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Conformational Flexibility in a Carbobicyclic Diphosphinite Ligand

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An unsymmetrical bicyclo[3.2.0]heptanyl diphosphinite ligand, FLEXIphosO, shows flexible coordination modes to palladium centres. The X-ray crystal structure for [$Pd^0_2(P,P')_3$] has been determined which reveals that the bicyclic backbone of the FLEXIphosO ligand exists in an *exo*-envelope conformation. The change in conformation stands in stark contrast to that observed in mononuclear neutral and cationic palladium(II) complexes containing the FLEXIphosO ligand, where an *endo*-envelope is observed in solution and in the solid-state. Theoretical studies provide an insight into the relative stability of palladium(0) complexes containing the FLEXIphosO ligand. Another large spanning angle ligand, SPANphos, does not form a similar palladium(0) dimer complex under identical reaction conditions, highlighting the unusual behaviour of the FLEXIphosO ligand.

Introduction

Bidentate phosphorus ligands are commonly used in coordination chemistry, synthesis and catalysis. The majority of these are rigid and on coordination to a transition metal possess a defined bite angle, a structural feature that is important in key steps in many transition metal-catalysed processes. The global complexity of the complete catalytic cycles of these reactions leads one to anticipate that bidentate ligands that can alter their bite angle could be beneficial to individual steps that are intrinsically different, e.g. oxidative addition and transmetallation, leading to an overall more efficient process. Although this proposition remains a significant challenge, it is evident that the identification of ligands that are capable of energetically accessible geometrical changes will be useful in addressing a key evolution in the design of efficient dynamic ligands. Ligands such as dioxop,[1] bisbi,[2] triptycene,[3] TRANSphos,[4] TRAP,[5] dppf,[6] xantphos,[7] and others[8] offer *cis* and *trans* coordination modes in square-planar complexes. SPANphos, a second generation variant of Xantphos developed by van Leeuwen and co-workers,[9] exhibits interesting catalytic properties in methanol carbonylation,[10] a facile *cis* to *trans* coordination mode switch, as well as the ability to form bimetallic complexes. Further additions to these ligand classes would be useful, particularly structures that utilise conformational changes imposed by a carbobicyclic skeleton – a potentially beneficial structural facet that has rarely been employed in ligand design strategies.[11] In this report we present evidence showing that the bicyclo[3.2.0]heptanyl ligand **1**, B[3.2.0]DPO[12] renamed as FLEXIphosO[13] (Figure 1), can undergo a conformational change on coordination to Pd^0. Our previous studies[14] have established that **1** exhibits an exclusive *cis*-coordination mode in neutral and cationic Pd^{II} and Pt^{II} complexes, e.g. **2**–**4**, where

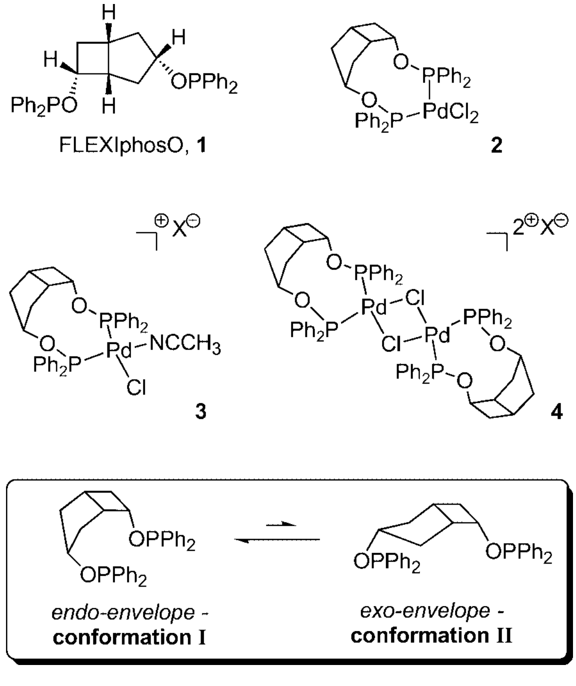

Figure 1. Bicyclo[3.2.0]heptanyl ligand and palladium complexes.

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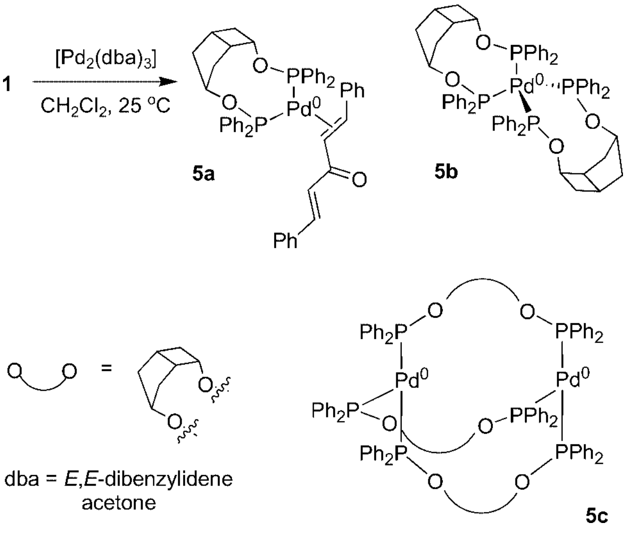
the ligand backbone possesses an *endo*-envelope conformation (**I**). Crucially, theoretical calculations support a conformational change from **I** to **II**, the latter an *exo*-envelope, for the stabilisation of cationic [Pd^{II}(H)L$_2$] species, which are proposed key intermediates in 1,6-diene cycloisomerization reactions.[15] Direct experimental evidence for the existence of conformation **II** is presented in this communication.

Results and Discussion

Generally, new bidentate ligands are often coordinated to Pd^{II}, Pt^{II} and Rh^{I}, perhaps due to their ease of preparation, stability and purification. Low oxidation state metal complexes are less often prepared, e.g. Pd^0, leading us to investigate the complexation of **1** to Pd^0. The reaction of **1** with [Pd$_2$(dba)$_3$] (**1**/Pd = 1:1) in CD_2Cl_2 at 25 °C affords one species as evidenced by ^{31}P NMR spectroscopy. Complexes **5a** (thermodynamic) and **5b** (kinetic) represent the most likely products. Two broad signals at {P1: δ = 108.1 and P2: δ = 109.8 (br. s); $\Delta\nu_{1/2}$ = 40 Hz} suggests **5a** as the product. The pseudo-molecular ion (MH$^+$ = *m*/*z* 837.1853; calculated 837.1873) was confirmed by APCI-ESI MS, exhibiting a correct isotopic distribution against calculated values for $C_{48}H_{45}O_3P_2Pd_1$. Repeats of this experiment resulted in the appearance of a minor species, possessing several phosphorus environments, as shown by ^{31}P NMR spectroscopy. The presence of excess **1** relative to Pd accounts for the formation of this species, confirmed by the reaction of ca. 3 equiv. of **1** with [Pd$_2$(dba)$_3$], which affords this species as the major component[16] (Scheme 1). Two sharp singlets in the ^{31}P NMR spectrum are observed at δ = 108.8 and δ = 116.6, as well as two sets of multiplets, the first collected between δ = 107.7–110.1 and the second between δ = 112.4–115.6. The ^{31}P NMR spectrum appears to be complicated by ligand **1** being unsymmetrical. The two sharp singlets could be attributed to either **5b** or **5c**. However, the multiplets could only arise through consideration of the possible isomeric forms **5c** and **5cc** (Figure 2).



Scheme 1. Synthesis of Pd^0 complexes containing ligand **1**.

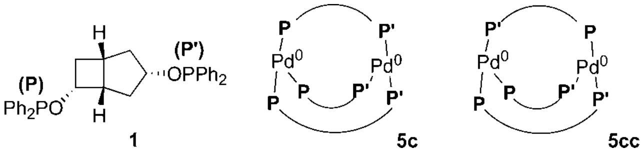


Figure 2. Isomeric forms of [Pd$_2$(FLEXIphosO)$_3$] complex (**5c**/**5cc**).

Simulation of the ^{31}P NMR spectrum for this mixture of compounds using the gNMR package confirmed that the muliplets were attributable to an isomeric form **5cc**, e.g. a six-spin system (Figure 3). The large $^2J_{PP}$ couplings (about 100–127 Hz) and small chemical shift differences between the phosphorus substituents in each of the cyclobutyl and cyclopentyl rings leads to pronounced second order effects, complicating the appearance of the ^{31}P NMR spectrum (Table 1 and Figure 3). The phosphorus environments in **5cc** are inequivalent due to the phosphinite group in the cyclobutyl ring in fragment (Pd1–P,P′,P′) breaking the overall symmetry, which directly affects the spin-spin coupling pattern for the other fragment (Pd2–P,P,P′). The larger ^2J(P,P′) couplings are observed in the (Pd1–P,P′,P′) fragment between P (environment D) and both P′ groups (environments B and C; 123.7 and 126.8 Hz, respectively). In

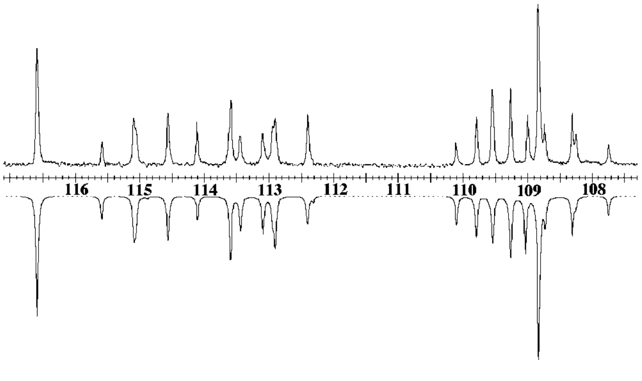
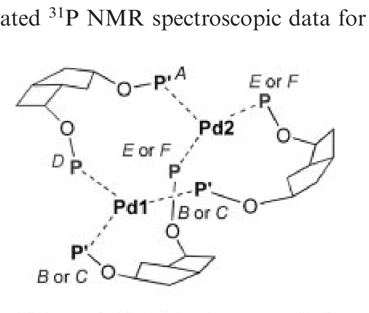


Figure 3. Experimental (upper) and simulated (lower) ^{31}P NMR spectra for **5c**/**5cc**.

Table 1. Simulated ^{31}P NMR spectroscopic data for complex **5cc**.



six inequivalent P environments in **5cc**

P environment	δ	J_A	J_B	J_C	J_D	J_E
A	109.3					
B	109.5	0				
C	108.4	0	116.0			
D	113.6	0	123.7	126.8		
E	112.9	107.8	0	0	0	
F	115.0	108.7	0	0	0	100.4

contrast there is a smaller $^2J_{P',P'}$ coupling between B and C (is 116 Hz). Smaller couplings are seen in the (Pd2–P,P,P′) fragment, with P′ (environment A) coupling with both P groups (environments E and F; 107.8 and 108.7, respectively). As with the first fragment, the two similar phosphorus environments, in this case E and F, exhibit a $^2J_{P,P}$ coupling of 100.4 Hz. Isomer **5c** is much more straightforward, exhibiting only two singlets at δ = 108.8 and δ = 116.6, due to C_{3v} symmetry. Attributing these singlets to **5b** has been ruled out on the basis that this species is undetected by APCI-ESI MS, whilst **5a** and **5c** are. It is interesting to note that [**5c**]$^+$ is produced as a stable ion on ionizing **5a** by this technique, highlighting the gas-phase stability of this species.

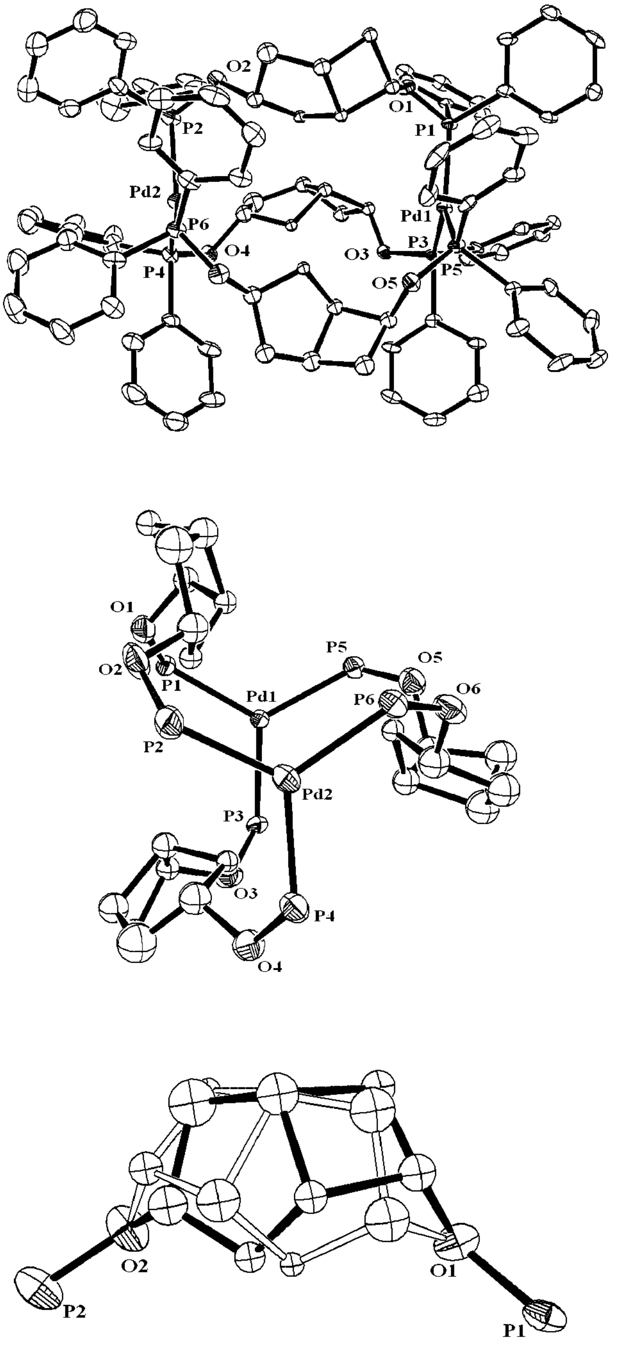


Figure 4. X-ray structure of complex **5c**/**5cc** (H atoms and CH_2Cl_2 omitted for clarity). Top structure: each ligand oriented in the same direction. Middle structure: phosphorus phenyl groups omitted. Bottom structure: showing the two orientations of the bicyclo[3.2.0]heptanyl structure in the ligand backbone. Selected bond lengths [Å] and angles [°]: O(1)–P(1) 1.632(6); O(2)–P(2) 1.624(6); O(3)–P(3) 1.641(6); O(4)–P(4) 1.637(6); O(5)–P(5) 1.631(6); O(6)–P(6) 1.618(6); P(1)–Pd(1) 2.294(2); P(2)–Pd(2) 2.284(2); P(3)–Pd(1) 2.295(2); P(4)–Pd(2) 2.284(2); P(5)–Pd(1) 2.289(2); P(6)–Pd(2) 2.275(2); P(5)–Pd(1)–P(1) 121.50(8); P(5)–Pd(1)–P(3) 119.89(8); P(1)–Pd(1)–P(3) 118.46(8); P(6)–Pd(2)–P(2) 117.98(9); P(6)–Pd(2)–P(4) 121.24(8); P(2)–Pd(2)–P(4) 120.08(9).

Layering a dichloromethane solution of the mixture of **5c** and **5cc**, under an inert atmosphere,[17] with diethyl ether (1:5, v/v) produced dark red crystals suitable for analysis by X-ray diffraction, which revealed the dimeric structure as a mixture of these isomeric forms (Figure 4).

The dimeric complex contains three bridging ligands and as ligand **1** is unsymmetrical it is found in two positions, which has been modelled with a 2:1 occupancy. The complex crystallizes with one molecule of dichloromethane. There is no evidence for a Pd–Pd bond in this structure and the total electron count for each metal is 16-electrons. The Pd(1)–Pd(2) distance is 7.191 Å. The average phosphorus–palladium bond length is slightly different for each Pd atom {Pd(1)–P 2.293(2) Å; Pd(2)–P 2.284(2) Å}, as is the average oxygen–phosphorus bond length around each Pd centre {O–P for Pd(1) 1.635(6); O–P for Pd(2) 1.626(6)}. The PdP_3 fragments are near eclipsed, and if one considers isomer **5c** possesses C_{3v} symmetry.

Of particular interest is the observation that this complex is isostructural with $[Pd^0_2(dba)_3\cdot CH_2Cl_2]$.[18] In the latter complex, each Pd^0 centre is coordinated by three alkenes, with the dba acting as a bridging ligand {the Pd(1)–Pd(2) bond length is 3.194 Å in this complex}.[18c] The dimeric complex is a rare example of a phosphorus variant of this ubiquitous dimeric Pd^0 alkenyl complex. Two more closely related $[Pd^0_2(P,P)_3]$ complexes are known, where P,P = bis(diphenylphosphanyl)methane[19] and bis(diphenoxy)-*N*-methylphospazane.[20] In each of these complexes, the Pd···Pd bond length is 2.959(2) and 2.855(2), respectively. Moreover, these ligands possess small spanning angle ligands, whereas ligand **1** exhibits a much larger angle.

Theoretical Studies

To study the geometric properties and relative stabilities of the species illustrated in Scheme 1, theoretical calculations were performed at the Becke3LYP level of DFT theory on the model complexes in which the phenyl groups were replaced by hydrogens.

As discussed above, the reaction of **1** with $[Pd_2(dba)_3]$ (**1**/Pd = 1:1) in CH_2Cl_2 affords **5a** initially. The absence of **5b** experimentally is intriguing. Bidentate phosphane ligands usually give this type of complex as the kinetic product.[21] To compare the relative stability of **5a** and **5b**, the reaction energy for Equation (1) was calculated.

$$\mathbf{5b} + \text{dba} \rightarrow \mathbf{5a} + \text{FLEXIphosO} \qquad (1)$$

The calculations reveal that the reaction energy ΔE is –0.5 kcal/mol. Once the phenyl groups are employed in the calculations, **5b** is expected to be even less favoured due to its relatively more congested structure. Experimentally an excess of dba may further tip the balance in favour of **5a**, more so than seen for other types of phosphanes. In the presence of a slight excess of ligand **1** relative to Pd, the reaction actually gives the dimeric complex **5c**; again **5b** is not formed. To study the relative stability of **5c**, the reaction energy for Equation (2) was calculated.

$$2\ \mathbf{5a} + \text{FLEXIphosO}\ (\mathbf{1}) \rightarrow \mathbf{5c} + 2\ \text{dba} \qquad (2)$$

The reaction energy ΔE was calculated to be –4.5 kcal/mol, confirming the experimental observation that the dimeric complex **5c** is the only species in the presence of a slight excess of **1** relative to Pd.

Since both the *endo*- and *exo*-envelope conformations for the free ligand are possible, it is interesting to assess how the stability of the complexes changes with the variation of the ligand's conformation. Both **5a** and **5b** shown in Scheme 1 have an *endo*-envelope conformation of ligand **1**. We were able to locate their conformational isomers **5a′** and **5b′** in which the ligand shows an *exo*-envelope conformation (Figure 5). **5a′** and **5b′** were found to be less stable by 2.7 and 4.8 kcal mol^{-1} than **5a** and **5b**, respectively. **5c** has an *exo*-envelope conformation of the ligand. Crucially, its *endo*-envelope conformational isomer **5c′** does not correspond to a local minimum on the potential energy surface.

In a previous study on related complexes with ligand **1** containing a Pd$^{\mathrm{II}}$ metal centre,[12] we found that when the ligand offers a *cis* coordination mode only the *endo*-envelope conformational isomer exists; when the ligand offers a *trans* coordination mode only the *exo*-envelope conformational isomer exists. In the Pd$^{\mathrm{II}}$ complexes studied, the geometry around the metal centre is square-planarly-based and the P–Pd–P bite angles are forced to be close to either 90° or 180°.

The trigonal planar geometry of Pd^{0}L$_3$ complexes and the tetrahedral geometry of Pd^{0}L$_4$ complexes allows ligand **1** to show its binding flexibility since the P–Pd–P bite angles are no longer limited to those close to either 90° or 180°. Therefore, in the mononuclear Pd^0 complexes shown in Scheme 1, both the *endo*- and *exo*-envelope conformations of ligand **1** are local minima on the potential energy surface.

In the dimeric palladium complex **5c**, the long distance between the two phosphorus atoms in each of the three bridging ligands, a situation similar to that when ligand **1** offers a *trans* coordination mode in Pd$^{\mathrm{II}}$ complexes, forces each ligand to adopt the *exo*-envelope conformation.

A final note is that in addition to **5c**, the calculations show that the dimeric complex can easily access the isomeric form **5cc** as shown in Figure 2, considering the (P,P′) structure of the ligand. The isomers **5c** and **5cc** share comparable stability. The difference in energy between **5c** and **5cc** is only 0.3 kcal/mol, implying that both **5c** and **5cc** coexist in solution, a finding supported by the ^{31}P NMR spectroscopic studies. In the calculated structures the distance between the two Pd atoms is 6.58 Å in **5c** and 6.60 Å in **5cc**.

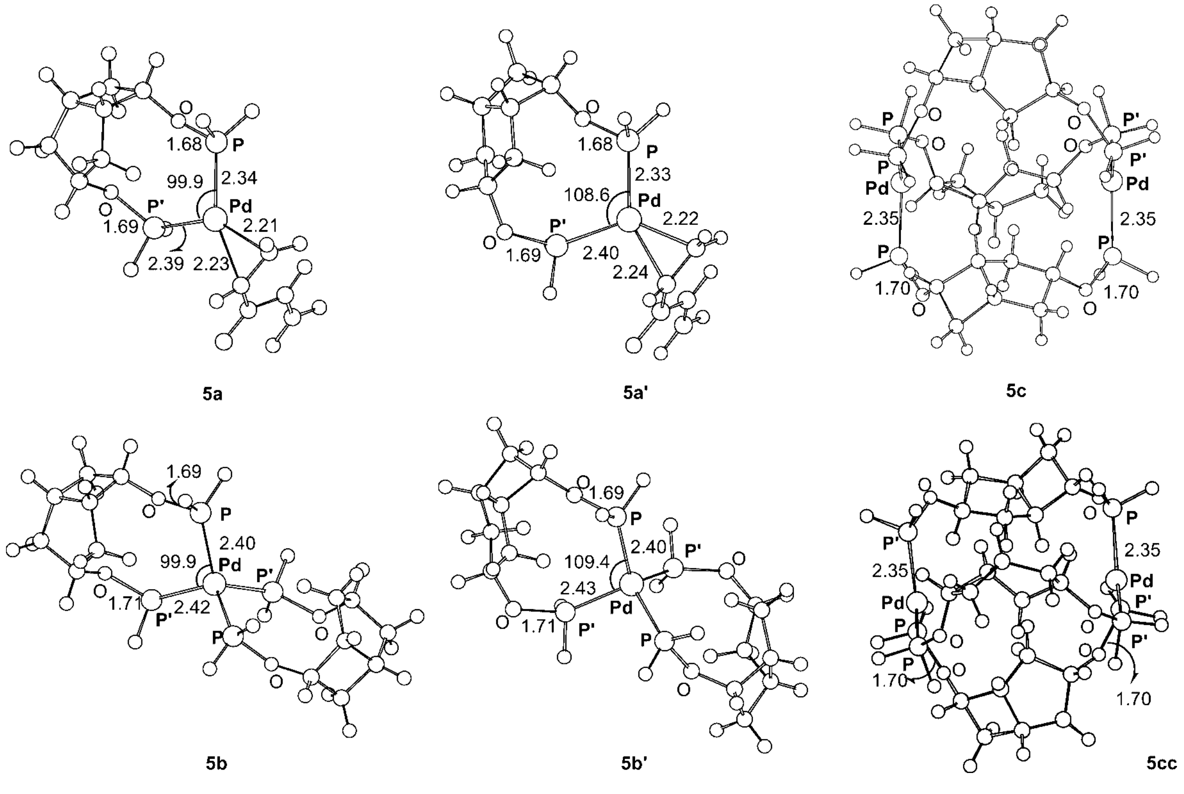
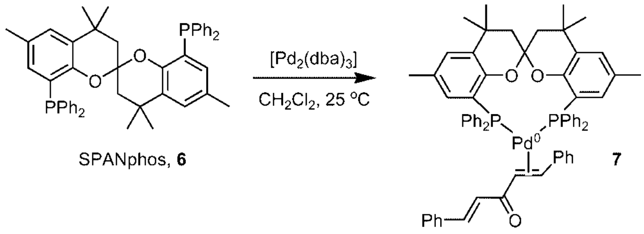


Figure 5. Calculated structures for the model Pd^0 complexes. The bond lengths are given in angstrom and the bond angles in degrees.

It is clear that there is no interaction between these two atoms. The long P–P′ distance (≈ 6.7 Å) in each ligand can only be accessed via the *exo* conformation. In the solid state, the phenyl groups cause significant lengthening (to 7.191 Å). All the P–O and Pd–P bonds in two isomers are about 1.70 and 2.35 Å respectively, which are longer than that found in the solid-state structure of **5c**.

We envisaged that other ligands possessing large bite angles would allow for the preparation of similar complexes. The reaction of SPANphos **6** with $[Pd_2(dba)_3]$ (**1**/Pd = 1:1) in CD_2Cl_2 at 25 °C was monitored by ^{31}P NMR spectroscopy which showed one very broad signal at δ = 22.7–24.8, characterized as [Pd(**6**)(η^2-dba)] (**7**), the pseudo-molecular ion (MH^+ = *m*/*z* 1045.3135; calculated 1045.3125) was confirmed by APCI-ESI MS, exhibiting a correct isotopic distribution against calculated values for $C_{64}H_{61}O_3P_2Pd_1$ (Scheme 2). The same reaction with excess SPANphos (ca. 3 equiv.) affords once again this complex, in addition to free ligand (δ = –16.2 ppm). It is interesting to note that ligand **6** does form rhodium dimer complexes of the type $[Rh_2(\mu\text{-}Cl)_2(\mathbf{6})(CO)_2]$, where the ligand exhibits a conformational change in the bichroman backbone.[9a,10] Molecular models suggest that unfavourable steric factors may explain why $[Pd_2(\mathbf{6})_3]$ is not formed under similar conditions to ligand **1**.



Scheme 2. Synthesis of a Pd^0 complex containing SPANphos.

Conclusions

In summary, the bicyclo[3.2.0]heptanyl ligand **1**, renamed as FLEXIphosO, shows flexible coordination modes[22] to transition metal centres. The influence of substituents on this bicyclic ring system is currently being assessed in our laboratories. We envisage that other carbobicyclic compounds will exhibit similar behaviour. Finally, conformational flexibility is a structural facet that could readily be exploited in transition metal–ligand catalyst design.

Experimental Section

NMR Experiments: All reactions were conducted in a dry box (O_2 and H_2O levels $<$ 0.5 ppm). A typical experiment: $[Pd_2(dba)_3]$ (5 mg) was added to ligand **1** (1 equiv.) in CD_2Cl_2 (0.5 mL) at 25 ± 0.5 °C. The mixture was stirred for 0.5 h, and then filtered through Celite™ (pipette and glass wool used); the filtrate was analysed directly by NMR spectroscopy. The ratio of **1**/Pd and solvent was changed according to the details supplied in the main text. Similar experiments were performed for the SPANphos ligand **6**. It should be noted that all the phosphane–palladium–alkene complexes are air sensitive.

Crystallography: X-ray quality single crystals of **5c/5cc** were grown layering a CH_2Cl_2 solution containing the complex with diethyl ether (1:5, v/v) in a dry-box, which gave dark red crystals. The X-ray diffraction experiment was carried out on a Bruker Smart Apex diffractometer with Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å) using a SMART CCD camera. The low temperature of the crystal was maintained with a Cryostream (Oxford Cryosystems) open-flow gas cryostat. The reflection intensities were corrected for absorption by a semi-empirical method based on the intensities of Laue equivalents and multiple measurements of identical reflections. The structures were solved by the Patterson and Fourier technique and refined by full-matrix least-squares against F^2 of all reflections, using SHELXTL software. The atoms of the bicyclo[3.2.0]heptanyl ring systems (x3) are disordered over two positions (50:50), as depicted in Figure 2. **Crystal data**: $C_{94}H_{92}Cl_2O_6P_6Pd_2$, M = 1787.20, triclinic, a = 12.1575(15), b = 12.2884(16), c = 32.357(4) Å, U = 4184.9(9) $Å^3$, α = 81.132(3), β = 79.892(3), γ = 61.929(2), T = 110(2) K, space group = $P\bar{1}$, Z = 2, μ(Mo–K_a) = 0.663 mm^{-1}, 15636 reflections measured, 8992 unique (R_{int} = 0.0358) which were used in all calculations. Final $R1$ = 0.0627 and $wR(F^2)$ = 0.1595 (all data). CCDC-642869 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

APCI-ESI MS Experiments: Bruker MicroTOF from Bruker Daltonics, Bremen, Germany. ESI was performed by injecting a 5 µl of the sample prepared in a dry-box (50 µg in CH_2Cl_2/MeOH; 95:5 v/v) into a stream of 200 µl/min methanol on a LC system Agilent 1200 (capillary 4500V; nebulizer 1.3 Bar; dry gas 8 L min^{-1}; dry temp. 180 °C).

Theoretical Calculations: Density functional theory calculations were performed at the B3LYP level using Gaussian 03.

Supporting Information (see also the footnote on the first page of this article): The ^{31}P NMR spectroscopic data for all the palladium complexes described in this paper. X-ray data for complex **5c/5cc** and the computational details and Cartesian coordinates for the calculated structures (depicted in Figure 5) are included.

Acknowledgments

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[16] APCI-ESI MS analysis confirmed a molecular ion at 1702.32, which is $C_{93}H_{90}O_6P_6Pd_2$, confirmed by comparison with the calculated isotopic distribution; an accurate mass determination for this ion was not attainble.

[17] The Pd^0 dimer complex is air sensitive and degrades to give palladium nanoparticles within minutes in the presence of air.

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