Palladium-MOP Chemistry: Pseudo-*cis*-Allyl MOP Complexes and Flexible Olefin Bonding

Preliminary Communication

by **Pascal Dotta**, **P. G. Anil Kumar**, and **Paul S. Pregosin***

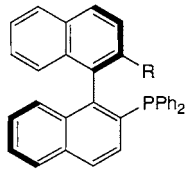
Laboratory of Inorganic Chemistry, ETHZ, CH-8093 Zürich

and **Alberto Albinati***

Department of Structural Chemistry (DCSSI), University of Milan, I-20133 Milan

We show that both palladium(0) and palladium(II) metal centers are capable of coordinating two monodentate MOP (=(*R*)-2-(diarylphosphino)-1,1′-binaphthalene) ligands in a pseudo-*cis* orientation, despite published statements to the contrary. In addition to $[Pd(\eta^3\text{-}C_3H_5)(MeO-MOP)_2]BF_4$ (MeO–MOP=(*R*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthalene), the first examples of chiral bis κC^1-prop-2-enyl (η^1-$CH_2CH{=}CH_2$) complexes [*cis*-$Pd(\kappa C^1\text{-}C_3H_5)_2$(MeO–MOP or MOP)$_2$], are shown to be relatively stable. Further, coordinated MOP and MeO–MOP both show stronger propensity towards novel intramolecular π-olefin complexation than the CN–MOP analogue. The solid-state structure of [Pd(fumaronitrile)$(MOP)_2$] is reported.

Applications of homogeneous catalysis involving chiral monodentate phosphine ligands continue to increase. One of the more-successful classes, the so-called MOP ligands, **1**–**3**, introduced by *Hayashi* [1a], has been used in enantioselective allylic alkylation [1b,c], hydrosilylation[1]) [1d–g], and allylic reduction [1a,h].



1 R = H ((*S*)-MOP)
2 R = CN ((*R*)-CN-MOP)
3 R = MeO ((*R*)-MeO-MOP)

Since the MOP ligand is relatively large, there is some uncertainty as to the number of MOP molecules capable of coordinating to a transition metal. Specifically, for **3** (=(*R*)-(2′-methoxy-[1,1′]binaphthalen-2-yl)diphenylphosphine), which has a cone angle of *ca.* 200° [1b], it has been stated [1b] that for 'MeO–MOP… the π-allyl Pd cannot accommodate two molecules of phosphine ligand because of the steric bulkiness…'. In connection with our studies on enantioselective allylic alkylation [2], we have prepared several new chiral Pd-MOP complexes and show here that *a*) indeed, two MOP ligands can readily complex Pd in a *cis*-orientation, *b*) an unprecedented bis

[1]) *trans*-$PdCl_2$((*R*)-MeO-MOP)$_2$ is known [1g].

κC^1 allyl-bis(MOP) compound is relatively stable, and *c*) several MOP complexes of Pd^{II} reveal a diene π-olefin bonding mode.

As the allylic alkylation and hydrosilylation reactions involve oxidative addition reactions to Pd^0, we prepared a stable fumaronitrile (*trans*-but-2-enedinitrile) Pd^0 complex by adding two equivalents of the smallest conventional MOP, **1** (=(*S*)-([1,1′]binaphthalen-2-yl)diphenylphosphine) to $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one) followed by addition of fumaronitrile. The solid-state structure of the product, [Pd(fumaronitrile)(**1**)$_2$], **4** (=bis[(*S*)-([1,1′]binaphthalen-2-yl)diphenylphosphine-κP][(2,3-η)-but-2-enedinitrile]palladium), is shown in *Fig. 1*. Interestingly, the two MOP ligands sit comfortably in a pseudo *cis*-orientation around the Pd-atom with a modest P–Pd–P angle of *ca.* 114°, *i.e.*, there are no untoward steric interactions that might have resulted in a P–Pd–P angle of > 120°. We note that this structure shows the two PPh_2 groups placed relatively close to each other, and the two naphthalenyl moieties in rather remote positions. The fumaronitrile olefinic C-atoms are located approximately in the P–Pd–P plane. The various bond lengths within the coordination sphere are normal; however, the Pd–P distance is somewhat long, Pd(1)–P(1) = 2.358(1) Å[2]).

To expand on the zero-valent class of MOP complexes, Pt(diphenylacetylene)$_2$ was allowed to react with 2 equiv. of **1** to afford [Pt(PhC≡CPh)(**1**)$_2$], in solution as the only product (*Eqn. 1*). This complex was not isolated; however, its ^{195}Pt-NMR spectra revealed the triplet multiplicity expected for a bis-phosphine complex (^1J(Pt,P) = 3590 Hz, δ ^{195}Pt = −4968, CD_2Cl_2, 233 K), thereby confirming the presence of two complexed MOP ligands within the coordination sphere.

$$Pt(PhC{\equiv}CPh)_2 + 2\ \mathbf{1} \rightarrow Pt(PhC{\equiv}CPh)(\mathbf{1})_2 - PhC{\equiv}CPh \qquad (1)$$

As a structural model for the Pd^{II} oxidation state, we allowed 1 equiv. of the dinuclear allyl complex $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Cl)_2]$, to react with 2 equiv. of $AgBF_4$ and 4 equiv. of MeO–MOP, **3**. The yellow-orange product was isolated (53%); the ^{31}P-NMR spectrum, shown in *Fig. 2*, contains three components in the ratio 1.0 : 0.8 : 1.4 and a small amount of phosphine oxide. Based on detailed NMR studies, the three MOP-containing species are suggested to be **6**–**8**.

Compound **6** (=bis[(*R*)-(2′-methoxy-[1,1′]binaphthalen-2-yl)diphenylphosphine-κP](η^3-prop-2-enyl)palladium(1+)[3]) represents the now expected bis-phosphine product. Its ^{31}P-NMR reveals an AB spin system, plus the five ^{1}H- and three ^{13}C-NMR resonances of the allyl-ligand. The axial and equatorial nature of the two PPh_2 groups renders the two ^{31}P signals (just barely) non-equivalent with respect to the allyl group.

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[2]) In keeping with this longish bond, we note that the ^{13}C chemical shifts for the fumaronitrile olefinic C-atoms in the two diastereomers of **4**, δ^{13}C = 32.5 and 36.7, are found at *ca.* 10 ppm higher frequency relative to those of related Pd^0 fumaronitrile complexes [2a], *i.e.*, the π-bonding to the olefin is not quite so marked.

[3]) NMR-Data of **6** (δ in ppm, *J* in Hz): ^{1}H-NMR (CD_2Cl_2, 400 MHz): 3.21 (*m*, ^3J(P,H) = 10.4, H_{anti}–C(1)); 3.52 (*m*, ^3J(P,H) = 10.4, H_{anti}–C(3)); 4.06 (br. *t*, ^3J(H,H) = 5.4, H_{syn}–C(3)); 4.29 (br. *t*, ^3J(H,H) = 4.9, H_{syn}–C(1)); 5.74 (*m*, H–C(2)). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 78.7 (C(1)); 80.1 (C(3)); *ca.* 123 (C(2)). ^{31}P-NMR (CD_2Cl_2, 121 MHz): 29.7, 30.0 (^2J(P,P) = 36).

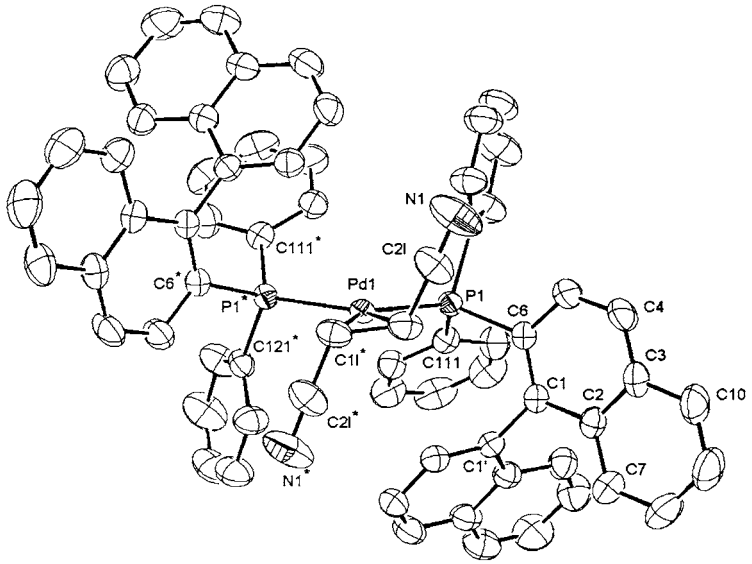

Fig. 1. *ORTEP View of the MOP-complex* **4**. Selected bond lengths [Å] and bond angles [°]: Pd–C(1L), 2.119(2); Pd(1)–P(1), 2.3588(8); P(1)–C(6), 1.855(2); P(1)–C(111), 1.828(2); P(1)–C(121), 1.847(2); C(1L)–C(1L)*, 1.431(5); C(2L)–N(1), 1.130(4); P(1)–Pd(1)–P(1)*, 114.11(3); P(1)–Pd(1)–C(1L), 142.4(1); P(1)–Pd(1)–C(1L)*, 103.4(1); C(1L)*–C(1L)–C(2L), 117.8(3); C(1L)–C(2L)–N(1), 177.5(4). The molecule lies on a *C*2 axis passing through the Pd-atom and the midpoint of the coordinated double bond. Symmetry related (starred) atoms are obtained by the symmetry operation $-x; y; -z$. Crystal data for **4**: $C_{68}H_{48}N_2P_2Pd$, $M = 1061.42$, monoclinic, space group $C2$ (no. 5), $a = 22.318(7)$, $b = 8.930(3)$, $c = 16.679(5)$ Å, $\beta = 117.199(5)$ deg, $U = 2956.8(15)$ Å^3, $Z = 2$, $d = 1.192$ g cm^{-3} $\mu = 4.08$ cm^{-1}, $T = 295(2)$ K. All atoms were refined anisotropically by full-matrix least-squares on F^2. Final agreement factors are: $R_1 = 0.0290$ (for 6595 unique reflections with $I > 2\sigma(I)$), 0.0311 (for all 6862 independent reflections).

The bis-allyl complex, **7** (= bis[(*R*)-2′-methoxy-[1,1′]binaphthalen-2-yl)diphenylphosphine-κP]bis(prop-2-enyl-κC^1)palladium), represents the first example of a stable bis-κC^1-allyl chiral compound. Generally, end-on allyl complexes are rarely observed. For complexes of chiral ligands, we know of only one other example, **9**, in which this isomeric form is stable [3].

The κC^1 allyl form in **7** is recognizable by its characteristic ^{1}H- and ^{13}C-NMR resonances, *i.e.*, diastereotopic aliphatic CH_2 protons and an ABX spin system at relatively high frequency, typical for a vinyl group (*Fig. 3*)[4]).

The presence of the two MOP ligands in **7** is confirmed by pulsed-gradient spin-echo (PGSE) diffusion measurements [4–6]. The smaller diffusion constants, *D*, for **7**, in CH_2Cl_2 ($D = 8.71$ and 8.63×10^{-10} m^2 s^{-1} from ^{1}H- and ^{31}P-NMR measurements, respectively), reflect the observed difference in volume between a single MOP ligand

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[4]) NMR Data of **7** (δ in ppm, *J* in Hz): ^{1}H-NMR (CD_2Cl_2, 400 MHz): 3.24 (*m*, ^3J(H,H) = 7.3, ^2J(H,H) = ^3J(P,H) = *ca.* 15, PdCH_2CH=CH$_2$); 3.35 (*m*, ^3J(H,H) = 7.2, ^2J(H,H) = ^3J(P,H) = *ca.* 15, 2 H, PdCH_2CH=CH$_2$); 5.06 (*dd*, ^3J(H,H) = 16.9, ^2J(H,H) = 3.7, 2 H, PdCH$_2$CH=CH_2, *trans*-H); 5.18 (*dd*, ^3J(H,H) = 10.2, ^2J(H,H) = 3.7, 2 H, PdCH$_2$CH=CH_2, *cis*-H); 5.32 (*m*, 2 H, PdCH$_2$CH=CH$_2$). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 29.5 (PdCH_2CH=CH$_2$); 124.4 (PdCH$_2$$C$H=CH$_2$); 126.3 (PdCH$_2$CH=$CH_2$). ^{31}P-NMR ($CD_2Cl_2$, 121 MHz): 21.3.

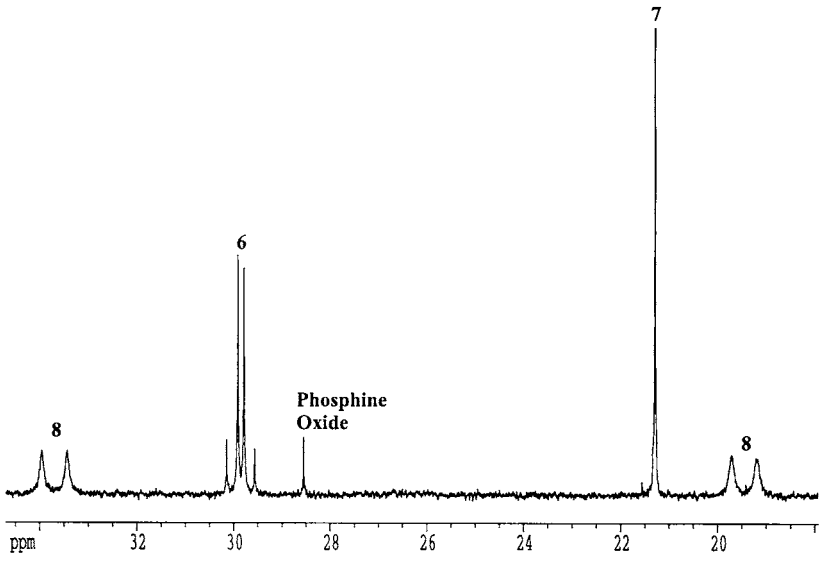
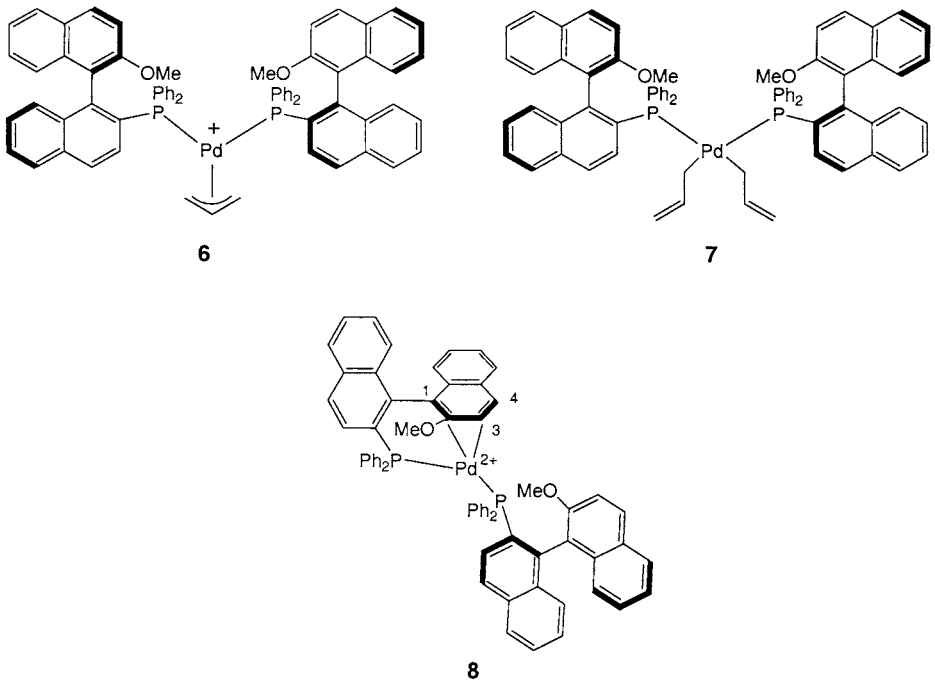
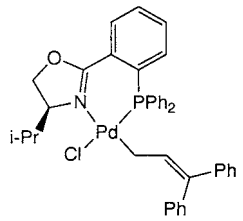


Fig. 2. *^{31}P-NMR Spectra of* **6**–**8** *at ambient temperature.* Complex **6** shows an AB spectrum, complex **7** a *singlet*, and **8** and AX spin system. The ^{31}P-NMR line widths in **8** indicate an exchange process and 2D exchange spectroscopy at 253 K confirms that the two MeO–MOP ligands exchange places.





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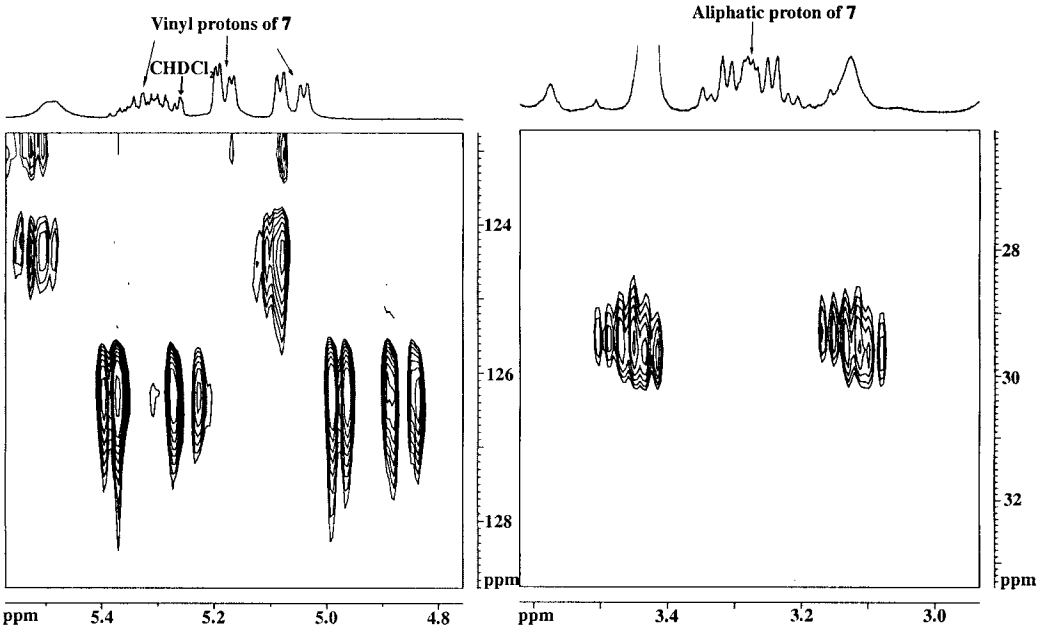

Fig. 3. *The proton resonances of the vinyl group of* **7**. The 1D spectra show the normal ^{1}H chemical shifts for a vinyl group at δ *ca.* 5.0–5.4. The cross-peaks arise from two sections of a 2D C,H one-bond correlation and show the expected vinyl ^{13}C chemical shifts at δ *ca.* 124–126, and not those expected for a Pd-allyl ligand.

($D = 10.59$ and 10.89×10^{-10} m^2 s^{-1} from ^{1}H- and ^{31}P-NMR data, resp.) and a complex containing two such large molecules. The ratio of D-values, *ca.* 1.24, is exactly what is expected for *ca.* double the volume[5]). Clearly, there is facile transfer of an allyl ligand from one metal center to another, perhaps due to the ease of η^3 to κC^1 isomerisation.

Diene complex **8** (={(*R*)-[2′-methoxy-[1,1′]binaphthalen-2-yl-(1′,2′,3′,4′-η)]diphenylphosphine-κP}[(*R*)-(2′-methoxy-[1,1′]binaphthalen-2-yl)diphenylphosphine-κP]palladium(2+)) shows two very different ^{31}P resonances ($\delta = 19.4$ and 33.7, ^2J(P,P) = 83 Hz), with the former signal associated with the chelate ring. This difference arises due to a novel Pd–MOP interaction, *i.e.*, one MOP ligand serves as a six-electron

[5]) The value 1.24 is arrived at by taking the average of the two values (^{31}P and ^{1}H) for the ligand and dividing it by the average of the two for the complex.

donor. The η^4-complexation in **8** was identified *via* a set of $^{13}C,^{1}H$ correlations with the key ^{13}C signals for the complexed arene assigned (at 253 K) to δ 103.6 (C(1′)), 127.7 (C(2′)), 80.4 (C(3′)), and 86.3 (C(4′)). The corresponding ^{1}H-signals for protons at C(3′) and C(4′) appear at δ 5.49 and 7.35. *The use of* **1**, *the unsubsubstituted MOP analog, affords the three analogous products.* Clearly this chemistry is not restricted to MOP derivatives that possess electron-donating substituents.

Although there is now some literature for MOP naphthalenyl bonding [7], the 'normal' π-(or σ)-complexation occurs *via* the fully substituted-C(1) and C(2) and *not via* C(3) and C(4). Consequently, the π-bond complexation in **8** is unique for Pd. Interestingly, the same reaction with **2** (R = CN) instead of either **1** or **3** gave only complexes analogous to **6** and **7**, some phosphine oxide, *but no π-bond complexation analogous to* **8**. We believe that the CN group of **2** decreases the electron-donating capacity of the naphthalene moiety, thus suppressing chelate formation in **8**. Consequently, the structural chemistry of the MOP class is not trivial, and postulated reaction mechanisms involving this group of compounds may need to clearly differentiate between **2** and **1** or **3**.

Our results clearly show that both Pd^0 and Pd^{II} are capable of coordinating two MOP ligands in pseudo *cis*-orientation. Interestingly, and, perhaps, because these MOP ligands are quite large, η^3 to κC^1 isomerisation is not only facile, but the end-on ligated form is relatively stable. Further, the choice of MOP ligand is not trivial in that both MOP complexes **1** and **3** show stronger propensity towards the novel intramolecular π-olefin complexation than does the CN-analogue, **2**.

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