Competing mechanisms in the carbonylation of neutral palladium(II) complexes containing bidentate ligands: theoretical insights

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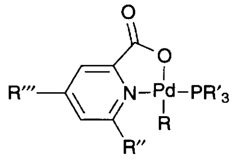
Correlated *ab initio* calculations identify the rate-determining step in the carbonylation reaction of palladium(II) complexes of mixed bidentate anionic ligands, and supply new evidence for the participation of five-coordinate intermediates and transition structures.

Carbonylation reactions employing palladium(II) chelate complexes as catalysts are of significant industrial interest.[1–3] Traditionally, catalyst design has relied upon the accumulation of experimental information.[1,4] Experimental methods have been skilfully employed in the identification of intermediates[5] and mechanistic steps.[6] However, a fundamental understanding of the details of various transformations remains elusive. With the rapid advances in computational techniques, significant contribution from the theoretical modelling of such reactions is becoming possible. More use is being made of these techniques to understand reaction mechanisms[7] and there is growing interest in combining theoretical and experimental methods to study CO insertion reactions.[8,4d] Prior theoretical research in the area of palladium- or platinum-catalysed carbonylation and polymerisation[8–10] has focussed on systems in which the non-participatory ligands are ignored or are simple monodentate ligands. We provide here the first theoretical investigation into the carbonylation of palladium(II) complexes with hemilabile bidentate ligands.

Experimental studies on the carbonylation of platinum- and palladium-alkyl complexes of picolinic acid derivatives[11–13] **1** have indicated that coordination and subsequent insertion of CO may proceed *via* a number of competing pathways. The donor capacity of the phosphine and the hemilability of the chelate influence the mechanism and rate of carbonylation. From initial experimental work[12] the mechanistic proposals illustrated in Scheme 1 are postulated as possible reaction pathways.

We are studying the model system **5** to identify competitive reaction pathways, and provide some insight into how these may be manipulated.[14] We have investigated the potential-energy surface at a correlated level,† employing polarised basis sets and a small-core relativistic pseudopotential on the metal.[15] Each intermediate and transition structure involved in these reactions has been fully optimised. In agreement with previous studies[16] methyl migration is favoured over carbonyl insertion. We have identified four reaction mechanisms in which the alkyl migration step is rate determining. Two related pathways (p and p′ in Scheme 1) involve either dissociation (*via* **3**) or partial dissociation (*via* **3′**) of the nitrogen and produce only the *trans* product (**4a**), isomerisation having taken place beforehand. The other two pathways (labelled d and d′ in Scheme 1) involve a migration step from **2** or **2′** to give **4** directly. As there is no specific isomerisation step the latter two pathways may proceed to form either the *cis*-(N,P) (**4b**) or *trans*-(N,P) (**4a**) products.



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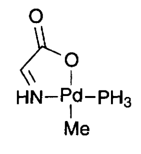

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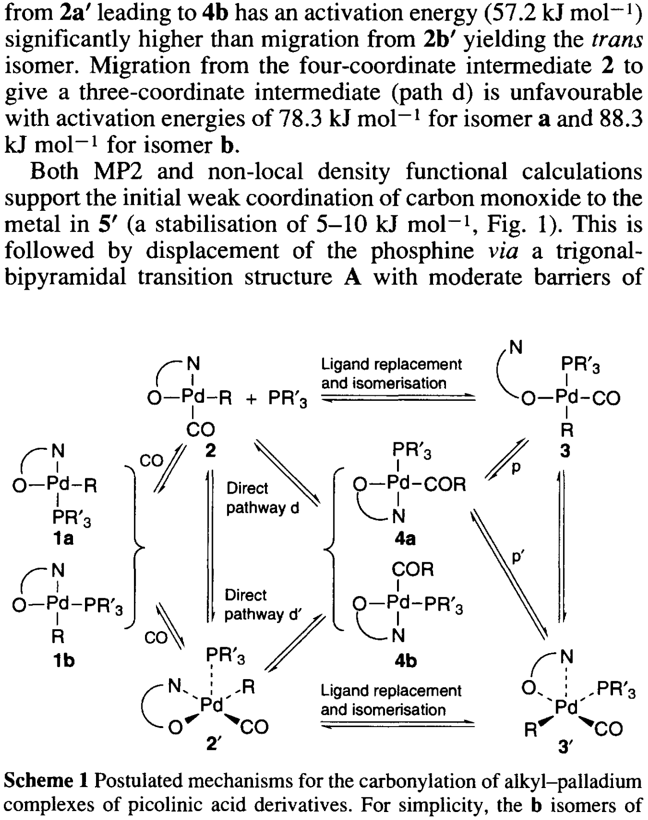
Three of the possible migration steps have been found to be competitive, with activation energies relative to the separated reactants of 38.3, 43.0 and 43.1 kJ mol^{-1} for migrations from **3′**,**2b′**, and **3** respectively. All three mechanisms produce the *trans* product, consistent with experimental observations and are stabilised by an ‘incoming’ coordinating group. Migration from **2a′** leading to **4b** has an activation energy (57.2 kJ mol^{-1}) significantly higher than migration from **2b′** yielding the *trans* isomer. Migration from the four-coordinate intermediate **2** to give a three-coordinate intermediate (path d) is unfavourable with activation energies of 78.3 kJ mol^{-1} for isomer **a** and 88.3 kJ mol^{-1} for isomer **b**.

Both MP2 and non-local density functional calculations support the initial weak coordination of carbon monoxide to the metal in **5′** (a stabilisation of 5–10 kJ mol^{-1}, Fig. 1). This is followed by displacement of the phosphine *via* a trigonal-bipyramidal transition structure **A** with moderate barriers of



Scheme 1 Postulated mechanisms for the carbonylation of alkyl–palladium complexes of picolinic acid derivatives. For simplicity, the **b** isomers of intermediates **2** and **2′** are not shown although they may form.

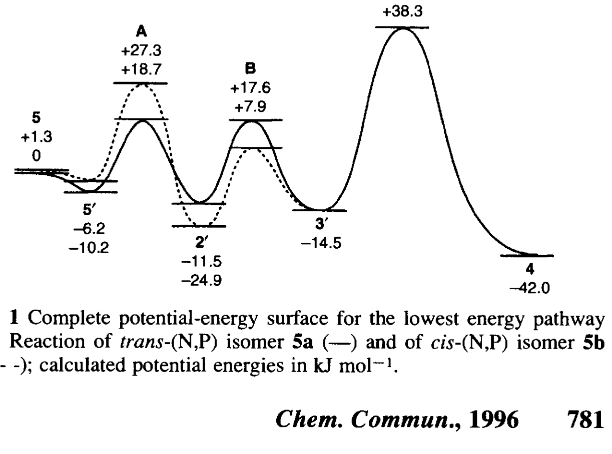
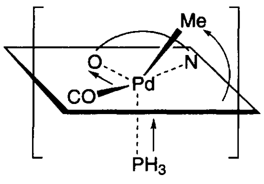


Fig. 1 Complete potential-energy surface for the lowest energy pathway (p′). Reaction of *trans*-(N,P) isomer **5a** (—) and of *cis*-(N,P) isomer **5b** (- - - -); calculated potential energies in kJ mol^{-1}.



B

18.7 kJ mol^{-1} (for isomer **a**) and 27.3 kJ mol^{-1} (for isomer **b**).

Mechanisms for isomerisation in organometallic systems are not well understood with few studies being done in this area. To our knowledge prior theoretical studies on isomerisation steps in reactions of planar complexes do not exist. We have identified a novel pathway for isomerisation with a modest barrier of 17.6 kJ mol^{-1} with respect to the separated reactants. This proceeds *via* a five-coordinate transition structure **B** from the square-pyramidal intermediate **2′**. The methyl group moves out of the plane to occupy a position *trans* to the phosphine. For this isomer where the methyl group is *trans* to the oxygen this motion lengthens the relatively strong palladium–oxygen bond providing the driving force for isomerisation. In a single step the carbonyl group moves around to occupy the position *trans* to the oxygen and the nitrogen is pushed out to give **3′**. Finally, migration of the methyl group to the carbonyl group occurs to complete the reaction.

In conclusion, four possible reaction mechanisms have been investigated and at this stage three different routes appear to be competitive with moderate activation energies, and are consistent with the product obtained experimentally. The participation of a five-coordinate intermediate where the nitrogen donor is weakly bound appears likely.

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Footnote

† Geometries were generated using gradient corrected density functional methods, improved energies were obtained using second-order Møller–Plesset theory with the density functional geometries. Hay and Wadt's small-core pseudopotential (P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299) was adopted for the metal with a double-ζ valence basis set, and 6-31G(d) on the main elements.

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