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Stereospecific isomerisation of P-heterocycles triggered by coordination: synthesis of the first P,N-chelates featuring a 2-phospholene moiety

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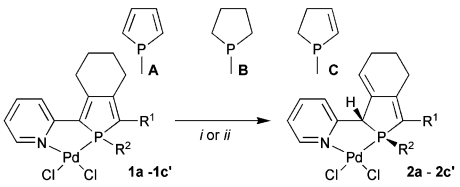
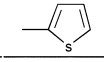
Coordination of 2-(2-pyridyl)phospholes on Pd(II) centres results in a ring strain sufficient to induce a stereospecific [1,3]-H migration affording the corresponding phospholene ligands.

Phosphorus heterocycles are versatile building blocks for the engineering of ligands,[1] including heteroditopic P,N-chelates that are nowadays key ligands in homogeneous catalysis.[2,3c–e] In this context, phospholes **A** and phospholanes **B** (Scheme 1) have been extensively investigated.[1,3] In marked contrast, ligands incorporating 2-phospholene moieties **C** are rare,[4a,b] although this P-heterocycle is attractive with a configurationally stable stereogenic and electron-rich P-centre.[4] Herein, we describe a straightforward route to 2-phospholenes involving an isomerisation of a phosphole ring **A** induced by complexation. This versatile methodology allows for the stereospecific synthesis of the first family of P,N-chelates featuring 2-phospholene units.

2-(2-Pyridyl)phospholes[5a,b] act as P,N-chelates toward Pd(II) centres affording complexes **1a–c′** (Scheme 1), characterised by a sharp singlet in their $^{31}P\{^1H\}$ NMR spectra (δ: **1a**[5c]–**c**, *ca.* 57 ppm; **1a′**[5c]–**c′**, *ca.* 70 ppm). They are stable for weeks in CH_2Cl_2 solutions at room temperature, except for complexes **1a**,**a′** that bear a pendant 2-pyridyl substituent. After one day, $^{31}P\{^1H\}$ NMR spectroscopy revealed the appearance of a new lower field singlet ($\Delta\delta$, *ca.* 10 ppm), in addition to the signals of **1a** and **1a′**. Complete transformation occurred within a period of five days, the new compounds **2a**,**a′** being isolated as air stable yellow powders in excellent yields (**2a**, 91%; **2a′**, 94%). High resolution mass spectroscopy and elemental analysis revealed that the new complexes **2a** and **2a′** are isomers of their precursors **1a** and **1a′**, respectively. They share intriguing ^1H and ^{13}C NMR spectroscopic data.[6] Of particular interest, the $^{13}C\{^1H\}$ NMR spectra show a doublet due to a PCH moiety (**2a**, 57.6 ppm, J_{PC} = 36.6 Hz; **2a′**, 48.3 ppm, J_{PC} = 32.6 Hz) and only three remaining signals assignable to the CH_2 of the fused carbocycle. X-Ray diffraction studies performed on **2a** and **2a′**† revealed that they possess the same general frame with an almost square-planar Pd-centre linked to two chlorine atoms and a P,N-chelate (Fig. 1). In both cases, the most striking feature is the tetrahedral geometry about the C(1) carbon atom in accordance with sp^3-hybridisation. The two endocyclic P–C distances are characteristic of single bonds [1.802(5)–1.835(4) Å], while the C(1)–C(2) [1.527(6); 1.512(5) Å] and C(7)–C(8) [1.357(6); 1.364(5) Å] bond distances are typical for a single and a double C–C bond, respectively. Hence, these solid state studies are clearly consistent with a 5-(2-pyridyl)-2-phospholene skeleton. Conversely, the short C(2)–C(3) [1.340(7); 1.345(5) Å] separation and the planar geometry at C(3) clearly show that the fused carbocycle is now a cyclohexene fragment. These solid state structures are in agreement with the spectroscopic data and reveal that the phosphole ring of complexes **1a**,**a′** has isomerised into 2-phospholene, something occurring *via* an allylic rearrangement. Two features are worthy of note: (*i*) the H-migration occurred on the side of the coordinated pyridine and not on that of the pendant one, (*ii*) complexes **2a**,**a′** were obtained as single diastereoisomers with the H-atom residing on the C(1) atom and the P-substituent being in mutual *cis*-configuration (Fig. 1).

This remarkable regioselectivity and stereospecificity prompted us to generalise this synthetic pathway with the aim of generating a family of pyridyl-phospholene ligands bearing substituents with different steric and electronic properties. Complexes **1b**,**b′** and **1c**,**c′** (Scheme 1) are stable for days in refluxing CH_2Cl_2 or THF solutions. This suggests that the pendant 2-pyridine of complexes **1a**,**a′** plays a key role in the isomerisation process. Indeed, in the presence of excess pyridine, complexes **1b–c′** gave rise to their respective isomers **2b–c′** following heating at reflux in CH_2Cl_2 for 3 days.[7] The new complexes were obtained as single diastereoisomers in high yields (Scheme 1). They exhibited spectroscopic NMR data that are very similar to those of their related analogues **2a**,**a′**,[6] including the $^2J_{PH}$ values within a given series (R^2 = Ph or Cy) (Scheme 1). These data suggest that complexes **2b–c′** feature 5-(2-pyridyl)-2-phospholene ligands with a *cis*-arrangement of the P-substituent and the H-atom on C(1). These



	R^1	R^2		Yield	$\delta(^{31}P)$ (ppm)	$^2J_{P\text{-}H}$ (Hz)
a		Ph	**2a**	91 %	67.3	11.9
a'		Cy	**2a'**	94 %	86.5	7.3
b		Ph	**2b**	91 %	69.8	13.0
b'		Cy	**2b'**	90 %	84.7	8.1
c		Ph	**2c**	88 %	68.1	10.8
c'		Cy	**2c'**	87 %	82.6	8.2

Scheme 1 *Reagents and conditions*: *i*, CH_2Cl_2, RT, 5 days (**1a**,**a′**); *ii*, refluxing CH_2Cl_2, 3 equiv. of pyridine, 3 days (**1b**,**b′** and **1c**,**c′**).

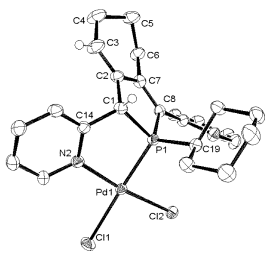


Fig. 1 Crystal structure of **2a′**; thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å]: Pd(1)–P(1), 2.193(1); Pd(1)–N(2), 2.076(4); C(2)–C(7), 1.462(6); C(3)–C(4), 1.501(7); C(4)–C(5), 1.521(8); C(5)–C(6), 1.529(7); C(6)–C(7), 1.512(6).

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conclusions were fully confirmed by an X-ray diffraction study performed on derivatives **2b** and **2c′**.† Related isomerisations of 3-methylphospholes into 3-methylene-2-phospholenes have been previously accomplished either by metallation with alkyllithiums of phosphole–BH_3 adducts followed by hydrolysis (70% yield),[4d] or by thermolysis of (phosphole)Ru(II)-complexes (3.9% yield).[4b] However, our method offers several advantages: the reaction takes place under mild reaction conditions (weak base, moderate temperatures) and the yields are almost quantitative with a range of substituents on the P-ring.

The metal centre plays a crucial role in this process since no isomerisation of free (2-pyridyl)phospholes into the corresponding (2-pyridyl)phospholenes occurs in refluxing pyridine/CH_2Cl_2 solutions. In order to elucidate the metal's role, DFT calculations[8] were performed on the free derivatives **3a′** and **4a′** (Fig. 2) and their $PdCl_2$-complexes **1a′** and **2a′**. This study indicates that phosphole **3a′** is more stable than its 2-phospholene isomer **4a′**, probably due to the presence of an extended π-conjugated system.[5a] Remarkably, the (phosphole)$PdCl_2$ complex **1a′** is less stable than the (2-phospholene)$PdCl_2$ complex **2a′** (Fig. 2), *revealing that upon coordination, the stability of the two P,N-isomers is reversed*!

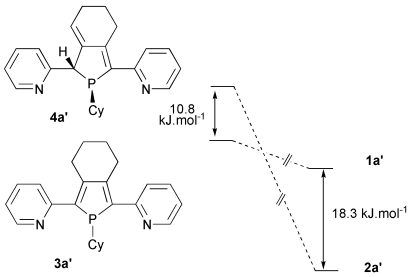

Fig. 2 Relative energy of isomers **3a′** and **4a′** and of their $PdCl_2$ complexes **1a′** and **2a′** according to DFT calculations.

An X-ray diffraction study of (phosphole)$PdCl_2$ **1c′** showed that the tetracoordinate P-atom exhibits a severely distorted tetrahedral geometry (Fig. 3, view a) and that the C(1) atom does not possess the expected trigonal planar geometry.[9] These features reveal an important ring strain imposed by the rigidity of the 1,4-P,N chelate backbones which contain sp^2-C atoms. In marked contrast, the geometry about the P-atom of the corresponding Pd(II)-coordinated phospholene is close to an ideal tetrahedron (Fig. 3, view b). This suggests a release of the ring strain upon creation of the sp^3-centre that can account for the higher stability of the phospholene complexes. Furthermore, DFT calculations reveal that the (2-pyridyl)phospholene–Pd(II) complex **2a′** with a *cis*-configuration of the P-substituent and the H-atom on C(1) is 42.7 kJ mol^{-1} more stable than its *trans*-stereoisomer. Thus, the palladium(II) centre plays a double role *via* the formation of a five-membered metallacycle: it reverses the relative stability of 2-pyridylphospholes *vs.* 2-pyridylphospholenes, allowing a thermodynamically controlled isomerisation, and imposes a stereospecificity.

Significantly, the free 5-(2-pyridyl)-2-phospholenes can be readily obtained in almost quantitative yields by addition of one equivalent of bis(diphenylphosphino)ethane to complexes **2a–c′**. This decomplexation step takes place without racemisation of the P-centre and the separation of the enantiomers is in progress.

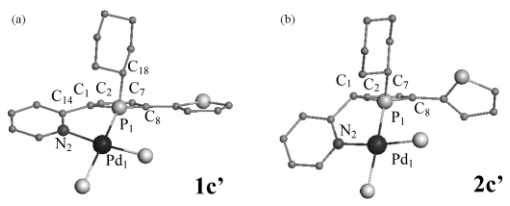

Fig. 3 Simplified views of the solid state structures of phosphole– (a) and phospholene– (b) $PdCl_2$ complexes.

In conclusion, we have described a straightforward and stereospecific route to the first P,N-ligands bearing a phospholene moiety. This synthetic path allows for the preparation of ligands with different electronic and steric properties.

Notes and references

† *Crystal data* for: $C_{23}H_{26}NPSCl_2Pd$, **1c′**, M = 556.78, monoclinic, $P2_1/n$, a = 10.3320(2), b = 17.1370(5), c = 13.1100(4) Å, β = 106.6950(10)°, V = 2223.40(10) Å^3, T = 95 K, Z = 4, μ = 1.252 mm $^{-1}$, 5046 reflections collected, 5046 unique, $R1$ = 0.044 for 3887 reflections with $I > 2\sigma(I)$. $C_{48}H_{42}N_4P_2Cl_4Pd_2$, **2a**·3 CH_2Cl_2, M = 1346.17, monoclinic, $C2/c$, a = 14.985(5), b = 9.785(5), c = 37.375(5) Å, β = 98.388(5)°, V = 5422(3) Å^3, T = 293(2) K, Z = 4, μ = 1.255 mm $^{-1}$, 6991 reflections collected, 5167 unique (R_{int} = 0.02), $R1$ = 0.0397 for 4216 reflections with $I > 2\sigma(I)$. $C_{24}H_{27}N_2PCl_2Pd$, **2a′**·CH_2Cl_2, M = 636.67, orthorhombic, $P2_12_12_1$, a = 8.7170(2), b = 16.2360(3), c = 18.9070(4) Å, V = 2675.89(10) Å^3, T = 293 K, Z = 4, μ = 1.170 mm $^{-1}$, 3452 reflections collected, 3452 unique, $R1$ = 0.0336 for 3351 reflections with $I > 2\sigma(I)$. $C_{50}H_{44}N_2P_2Cl_4Pd_2$, **2b**, M = 1089.41, monoclinic, $I2/a$, a = 21.587(5), b = 8.979(5), c = 26.183(5) Å, β = 104.844(5)°, V = 4906(3) Å^3, T = 293(2) K, Z = 4, μ = 1.051 mm $^{-1}$, 4831 reflections collected, 4831 unique, $R1$ = 0.158 for 3352 reflections with $I > 2\sigma(I)$. $C_{23}H_{25}NPSCl_2Pd$, **2c′**·0.5 CH_2Cl_2, M = 598.23, monoclinic, $P2_1/n$, a = 10.866(5), b = 15.475(5), c = 16.973(5) Å, β = 106.722(5)°, V = 2733.3(17) Å^3, T = 293 K, Z = 4, μ = 1.118 mm $^{-1}$, 12092 reflections collected, 6251 unique, (R_{int} = 0.0171), $R1$ = 0.0570 for 4972 reflections with $I > 2\sigma(I)$. CCDC 208509–208513. See http://www.rsc.org/suppdata/cc/b3/b304308h/ for crystallographic data in .cif format.

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6 Selected ^{1}H (200 MHz) and ^{13}C{^{1}H} (75.469 MHz) NMR data in CD_2Cl_2. **2a**: ^{1}H NMR, δ 4.66 (dd, J(HH) = 1.6 Hz, J(PH) = 11.9 Hz, 1H; PC*H*), 6.26 (ddd, J(HH) = 1.6, 4.2 and 5.8 Hz; C=CH). **2a′**: ^{1}H NMR, δ 4.59 (br d, J(PH) = 7.3 Hz, 1H; PC*H*), 6.26 (m, 1H; C=CH). **2b**: ^{1}H NMR, δ 4.61 (d, J(PH) = 13.0 Hz, 1H; PC*H*), 6.15 (m, 1H; C=C*H*); ^{13}C{^{1}H} NMR, δ 53.7 (d, J(PC) = 28.1 Hz, P*C*H), 132.6 (d, J(PC) = 6.1 Hz, C=*C*H). **2c**: ^{1}H NMR 4.56 (d, J(PH) = 10.8 Hz, 1H; PC*H*), 6.26 (m, 1H; C=CH); ^{13}C{^{1}H} NMR δ 57.2 (d, J(PC) = 36.6 Hz, P*C*H), 132.5 (d, J(PC) = 6.2 Hz, C=*C*H). **2c′**: ^{1}H NMR, δ 4.63 (br d, ^2J(PH) = 8.2 Hz, 1H; PC*H*), 6.22 (m, 1H; C=CH); ^{13}C{^{1}H} NMR, δ 48.9 (d, ^1J(PC) = 33.6 Hz, P*C*H), 134.8 (br s, C=*C*H).

7 Pyridine is the most efficient base to promote this isomerisation since with both DBU and Et_3N, complicated mixtures of products were obtained.

8 DFT calculations (E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.*, 1973, **2**, 41) were carried out with the Amsterdam Density Functional (ADF) program (ADF 2000.02, Vrije Universteit, Amsterdam, The Netherlands), using nonlocal exchange (A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098) and correlation (J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822; 1986, **34**, 7406 (erratum)) corrections. Standard ADF STO basis set IV was used. The frozen-core approximation was considered.

9 The value of the angle between the planes containing the C(1)–P(1)–C(8) and the Pd(1)–P(1)–C(18) fragments is 78.2(2)° (ideal value, 90°) while the value of the angle between the planes containing the P(1)–C(1)–C(2) and the C(2)–C(1)–C(14) fragments is 13.6(2)°.