A chiral amidophosphine bearing a P–N bond and its π-allyl palladium(II) chemistry

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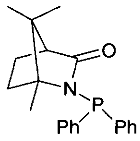
Camphor lactam phosphines 1 and 2, prepared from D-camphoric acid and D-camphor, respectively, act as bidentate P,O-ligands of palladium(II) where 1 is less hemilabile than 2, and in the dynamic behaviour of (π-allyl)palladium(II) complex 8 bearing 1, the bidentate coordination of this ligand is retained.

Transition-metal complexes having coordinated carbonyl groups such as ketones, aldehydes and esters are well documented;[1] however, very little is known of those with amidocarbonyl coordination.[2] Furthermore, no precedent has been reported for transition-metal complexes with chiral amidophosphines bearing a P–N bond.[3] We describe here the first synthesis of such compounds 1 and 2 which act as bidentate P,O-ligands. Interestingly, the study of the dynamic behaviour of (π-allyl)palladium complex 8 containing 1 clearly shows that a π–σ–π rotation of the allylic moiety predominates over a rotation expected from the cleavage of the weaker coordination of the amidocarbonyl.

In view of the rigidity of the camphor skeleton, the amidocarbonyl of camphor lactam phosphine 1 is expected to readily coordinate to metals. Indeed, 1, prepared from D-camphoric acid,† was found to act as a bidentate P,O-ligand towards Pd^{II}. Thus, treatment of 1 with $[PdCl_2(MeCN)_2]$ in dichloromethane gave complex 3 (93% yield), the structure of which was determined by a single-crystal X-ray analysis.‡ The ORTEP drawing of 3 (Fig. 1) shows that both the O and the P atoms of 1 coordinate to Pd as a bidentate ligand with Pd–P 2.18 Å and Pd–O 2.09 Å. In accordance with this structure, the IR spectrum of 3 (KBr) shows ν(C=O) at 1601 cm^{-1} which is lower by 114 cm^{-1} than that of the parent compound 1. For 2, prepared from D-camphor,† two palladium complexes 4 (77%) and 5 (11%) were obtained upon treatment with $[PdCl_2(MeCN)_2]$.§ The formation of monodentate complex 5 shows that 2 is more hemilabile than 1. Lactam phosphines do not necessarily coordinate to Pd^{II} as bidentate P,O-ligands. For example, lactam phosphine 6 and oxazolidinone phosphine 7, when treated with $[PdCl_2(MeCN)_2]$, gave the dimeric $PdCl_2$ complexes bearing η^1-P-ligands corresponding to 5.



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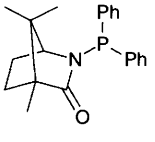

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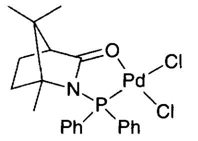

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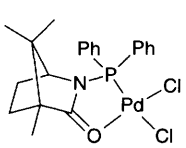

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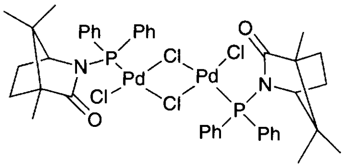

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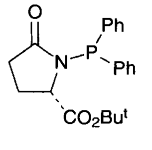

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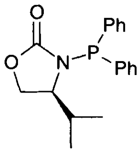

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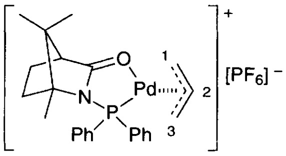


8

Chiral ligands in metal complexes bearing an achiral π-allyl moiety serve as a good probe for studying the dynamic behaviour of the π-allyl complexes, since the two diastereoisomeric structures can be discernible in their NMR spectra. Recently, a π–σ–π allyl rotation of allylic moieties has been elegantly revealed by using chiral diphosphine,[4] P,S-[5] or P,N-bidentate ligands.[6] Our attention has been thus directed towards the study of the dynamic behaviour of π-allyl complex 8 bearing chiral amidophosphine 1. Complex 8 was prepared in 75% yield by treating a solution of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ and 1 in CH_2Cl_2 with a solution of KPF_6 in MeCN.¶ The ν(C=O) in the IR spectrum appears at 1620 cm^{-1} which is also lower by 95 cm^{-1}. The ^{1}H NMR spectrum of 8 at ambient temperature shows broad signals due to the π-allyl moiety, but lowering the temperature results in separation of two sets of π-allyl moieties. In this spectrum, the C^3 protons (H^{3a} and H^{3s}) which suffer anisotropic shielding of the phenyl ring on the phosphorus atom

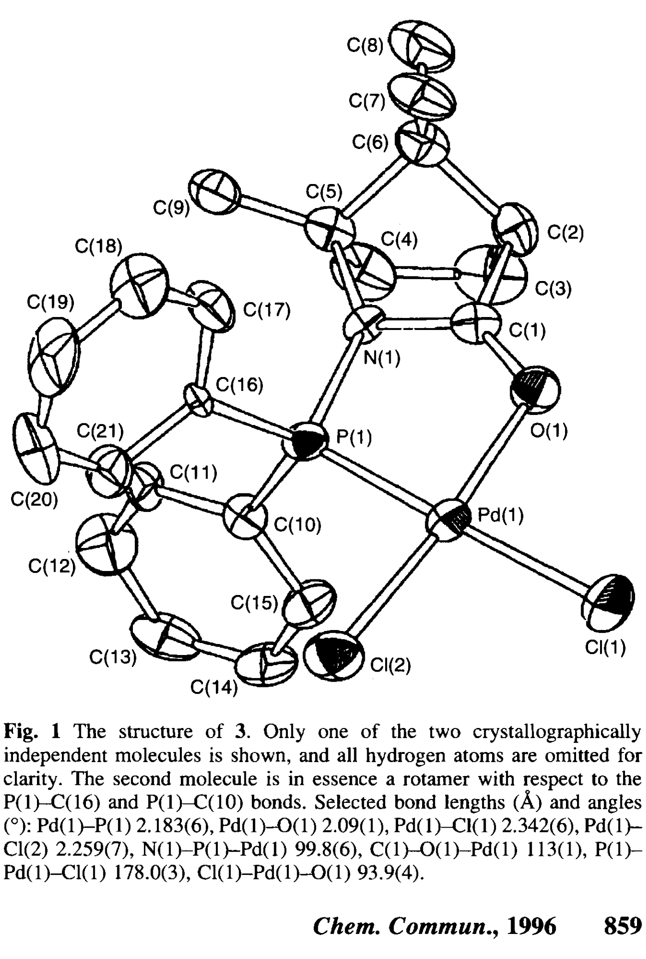
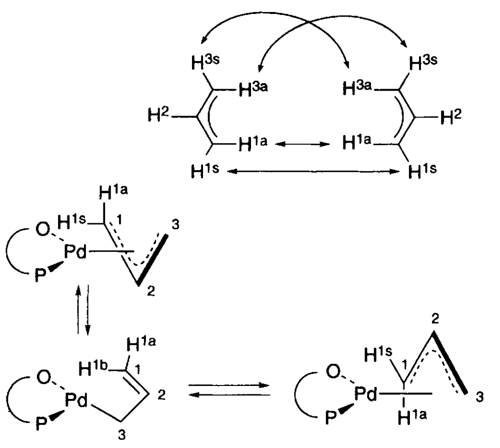


Fig. 1 The structure of 3. Only one of the two crystallographically independent molecules is shown, and all hydrogen atoms are omitted for clarity. The second molecule is in essence a rotamer with respect to the P(1)–C(16) and P(1)–C(10) bonds. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.183(6), Pd(1)–O(1) 2.09(1), Pd(1)–Cl(1) 2.342(6), Pd(1)–Cl(2) 2.259(7), N(1)–P(1)–Pd(1) 99.8(6), C(1)–O(1)–Pd(1) 113(1), P(1)–Pd(1)–Cl(1) 178.0(3), Cl(1)–Pd(1)–O(1) 93.9(4).



Scheme 1

appear at higher field compared to the C^1 protons (H^{1a} and H^{1s}).

The phase-sensitive two-dimensional ^1H NOESY spectrum for **8** (−30 °C)|| clearly shows the exchange cross-peaks for the allylic protons, and the results are shown in Scheme 1. Thus, for the C^1 protons (H^1) *trans* to the P-atom, the selective exchange of *syn* ⟶ *syn* and *anti* ⟶ *anti* protons are observed. The *syn* ⟶ *anti* exchange occurs only for the C^3 protons (H^3) *trans* to the O atom. No exchange between *syn*-H^1 and *syn*-H^3 protons takes place. Thus, two diastereoisomers exclusively exchange *via* a $\pi \longrightarrow \sigma$ allylic isomerization with the elective formation of a Pd–C^3 σ bond. A rotation expected from the cleavage of weaker C=O coordination does not take place.[7] The selectivity of $\pi \longrightarrow \sigma$ opening has been reported to be controlled by either electronic or steric effects.[5] If the rotation of the π-allyl moiety is not sterically hampered, it is governed by the electronic factor, and a σ-allyl bond is formed in a position *trans* to the weaker donor atom. Unambiguously, this is the case for the present study, as shown in Scheme 1.

Footnotes

† Camphor lactam phosphine **1** was prepared from D-camphoric acid by the following treatments: i, MeOH–HCl; ii, PCl_5, NH_4OH; iii, MeONa, Br_2; iv, NaH; v, NaH–Ph_2PCl. Camphor lactam phosphine **2** was prepared from D-camphor by the following treatments: i, LDA–isoamyl nitrile; ii, HCl; iii, K_2CO_3–MeI; iv, MeONa, Br_2; v, NaH; vi, NaH–Ph_2PCl. We are grateful to Professor R. K. Boeckman, Jr., for informing us of the procedures for the preparation of the camphor lactams, namely, the precursors of **1** and **2**; see R. K. Boeckman, Jr., S. G. Nelson and M. D. Gaul, *J. Am. Chem. Soc.*, 1992, **114**, 2258.

‡ *Crystal data* for $C_{21}H_{24}Cl_2NOPPd$: M = 514.7, monoclinic, space group $P2_1$ (no. 4), a = 14.113(3), b = 9.89(1), c = 15.606(6) Å, α = 90.01(7), β = 94.35(3), γ = 90.01(4)°, U = 2171(1) Å^3, Z = 4, D_c = 1.58 g cm^{-3}, $F(000)$ = 1040, μ(Mo-Kα) = 1.17 mm^{-1}. A yellow prismatic crystal (0.20 × 0.20 × 0.30 mm) was grown from dichloromethane–diethyl ether, and mounted on a Rigaku AFC7R four-circle diffractometer (12 kW). 4229 reflections (4070 unique reflections, R_{int} = 0.090) were collected using graphite-monochromated Mo-Kα (λ = 0.71069 Å) radiation with ω–2θ scans of which 3144 were observed [$I > 3.00\sigma(I)$]. The structure was solved by direct methods (SHELX86) and refined by full-matrix least squares to R = 0.037, R_w = 0.034, S = 2.82 for 486 variables; ρ_{max}, ρ_{min} 0.73, 0.94 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/10.

§ The ν(C=O) absorption of complex **4** appears at 1599 cm^{-1} (Nujol), also lower by 104 cm^{-1} than that of **2**, indicating that the O atom of **2** coordinates to Pd. By contrast, no such lowering was observed in complex **5** [ν(C=O) 1720 cm^{-1} (Nujol)].

¶ The structure of **8** was confirmed by a single-crystal X-ray determination but structural details are omitted here.

|| The phase-sensitive two-dimensional ^1H NOESY spectrum for **8** was measured at −30 °C in $CDCl_3$ with a mixing time of 720 ms. To simplify Scheme 1, the observed exchange between H^2 protons is omitted. Selected ^1H NMR data (270 MHz, −60 °C) for the two diastereoisomers of **8** (53 : 47) are: δ 2.77 (H^{3a}), 3.90 (H^{3s}), 4.12 (H^{1a}), 5.24 (H^{1s}), 6.08 (H^2); and 3.23 (H^{3a}), 3.62 (H^{3s}), 4.38 (H^{1a}), 5.24 (H^{1s}), 5.75 (H^2).

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Received, 18th December 1995; Com. 5/08203J