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Decarbonylation of ethanol to methane, carbon monoxide and hydrogen by a [PNP]Ir complex†

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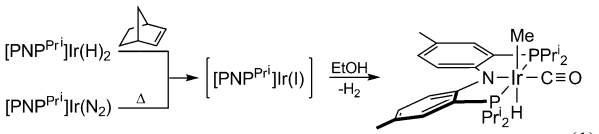
The putative three-coordinate Ir(I) PNP$^{Pr^i}$ (PNP$^{Pr^i}$ = [N{2-P(CHMe$_2$)$_2$-4-MeC$_6$H$_3$}$_2$]$^-$) pincer complex decarbonylates ethanol to yield methane, hydrogen and [PNP$^{Pr^i}$]Ir(CO). The mechanism involves the isolable *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO), which is susceptible to photochemical reductive elimination of methane.

The oxidative addition of hydroxyl functionalities is of importance for a variety of energy conversion reactions. For example, oxidative addition of water[1–3] is a potential method for water oxidation,[4] an important reaction for chemical energy storage.[5–7] In addition, hydroxyl oxidative addition is pertinent to the increasing interest of using low-molecular weight alcohols, the most prominent of which is ethanol,[8,9] as a primary fuel source. Consequently, a deeper understanding of alcohol synthesis and decomposition at catalytic centers may prove relevant to a range of energy conversion applications.

Whereas Ir(I) complexes promote alcohol dehydrogenation[10–12] and aldehyde decarbonylation,[13–16] the coupling of these two steps to drive alcohol decarbonylation is less explored.[17,18] We have undertaken studies on ethanol decarbonylation, employing iridium(I) complexes of the PNP$^{Pr^i}$ ligand (PNP$^{Pr^i}$ = [N{2-P(CHMe$_2$)$_2$-4-MeC$_6$H$_3$}$_2$]$^-$).[19] Alcohol decarbonylation has been promoted by Ir pincer complexes in only two cases: an Ir(I) PCP (PCP = [C$_6$H$_3$-2,6-(CH$_2$PBu$^t_2$)$_2$]) pincer complex promotes methanol decarbonylation to generate hydrogen equivalents and the corresponding Ir–CO complex;[20] and treatment of an Ir(I) PNP (PNP = [C$_5$H$_3$N-2,6-(CH$_2$PBu$^t_2$)$_2$]) complex with methanol gives *trans*-Ir(H)$_2$(CO), which is stable to dehydrogenation.[21] We now report that [PNP$^{Pr^i}$]Ir(I) reacts with EtOH *via* initial O–H oxidative addition to afford the isolable *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO), which has been structurally characterized.‡ Photolysis of the hydrido-methyl complex subsequently drives the reductive elimination of methane to effect overall decarbonylation of ethanol.

Photolysis of [PNP$^{Pr^i}$]Ir(N$_2$)§ (Fig. S3, ESI†) in EtOH yields the known compound [PNP$^{Pr^i}$]Ir(CO)[22] as the only metal containing product and H$_2$ and CH$_4$ as the organic products in 79% and 94% yield, respectively, as determined by GC. To determine intermediates along the reaction pathway, possible EtOH addition products were targeted by non-photochemical means. Treatment of [PNP$^{Pr^i}$]Ir(H)$_2$ and norbornylene with EtOH at room temperature yields *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO); the same product is obtained by the thermolysis of [PNP$^{Pr^i}$]Ir(N$_2$) in EtOH at 80 °C:



(1)

[PNP$^{Pr^i}$]Ir is capable of decarbonylating longer chain alcohols as well. Treatment of a mixture of [PNP$^{Pr^i}$]Ir(H)$_2$ and NBE with *n*-PrOH gives *trans*-[PNP$^{Pr^i}$]Ir(H)(Et)(CO).¶ The *trans* configuration of alkyl and hydride ligands in the decarbonylation product is analogous to the reported *trans*-dihydride carbonyl obtained *via* decarbonylation of paraformaldehyde with Ir(I) pincer complexes, which has been attributed to stereoselective migratory deinsertion of the aldehyde following C–H activation.[21]

The products from the thermal decarbonylation reactions of EtOH and *n*-PrOH were isolated and their structures were characterized by X-ray diffraction, the results of which are shown in Fig. 1. The solid-state structure reveals iridium in an octahedral coordination environment with the carbonyl ligand *trans* to the amide nitrogen of the [PNP$^{Pr^i}$]. The decarbonylation product can be furnished independently. *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) can also be prepared from the reaction of [PNP$^{Pr^i}$]Ir(H)$_2$[23] with acetaldehyde.[24] The observation that EtOH and acetaldehyde both furnish the same decarbonylation product suggests that the acetaldehyde is an intermediate along the alcohol decarbonylation pathway. Thermolysis or photolysis of [PNP$^{Pr^i}$]Ir(N$_2$) is known to liberate N$_2$ to generate the coordinatively unsaturated species, [PNP$^{Pr^i}$]Ir(I).[25] EtOH addition to this coordinatively unsaturated intermediate to yield acetaldehyde and H$_2$ followed by subsequent decarbonylation would result in *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) as illustrated in Scheme 1.

To determine whether *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) is a viable intermediate for EtOH decarbonylation, we sought to effect reductive elimination of methane from the complex. Methane reductive elimination from *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) is not observed to temperatures of 80 °C. However, methane elimination was observed under photolysis reaction conditions. As Fig. 2 displays, solutions of *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) smoothly and quantitatively convert to [PNP$^{Pr^i}$]Ir(CO) under irradiation with $\lambda_{exc} \geq 338$ nm; the product and its quantitative formation were corroborated by ^{1}H NMR spectra of photolyzed solutions.[26] The maintenance of isosbestic points in the absorption spectra of Fig. 2 indicates that no long-lived

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† Electronic supplementary information (ESI) available: Experimental procedures, additional spectra and charts. CCDC 740056–740058. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b914083b

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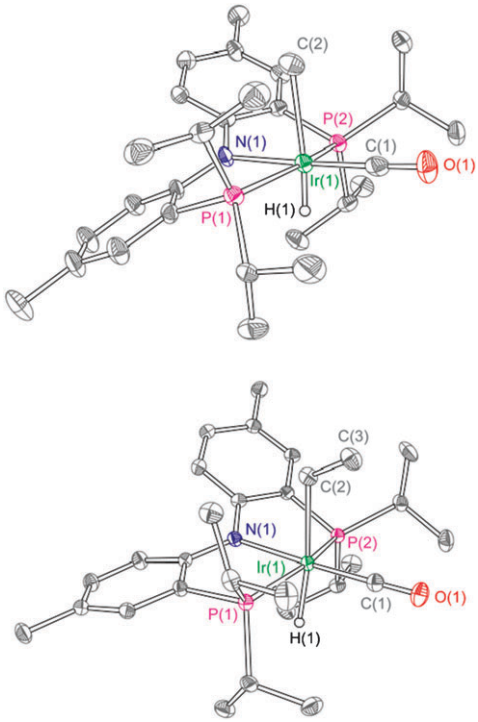
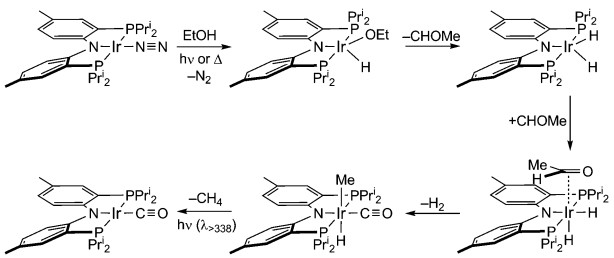


Fig. 1 Molecular structures of (top) *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) and (bottom) *trans*-[PNP$^{Pr^i}$]Ir(H)(Et)(CO), which are the products obtained from the thermal decarbonylation of EtOH and *n*-PrOH, respectively. H-atoms (refined at calculated positions) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.



Scheme 1

intermediates form during the photoreductive elimination reaction.

Examples of photochemical *trans* reductive elimination from octahedral complexes are rare and typically involve homolytic bond cleavage.[27,28] However, in our photolytic experiments with *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) neither H_2 nor C_2H_6 is observed, indicating that a homolytic bond cleavage mechanism is unlikely. Rather, ligand isomerization *via* photodissociation of CO could give *cis*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO), permitting spontaneous unimolecular reductive elimination of CH_4. This mechanism is consistent with the observation that treatment of [PNP$^{Pr^i}$]Ir(H)$_2$ with CO furnishes [PNP$^{Pr^i}$]Ir(CO) along with putative elimination of H_2.[22]

The initial dehydrogenation of EtOH can occur across the O(H)–C(H) bond to directly furnish the acetaldehyde or from across C(H)–C(H) to produce the enol, which then can isomerize to acetaldehyde. Iridium catalyzed alkane dehydrogenation is common,[29–32] and fewer examples of diethyl

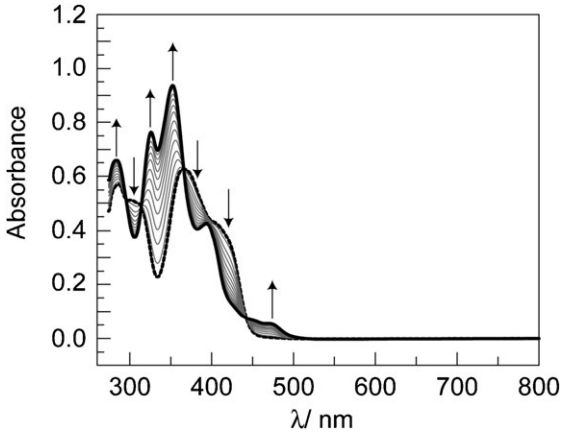


Fig. 2 Spectral changes of the absorption profile upon photolysis (λ_{exc} > 338 nm) of *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO) (---). The final product spectrum corresponds to [PNP$^{Pr^i}$]Ir(CO) (—). Spectra were recorded over the span of 6 min every 30 s.

ether dehydrogenation with iridium to give an Ir(η^2-$CH_2CHOCH_2CH_3$) species have been reported.[33–35] In fact, the reaction of a mixture of [PNP$^{Pr^i}$]Ir(H)$_2$ with NBE in Et_2O yields [PNP$^{Pr^i}$]Ir(η^2-$CH_2CHOCH_2CH_3$).[36] Its availability suggests the possibility that initial dehydrogenation proceeds from the ethoxy fragment to generate the enol. To address this question more incisively, [PNP$^{Pr^i}$]Ir(N_2) was photolyzed in EtOD and the isotope distribution of methane, CH_xD_{4-x}, was analyzed. Mass spectra of the evolved methane show all possible isotopomers. The fact that higher order deuterium incorporation occurs requires that a mechanism for isotopic scrambling involving solvent is present. Indeed, D_2O exchange with the hydride ligands of *trans*-Ir(H)$_2$(CO)(Cl)(PR$_3$)$_2$ has been observed.[37] The H–D exchange of Ir–H intermediates involving solvent necessarily obscures a detailed mechanistic description based on isotope experiments. Notwithstanding, an appreciable amount of CH_4 (*ca.* 25%) is observed. This implies that dehydrogenation occurs across the O(H)–C(H) bond. If dehydrogenation were to exclusively occur from the C(H)–C(H) bond, the maximum proton composition of the liberated methane would be CH_3D, since after H_2 liberation, the generated acetaldehyde would only contain three protons. Although C(H)–C(H) dehydrogenation cannot be excluded as a competing mechanism, only dehydrogenation across the O(H)–C(H) can account for a 4H equivalency.

Of the two possible initial addition products involving the dehydrogenation of EtOH across the O(H)–C(H) bond, DFT computations support that the lowest energy addition product arises from addition across the O–H bond as opposed to the methylene C–H bond. The geometries of the respective transition states were calculated by scanning the reaction trajectories for O–H (Fig. S18–S20, ESI†) and C–H (Fig. S21–S23, ESI†) oxidative addition. The activation energy for O–H oxidative addition is 14.6 kcal mol^{-1}, while the activation barrier for C–H is 18.9 kcal mol^{-1} (Fig. 3). In addition, the reverse reaction, reductive elimination to regenerate EtOH and [PNP$^{Pr^i}$]Ir(I), is more favorable for the C–H activation pathway by 7.4 kcal mol^{-1}.

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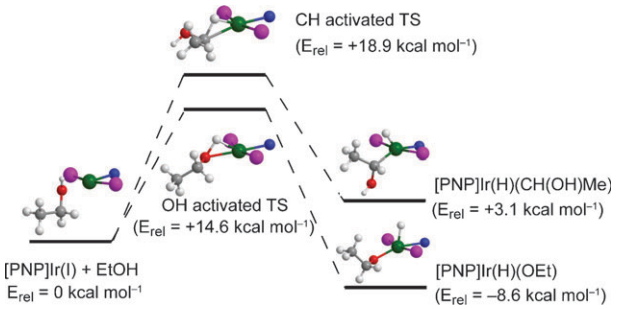

Fig. 3 DFT calculated structures and transition states of the oxidative addition of the O–H and methylene C–H of EtOH to [PNP$^{Pr^i}$]Ir(I). Only the EtOH and immediate coordination sphere are shown (Ir shown in green, P purple, N blue, O red, C gray, H white).

The mechanism shown in Scheme 1 for the decarbonylation of ethanol to methane, dihydrogen and carbon monoxide is consistent with the foregoing observations.

In summary, we have observed room temperature decarbonylation of EtOH by [PNP$^{Pr^i}$]Ir(I) to generate H_2 and *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO), which quantitatively undergoes photolytically induced reductive elimination of methane to generate [PNP$^{Pr^i}$]Ir(CO). Experiments and computations indicate the mechanism involves initial oxidative addition of the hydroxyl moiety of EtOH to the coordinatively unsaturated [PNP$^{Pr^i}$]Ir(I) center followed by dehydrogenation to produce the *in situ* generated acetaldehyde.

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Notes and references

‡ Crystallographic data for *trans*-[PNP$^{Pr^i}$]Ir(H)(Me)(CO): $C_{28}H_{44}IrNOP_2$, M = 664.78, triclinic, space group $P\bar{1}$, a = 8.3135(8), b = 9.8060(10), c = 17.8528(17), α = 84.829(2)°, β = 83.244(2)°, γ = 75.962(2)°, V = 1399.3(2), Z = 2, μ = 4.906 mm^{-1}, T = 100 K, R_1 = 0.0471, wR_2 = 0.0732 (based on observed reflections), GooF = 1.024, reflections measured = 29 281, R_{int} = 0.0855, CCDC 740057.
§ Crystallographic data for [PNP$^{Pr^i}$]IrN$_2$·MesNH$_2$: $C_{35}H_{53}IrN_4P_2$, M = 783.95, triclinic, space group $P\bar{1}$, a = 9.8992(12), b = 11.2251(14), c = 16.388(2), α = 101.780(2)°, β = 93.376(2)°, γ = 93.801(2)°, V = 1773.9(4), Z = 2, μ = 3.882 mm^{-1}, T = 100 K, R_1 = 0.0535, wR_2 = 0.0944 (based on observed reflections), GooF = 1.005, reflections measured = 39 573, R_{int} = 0.0882, CCDC 740058.
¶ Crystallographic data for *trans*-[PNP$^{Pr^i}$]Ir(H)(Et)(CO): $C_{29}H_{46}IrNOP_2$, M = 678.81, monoclinic, space group $P2(1)/n$, a = 14.7286(13), b = 12.3197(11), c = 16.0250(14), β = 90.754(2)°, V = 2907.5(4), Z = 4, μ = 4.724 mm^{-1}, T = 100 K, R_1 = 0.0226, wR_2 = 0.0529 (based on observed reflections), GooF = 1.002, reflections measured = 67 091, R_{int} = 0.0415, CCDC 740056.

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