Showcasing collaborative research from the Laboratories of Richard O’Hair (University of Melbourne), Allan Canty (University of Tasmania), Victor Ryzhov (Northern Illinois University) and Philippe Maitre (Université Paris-Sud)

Ligand-induced decarbonylation in diphosphine-ligated palladium acetates \([\text{CH}_3\text{CO}_2\text{Pd(\text{PR}_2\text{CH}_2)}]^{+}\) (R = Me and Ph)

The powerful combination of mass spectrometry experiments, gas-phase IR spectroscopy and DFT calculations have been used to shed light on a new mode of reactivity: formation of organometallic complexes via ligand-induced decarbonylation reactions of \([\text{K}^2\text{-acetate}\text{Pd(\text{K}^2\text{-diphosphine})}]^{+}\) complexes.

As featured in:

Ligand-induced decarbonylation in diphosphine-ligated palladium acetates \( [\text{CH}_3\text{CO}_2\text{Pd}((\text{PR}_2)_2\text{CH}_2)]^+ \) 
\((\text{R} = \text{Me and Ph})^{\dag}\)

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A new decarbonylation reaction is observed for \( [\text{(K}^2\text{-acetate})\text{Pd}(\text{K}^2\text{-diphosphine})]^{\dag} \) complexes. Gas-phase IR experiments identify the product as \( [\text{CH}_3\text{Pd(OP}2\text{Ph})_2\text{CH}_2\text{PPh}_2)]^+ \). DFT calculations uncovered a plausible mechanism involving O atom abstraction by the diphosphine ligand within the coordination sphere to yield the acetyl complex, \( [\text{CH}_3\text{OPd(OP}2\text{Ph})_2\text{CH}_2\text{PPh}_2)]^+ \), which then undergoes decarbonylation.

Gas-phase studies utilising tandem mass spectrometry (MS/MS) methods in conjunction with DFT calculations provide valuable fundamental information on how the auxiliary ligands in metal complexes can tune the fragmentation chemistry of coordinated carboxylates under collision-induced dissociation (CID) conditions (Scheme 1).\textsuperscript{1} For example, the acetate ligand in Pd(\textit{i}) cationic complexes can undergo decarbonylation to give an organometallic cation (eqn (1))\textsuperscript{2} or act as an intramolecular base to promote C–H bond activation (eqn (2)).\textsuperscript{3} Both of these modes of reactivity have been widely exploited in the condensed phase\textsuperscript{7–9} and is thus of considerable mechanistic interest.

A recent study has used mechanistic insights from MS/MS experiments to develop a new decarboxylative protocol for the synthesis of thioamides,\textsuperscript{6} highlighting the value of gas-phase model systems. Here we report on a newly discovered mode of reactivity, ligand-induced decarbonylation (eqn (3)), one that has little precedence in the condensed phase\textsuperscript{7–9} and is thus of considerable mechanistic interest.

Electrospray ionisation (ESI) of methanolic solutions containing palladium acetate and a diphosphine ligand, \( \text{R}_2\text{PCH}_2\text{PR}_2 \) (\( \text{R} = \text{Ph} = \text{dppm ligand}; \text{R} = \text{Me} = \text{dmpm ligand} \)) gave rise to the desired diphosphine-ligated palladium acetates \( [\text{CH}_3\text{CO}_2\text{Pd}((\text{PR}_2)_2\text{CH}_2)]^+ \), \textit{1a}, \( \text{R} = \text{Ph} \) and \( \text{1b}, \text{R} = \text{Me} \), which were mass selected and subjected to low-energy CID in ion trap mass spectrometers. The unimolecular chemistry of \( \text{1a} (m/z 549, \text{Fig. } 1a) \) is dominated by loss of CO to give an ion at \( m/z 521 \) (eqn (3), Scheme 1). Minor fragment ions at \( m/z \) 305 and 397 are assigned as \( [\text{Ph}_2\text{PCH}_2\text{Pd}]^+ \) and \( [\text{Ph}_2\text{PCH}_2\text{Pd}((\text{Me})\text{Ph})]^+ \), respectively, and arise from subsequent C–P activation of the dppm ligand, as established by MS\textsuperscript{3} on \( m/z 521 \), which gave \( m/z \) 305 and 397 (Fig. S1, ESI\textsuperscript{f}). CID of the labelled acetate complexes \( [\text{CH}_3^{13}\text{CO}_2\text{Pd}((\text{PR}_2)_2\text{CH}_2)]^+ \) \( (m/z 550, \text{Fig. } 1b) \) and \( [\text{CD}_3\text{CO}_2\text{Pd}((\text{PR}_2)_2\text{CH}_2)]^+ \) \( (m/z \) 550, Fig. 1c) confirmed these assignments. Complex \( \text{1b} \) also underwent decarbonylation (Fig. S2, ESI\textsuperscript{f}). Decarbonylation is only a very...
minor pathway in the CID spectra of 1a (< 0.1%) and 1b (< 1%), which is in stark contrast to CID on [CH3CO2Pd(phen)]+, where decarboxylation dominates (eqn (1), Scheme 1). This highlights the unique role of the diphosphine auxiliary ligand in promoting decarboxylation.

Since the structure(s) of the decarboxylation product is unknown, we next: (1) used DFT calculations to optimise four chemically reasonable isomers, including the organopalladium complexes, [CH3Pd(OP(Ph2)CH2PPh2)]+, (2) compared the theoretically predicted IR spectra of these isomers to the gas-phase infrared multiphoton dissociation (IRMPD) spectrum of 1a-CO acquired using a 3D ion-trap tandem mass spectrometer coupled with the CLIO free electron laser.

Although 4a benefits from an agostic interaction between the methyl group and Pd (Fig. S3, ESI†), calculations at the M06/SDD-6-31G(d) level of theory show the following stability order: 2a (0 kcal mol−1) > 3a (+22 kcal mol−1) > 4a (+30 kcal mol−1). 3a is unstable, undergoing rearrangement to 4a. Although the experimental IRMPD spectrum of 1a-CO exhibits quite broad features, an examination of Fig. 2 reveals that the lowest-energy isomer 2 displays the best match (Fig. 2a and Table S1, ESI†). The most intense absorption band in the experimental spectrum (the broad band at 1076–1200 cm−1) matches the predicted P-O and P-C asymmetric stretches at 1134 cm−1 flanked by the shoulder peaks at 1076 cm−1 (Ph ligand C-H bend coupled with P-O stretch) and 1196 cm−1 (CH3 rocking mode). The experimental absorption between 1400 and 1450 cm−1 matches the aromatic ring deformation of the ligand, calculated to be at 1442 cm−1. The smaller experimental peaks at around 1300 and 1000 cm−1 can be assigned to the aromatic ligand C-H bending (1299 cm−1) and C-H/C-C stretching/bending (988 cm−1), respectively. In contrast, the higher-energy isomers 3a and 4a show substantially poorer matches to the experimental IRMPD spectrum (Fig. 2b and (c)). Isomer 3a is predicted to have a strong band at 1042 cm−1, corresponding to the P-O stretching and Pd-O bending motions. This band is absent from the experimental spectrum (Fig. 2b). Isomer 4a has the CH3 umbrella band calculated to be at 1580 cm−1, which is also absent from the experimental spectrum. Thus, the IRMPD data is consistent with structure 2a for the 1a-CO ion.

Having established the product structure as 2a, we next used DFT calculations to examine potential mechanisms for the decarboxylation of 1a and 1b and to establish that the barrier for decarboxylation is lower than that for decarbonylation, a requirement for formation of 2a and 2b as the major products under the low energy CID conditions used (Fig. 1 and Fig. S2, ESI†). The pathways for the decarboxylation and decarbonylation reactions are compared for 1b in Fig. 3 and Fig. S4 (ESI†), while the related reactivity for 1a is shown in Fig. S5 (ESI†). The decarboxylation pathway follows the same mechanism reported for [CH3CO2Pd(phen)]+.28

Multiple decarbonylation pathways were considered. The lowest energy pathway connects 1b, 6b and 7b via TSb-6b and TSb-7b. Cleavage of the C-O bond via TSb-6b gives the Pd-acetyl cation coordinated to a dmpmO ligand, 8b. Just as in the decarboxylation pathway, the coordinated acetyl cation needs...
to adopt reactive conformation 10b in order for decarboxylation to occur. This involves changing the conformation of the coordinated acetyl anion relative to the dmpmO ligand. Of the two pathways to connect 8b to 10b that were found (Fig. S4 and S5, ESI†), the lowest one involves traversing two transition structures TS8b-9b and TS9b-10b. Once formed, 10b decarboxylates via TS10b-11b to give the CO coordinated organometallic cation, 11b, from which CO loss produces the experimentally observed cation, 2b. TS1b-6b. The most energetically demanding TS for decarbonylation (+17.2 kcal mol$^{-1}$) is lower in energy than TS12b-13b (+36.7 kcal mol$^{-1}$) for decarboxylation, consistent with the experimental observation that decarboxylation occurs predominantly. Related calculations were carried out for the competition between CO and CO$_2$ loss for 1a (Fig. S6 and S7, ESI†). Similar reaction profiles were found, with TS6a-7a, the most energetically demanding TS for decarboxylation (+29.2 kcal mol$^{-1}$) being lower in energy than TS12a-13a (+37.9 kcal mol$^{-1}$) for decarbonylation, consistent with the experimental observation that decarbonylation occurs predominantly.

Metal-mediated decarboxylation of carboxylic acid derivatives finds wide application in synthesis,$^7$14,15 although most processes show poor atom economy as they require an anhydride additive to facilitate formation of an acyl complex which then undergoes decarboxylation.$^8$ Here we have shown that diphosphine and acetate ligands react with each other within the coordination sphere of complexes to trigger decarbonylation. While this mechanism appears to be unprecedented, there is a growing literature on ligand oxidation reactions occurring within the coordination sphere of metal complexes.$^{16,17}$ Finally, the observed chemistry is not limited to acetate ligands, but occurs with a range of other coordinated carboxylates (e.g. benzoate and hydrocinnamate) as will be reported in due course.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
8 For transition metal mediated decarboxylation reactions of carboxylic acids that utilize activating anhydride reagents, see: (a) A. John, M. O. Miranda, K. Ding, B. Dereli, M. A. Ortuno, A. M. LaPointe, and
9 Transition metal mediated decarbonylation reactions of carboxylic acids that do not require activating anhydride reagents have only rarely been described, and it has typically been assumed that they proceed via the coordinated carboxylate: (a) R. H. Prince and K. A. Raspin, *Chem. Commun.*, 1966, 156; (b) D. Fenton, *US Pat.*, 3530198, 1970; (c) T. A. Foglia and P. A. Barr, *J. Am. Oil Chem. Soc.*, 1976, 53, 737; (d) A. John, M. A. Hillmyer and W. B. Tolman, *Organometallics*, 2017, 36, 506.


