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Monohapto-allyl Pd(II) complexes with bidentate hybrid P,N ligands †

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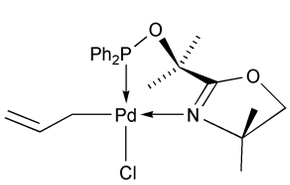
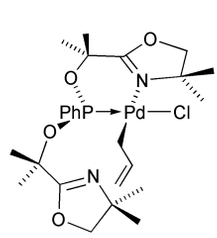
Using a new oxazoline-phosphonite P,N ligand, we establish that in contrast with commonly held belief, bidentate ligands can lead to unusually stable η^1-allyl complexes of Pd(II); CO insertion into their Pd–C σ-bond affords the corresponding 3-butenoyl complexes under mild conditions.

Transition metal allyl complexes display a rich chemistry and have a considerable importance in homogeneous catalysis where they often represent key intermediates.[1] Whereas η^3 bonding mode is the most general for this ligand, η^1-allyl complexes have been isolated mainly with platinum,[2] rhodium,[3] very recently with iridium,[4] or early transition metals.[5] The bonding features of an allyl fragment to a transition metal affect the stereochemistry of reactions proceeding *via* allyl intermediates and it is well known in Pd-allyl chemistry that an η^3–η^1–η^3 dynamic behaviour has considerable relevance to enantioselection.[1] It is therefore essential to recognize the exact bonding mode of the allyl ligand in a complex in order to understand or rationalize its reactivity. In Pd chemistry, the η^3-bonding mode of the allyl ligand is the rule and only very few Pd complexes containing η^1-allyl ligands have been characterized in solution,[6] and even more rarely in the solid-state,[7,8] despite their considerable importance as reactive species or proposed intermediates in C–C coupling reactions.[1] Although the idea that a strong and rigid tridentate ancillary ligand coordinated to a Pd(II) centre will trigger the occurrence of the rare η^1-bonding mode of the allyl ligand is completely logical,[6,7] we now establish that this does not represent a prerequisite. Reaction of the new bidentate ligand 1-(4,4′-dimethyl-4,5-dihydrooxazol-2-yl)-1-methyl)diphenylphosphonite,[9] abbreviated NOP^{Me2}, with $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$[10] afforded in 89% yield the new η^1-allyl chloro Pd(II) complex **1** which has been fully characterized (see ESI), † including by X-ray diffraction. ‡ There are two different but almost identical molecules in the asymmetric unit. One of them is represented in Fig. 1.



1

The ^{31}C NMR spectrum is very diagnostic for a η^1-allyl ligand, with characteristic chemical shifts at δ 29.5, 105.9, and 141.0 for the Pd–CH_2, =CH_2 and –CH= carbons.[8a] Consistent with Pearson's antisymbiotic effect,[11] the η^1-allyl ligand is *trans* to the nitrogen donor (Fig. 1), a ligand of weaker *trans* influence than phosphorus. These results allow us to answer the question of the need or not for a tridentate ligand to stabilize η^1-allyl Pd(II) complexes. With the ligand bis(2-oxazoline-4,4-dimethyl-2-hydroxydimethyl)phenylphosphonite, abbreviated $NOPON^{Me2}$, we recently characterized another η^1-allyl chloro Pd complex, **2**, in which $NOPON^{Me2}$ did not behave as a tridentate, but as a chelating ligand with a dangling oxazoline moiety.[8a]



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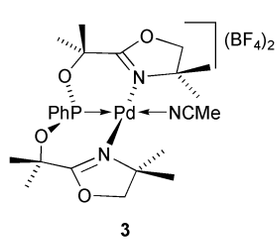

3

This behaviour was not due to an impossibility for $NOPON^{Me2}$ to function as a planar tridentate ligand since $[Pd(NCMe)(NOPON^{Me2}\text{-}N,P,N)](BF_4)_2$ **3** is perfectly stable.[8a] Although the dangling oxazoline arm in **2** was involved in the dynamic behaviour of the complex, our present results indicate that it did not play any significant role in promoting the η^1-allyl bonding mode. This establishes that the paradigm for a strong

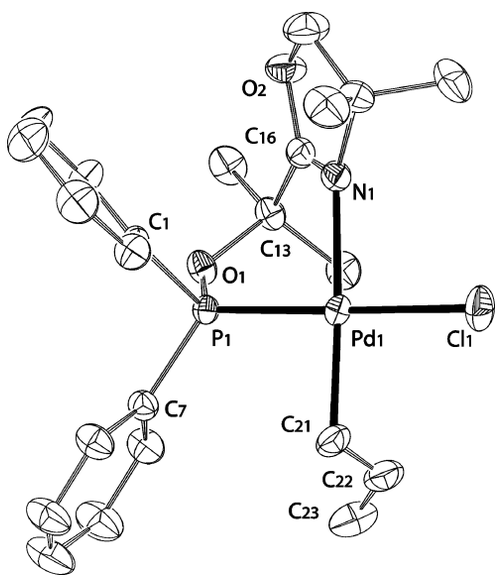

Fig. 1 ORTEP[18] view of the structure of $[Pd(\eta^1\text{-}C_3H_5\}Cl(NOP^{Me2}\text{-}N,P)]$ **1**. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.200(1), Pd(1)–N(1) 2.180(2), Pd(1)–Cl(1) 2.387(1), Pd(1)–C(21) 2.070(2), C(21)–C(22) 1.475(3), C(22)–C(23) 1.322(4); C(21)–Pd(1)–P(1) 92.31(7), C(21)–Pd(1)–Cl(1) 88.43(7), N(1)–Pd(1)–P(1) 83.22(5), N(1)–Pd(1)–Cl(1) 96.15(5), Pd(1)–C(21)–C(22) 101.5(1), C(21)–C(22)–C(23) 126.5(2), Pd(1)–P(1)–O(1) 112.5(6), P(1)–O(1)–C(13) 123.2(1), O(1)–C(13)–C(16) 107.9(1), C(13)–C(16)–N(1) 125.1(2), C(16)–N(1)–Pd 121.5(1).

† Electronic supplementary information (ESI) available: preparations and selected spectroscopic data for **1** and **4**–**6**. See http://www.rsc.org/suppdata/dt/b2/b212393m/

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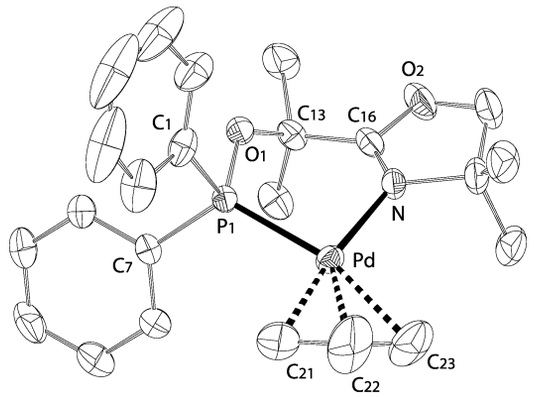


Fig. 2 ORTEP[18] view of the structure of $[Pd(\eta^3\text{-}C_3H_5\}(NOP^{Me2}\text{-}N,P)]PF_6$ **4**. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): Pd–P 2.244(1), Pd–N 2.112(2), Pd–C(21) 2.102(3), Pd–C(22) 2.144(4), Pd–C(23) 2.268(3), C(21)–C(22) 1.330(5), C(22)–C(23) 1.245(6); N–Pd–P 91.41(5), N–Pd–C(21) 173.4(1), N–Pd–C(23) 106.5(1), P–Pd–C(21) 95.17(9), P–Pd–C(22) 130.1(1), P–Pd–C(23) 162.1 (1), C(21)–Pd–C(23) 66.9(1), P–O(1)–C(13) 123.3(1), O(1)–C(13)–C(16) 109.0(1), C(13)–C(16)–N 129.0(2).

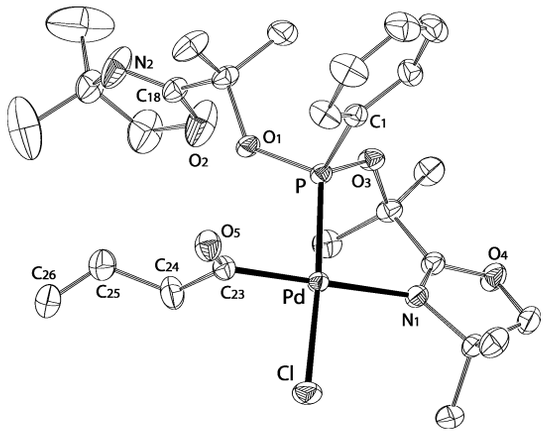
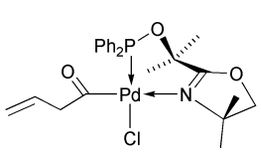


Fig. 3 ORTEP[18] view of the structure of $[Pd\{C(O)C_3H_5\}\text{-}Cl(NOPON^{Me2}\text{-}N,P)]$ **6**. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): Pd–P 2.210(1), Pd–N(1) 2.222(1), Pd–Cl 2.372(1), Pd–C(23) 1.983(2), C(23)–O(5) 1.201(2), C(23)–C(24) 1.535(3), C(24)–C(25) 1.493(3), C(25)–C(26) 1.306(3); C(23)–Pd–P 88.69(5), C(23)–Pd–Cl 85.29(5), N(1)–Pd–P 88.49(4), N(1)–Pd–Cl 98.20(4), Pd–P–O(1) 112.07(5), Pd–P–O(3) 112.94(5).

tridentate ligand being required to observe the η^1-allyl bonding mode in Pd(II) chemistry is no longer valid.

As expected, chloride abstraction from **1** led to the cationic η^3-allyl Pd(II) complex **4** (Fig. 2).†‡ The longer Pd–C(23) distance compared to Pd–C(21) reflects the larger *trans* influence of the P donor. Its ^{1}H NMR spectrum in $CDCl_3$ at 297 K shows an AB spin system for the two methylenic protons of the oxazoline and the methyl region exhibits two peaks at δ 1.70 and 1.79 for the diastereotopic $OC(CH_3)_2$ protons. Unlike the situation in $[Pd(\eta^3\text{-}C_3H_5\}(NOPON^{Me2}\text{-}N,P)]PF_6$,[8a] the five protons of the allyl fragment of **4** give rise to five peaks at room temperature, with the terminal protons *cis* to P exhibiting two doublets at δ 2.89 ($^3J_{HH}$ = 12.3 Hz) and 3.69 ($^3J_{HH}$ = 6.9 Hz), respectively. These data indicate either a static situation or slow rotation on the NMR time scale of the allyl ligand about the $(\eta^3\text{-}C_3H_5)$–Pd axis and no η^3–η^1–η^3 interconversion, the terminal *syn*- and *anti*-protons remaining non-equivalent.[12]

Bubbling of CO through a solution of **1** in toluene led to the formation of the insertion product **5**.†



5

Its ν(C=O) band at 1688 cm^{-1} is indicative of the formation of an acyl ligand and a resonance at δ = 226.7 ppm in the ^{13}C NMR spectrum with a small ^2J(P,C) coupling of 10.0 Hz shows that the acyl group resides in a *cis* position relative to the phosphorus.[13] For comparison, the related insertion product **6** was prepared from **2** (Fig. 3).†‡ The large high-field shift ($\Delta\delta$ = −20 ppm) of the ^{31}P NMR resonance (δ = 118.4), compared to **2** (δ = 138.1), also indicates the *cis* arrangement of the acyl group relative to the P atom.[13a,14] The geometry around palladium approximates square-planar, with slight deviations arising from the angles P–Pd–C(23) and N(1)–Pd–Cl of 85.29(5) and 98.20(4)°, respectively. The ^{1}H NMR spectrum of **6** at room temperature shows only one AB spin system assigned to the four OCH_2 protons.† The methyl region contains four lines including a broad singlet for the diastereotopic $NC(CH_3)_2$, which is similar to the situation in *cis*-$[PdCl_2(NOPON^{Me2}\text{-}N,P)]$,[8a] and indicates that the ligand behaves as a fluxional, hemilabile P,N chelate. In both **5** and **6**, the preference for the soft carbon ligand to avoid a position *trans* to P is again consistent with the antisymbiotic effect.[11]

These carbonylation reactions under very mild conditions contrast with the inactivity of $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Cl(PMe_3)]$[15] and support the view that CO insertion into η^3-allyl palladium cationic complexes occurs *via* first coordination of the counter ion to form an η^1-allyl intermediate. This hypothesis was presented Ozawa, Yamamoto and co-workers although they had not succeeded in isolating such η^1-allyl intermediates.[15] In contrast to *e.g.* *trans*-$[Pd\{C(O)CH_2CH{=}CH_2\}Br(PMePh_2)_2]$,[15] complexes **5** and **6** exhibit remarkable stability towards decarbonylation or decomposition, probably because of the energetically favourable *trans*-P–Pd–Cl and *trans*-N–Pd–C arrangements.[8a] Attempts to isolate further insertion products with ethylene were unsuccessful, consistent with the lower reactivity of neutral complexes,[16] and prolonged reaction times (>1 day) led to progressive decarbonylation and formation of the corresponding η^3-allyl complexes (*in situ* ^{1}H NMR monitoring).

In conclusion, we have clearly established that appropriate bidentate chelating ligands are suitable to stabilize η^1-allyl Pd complexes and this still rare bonding situation may occur more often than expected in numerous stoichiometric or catalytic transformations involving Pd(II) allyl complexes. The importance of halide effects on stoichiometric and catalytic reaction involving transition metal complexes has been recently reviewed.[17] In particular, it is noteworthy that the *syn-anti* isomerization of cationic, π-allyl Pd(II) complexes is considerably enhanced in the presence of added chloride and that catalytic amounts of halide were found to beneficially influence both the regio- and enantio-selectivity of asymmetric allylic alkylations.[17]

Acknowledgements

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Notes and references

‡ X-Ray structural analyses: the diffraction intensities were collected on a Kappa CCD diffractometer using Mo-Kα graphite monochromated radiation (λ = 0.71069 Å). The structures were solved by heavy-atom Patterson methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions with C–H = 0.98 Å.

Crystal data for **1**: $C_{23}H_{29}ClNO_2PPd$, M_r = 524.29, triclinic, space group $P\bar{1}$, a = 9.952(5), b = 12.957(5), c = 18.271(5) Å, α = 89.915(5), β = 89.447(5), γ = 86.007(5)°, V = 2350.2(16) Å^3, F(000) = 1072, Z = 4, D_c = 1.482 g cm^{-3}, μ = 0.990 mm^{-1}, T = 173(2) K, $R1$ = 0.0335, $wR2$ = 0.0853, GOF = 1.032 for 523 parameters.

Crystal data for **4**: $C_{23}H_{29}F_6NO_2P_2Pd$, M_r = 633.81, orthorhombic, space group *Pbca*, a = 15.136(5), b = 17.392(5), c = 20.248(5) Å, V = 5330(3) Å^3, F(000) = 2560, Z = 8, D_c = 1.580 g cm^{-3}, μ = 0.879 mm^{-1}, $R1$ = 0.0393, $wR2$ = 0.1058, GOF = 0.942 for 316 parameters.

Crystal data for **6**: $C_{26}H_{38}ClN_2O_5PPd$, M_r = 631.4, monoclinic, space group $P2_1/c$, a = 14.643(2), b = 10.970(2), c = 18.216(3) Å, β = 97.017(5)°, V = 2904.2(8) Å^3, F(000) = 1304, Z = 4, D_c = 1.444 g cm^{-3}, μ = 0.823 mm^{-1}, T = 173(2) K, $R1$ = 0.0467, $wR2$ = 0.1215, GOF = 1.013 for 325 parameters. CCDC reference numbers 193036–193038. See http://www.rsc.org/suppdata/dt/b2/b212393m/ for crystallographic data in CIF or other electronic format.

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