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Heterobimetallic intermediates in alkene insertion reactions into a Pd–acetyl bond†

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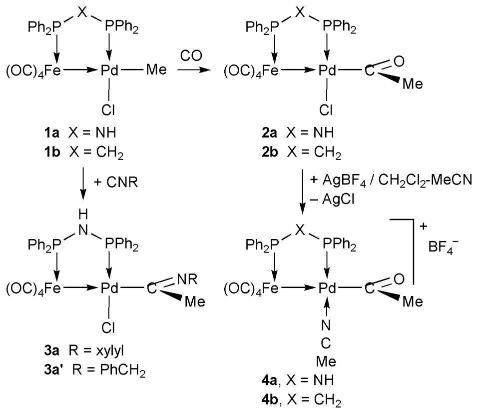
The reactivity of diphosphine-bridged heterobimetallic Fe–Pd alkyl complexes was evaluated for the insertion of CO, isonitriles, ethylene, methyl acrylate and norbornadienes and the crystal structures of the precursor alkyl complex, the iminoacyl derivative and the five-membered ring complex resulting from ethylene insertion into the palladium–acyl bond are reported.

The insertion of small molecules such as CO, isonitriles, olefins and alkynes into palladium–carbon bonds represents reactions of fundamental importance for stoichiometric organic synthesis and industrial catalysis.[1] An example of the latter is the alternating copolymerisation of CO and olefins, which has triggered considerable research on alkene insertion into the palladium–acyl bond.[1,2] Whereas previous studies have been concerned with the influence of the stereoelectronic properties of the (usually chelating) ligand bonded to the Pd centre on this chemistry, we present here a different approach aimed at evaluating the influence of a metal adjacent to the reactive Pd on its reactivity, with the hope that cooperativity effects may lead to beneficial bimetallic effects.[3]

In the alkyl complexes $[(OC)_4\overline{Fe(\mu\text{-dppx})Pd}Cl(Me)]$ [**1a**, dppx = $Ph_2PNHPPh_2$ (dppa); **1b**, dppx = $Ph_2PCH_2PPh_2$ (dppm)], prepared by reaction of $[Fe(CO)_4(dppx\text{-}P)]$ with [PdCl(Me)(cod)], the methyl ligand is *trans* to the formally dative Fe→Pd bond, both in solution, as deduced from the small $^3J(PH)_{cis}$ coupling constant (< 4 Hz) with the Pd-bound P atom, and in the solid state, as established by X-ray diffraction for **1b** (Scheme 1, Fig. 1).‡§



Scheme 1

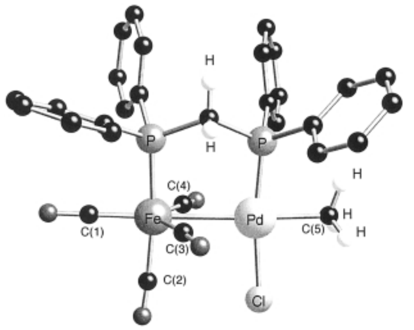


Fig. 1 View of the crystal structure of **1b**. Selected bond lengths (Å) and angles (°): Fe–Pd 2.8408(9), Pd–P(2) 2.2098(14), Pd–C(5) 2.066(6), Pd–Cl 2.361(2), Fe–P(1) 2.256(2), Fe–C(1) 1.761(7), Fe–C(2) 1.897(9), Fe–C(3) 1.799(8), Fe–C(4) 1.869(8); Cl–Pd–Fe 94.10(5), Cl–Pd–C(5) 87.4(2), P(2)–Pd–C(5) 85.2(2), P(2)–Pd–Cl 172.42(6), C(5)–Pd–Fe 174.3(2), Pd–Fe–P(1) 92.35(4), Fe–Pd–P(2) 93.40(4), C(2)–Fe–Pd 93.5(2).

These complexes react with CO under atmospheric pressure, more rapidly (3 h) in the case of **1b** because of its higher solubility, to form **2a**,**b**. Quantitative carbonylation of **1a** was achieved in CH_2Cl_2 in < 1 h under 20 atm CO. The *trans* arrangement of the acetyl ligand and the metal–metal bond suggested by the spectroscopic data is retained in the solid state, as shown by comparison with the spectroscopic data for the corresponding iminoacyl complexes **3a**,**a′** which were prepared by instantaneous reaction of **1a** with a stoichiometric amount of (xylyl)N≡C or $PhCH_2N$≡C, respectively, and characterised by X-ray diffraction in the case of **3a** (Fig. 2).‡§ As expected, the iminoacyl ligand is almost orthogonal to the palladium coordination plane.[4]

Since **2a** did not react with ethylene (at 1 atm), we turned our atttention to more electrophilic, cationic systems and prepared complex **4b** by chloride abstraction in CH_2Cl_2 in the presence of MeCN (Scheme 1). Interestingly, this reaction did not lead to CO deinsertion, a reaction often observed with Pd(II) acyl complexes. Complexes **4a**,**b** are more readily prepared by

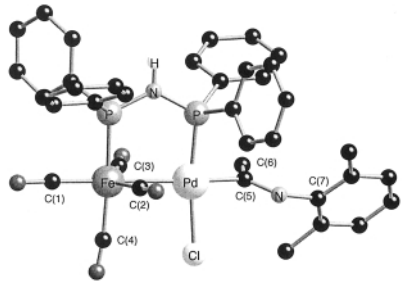


Fig. 2 View of the crystal structure of **3a**. Selected bond lengths (Å) and angles (°): Fe–Pd 2.7356(12), Pd–P(2) 2.274(2), Pd–C(5) 1.978(2), Pd–Cl(1) 2.402(2), Fe–P(1) 2.271(2), Fe–C(1) 1.758(8), Fe–C(2) 1.785(9), Fe–C(3) 1.795(10), Fe–C(4) 1.806(10), C(5)–N(1) 1.319(8); Cl(1)–Pd–C(5) 84.0(2), P(2)–Pd–C(5) 90.8(2), Pd–C(5)–C(6) 116.4(5), Pd–C(5)–N(1) 124.6(5), C(5)–Pd–Fe 164.4(2), C(5)–N(1)–C(7) 127.0(6), Pd–Fe–P(1) 91.86(6), Fe–Pd–P(2) 91.27(5), Cl(1)–Pd–P(2) 171.75(6).

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† Electronic supplementary information (ESI) available: Experimental. See http://www.rsc.org/suppdata/cc/b0/b007171o/

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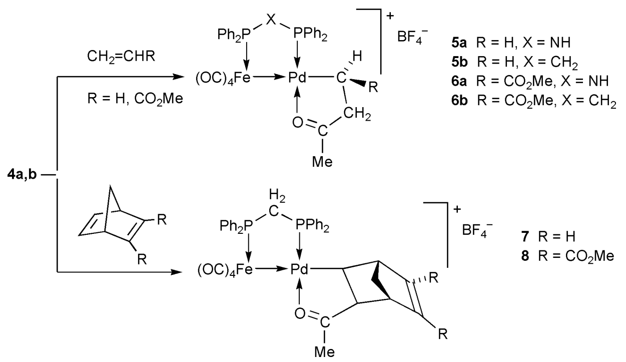


Scheme 2

halide abstraction from **1a**,**b** using $AgBF_4$ in CH_2Cl_2–MeCN, which generates $[(OC)_4\overline{Fe(\mu\text{-dppx})Pd}(Me)(NCMe)]^+$, followed by instantaneous *in situ* reaction with CO. Complexes **4a**,**b** were indeed more reactive than **2a**,**b** since ethylene insertion into the Pd–acetyl bond occurred under atmospheric pressure to afford after *ca.* 15 h the stable complexes **5a**,**b** in quantitative spectroscopic yields (Scheme 2).‡ The latter represent rare examples of isolable insertion products of an unstrained alkene into a Pd–acyl bond.[5]

IR spectra show an absorption at 1634 cm^{-1} (**5a**) and 1633 cm^{-1} (**5b**) for the acetyl carbonyl coordinated to Pd. The crystal structure of **5a** (Fig. 3)§ established that the σ-bonded carbon atom is *trans* to the metal–metal bond. The BF_4^- counter ion weakly interacts with the N–H proton [$d(N\cdots F) = 3.105$ Å]. To the best of our knowledge, there are only two precedents for the structural characterisation of a $-CH_2CH_2C(O)Me$ ligand, both in mononuclear Pd complexes.[5]

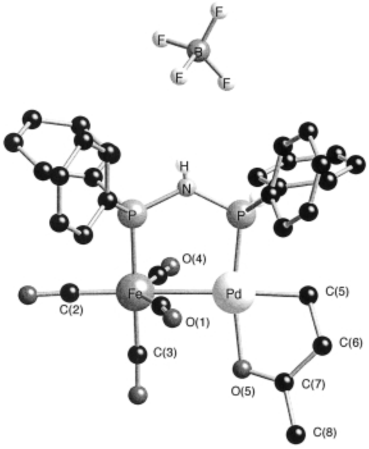
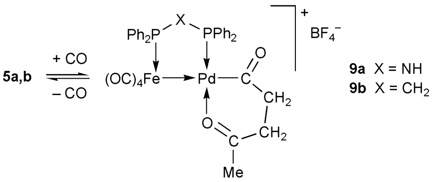


Fig. 3 View of the crystal structure of **5a**. Selected bond lengths (Å) and angles (°): Fe–Pd 2.7208(9), Pd–P(2) 2.1861(14), Pd–C(5) 2.054(6), Pd–O(5) 2.130(4), Fe–P(1) 2.240(2), Fe–C(1) 1.802(6), Fe–C(2) 1.791(7), Fe–C(3) 1.786(6), Fe–C(4) 1.806(6), C(7)–O(5) 1.256(8); O(5)–Pd–Fe 96.13(12), O(5)–Pd–C(5) 81.5(2), P(2)–Pd–C(5) 87.4(2), Pd–C(5)–C(6) 105.7(4), Pd–C(5)–N(1) 124.6(5), C(5)–Pd–Fe 172.5(2), Pd–O(5)–C(7) 112.7(4), Pd–Fe–P(1) 91.12(5), Fe–Pd–P(2) 95.48(5), O(5)–Pd–P(2) 167.93(12), C(6)–C(7)–O(5) 119.0(5), C(3)–Fe–Pd 88.9(2).

The stable methyl acrylate insertion products **6a**,**b** were isolated in *ca.* 90% yield after stirring **4a**,**b** for 18 h in the presence of 10 equiv. of methyl acrylate (Scheme 2). Insertion of norbornadiene or dimethyl norbornadiene-2,3-dicarboxylate into the Pd–C bond of **4b** occurred within *ca.* 30 min with complete regio- and stereo-selectivity to afford yellow **7** or orange **8**, respectively. The ^1H NMR data of **8** unambiguously indicate that insertion across the *exo*-face of the sterically less hindered CH=CH double bond is preferred over that of the more 'activated' MeO_2C–C=C–CO_2Me double bond.

In order to mimic the next step in the alternating CO/olefin insertion chemistry, **5a**,**b** were reacted with CO under atmospheric pressure and the six-membered chelate complexes **9a**,**b** were obtained after *ca.* 4 h [eqn. (1)].



(1)

This reaction is reversible since **5a**,**b** are regenerated under reduced pressure. The lower reactivity of **5a**,**b** compared to $[(OC)_4\overline{Fe(\mu\text{-dppa})Pd}(Me)(NCMe)]^+$ is most likely due to the presence of a chelating ligand at Pd, suggesting that opening of the dative ketone→Pd bond is necessary for CO insertion into the Pd–CH_2 bond to proceed. The reaction leading to **9a** is indeed much faster in the presence of a few drops of MeCN.

The bimetallic templates around which various C–C coupling reactions have been performed in this work do not appear, at the moment, to be more reactive than mononuclear cationic Pd(II) complexes reported recently.[5b] However, they have allowed the complete characterization of key intermediates, including in the chemistry of functional monomers.

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Notes and references

‡ The dppm complexes are generally more soluble than their dppa analogs and therefore better amenable to NMR studies. Selected spectroscopic data (all ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ at 298 K) are provided as ESI.†

§ *Crystal data*: **1b**: $C_{30}H_{25}ClFeO_4P_2Pd$, $M_w = 709.14$, monoclinic, space group $P2_1/c$, $a = 10.931(2)$, $b = 12.0774(15)$, $c = 22.688(3)$ Å, $\beta = 98.48(3)$, $V = 2962.5(7)$ Å^3, $Z = 4$, $D_c = 1.590$ g cm^{-3}, μ(Mo-Kα) = 1.328 mm^{-1}, 24 209 reflections collected, indep. reflections 5811 ($R_{int} = 0.0549$), GOF 1.110; final R, R_w indices [$I > 2\sigma(I)$] 0.0599 and 0.1677 for 353 parameters.

3a: $C_{38}H_{33}ClFeN_2O_4P_2Pd\bullet 0.5CHCl_3$, $M_w = 900.99$, monoclinic, space group $C2/c$, $a = 39.920(8)$, $b = 11.851(2)$, $c = 16.940(3)$ Å, $\beta = 105.60(3)$, $V = 7719.0(24)$ Å^3, $Z = 8$, $D_c = 1.551$ g cm^{-3}, μ(Mo-Kα) = 1.140 mm^{-1}, 24 525 reflections collected, 6796 indep. reflections ($R_{int} = 0.0867$), GOF 1.042; final R, R_w indices [$I > 2\sigma(I)$] 0.0574 and 0.1241 for 448 parameters.

5a: $C_{32}H_{28}BF_4FeNO_5P_2Pd\bullet CH_2Cl_2$, $M_w = 902.52$, monoclinic, space group $P2_1/n$, $a = 12.468(2)$, $b = 14.540(3)$, $c = 20.969(4)$ Å, $\beta = 103.40.3$, $V = 3697.9(12)$ Å^3, $Z = 4$, $D_c = 1.623$ g cm^{-3}, μ(Mo-Kα) = 1.170 mm^{-1}, 29 287 reflections collected, 7202 indep. reflections ($R_{int} = 0.0607$), GOF 1.001; final R, R_w indices [$I > 2\sigma(I)$] 0.0573 and 0.1404 for 457 parameters.

CCDC 182/1872. See http://www.rsc.org/suppdata/cc/b0/b007171o/ for crystallographic files in .cif format.

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