring formed through chelation of the Pd center by the dicarbene adopts a boat configuration³⁵ with a C1-Pd-C14 ligand bite angle of 84.8°. This angle is significantly smaller than the homologous complex supported by dppp. Although both these complexes contain a six-membered palladacycle, the corresponding phosphine adopts a conformation in which the ligand cleft is splayed open by nearly 94°. ²⁷ The two Pd-Me bond lengths observed for (MDC^{Mes})PdMe₂ are indistinguishable at 2.075(4) and 2.079(4) Å, which is significantly longer than those observed for the homologous dimethyl palladium(II) complex supported by tmeda (Figure 2).²⁶ The increased Pd-Me bond distances observed for (MDC^{Mes})PdMe₂ is indicative of the strong trans-influence imparted by carbene ligands and attests to the excellent σ-donor properties that are intrinsic to NHCs.^{36,37} Dimethyl Pd(II) complexes supported by chelating bis-phosphines show similar Pd-Me bonding metrics (Figure 2).^{26,27}

The reactivity of (MDC^{Mes})PdMe₂ with CO₂ was monitored by ¹H NMR spectroscopy in CD₃CN at 25 °C. Over the course of 4 hrs, the starting dimethyl complex was converted to a new product concomitant with the production of CH₄, which has a diagnostic ¹H resonance

at 0.2 ppm.³⁸ The final ^1H NMR spectrum is consistent with an asymmetric product in which the Pd–Me resonance (-1.05 ppm) of the starting material is replaced by a new signal at -0.65 ppm that integrates to three protons (Figure S-1). The APT/JVERT NMR for this new product also indicated that this ^1H resonance was a primary carbon (Fig. S-2). ^1H NMR time course experiments clearly indicate that the CH_4 generated upon reaction of the dimethyl complex with CO_2 is linked to consumption of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ and formation of an organometallic product containing a single Pd–Me functionality (Fig. S-3). The NMR spectrum of this organometallic component may be consistent with insertion of CO_2 into one of the Pd–Me functionalities to give a methyl acetate complex $(\text{MDC}^{\text{Mes}})\text{PdMe}(\text{OAc})$, however, the CH_4 byproduct is consistent with acidolysis induced by CO_2 and water. Furthermore, the solid state IR spectrum recorded for this product shows strong stretches in the carbonyl region at 1655 and 1626 cm^{-1} , which significantly differs from IR absorptions reported for Pd–OAc complexes, which are typically in the 1570 – 1610 cm^{-1} range.³⁹ Taken together, these results suggest that the observed reactivity of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with CO_2 proceeds via protonolysis to generate a bicarbonate complex in a manner similar to that observed for diamine and bisphosphine PdMe_2 complexes.¹⁷

In an effort to confirm the identity of the product described above, we sought to prepare an authentic sample of the Pd–OAc complex for spectroscopic comparison. Reaction of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with excess acetic acid at room temperature generates $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{OAc})_2$ in high yield (93%). The ^1H -NMR spectrum of this compound is consistent with a symmetric complex, which lacks Pd–Me functionalities. The solid state IR spectrum obtained for this material shows a characteristic C=O stretch at 1589 cm^{-1} , which is typical for Pd–OAc complexes.⁴⁰ Single crystals of $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{OAc})_2$ were obtained by diffusion of ether into a concentrated CH_3CN solution. X-ray diffraction analysis confirmed the structure of this complex (Fig. 3).

Reaction of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with a single equivalent of acetic acid generates a product with a ^1H -NMR spectrum that is similar to, but distinct from that obtained for the reaction with CO_2 (*vide supra*). As shown in Fig. S-1, acidolysis of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ by AcOH generates an equivalent of CH_4 along with an asymmetric organometallic product containing a single Pd–Me resonance at -0.65 ppm. These results are consistent with formation of $(\text{MDC}^{\text{Mes}})\text{PdMe}(\text{OAc})$. Solid state IR analysis of this product delivers a spectrum with a characteristic Pd–OAc carbonyl stretching frequency of 1583 cm^{-1} . Furthermore, this product has a resonance in its ^1H NMR spectrum at 1.27 ppm, which is presumed to correspond to the protons of the Pd-bound acetate ligand. Notably, this resonance is lacking in the spectrum obtained upon reaction of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with CO_2 and indicates that the former product is not the insertion product.

The facile nature with which $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ undergoes protonolysis with acetic acid, bolsters the contention that trace H_2O contributes to the observed reactivity with CO_2 . This contention is supported by the fact that no reaction was observed between $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ and CO_2 that had been rigorously dried by passage through a column of molecular sieves, by either NMR or React-IR analysis. Further confirmation that protonolysis is the dominant reactivity mode observed for $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$, was obtained upon monitoring the reaction of this complex with CO_2 that had been passed through a water bubbler by React-IR spectroscopy. Figure 4 displays the spectral changes that accompany this reaction, with emergent peaks at ~ 1665 , 1630 and 1250 cm^{-1} (Fig. 4). By contrast, React-IR analysis of the reaction of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with acetic acid in dry MeCN produces a completely different set of spectral changes with an emergent peak at $\sim 1573\text{ cm}^{-1}$ (Fig. S-4), which is similar to stretches observed for Pd–OAc complexes (*vide supra*).³⁹

The discrepancy in the React-IR spectra obtained upon reaction of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with CO_2 versus acetic acid, confirms that the CO_2 reaction does not generate a Pd-OAc species. These spectra are consistent with direct reaction of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with $\text{CO}_2/\text{H}_2\text{O}$, as shown in Scheme 2, to give the bicarbonate complex $(\text{MDC}^{\text{Mes}})\text{PdMe}(\text{O}_2\text{COH})$. The formulation of the bicarbonate complex as a mononuclear compound containing a terminal $\text{Pd-O}_2\text{COH}$ ligand is consistent with the spectroscopic data recorded for this compound. Binuclear complexes of Pd(II) with bridging carbonate ligands typically display strong absorptions at ~ 1540 and 1300 cm^{-1} . By contrast, Pd(II) complexes containing terminal bicarbonate ligands are distinguished by absorptions at ~ 1655 and 1620 cm^{-1} , which correspond to $\nu(\text{C=O})$ and at $\sim 1300\text{ cm}^{-1}$, which corresponds to $\nu_{\text{as}}(\text{C-O})$. The observed absorptions in the React-IR spectrum at 1665 , 1630 and 1250 cm^{-1} (Fig. 4) clearly indicate protonolysis leads to formation of a terminal bicarbonate ligand. Moreover, the ^1H NMR spectrum of the bicarbonate complex displays a resonance at 11.4 ppm , which can be attributed to the $\text{Pd-O}_2\text{CO-H}$ proton.

In principle, formation of the $\text{Pd-O}_2\text{COH}$ complex could proceed via hydrolysis of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ by water to generate the hydroxide complex $(\text{MDC}^{\text{Mes}})\text{Pd(OH)Me}$, followed by subsequent insertion of CO_2 into the Pd-OH bond to give the final product.^{41,42} In an effort to determine whether a Pd-OH complex is a competent intermediate for the observed reaction, the protonolysis of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ by 100 equivalents of water in CD_3CN was monitored by ^1H NMR spectroscopy. After several hours, more than 75% of the starting PdMe_2 complex remained unreacted. Accordingly, protonolysis of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ by water proceeds much more slowly compared to the observed acidolysis with wet CO_2 . These results suggest that the reaction to generate $(\text{MDC}^{\text{Mes}})\text{PdMe}(\text{O}_2\text{COH})$ proceeds via direct protonolysis of the $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ complex by carbonic acid formed upon reaction of carbon dioxide with water. This reaction pathway has been suggested to be operative for analogous PdMe_2 complexes supported by diamines and bisphosphines, as well.¹⁷

The $(\text{MDC}^{\text{Mes}})\text{PdMe}(\text{O}_2\text{COH})$ complex is robust in solution,⁴³ however, crystallization of this complex leads directly to formation of the related κ^2 -carbonato complex $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{CO}_3)$, the structure of which is shown in Fig. 5. Accordingly, $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{CO}_3)$ is one of a handful of structurally characterized κ^2 -carbonato complexes of palladium^{17,44–46} and represents the first such complex supported by NHC ligands. This compound is analogous to a recently described $(\text{MDC}^{\text{tBu}})\text{Pt}(\text{CO}_3)$ analogue⁴⁷ and is likely formed via a similar pathway. Moreover, dimethyl palladium complexes supported by either *tmEDA* or *dppe* have also been shown to give κ^2 -carbonato complexes upon reaction with wet CO_2 .¹⁷ The $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{CO}_3)$ complex was also prepared by metathesis of $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{Br})_2$ with one equivalent of Ag_2CO_3 in hot MeCN . Spectroscopic data recorded for this complex correlates with that for other Pd -carbonates. The solid state IR spectrum obtained for $(\text{MDC}^{\text{Mes}})\text{Pd}(\text{CO}_3)$ shows an intense stretching frequency at 1601 cm^{-1} , which matches that reported for similar complexes.^{47,44,48–49}

Summary and Conclusions

We have shown that a dimethyl palladium complex supported by a chelating dicarbene ligand does not readily insert CO_2 . Instead, this compound behaves similarly to dimethyl palladium complexes supported by other chelating ligands and readily undergoes protonolysis. As such, although $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ does not react directly with CO_2 , in the presence of trace H_2O protonolysis ensues to generate a bicarbonate complex, which ultimately gives the corresponding κ^2 -carbonato complex. In the course of these studies, we have also demonstrated the reactivity of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with acetic acid. As a whole, this work demonstrates the need for exceptionally nucleophilic Pd-alkyl complexes to engender

a successful insertion chemistry with CO₂. Future work will be aimed at the synthesis and study of such compounds for applications in the field of CO₂ conversion.

Experimental

General experimental procedures

Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under a positive pressure of N₂ using flasks fitted with Suba-Seal rubber septa or in a nitrogen filled glove box. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Reagents and solvents were purchased from Sigma Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Solvents for synthesis were of reagent grade or better and were dried by passage through activated alumina and then stored over 4 Å molecular sieves prior to use.⁵⁰ All other reagents were used as received. Synthetic work required 1-(2,4,6-trimethylphenyl)-1*H*-imidazole,^{29,30} 1,1'-di(mesityl)-3,3'-methylene-diimidazolium dibromide, (**1**)²⁸ and (tmeda)PdMe₂,^{51,52} which were each synthesized as previously described. The palladium precursor (CH₃CN)₂PdCl₂ was prepared by refluxing PdCl₂ in acetonitrile,⁵³ and collecting the resulting yellow solid by vacuum filtration. CO₂ was dried by passing through a Glass Indicating Moisture Trap (3.5 × 26 cm) containing 5 Å molecular sieves (Restek).

Physical Measurements

¹H NMR and ¹³C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent (CD₃CN = δ 1.94) and carbon spectra are referenced to the carbon resonances of the solvent (CD₃CN = δ 1.32). All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. Elemental analyses were performed by Intertek QTI, White House, NJ. React IR experiments were performed using an IC10USER ReactIR 10 with MCT Detector and DiComp (Diamond) probe connected via AgCl 6mm × 1.5m Fiber. Infrared spectra were recorded in KBr using a Nicolet Magna-IR 750 spectrometer.

X-ray Structural Solution and Refinement

Data were collected on a Bruker-AXS Smart APEX diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters and orientation matrices were determined by gathering reflections from three sets of 15–20 frames using 0.3° ω scans. The systematic absences, together with the unit cell parameters, in the diffraction data are uniquely consistent with the reported space groups for (MDC^{Mes})PdMe₂, and (MDC^{Mes})Pd(CO₃). No symmetry higher than triclinic was observed for (MDC^{Mes})Pd(OAc)₂ and solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. Two symmetry unique but chemically identical compound molecules were located in the asymmetric unit of (MDC^{Mes})Pd(OAc)₂. The structures display cocrystallized molecules of solvation with varying degrees of disorder in their unit cells. The two THF molecules in the (MDC^{Mes})PdMe₂ asymmetric unit were treated with rigid bond constraints. The acetonitrile molecule in the (MDC^{Mes})Pd(CO₃) asymmetric was modeled as two disordered contributions with a refined site occupancy ratio of 58/32. The 10 acetonitrile molecules in the (MDC^{Mes})Pd(OAc)₂ unit cell were treated as diffused contributions.⁵⁴ All structure factors, anomalous dispersion coefficients, and the applied SADABS absorption correction program are contained in various versions (5.1 – 6.12) of SHELXTL program library.⁵⁵ All other non-hydrogen atoms were anisotropically refined using the conventional full-matrix least-squares method. All hydrogen atoms were treated as idealized contributions. The CIFs

are available from the Cambridge Crystallographic Data Centre under the depositary numbers CCDC 871921 – 871923.

React IR Spectroscopy

In a glove box, 50 mL of a 2 mM solution of (MDC^{Mes})PdMe₂ in CH₃CN was placed in a three neck Schlenk flask, which was sealed with Suba-Seal rubber septum and transferred to a chemical fume hood. Under positive pressure of N₂, one septum was removed and replaced with a Teflon adapter connected to either a DiComp diamond or silicon IR probe, which was then submerged in the solution to be analyzed. Following acquisition of an initial IR spectrum of the starting solution, a continuous stream of CO₂ was flowed through the gas inlet line of the reaction vessel and the subsequent reaction was monitored by recording solution IR spectra of the course over 8.5 hrs in various intervals.

React IR analysis of the reaction between (MDC^{Mes})PdMe₂ and acetic acid in CH₃CN was carried out in a similar manner, except that CH₃CO₂H was injected via syringe into the reaction solution under a constant flow of N₂.

NMR Time-Course Experiments

In a glove box, 1.0 mL of a 20 mM solution of (MDC^{Mes})PdMe₂ in CD₃CN was added to a J-Young NMR tube. An external standard of 1,4-dioxane in CD₃CN was sealed within a capillary tube that was placed in the NMR tube. The CD₃CN solution was subjected to three freeze–pump–thaw cycles and an initial NMR of the starting (MDC^{Mes})PdMe₂ complex was obtained. The solution was refrozen and evacuated a fourth time, prior to backfilling the NMR tube headspace with CO₂. The reaction of (MDC^{Mes})PdMe₂ with CO₂ was monitored by recording ¹H NMR spectra in 7 min intervals over a 4 hr period. Spectra were analyzed by referencing consumption of starting material and product formation versus external 1,4–dioxane standard. The reaction was roughly 80% complete within the first 5 min of the experiment and slowly reached completion over the course of the 4 hr experiment. Methane was observed as a byproduct of the reaction at 0.20 ppm.

Synthesis of (MDC^{Mes})PdMe₂

A stirred suspension of 273 mg (0.5 mmol) of compound **1** in 15 mL of THF was cooled at –40 °C for 3 hrs, following which, 140 mg (1.25 mmol) of KO^tBu was added to the mixture. The resulting off white suspension was allowed to warm to room temperature and stirred for 10 hrs, during which time, the reaction mixture turned brown in color. The crude dicarbene was slowly filtered through a plug of celite and directly added to a solution of (tmeda)PdMe₂ (0.126 g, 0.5 mmol) in 10 mL of THF. This resulting brown solution was stirred at room temperature for an additional 8 hrs, after which time the solvent was removed under reduced pressure. The resulting crude tan colored material was redissolved in a minimal amount of THF and precipitated by addition to approximately 100 mL of Et₂O. The resulting tan precipitate was collected by filtration, washed with additional Et₂O and dried in vacuo to deliver 243 mg of the title compound in 93 % yield. Spectroscopic data obtained for this material matched that which has been previously reported and is reproduced below. ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 7.37 (d, *J* = 7.2 Hz, 2H, Im–*H*), 6.94 (s, 4H, Mes–*H*), 6.81 (d, *J* = 7.2 Hz, 2H, Im–*H*), 6.08 (s, 2H, –CH₂–), 2.30 (s, 6H, *p*–CH₃), 2.02 (s, 12H, *o*–CH₃), –1.06 (s, 6H, Pd–CH₃); ¹³C NMR (100 MHz; CD₃CN, 25 °C) δ/ppm: 191.2, 139.0, 138.0, 136.2, 129.2, 122.6, 120.5, 64.2, 21.1, 18.7, 15.6, –5.7.

Synthesis of (MDC^{Mes})PdMe(O₂COH)

In a Schlenk flask, A solution of (MDC^{Mes})Me₂ (0.110g, 0.21 mmol) in 100 mL of dry acetonitrile was stirred at room temperature under a nitrogen atmosphere. The reaction

vessel was connected to a tank of carbon dioxide and the solution was stirred under a constant stream of CO₂ for 12 hrs. Upon introduction of CO₂ to the reaction, slight effervescence was observed and over the course of the reaction the solution changed appearance from a maroon color to light tan. Following removal of all volatiles under reduced pressure, the sealed reaction vessel was transferred to the glove box and the crude tan solid was redissolved in minimum amount of acetonitrile and precipitated by addition to approximately 100 mL of Et₂O. The resulting off-white precipitate was collected by filtration, washed with additional Et₂O and dried in vacuo to deliver 86 mg of the title compound in 75% yield. ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 11.4 (s, 1H, Pd–O₂CO–H), 7.59 (d, *J* = 8 Hz, 1H, Im–H), 7.56 (d, *J* = 2 Hz, 1H, Im–H), 7.05 (s, Mes–H), 7.04 (d, *J* = 8 Hz, 1H, Im–H), 7.00 (d, *J* = 2 Hz, 1H, Im–H), 6.98 (s, 2H, Mes–H), 6.27 (s, 2H, –CH₂–), 2.33 (s, 3H, *p*–CH₃), 2.30 (s, 3H, *p*–CH₃), 2.05 (s, 6H, *o*–CH₃), 1.97 (s, 6H, *o*–CH₃), –0.65 (s, 3H, Pd–CH₃); ¹³C NMR (100 MHz; CD₃CN, 25 °C) δ/ppm: 182.3, 170.6, 167.7, 162.1, 140.4, 140.2, 140.0, 136.7, 136.5, 136.4, 135.9, 135.5, 129.7, 129.6, 129.5, 124.4, 123.9, 123.2, 122.9, 122.8, 122.2, 63.9, 21.3, 21.1, 18.1, 17.9, –8.3. ν_{max} (KBr)/cm^{–1} 1655, 1627 (s, C=O). Anal. Calcd for C₂₇H₃₂N₄O₃Pd: C, 57.20; H, 5.69; N, 9.88. Found: C, 57.39; H, 5.47; N, 9.94.

Synthesis of (MDC^{Mes})PdMe(OAc)

To a stirred suspension of (MDC^{Mes})Me₂ (0.052g, 0.1 mmol) in 20 mL of CH₃CN was added 5.7 μL (0.1 mmol) of acetic acid. Addition of acid was accompanied by effervescence and the resulting suspension was stirred overnight to give a brown solution. Following removal of solvent under reduced pressure, the residual brown material was redissolved in 5 mL of CH₃CN and added to approximately 100 mL of Et₂O to deliver an off-white powder. This powder was collected, washed with Et₂O and dried under vacuum. Yield 88 % (50 mg). ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 7.63 (d, *J* = 6, 1H, Im–H), 7.59 (d, *J* = 2, 1H, Im–H), 7.06 (s, 2H, Mes–H), 7.04 (d, *J* = 6 Hz, 1H, Im–H), 7.02 (d, *J* = 2 Hz, 1H, Im–H), 6.98 (s, 2H, Mes–H), 6.29 (s, 2H, –CH₂–), 2.33 (s, 3H, *p*–CH₃), 2.30 (s, 3H, *p*–CH₃), 2.05 (s, 6H, *o*–CH₃), 1.98 (s, 6H, *o*–CH₃), 1.27 (s, 3H, Pd–O₂CCH₃), –0.65 (s, 3H, Pd–CH₃); ν_{max} (KBr)/cm^{–1} 1583 (s, C=O). Anal. Calcd for C₂₈H₃₄N₄O₂Pd: C, 59.52; H, 6.07; N, 9.92. Found: C, 59.31; H, 6.33; N, 10.07.

Synthesis of (MDC^{Mes})Pd(OAc)₂

To a stirred suspension of (MDC^{Mes})Me₂ (0.130g, 0.25 mmol) in 50 mL of THF was added 30 μL (0.50 mmol) of acetic acid. Addition of acid was accompanied by slight effervescence and the resulting solution was allowed to stir for 4 hrs to give a light colored solution. Following removal of solvent under reduced pressure, the residual off-white material was redissolved in 5 mL of CH₃CN and added to approximately 100 mL of Et₂O to deliver an off-white powder. This powder was collected, washed with Et₂O and dried under vacuum to deliver 114 mg of the title compound in 93% yield. ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 7.52 (s, 2H, Im–H), 6.95 (s, 4H, Mes–H), 6.93 (s, 2H, Im–H), 6.30 (s, 2H, –CH₂–), 2.30 (s, 6H, *p*–CH₃), 2.06 (s, 12H, *o*–CH₃), 1.25 (s, 6H, Pd–O₂CCH₃); ¹³C NMR (100 MHz; CD₃CN, 25 °C) δ/ppm: 176.8, 157.6, 139.6, 138.4, 136.1, 129.7, 126.3, 124.7, 122.3, 63.7, 30.8, 21.3, 18.7. ν_{max} (KBr)/cm^{–1} 1589 (s, C=O). Anal. Calcd for C₂₉H₃₄N₄O₄Pd: C, 57.19; H, 5.63; N, 9.20. Found: C, 56.82; H, 5.99; N, 8.87.

Synthesis of (MDC^{Mes})Pd(CO₃)

To a stirred suspension of 260 mg (0.40 mmol) of (MDC^{Mes})PdBr₂ in 100 mL of acetonitrile was added 120 mg (0.43 mmol) of Ag₂CO₃. The resulting mixture was allowed to stir for 12 hrs at 65 °C in the dark, after which time the precipitated AgBr was removed by filtration through celite. The resulting pink solution was concentrated under reduced

pressure to yield a tan solid, which was washed with Et₂O and dried in vacuo to deliver 88 mg of the title compound in 40% yield. ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 7.57 (d, *J* = 2 Hz, 2H, Im-*H*), 7.04 (d, *J* = 2 Hz, 2H, Im-*H*), 7.01 (s, 4H, Mes-*H*), 6.27 (s, 2H, -CH₂-), 2.34 (s, 6H, *p*-CH₃), 1.99 (s, 12H, *o*-CH₃). ¹³C NMR (100 MHz; CD₃CN, 25 °C) δ/ppm: 162.3, 140.1, 136.5, 129.4, 126.3, 124.0, 122.6, 66.5, 21.3, 15.6. ν_{max} (KBr)/cm⁻¹ 1601 (s, C=O). Anal. Calcd for C₂₆H₂₈N₄O₃Pd: C, 56.68; H, 5.12; N, 10.17. Found: C, 56.92; H, 4.79; N, 10.43.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Glossary

MDC^{Mes} 1,1'-di(mesityl)-3,3'-methylene-diimidazolium

References

1. Aresta M, Dibenedetto A. Dalton Trans. 2007; 37:2975–2992. [PubMed: 17622414]
2. Peters M, Köhler B, Kuckshinrichs W, Leitner W, Markewitz P, Müller TE. ChemSusChem. 2011; 4:1216–1240. [PubMed: 21866580]
3. Quadewlli EA, Centi G, Duplan J-L, Perathoner S. ChemSusChem. 2011; 4:1194–1215. [PubMed: 21922677]
4. Benson EE, Kubiak CP, Sathrum AJ, Smieja JM. Chem. Soc. Rev. 2009; 38:89–99. [PubMed: 19088968]
5. Olah GA, Surya Prakash GK, Goeppert Alain. J. Am. Chem. Soc. 2011; 133:12881–12898. [PubMed: 21612273]
6. Jiang Z, Xiao T, Kuznetsov VL, Edwards PP. Phil. Trans. R. Soc. A. 2010; 368:3343–3364. [PubMed: 20566515]
7. Centi G, Perathoner S, Wine G, Gangeri M. Green Chem. 2007; 9:671–678.
8. Braunstein P, Matt D, Nobel D. Chem. Rev. 1988; 88:747–764.
9. Sakakura T, Choi JC, Yasuda H. Chem. Rev. 2007; 107:2365–2387. [PubMed: 17564481]
10. Riduan SN, Zhang Y. Dalton Trans. 2009; 39:3347–3357. [PubMed: 20379526]
11. Mankad NP, Gray TG, Laitar DS, Sadighi JP. Organometallics. 2004; 23:1191–1193.
12. Johansson R, Wendt OF. Dalton Trans. 2007; 37:488–492. [PubMed: 17213935]
13. Wu J, Hazari N. Chem. Commun. 2011; 47:1069–1071.
14. Hruszkewycz DP, Wu J, Hazari N, Incarvito CD. J. Am. Chem. Soc. 2011; 133:3280–3283. [PubMed: 21329388]
15. Hruszkewycz DP, Wu J, Green JC, Hazari N, Schmeier TJ. Organometallics. 2012; 31:470–485.
16. Johansson R, Jarenmark M, Wendt OF. Organometallics. 2005; 24:4500–4502.
17. Pushkar J, Wendt OF. Inorg. Chim. Acta. 2004; 357:1295–1298.
18. Laitar DS, Müller P, Sadighi JP. J. Am. Chem. Soc. 2005; 127:17196–17197. [PubMed: 16332062]
19. Lee CH, Laitar DS, Mueller P, Sadighi JP. J. Am. Chem. Soc. 2007; 129:13802–13803. [PubMed: 17944470]

20. Bhattacharyya KX, Akana JA, Laitar DS, Berlin JM, Sadighi JP. *Organometallics*. 2008; 27:2682–2684.
21. Hermann WA. *Angew. Chem. Int. Ed.* 2002; 41:1290–1309.
22. Huang J, Stevens ED, Nolan SP, Petersen JL. *J. Am. Chem. Soc.* 1999; 121:2674–2678.
23. Arduengo AJ III, Rasika Dias HV, Harlow RL, Kline M. *J. Am. Chem. Soc.* 1992; 114:5530–5534.
24. Díez-González S, Nolan SP. *Coord. Chem. Rev.* 2007; 251:874–883.
25. Jacobsen H, Correa A, Poater A, Costabile C, Cavallo L. *Coord. Chem. Rev.* 2009; 253:687–703.
26. de Graaf W, Boersma J, Smeets WJJ, Spek AL, van Koten G. *Organometallics*. 1989; 8:2907–2917.
27. Ledford J, Schultz CS, Gates DP, White PS, DeSimone JM, Brookhart M. *Organometallics*. 2001; 20:5266–5276.
28. Gardiner MG, Herrmann WA, reisinger C-P, Schewarz J, Spiegler M. *J. Organomet. Chem.* 1999; 572:239–247.
29. Liu J, Chen J, Zhao J, Zhao Y, Li L, Zhang H. *Synthesis*. 2003; 17:2661–2666.
30. Scherg T, Schneider S, Frey G, Schwarz J, Herdtweck E, Herrmann WA. *Synlett*. 2006; 18:2894–2907.
31. Cámpora J, Del M. Conejo A, Merieiter K, Palma P, Perez C, Reyes ML, Ruiz C. *J. Organomet. Chem.* 2003; 683:220–239.
32. Danopoulos AA, Pugh D. *Dalton Trans.* 2008; 38:30–31. [PubMed: 18399222]
33. Subramaniam SS, Slaughter LM. *Dalton Trans.* 2009; 39:6930–6933. [PubMed: 20449132]
34. Douthwaite RE, Green MLH, Silcock PJ, Gomes PT. *Dalton Trans.* 2002:1386–1390.
35. Taige MA, Zeller A, Ahrens S, Goutal S, Herdtweck E, Strassner T. *J. Organomet. Chem.* 2007; 692:1519–1529.
36. Khranov DM, Lynch VM, Bielawski CW. *Organometallics*. 2007; 26:6402–6049.
37. Fantasia S, Petersen JL, Jacobsen H, Cavallo L, Nolan SP. *Organometallics*. 2007; 26:5880–5889.
38. Fulmer GR, Miller AJM, Sherden NH, Gottlieb HE, Nudelman A, Stoltz BM, Bercaw JE, Goldberg KI. *Organometallics*. 2010; 29:2176–2179.
39. Henderson WH, Alvarez JM, Eichman CC, Stambuli JP. *Organometallics*. 2011; 30:5038–5044.
40. Stephenson TA, Wilkinson G. *J. Inorg. Nuc. Chem.* 1967; 29:2122–2123.
41. Crutchley RJ, Powell J, Faggiani R, Lock CJL. *Inorg. Chim. Acta*. 1977; 24:L15–L16.
42. Ganguly S, Mague JT, Roundhill DM. *Inorg. Chem.* 1992; 31:3831–3835.
43. ¹H NMR time course experiments show that (MDC^{Mes})PdMe(O₂COH) is stable in dry MeCN over the course of several days.
44. Yasuda H, Choi J–C, Lee S–C, Sakakura T. *Organometallics*. 2002; 21:1216–1220.
45. Cecconi F, Ghilardi CA, Midollini S, Moneti S, Orlandini A, Scapacci G. *Dalton Trans.* 1989:211–216.
46. Mandal SK, Sigman MS. *J. Org. Chem.* 2003; 68:7535–7537. [PubMed: 12968915]
47. Jamali S, Mili D, Kia R, Mazloomi Z, Abdolahi A. *Dalton Trans.* 2011; 40:9362–9365. [PubMed: 21660338]
48. Di Bugano C, Pasquali M, Leoni P. *Inorg. Chim. Acta*. 1988; 149:19–20.
49. Hayward PJ, Blake DM, Wilkinson G, Nyman CJ. *J. Am. Chem. Soc.* 1970; 92:5873–5878.
50. Pangborn AB, Giardello MA, Grubbs RH, Rosen RK, Timmers FJ. *Organometallics*. 1996; 15:1518–1520.
51. Van Koten G, De Graaf W, Boersma J, Smeets WJJ, Spek AL. *Organometallics*. 2008; 8:2907–2917.
52. Byers PK, Canty AJ, Jin H, Kruis D, Markies BA, Boersma J, Van Koten G. *Inorg. Synth.* 1998; 32:162–172.
53. Abrunhosa I, Delain–Bioton L, Gaumont A–C, Gulea M, Masson S. *Tetrahedron*. 2004; 60:9263–9272.
54. Spek AL. *Appl. J. Cryst.* 2003; 36:7–13.
55. Sheldrick GM. *Acta Cryst. A*. 2008; 64:112–122. [PubMed: 18156677]

Fig. 1. Thermal ellipsoid plot of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ shown from above (left) and in profile (right). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except those on C26 and C27) and solvent molecules are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Pd–C1 2.065, Pd–C14 2.072, Pd–C26 2.079, Pd–C27 2.075, C1–Pd–C14 86.81, C26–Pd–C27 84.60.

avg. Pd—Me = 2.077 Å

avg. Pd—Me = 2.028 Å

avg. Pd—Me = 2.095 Å

avg. Pd—Me = 2.087 Å

Fig. 2.
Bonding metrics for a set of palladium dimethyl complexes supported by bidentate chelating ligands.

Fig. 3. Thermal ellipsoid plot of (MDC^{Mes})Pd(OAc)₂ with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except those on C27 and C29) are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–C14 1.955, Pd–C10 1.977, Pd–O1 2.077(3), Pd–O3 2.069, O1–Pd–O3 86.46, C14–Pd–C10 86.46.

Fig. 4. Stacked React-IR spectra recorded over the course of 8.5 hrs for the reaction of (MDC^{Mes})PdMe₂ with CO₂. Emergent peaks at 1665, 1630 and 1250 cm⁻¹ suggest formation of (MDC^{Mes})PdMe(O₂COH).

Fig. 5. Thermal ellipsoid diagram of one of the asymmetric units of **3** with 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C10 1.980(5), Pd1–C14 1.986(5), Pd1–O1 2.064(3), Pd1–O2 2.069(4), C10–Pd1–O2 64.96(14), C10–Pd1–C14 84.9(2), O1–C26–O2 113.5(4).

Scheme 1.

Synthesis of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ and $(\text{MDC}^{\text{Mes}})\text{PdBr}_2$. (a) $\text{Pd}(\text{OAc})_2$, Δ , DMSO; (b) 2 MeLi, THF; (c) **1**. KOtBu, THF; **2**. (tmeda) PdMe_2 , THF.

Scheme 2.
 Reactivity of $(\text{MDC}^{\text{Mes}})\text{PdMe}_2$ with $\text{CO}_2/\text{H}_2\text{O}$ and AcOH.

Table 1Crystallographic data for (MDC^{Mes})PdMe₂, (MDC^{Mes})Pd(OAc)₂, and (MDC^{Mes})Pd(CO₃).

	(MDC ^{Mes})PdMe ₂	(MDC ^{Mes})Pd(OAc) ₂	(MDC ^{Mes})Pd(CO ₃)
Formula	C ₃₅ H ₅₀ N ₄ O ₂ Pd	C ₃₁ H _{35.50} N _{6.50} O ₃ Pd	C ₃₃ H ₄₀ N ₆ O ₄ Pd
fw	665.19	653.56	691.11
Cryst syst	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	P-1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , (Å)	14.176(4)	14.015(7)	13.403(7)
<i>b</i> , (Å)	8.709(2)	16.141(9)	19.118(10)
<i>c</i> , (Å)	27.584(7)	17.230(9)	14.849(8)
α, (°)	90.00	101.769(18)	90.00
β, (°)	93.076(5)	110.124(17)	114.089(7)
γ, (°)	90.00	102.20(2)	90.00
<i>V</i> (Å ³)	3400.6(16)	3411(3)	3473(3)
<i>Z</i>	4	4	4
Temp (K)	203(2)	200(2)	200(2)
<i>D</i> _{calcd} , g/cm ³	1.299	1.273	1.322
2θ range, deg	1.58–28.30	1.32–28.26	1.98–28.24
μ (Mo, Kα) mm ⁻¹	0.71073	0.71073	0.71073
Reflections	42760	42475	43918
Unique	8436	16756	8565
<i>R</i> (int)	0.0912	0.1184	0.0712
<i>R</i> 1	0.0564	0.0693	0.0466
<i>wR</i> 2	0.1298	0.1503	0.1133