

Palladium and Platinum Complexes Containing Diphenyl-2-(3-methyl)indolylphosphine

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Abstract: Syntheses and characterisation of group ten complexes containing the ligand diphenyl-2-(3-methyl)indolylphosphine are presented herein. The complexes [*trans*-PdCl₂{PPh₂(C₉H₈N)}₂] (**1**), [*cis*-PtCl₂{PPh₂(C₉H₈N)}₂] (**2**), [*trans*-Pd(CH₃)Cl{PPh₂(C₉H₈N)}₂] (**3**) and [*trans*-Pt(CH₃)Cl{PPh₂(C₉H₈N)}₂] (**4**) have all been structurally characterized by X-ray crystallography. In all cases, the ligands coordinate to the metal centres via the phosphorus donor atom (κ^1 -P) and the pendent NH groups on the indolyl rings of the ligand are orientated so that there is some degree of interaction with the metal-chloride bonds. The unexpected reactivity of **4** with Na[B{3,5-C₆H₃(CF₃)₂}]₄ is also reported. In this case, the product resulting from this reaction was found to be [Pt{3,5-C₆H₃(CF₃)₂}₂{PPh₂(C₉H₈N)}₂].

scaffolds within a range of homogeneous catalysts.^[11-17] Finally, it has also been reported that the N-H functional group in this type of ligand can undergo hydrogen bonding with co-ligands^[8,18] via secondary coordination sphere interactions.^[19] For example, the solid state structure of the complex [PdCl(μ -Cl)L]₂ reveals intramolecular hydrogen-bonding contacts between the N-H and the terminally bound Cl (with a distance of 2.447 Å).^[8] In these cases, a downfield shift for the NH resonance is observed in the corresponding ¹H NMR spectra.

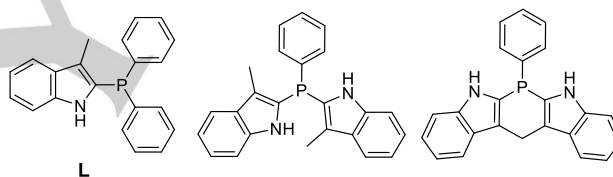


Figure 1. Diphenyl-2-(3-methyl)indolylphosphine (**L**) and selected examples of related ligands

Introduction

There has been much interest in the coordination chemistry of transition metal complexes containing mixed donor ligands. These have been utilised for the purposes of fine tuning reactivity, controlling the properties of the resulting complexes and the development of enhanced catalytic applications.^[1] Many known mixed donor systems are based on phosphine and nitrogen functional groups.^[2-4] Our research group has been interested in the ligand diphenyl-2-(3-methyl)indolylphosphine (**L**) (Figure 1) for some time.^[5,6] This ligand contains a phosphorus donor in addition to a pendent N-H functional group which has the potential to interact directly at the metal centre itself or with co-ligands within the coordination sphere. The synthesis and coordination chemistry of **L** was first published by Browning back in 2004 alongside related derivative ligands.^[7,8]

As a soft σ -donor and π -acceptor, the phosphorus centre preferentially coordinates to soft transition metals such as the platinum group metals. We have previously published a series of rhodium and iridium complexes,^[5] and ruthenium complexes^[6] containing **L**. In the complexes reported to date, this ligand has exhibited both κ^1 -P and κ^1 -P, η^6 -C₆ coordination modes, where in this latter coordination mode, the arene unit of the ligand bridges to an additional metal centre.^[5-9] Other coordination modes including μ_2 -P,N and μ_3 -P,N,N, η^2 -N have also been observed for the deprotonated version of this ligand.^[7,8] Furthermore, dinuclear A-frame type complexes of the deprotonated ligand have been reported with the coinage metals^[9] and palladium.^[10] The 3-methylindolyl moiety has also been utilised to form part of ligand

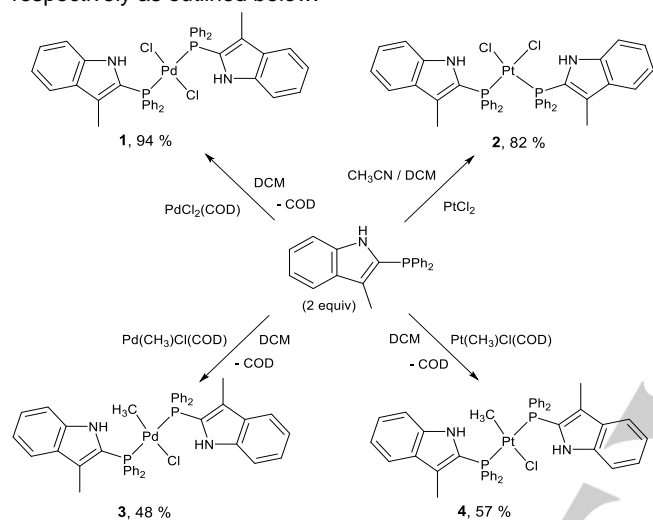
There is currently only one palladium complex containing **L** and a handful of palladium complexes containing the deprotonated version of **L** reported in the chemical literature.^[8,10] There are, however, no examples of any platinum complexes containing this ligand. To that end, we wish to report the results of our investigations involving the preparation of a series of palladium and platinum complexes containing diphenyl-2-(3-methyl)indolylphosphine. The results of these investigations are outlined below.

Results and Discussion

Synthesis of complexes

The synthesis of the complexes [PdCl₂L₂] (**1**), [PtCl₂L₂] (**2**), [Pd(CH₃)ClL₂] (**3**) and [Pt(CH₃)ClL₂] (**4**) were achieved by standard ligand substitution reactions utilising standard palladium and platinum precursors (Scheme 1). Complex **1**, [*trans*-PdCl₂{ κ^1 -P-PPh₂(C₉H₇NH)}₂] was prepared by addition of two equivalents of **L** to a DCM solution of [PdCl₂(COD)] (where COD = 1,5-cyclooctadiene).^[20] A yellow-orange solid was precipitated from the reaction mixture following addition of hexane, after which the target product was isolated by filtration and subsequent drying.

The ^1H NMR spectrum of the isolated solid confirmed the substitution of cyclooctadiene ligand by the disappearance of the signals corresponding to coordinated COD. Complex **2**, $[\text{cis-PtCl}_2\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$ was obtained directly from the reaction between PtCl_2 and two equivalents of **L**. The metal precursor was not soluble in DCM and so a 1:1 mixture of DCM:acetonitrile was used. A solid was isolated after 4 h by evaporation of all volatiles and washing the resulting solid with diethyl ether. For the synthesis of complexes **3** and **4**, two equivalents of **L** were added to DCM solutions of $[\text{MCl}(\text{CH}_3)(\text{COD})]$ (where $\text{M} = \text{Pd}, \text{Pt}$),^[21,22] respectively. The solid products were obtained upon addition of hexane to the mixtures. Complexes **3** and **4** were identified as $[\text{trans-PdCl}(\text{CH}_3)\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$ and $[\text{trans-PtCl}(\text{CH}_3)\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$, respectively as outlined below.



Scheme 1. Synthesis of palladium and platinum complexes **1** – **4**.

Characterisation of complexes

Complexes **1** – **4** were obtained as pure compounds which were fully characterised by spectroscopic and analytical methods. Selected spectroscopic data are highlighted in Table 1 along with a comparison with other platinum group metal complexes containing **L**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for all complexes consisted of a single resonance shifted downfield with respect to the free ligand ($\delta = -32.7$ ppm). The platinum satellites for complexes **2** and **4** were $^1J_{\text{PtP}} = 3529$ Hz and 3059 Hz, respectively.^[23] These constants are consistent with the phosphorus ligands being *trans* to a chloride ligand in **2** and *trans* to another phosphorus in **4**, thus confirming the $[\text{cis-PtCl}_2\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$ and $[\text{trans-PtCl}(\text{CH}_3)\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$ conformations for these two complexes.

The ^1H NMR signals corresponding to the *NH* peak of the indolyl group for the complexes were located in the range 9.89 ppm to 11.10 ppm (c.f. 7.80 ppm for the free ligand). This includes complexes **1** – **4** in addition to $[\text{PdCl}_2\text{L}_2]$, $[\text{RhCl}(\text{COD})\text{L}]$, $[\text{IrCl}(\text{COD})\text{L}]$, $[\text{RhCl}(\text{NBD})\text{L}]$ and $[\text{RuCl}_2(\text{cymeme})\text{L}]$. For those previously reported complexes which do not feature chloride co-ligands, i.e. $[\text{Rh}(\text{COD})\text{L}_2]\text{BF}_4$, $[\text{Ir}(\text{COD})\text{L}_2]\text{BF}_4$, $[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})\text{L}]\text{BF}_4$ and $[\text{Ir}(\text{COD})(\text{CH}_3\text{CN})\text{L}]\text{BF}_4$, the corresponding signals for the *NH* protons appear in the range 9.02 ppm to 9.61 ppm (Table 1). The clear distinction in these chemical shift ranges is consistent with a degree of hydrogen bonding

interaction with the chloride co-ligands present within the various complexes. This is explored further within our discussion on the crystal structures.

The IR spectra (ATR, powder film) for complexes **1** – **4** display characteristic bands for **L**, confirming its coordination to the metal centres. Of particular note are the N-H stretches which appear as single bands for the palladium complexes and two bands for the corresponding platinum complexes as outlined in Table 1. As shown in the table, the bands corresponding to the N-H stretches within all complexes containing **L** range from 3223 to 3389 cm^{-1} .

Mass spectrometry showed molecular ion peaks for complexes **1**, **2** and **4** with the corresponding loss of one halide. The molecular composition of the complexes was further confirmed by elemental analysis.

Table 1. Selected spectroscopic data for complexes **1** – **4** and related platinum group metal complexes.

	$^{31}\text{P}\{^1\text{H}\}$ [a]		^1H [δ (ppm)] [a]		IR [b] (cm^{-1})	Ref [c]
	δ (ppm)	$^1J_{\text{PtP}}/^1J_{\text{RhP}}$ (Hz)	(NH)	(CH ₃)		
$[\text{PdCl}_2\text{L}_2]$ (1)	6.3	-	10.40	1.78	3303	-
$[\text{PdCl}_2\text{L}_2]$	14.6	-	10.20	1.68	-	8
$[\text{PtCl}_2\text{L}_2]$ (2)	-1.0	3529	9.89	1.72	3379(s), 3223 (m)	-
$[\text{PdCl}(\text{CH}_3)\text{L}_2]$ (3)	12.2	-	11.10	1.83	3282	-
$[\text{PtCl}(\text{CH}_3)\text{L}_2]$ (4)	12.7	3059	10.68	1.87	3320 (m), 3257 (s)	-
$[\text{RhCl}(\text{COD})\text{L}]$	14.1	146	10.78	1.78	3290	5
$[\text{IrCl}(\text{COD})\text{L}]$	6.7	-	10.44	1.79	3325	5
$[\text{RhCl}(\text{NBD})\text{L}]$	15.8	167	10.86	1.82	3267	5
$[\text{RuCl}_2(\text{cymeme})\text{L}]$	9.5	-	10.44	1.75	3289	6
$[\text{RhCl}(\text{COD})\text{L}_2]\text{BF}_4$	9.1	142	9.61	1.81	3389	5
$[\text{Ir}(\text{COD})\text{L}_2]\text{BF}_4$	2.2	-	9.52	1.80	3379	5
$[\text{Rh}(\text{COD})(\text{CH}_3\text{CN})\text{L}]\text{BF}_4$	8.7	u.r. [d]	9.02 [e]	2.73	3372	5
$[\text{Ir}(\text{COD})(\text{CH}_3\text{CN})\text{L}]\text{BF}_4$	0.3	-	9.09 [e]	2.65	3364	5

[a] Recorded in CDCl_3 unless otherwise stated; [b] powder film; [c] complexes reported herein or in the reference indicated; [d] unresolved; [e] recorded in CD_3CN .

Crystal structures of complexes **1** – **4**

Single crystals of all four complexes were obtained and are presented in Figures 2 to 5. Selected bond distances and angles are highlighted in Table 2. Crystallographic parameters are provided below and the cif files are available in the Electronic Supplementary Information.

For the structure of complex **1**, there are two independent half molecules (**A** and **B**) within the asymmetric unit (i.e. $Z' = 2 \times 0.5$). The molecular structure for one of these is shown in Figure 2. The structure reveals a *trans* square planar configuration for both independent molecules with the metal centre positioned on an inversion centre. This means that the atoms P1, P1', Cl1 and Cl1' lie in the same plane. The configuration of the ligands is such that the indolyl rings are on opposite sides above and below the square plane, in accordance with the inversion symmetry. The

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indolyl rings are orientated in a way which directs the N–H groups towards the chloride ligands. As observed in later structures, the orientations are such that the N–H groups are directed more towards the bond than the ligands. It has long been recognised that metal-chloride bonds can act as hydrogen bond acceptors.^[24–26] The NH---ClPd distances in the complexes within the unit cell are 2.473 Å (**A**) and 2.452 Å (**B**). The corresponding NH---Pd distances are 3.244 Å and 3.085 Å. The NH---Cl–Pd angles are 85.59° (**A**) and 80.78° (**B**) whilst the corresponding N–H---Cl angles are 144.77° and 149.26°. This feature where the interaction appears on the bond rather than the halide is more apparent for some of the later structures. The Pd–P and Pd–Cl bond distances are 2.3412(4) Å and 2.2981(4) Å, respectively (for molecule **A**) within the unit cell). The corresponding values for molecule (**B**) are 2.3388(4) Å and 2.3052(4) Å. One of the angles between Cl–Pd–P was found to be 93.232(15)° whilst the complementary angle was 86.767(14)° [the corresponding angles for **B** are 87.642(15)° and 92.358(15)°]. The compression of one Cl–Pd–P bond angle in each case appears to be related to the NH---ClPd interaction which brings the corresponding P and Cl donors closer together.

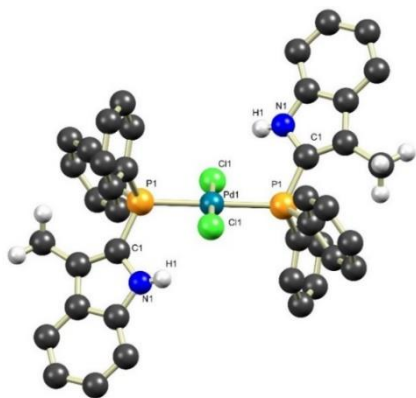


Figure 2. Molecular structure of $[trans-PdCl_2\{\kappa^1-P-PPh_2(C_9H_7NH)\}]$ (**1**). Hydrogen atoms (with the exception of H1 and methyl protons) have been omitted for clarity.

The molecular structure of complex **2** is shown in Figure 3. In this case, the NMR spectroscopic data is consistent with a *cis* square planar structure. The phosphorus ligands are orientated in a position where both indolyl units are situated above the square plane, as presented in the figure. One of the NH units is directed towards the Pt–Cl bond whilst the other indolyl unit is more closely directed to the platinum centre. For the case where the indolyl unit appears to interact with the Pt–Cl bond, the corresponding NH---Cl and NH---Pt distances are 2.692 Å and 3.071 Å, respectively. The distance from the hydrogen atom to the centroid of the Pt–Cl bond is shorter at 2.634 Å. For the second indolyl unit within the complex, the NH group is more directed towards the platinum centre where the NH---Cl and NH---Pt distances are 4.373 Å and, 2.811 Å. In addition to these, two phenyl groups (one from each phosphine ligand) are orientated so that an *ortho* C–H bond in each are positioned in close proximity to the platinum centre from below the square plane as shown in Figure 3. The CH---Pt distances are 2.989 Å and 3.331 Å. The phosphorus and chloride ligands lie on almost an idealised plane. The distance of the platinum centre from the plane defined by the four donor atoms is

0.007 Å. The sum of the *cis*-inter ligand angles is 360.51 [ranging between 84.69(4)° and 96.68(5)°]. The platinum-phosphorus distances within the complex are 2.2540(12) Å and 2.2678(13) Å, whilst the platinum-chloride distances are 2.3650(11) Å and 2.3445(13) Å.

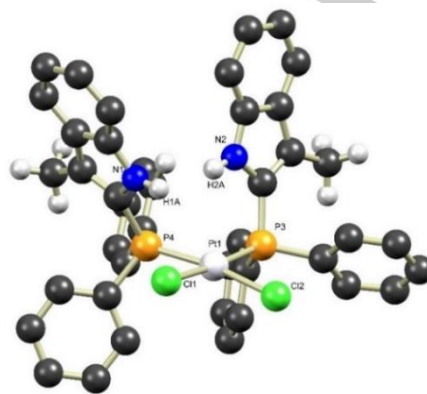


Figure 3. Molecular structure of $[cis-PtCl_2\{\kappa^1-P-PPh_2(C_9H_7NH)\}]$ (**2**). Hydrogen atoms (with the exception of H1) have been omitted for clarity.

The molecular structure of complex **3** is shown in Figure 4, confirming the *trans* square planar configuration for the complex. In this case, the two indolyl N–H units are positioned above and below the square plane, both pointing in the direction of the sole chloride ligand in this complex. In this complex, the NH---Cl distances are 2.442 Å and 2.530 Å, and the corresponding NH---Pd distances are 3.012 Å and 2.940 Å. In this case, one NH unit points more closely to the chlorine atom and the second one more closely to the Pt–Cl bond. The respective distances from the hydrogen atoms to the centroid of the Pt–Cl bonds is 2.457 Å and 2.458 Å. In addition to these, there are close distances involving the *ortho* C–H units of a phenyl group on each **L** ligand with the palladium centre. They approach the metal centre on opposite sides of the square plane with respect to the indolyl unit on the same ligand. The two shortest CH---Pd distances are 2.861 Å and 3.339 Å. The sum of the *cis*-inter ligand angles is 359.784 [ranging between 88.88(5)° and 93.18(5)°]. The palladium-phosphorus distances within the complex are 2.3104(4) Å and 2.3124(4) Å. The palladium-carbon distance is 2.0647(16) Å whilst the palladium-chloride distance is 2.4331(4) Å. The latter distance is consistent with the halide ligands being *trans* to a strong *trans* influence ligand such as a methyl group.

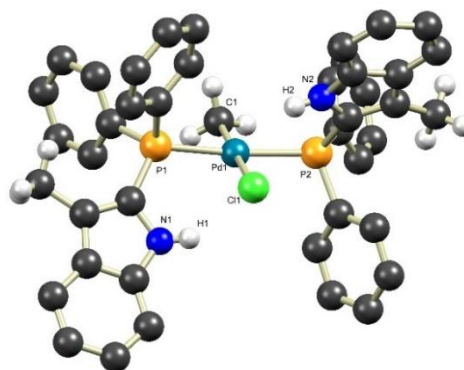


Figure 4. Molecular structure of $[trans-Pd(CH_3)Cl\{\kappa^1-P-PPh_2(C_9H_7NH)\}]$ (**3**). Hydrogen atoms (with the exception of H1) have been omitted for clarity.

Table 2. Selected bond distances Å and angles (deg.) for **1** – **4**.

	[PdCl ₂ (L) ₂] (1) ^[a]		[PtCl ₂ (L) ₂] (2)	[Pd(CH ₃)Cl(L) ₂] (3)	[Pt(CH ₃)Cl(L) ₂] (4)
	A	B			
M–P / M–P	2.3412(4)	2.3388(4)	2.2540(12) / 2.2678(13)	2.3104(4) / 2.3124(4)	2.3071(9) / 2.3017(9)
M–Cl (<i>trans</i> to Cl)	2.2981(4)	2.3052(4)	-	-	-
M–Cl (<i>trans</i> to PPh ₃)	-	-	2.3650(11) / 2.3445(13)	-	-
M–Cl (<i>trans</i> to CH ₃)	-	-	-	2.4331(4)	2.4405(9)
M–CH ₃ (<i>trans</i> to Cl)	-	-	-	2.0647(16)	2.077(3)
P–C (indole)	1.8025(17)	1.7977(17)	1.804(5) / 1.815(5)	1.8021(17) / 1.8041(17)	1.805(4) / 1.810(4)
N–H	0.803	0.796	0.880 / 0.880	0.823 / 0.828	0.828 / 0.838
NH...Cl ^[b]	2.473	2.452	2.692 / 4.373	2.442 / 2.530	2.513 / 2.347
M...HN ^[c]	3.244	3.085	3.071 / 2.811	3.012 / 2.940	3.070 / 2.982
M...HC ^[d]	3.753 / 3.655	3.157 / 3.823	3.331 / 2.989	2.861 / 3.339 / 3.833 ^[f]	3.237 / 3.208 / 3.813 / 3.883
P–M–P	180.0	180.0	96.68(5)	173.313(16)	172.90(3)
Cl–M–Cl	180.00(2)	180.0	87.36(4)	-	-
P–M–Cl ^[e]	86.767(14) / 93.232(15)	87.642(15) / 92.358(15)	84.69(4) / 91.78(5)	90.017(15) / 87.707(15)	87.47(3) / 89.82(3)
P–M–CH ₃	-	-	-	88.88(5) / 93.18(5)	91.16(10) / 92.06(10)
Cl–M–CH ₃	-	-	-	177.74(5)	175.16(10)
NH–Cl–Pd	85.59	80.78	74.47 / 35.36	72.63 / 76.33	76.58 / 77.04
N–H–Cl	144.77	149.26	120.17 / 105.64	134.93 / 143.54	142.22 / 158.96
∑ _{cis} angles around metal centre	360.00	360.00	360.51	359.784	360.51
∑ of 3 C–P–C angles of ligand (L)	317.18	315.89	314.9 / 311.6	318.45 / 316.67	315.78 / 312.76
N–C–P–Pd ^[g]	19.83(15)	24.89(14)	2.3(4) / 7.7(4)	1.03(14) / 3.89(15)	13.1(3) / 35.2(3)

[a] there are two independent molecules within the asymmetric unit for this complex each containing a centre of inversion at the palladium centre. For comparison they are labelled **A** and **B**. The bond distances and angles for **A** are provided along with the equivalent values for **B** in the adjacent column under the column labelled **B**; [b] – the distance involving the indole H and a Cl ligand; [c] – the distances involving the indole H and either Pd or Pt centre; [d] the distances involving CH...M units from one of the phenyl rings in L; [e] – only the cis P–M–Cl angles provided here; [f] only those distances less than 4 Å provided; [g] magnitude of this angle provided.

The structure for complex **4** is shown in Figure 5. This has a similar structure as that of complex **3**. The main difference is the orientation of the indolyl units. Whilst in complex **3**, the two indolyl groups are above and below the square plane, they are both on the same side of the plane in complex **4**. Furthermore, the N–H bond of the indolyl units are slightly closer to the chloride ligand than to the M–Cl bond. The NH...Cl distances are 2.347 Å and 2.513 Å; the corresponding NH...Pt distances are 2.982 Å and 3.070 Å. The indolyl rings are almost co-planar with each other with a C_{indolyl}–P1–P2–C_{indolyl} torsion angle of 9.88°. These groups are situated at just over 60° from the square plane (the torsion angles C2–P1–Pt1–Cl1 and C23–P2–Pt1–Cl1 are –60.17° and 70.15°, respectively). The sum of the *cis*-inter ligand angles is 360.51 [ranging between 87.47(3)° and 92.06(10)°]. The platinum-phosphorus distances within the complex are 2.3017(9) Å and 2.3071(9) Å. The platinum-carbon distance is 2.077(3) Å whilst the palladium-chloride distance is 2.4405(9) Å.

Reactivity of complex **4**

In an attempt to abstract the halide from complex **4**, we investigated its reactivity with Na[3,5-C₆H₃(CF₃)₂]₄ ([Na][BAR_F]). No reaction occurred at room temperature in toluene solvent. Heating the reaction to 80 °C for two and a half hours, however, led to the formation of a new species. This was evidenced by the disappearance of the signal corresponding to **4** and the appearance of a new singlet signal at 3.51 ppm (¹J_{PtP} = 2888 Hz) in the ³¹P{¹H} NMR spectrum of the reaction mixture.^[27] A new product, complex **5**, was isolated from the reaction mixture by

removal of all volatiles and extraction into diethyl ether. Complex **5** was identified as [Pt(3,5-C₆H₃(CF₃)₂)₂L₂] as shown in Scheme 2. The molecular structure of **5** is presented in Figure 6. A similar reaction involving the decomposition of the BAR_F anion mediated by a platinum-methyl complex was reported by Kubas in which two of the aryl units were transferred from the boron to a platinum centre.^[28] Similar transformations involving B–C bond cleavage in the BAR_F anion have also previously been reported^[29,30] although such reactivity is still rare.

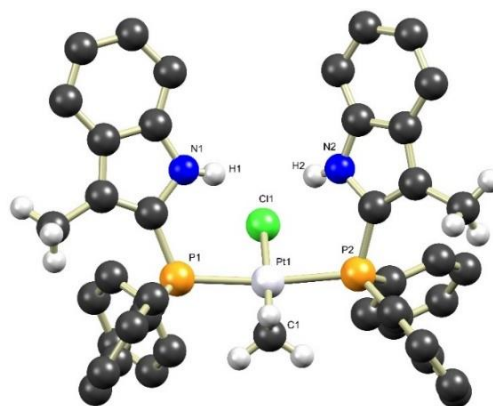
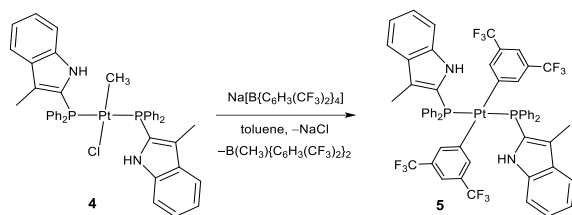


Figure 5. Molecular structure of [trans-Pt(CH₃)Cl{κ¹-P-PPh₂(C₉H₇NH)}] (**4**). Hydrogen atoms (with the exception of H1) have been omitted for clarity.



Scheme 2. Synthesis of $[\text{trans-Pt}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_2\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$

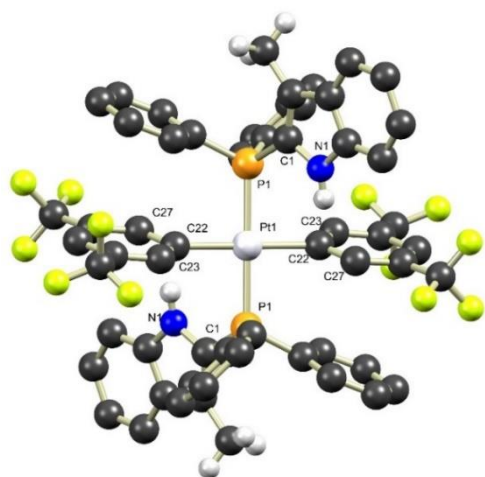


Figure 6. Molecular structure of $[\text{Pt}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_2\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}_2]$. Hydrogen atoms (with the exception of the NH protons) have omitted for clarity. Selected bond distances (Å) and angles (deg). Pt1–C22 2.101(5), Pt1–P1 2.3106(12), C1–P1 1.807(5), C22–Pt1–C22' 180.0, C22'–Pt1–P1 89.54(13), C22–Pt1–P1 90.46(13), P1–Pt1–P1' 180.00(5), N1–C1–P1–Pt1 11.7(4), P1–Pt1–C22–C27 –111.0, P1–Pt1–C22–C23 74.4.

The structure for complex **5** contains half of the complex within the asymmetric unit (*i.e.* $[\text{Pt}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}\{\kappa^1\text{-P-PPh}_2(\text{C}_9\text{H}_7\text{NH})\}]$). The structure reveals a *trans* square planar configuration with the metal positioned on an inversion centre and the atoms Pt, P1, P1', C22 and C22' lie on a plane. The C22–Pd–P1 angle was found to be $90.46(13)^\circ$ whilst the complementary angle was $89.54(13)^\circ$ confirming little distortion from the expected idealised square planar angles. The configuration of the phosphine ligands is such that the indolyl rings are positioned above and below the square plane. The N–H unit in each is orientated so that they are pointing towards the metal centre. The Pt–P1–N1–H1 torsion angle is 11.42° . There is a relatively short distance between the hydrogen of the indole unit and the hydrogen on C27 (2.190 Å). The Pd–P1 and Pd–C22 bond distances are 2.3106(12) Å and 2.101(5) Å. Of particular note is the orientation of the two 3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ groups within the complex. These aryl rings are both twisted from the position perpendicular to the square plane. The angle between two calculated planes defined by the atoms Pt, P1, P1', C22 and C22' (plane A) and Pt and all carbon atoms within the aryl rings of 3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ (plane B) was found to be 72.33° . This appears to be the result of minimising the steric repulsion resulting from the orientation of the indolyl group. Additionally, this also appears to accommodate π -stacking between the 3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ rings and a phenyl ring on the $\text{PPh}_2(\text{C}_9\text{H}_7\text{NH})$ ligand. The distance between the two calculated centroids involving these six membered rings was found to be 3.584 Å with an offset distance of 1.249 Å.

Conclusion

In summary, we have reported the synthesis and characterisation of a series of square planar group ten complexes containing the ligand diphenyl-2-(3-methyl)indolylphosphine (**L**). These were achieved via straightforward ligand substitution reactions. This has added to the small number of examples which currently exist within the chemical literature. The phosphorus ligand exhibits a $\kappa^1\text{-P}$ coordination mode in all cases. In all complexes, the indolyl unit within the ligands are orientated so that they point towards a position along the metal–chloride bond suggesting some degree of hydrogen bonding where the metal–halide bond acts a hydrogen bond acceptor. In addition to these, there are also further interactions between the *ortho*-CH units of the phenyl groups on **L** with the metal centres. Further exploration of the reactivity of complex **4** with $\text{Na}\{[3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2]_4\}$ led to the complex $[\text{Pt}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_2\text{L}_2]$ in which two aryl groups from the BAR_F anion were transferred to the platinum centre.

Experimental Section

General Remarks

All manipulations were performed in a Braun glovebox with an O_2 and H_2O atmosphere below 5 ppm or by using standard Schlenk techniques. Solvents (CH_2Cl_2 , Et_2O , CH_3CN and hexane) were dried using a Grubbs' alumina system and were kept in Young's ampoules under N_2 over molecular sieves (4 Å). Dry *n*-pentane (< 0.05 ppm H_2O) was purchased from Fluka and was stored in a Young's ampoule under N_2 over molecular sieves (4 Å). The ligand, diphenyl-2-(3-methyl)indolylphosphine,^[8] and the complexes $[\text{PdCl}_2(\text{COD})]$,^[20] $[\text{PdCl}(\text{CH}_3)(\text{COD})]$ ^[21] and $[\text{PtCl}(\text{CH}_3)(\text{COD})]$ ^[22] were synthesised according to standard literature procedures. The deuterated solvents CDCl_3 and CD_3CN were degassed by three freeze-thaw cycles then vacuum distilled and stored in J-Young's ampoules over 4 Å molecular sieves under N_2 . ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a JEOL Lambda 300 spectrometer operating at 300 MHz (^1H), a JEOL ECP300 spectrometer operating at 300 MHz (^1H), a JEOL ECP 400 spectrometer operating at 400 MHz (^1H) or a Varian VNMR S500 instrument operating at 500 MHz (^1H). $^{13}\text{C}\{^1\text{H}\}$ NMR, DEPT-135, and heteronuclear correlation experiments spectra were recorded on a JEOL ECP400 spectrometer operating at 400 MHz (^1H), or a Varian 400-MR spectrometer operating at 400 MHz (^1H). The spectra were referenced internally to the residual protic solvent (^1H) or the signals of the solvent (^{13}C). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are referenced relative to 85% H_3PO_4 . Mass spectra were recorded on a Bruker Daltonics Apex (7.0 Tesla) FT-ICR-MS mass spectrometer using ESI^+ ionization. Elemental analyses were performed at the microanalytical laboratory of the School of Chemistry at the University of Bristol. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (solid state, neat) from 4000 cm^{-1} to 650 cm^{-1} . Figure 7 highlights the numbering scheme used for the NMR assignments.

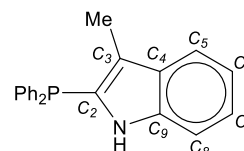


Figure 7. Numbering scheme for **L** used for NMR assignments

[Dichloro-bis(diphenyl-2-(3-methyl)indolylphosphine)palladium(II)], [PdCl₂L₂] (1)

A Schlenk flask was charged with dichloro(cycloocta-1,5-diene)palladium (50.0 mg, 0.175 mmol) and the ligand diphenyl-2-(3-methyl)indolylphosphine (110.5 mg, 0.350 mmol). CH₂Cl₂ (10 mL) was subsequently added to the mixture under stirring to give an orange solution after a few minutes. The mixture was further stirred at room temperature for 3 h. The solvent was reduced to a minimum and hexane (10 mL) was added to give the product as a yellow-orange powder which was isolated by filtration and dried under vacuum (133.0 mg, 0.164 mmol, 94%). ¹H NMR, (CDCl₃, 400.2 MHz): δ 1.78 (s, 6H, CH₃ (indole)), 7.16 (ddd, ³J_{HH} = 8.1 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.0 Hz, 2H, H⁶ (indole)), 7.31 (ddd, ³J_{HH} = 7.6 Hz, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.1 Hz, 2H, H⁷ (indole)), 7.40-7.52 (m, 14H, CH (m,p-PPh₂) & H^F (indole)), 7.58-7.68 (m, 10H, CH (o-PPh₂) & H^B (indole)), 10.40 (br s., 2H, NH). ³¹P {¹H} NMR (CDCl₃, 121.7 MHz): δ 6.3 (s, PPh₂(^{Me}indolyl)). ¹³C {¹H} NMR (CDCl₃, 100.6 MHz): δ 10.5 (s, CH₃), 112.1 (s, C⁵ (indole)), 119.25 (virtual t, ¹J_{PC} = 33.2 Hz, C² (indole)), 119.34 (s, C⁸ (indole)), 119.7 (s, C⁶ (indole)), 122.8 (virtual t, ²J_{CP} = 3.8 Hz, C³ (indole)), 124.3 (s, C⁷ (indole)), 128.39 (virtual t, ¹J_{CP} = 27.0 Hz, ipso-PPh₂), 128.40 (virtual t, ³J_{CP} = 5.4 Hz, o-PPh₂), 129.1 (virtual t, ³J_{CP} = 3.9 Hz, C⁴ (indole)), 130.7 (s, p-PPh₂), 133.7 (virtual t, ⁴J_{CP} = 6.3 Hz, m-PPh₂), 138.0 (virtual t, ³J_{PC} = 4.6 Hz, C⁹ (indole)). MS(ESI): m/z 771.11 [M-Cl+H]⁺ (15%), 735.14 [M-2HCl+H]⁺ (100%), 657.09 [M-2HCl-PH]⁺ (33%). Anal. Calcd. for C₄₂H₃₆Cl₂N₂P₂ (892.96): C, 57.84; H, 4.29; N, 3.14. Found: C, 57.70; H, 4.52; N, 3.50. IR (cm⁻¹): 3303 (s, ν_(N-H)), 3000 (w, ν_(C-H sp²)), 2980 (w, ν_(C-H sp³)), 1437 (s, PPh₂), 1329 (m), 1190 (m), 1091 (s).

[Dichloro-bis(diphenyl-2-(3-methyl)indolylphosphine)platinum(II)], [PtCl₂L₂] (2)

A Schlenk flask was charged with dichloroplatinum (100.0 mg, 0.380 mmol) and the ligand diphenyl-2-(3-methyl)indolylphosphine (260.0 mg, 0.824 mmol). CH₃CN (20 mL) and CH₂Cl₂ (20 mL) were subsequently added to the mixture under stirring to give a yellow solution. This was further stirred for 4 h after which time all volatiles were removed *in vacuo*. Diethyl ether (30 mL) was added to the residue, stirred for 5 min to give the product as a yellow powder which was isolated by filtration and dried under vacuum (280.0 mg, 0.312 mmol, 82%). ¹H NMR, (CDCl₃, 400.2 MHz): δ 1.72 (s, 6H, CH₃(indole)), 7.01 (d, ³J_{HH} = 8.2 Hz, 2H, H^F(indole)), 7.08 (ddd, ³J_{HH} = 8.0 Hz, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.6 Hz, 8H, o-PPh₂), 7.17 – 7.30 (m, 16H, m,p-PPh₂ & H^F(indole) & H^I(indole)), 7.55 (d, ³J_{HH} = 7.9 Hz, 2H, H^F(indole)), 9.89 (br, 2H, NH). ³¹P {¹H} NMR (CDCl₃, 121.7 MHz): δ -1.02 (s, ¹J_{PP} = 3529 Hz, PPh₂(^{Me}indolyl)). ¹³C {¹H} NMR (CDCl₃, 100.6 MHz): δ 11.8 (s, CH₃), 112.4 (s, C⁵(indole)), 119.86 (s, C⁸(indole)), 120.67 (s, C⁷(indole)), 119.8 (virtual t, ¹J_{PC} = 33.2 Hz, C²(indole)), 119.34 (s, C⁹(indole)), 122.8 (virtual t, ²J_{CP} = 3.8 Hz, C³(indole)), 128.39 (virtual t, ¹J_{CP} = 27.0 Hz, ipso-PPh₂), 128.40 (virtual t, ³J_{CP} = 5.4 Hz, o-PPh₂), 129.1 (virtual t, ³J_{CP} = 3.9 Hz, C⁴(indole)), 130.7 (s, p-PPh₂), 133.7 (virtual t, ⁴J_{CP} = 6.3 Hz, m-PPh₂), 138.0 (virtual t, ³J_{PC} = 4.6 Hz, C⁹(indole)). MS(ESI)⁺: m/z 938.22 [M + H + MeCN]⁺ (100%), 1139 [PtL₃]⁺ (10%). Anal. Calcd. for C₄₂H₃₆Cl₂N₂P₂Pt·H₂O (914.71): C, 55.15; H, 4.19; N, 3.06. Found: C, 54.84; H, 4.19; N, 3.39. IR (cm⁻¹): 3379 (s, ν_(N-H)), 3323 (m, ν_(N-H)), 3054 (w, ν_(C-H sp²)), 2910 (w, ν_(C-H sp³)), 1437 (s, PPh₂), 1329 (m), 1170 (m), 1095 (s).

[Chloro(methyl)-bis(diphenyl-2-(3-methyl)indolylphosphine)palladium(II)], [PdCl(Me)L₂] (3)

A Schlenk flask was charged with chloro(methyl)(cycloocta-1,5-diene)palladium (69.0 mg, 0.260 mmol) and CH₂Cl₂ (10 mL). The ligand diphenyl-2-(3-methyl)indolylphosphine (164.2 mg, 0.520 mmol) was subsequently added to the solution. The resulting pale yellow solution was stirred at room temperature for 16 h. The volume of solvent was reduced to a minimum and hexanes (10 mL) added to give the product as an off-white powder which was isolated by filtration, washed with diethyl ether and dried under vacuum (98.4 mg, 0.125 mmol, 48%). ¹H NMR, (CDCl₃, 400.2 MHz): δ 0.11 (t, ³J_{PH} = 6.3 Hz, 3H, PdCH₃),^[31] 1.83 (s, 6H, indoleCH₃), 7.16 (ddd, ³J_{HH} = 8.0 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 0.9 Hz, 2H, indoleC⁶H), 7.31

(ddd, ³J_{HH} = 8.2 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.1 Hz, 2H, indoleC⁷H), 7.41-7.49 (m, 14H, m,p-PPh₂CH & indoleC⁵H), 7.56-7.65 (m, 10H, o-PPh₂CH & indoleC⁸H), 11.10 (br, 2H, NH). ³¹P {¹H} NMR (CDCl₃, 121.7 MHz) δ [ppm] = 12.2 (s, PPh₂(^{Me}indolyl)). ¹³C {¹H} NMR (CDCl₃, 100.6 MHz) δ [ppm] = 9.9 (poorly resolved t, ²J_{CP} ≈ 2 Hz, PdCH₃), 10.9 (s, indoleCH₃), 112.3 (s, indoleC⁵H), 119.3 (s, indoleC⁸H), 119.5 (s, indoleC⁹H), 121.4 (virtual t, ²J_{CP} = 2.7 Hz, indoleC³), 121.5 (virtual t, ¹J_{PC} = 30.7 Hz, indoleC²), 124.0 (s, indoleC⁷H), 128.8 (virtual t, ³J_{CP} = 5.2 Hz, o-PPh₂CH), 129.4 (virtual t, ³J_{CP} = 3.8 Hz, indoleC⁴), 130.1 (virtual t, ¹J_{CP} = 24.6 Hz, ^{PPH₂}C_{ipso}), 130.4 (s, p-PPh₂CH), 133.7 (virtual t, ⁴J_{CP} = 6.5 Hz, m-PPh₂CH), 138.0 (virtual t, ³J_{PC} = 4.7 Hz, indoleC⁹). MS(ESI): m/z 751.15 [M-Cl]⁺. Anal. Calcd. for C₄₃H₃₉ClN₂P₂Pd (787.60): C, 65.57; H, 4.99; N, 3.56. Found: C, 65.37; H, 5.13; N, 3.84. IR (cm⁻¹): 3282 (m, ν_(N-H)), 3141 (w, ν_(C-H sp²)), 2891 (w, ν_(C-H sp³)), 1435 (s, PPh₂), 1331 (m), 1182 (m), 1093 (s).

[Chloro(methyl)-bis(diphenyl-2-(3-methyl)indolylphosphine)platinum(II)], [PtCl(Me)L₂] (4)

A Schlenk flask was charged with chloro(methyl)(cycloocta-1,5-diene)platinum (0.162 mg, 0.458 mmol) and the ligand diphenyl-2-(3-methyl)indolylphosphine (0.303 mg, 0.961 mmol). CH₂Cl₂ (10 mL) was subsequently added to the mixture to give a pale yellow solution which was further stirred for 3 h. All volatiles were removed and hexanes (10 mL) added to give the product as an off-white solid which was isolated by filtration and dried under vacuum (230.0 mg, 0.262 mmol, 57%). ¹H NMR, (CDCl₃, 400.2 MHz) δ [ppm] = 0.00 (t, 3H, ²J_{PH} = 6.8 Hz, ¹J_{PH} = 81.3 Hz, PtCH₃), 1.87 (s, 6H, indoleCH₃), 7.16 (t, ³J_{HH} = 7.3 Hz, 2H, indoleC⁶H), 7.31 (t, ³J_{HH} = 7.2 Hz, 2H, indoleC⁷H), 7.40-7.49 (m, 14H, m,p-PPh₂CH & indoleC⁵H), 7.59-7.68 (m, 10H, o-PPh₂CH & indoleC⁸H), 10.68 (br, 2H, NH). ³¹P {¹H} NMR (CDCl₃, 121.7 MHz) δ [ppm] = 12.7 (s, ¹J_{PP} = 3059 Hz, PPh₂(^{Me}indolyl)). ¹³C {¹H} NMR (CDCl₃, 100.6 MHz) δ [ppm] = -6.40 (t, ³J_{PC} = 5.0 Hz, ¹J_{PTC} = not observed), 11.0 (s, indoleCH₃), 112.2 (s, indoleC⁵H), 119.4 (s, indoleC⁸H), 119.6 (s, indoleC⁹H), 121.1 (virtual t, ¹J_{PC} = 35.3 Hz, indoleC²), 121.6 (virtual t, ²J_{CP} = 3.8 Hz, indoleC³), 124.1 (s, indoleC⁷H), 128.5 (virtual t, ³J_{CP} = 5.4 Hz, o-PPh₂CH), 129.2 (virtual t, ¹J_{CP} = 29.7 Hz, ^{PPH₂}C_{ipso}),^[32] 129.4 (virtual t, ³J_{CP} = 4.2 Hz, indoleC⁴),^[32] 130.6 (s, p-PPh₂CH), 133.8 (virtual t, ⁴J_{CP} = 6.2 Hz, m-PPh₂CH), 138.0 (virtual t, ³J_{PC} = 4.6 Hz, indoleC⁹). MS(ESI): m/z 773.15 [M-Cl]⁺. Anal. Calcd. for C₄₃H₃₉ClN₂P₂Pt (876.28): C, 58.94; H, 4.49; N, 3.20. Found: C, 58.92; H, 4.54; N, 3.13. IR (cm⁻¹): 3320 (m, ν_(N-H)), 3257 (s, ν_(N-H)), 3059 (w, ν_(C-H sp²)), 2955, 2928, 2886 (m, ν_(C-H sp³)), 1436 (s, PPh₂), 1096 (s).

Reaction of [PtCl(CH₃)L₂] with Na[B{3,5-C₆H₃(CF₃)₂]₄]

A Schlenk flask was charged with [PtCl(CH₃)L₂] (50.0 mg, 0.057 mmol) and Na[B{3,5-C₆H₃(CF₃)₂]₄] (51.0 mg, 0.058 mmol). Toluene (10 mL) was subsequently added and the resulting mixture heated to 80 °C for 2.5 h. After this time, all volatiles were removed. A solid product was obtained by extraction into diethyl ether and subsequent reduction of the solvent volume to provide a microcrystalline solid. Yield 44.3 mg, 0.035 mol, 62%). ¹H NMR, (C₆D₆, 400.2 MHz) δ [ppm] = 1.92 (s, 6H, indoleCH₃), 6.83 – 6.95 (m, 12H, Ar), 7.02 – 7.09 (m, 2H, Ar), 7.11 (m, 2H, Ar), 7.14-7.18 (m, 4H, Ar), 7.23 – 7.30 (8H, Ar), 7.43 [d, 2H, ³J_{HH} = 7.8 Hz, Ar], 7.68 [s, ¹J_{PH} = 31.5 Hz, 4H, o-(C₆H₃(CF₃)₂)], 8.47 (br, 2H, NH). ³¹P {¹H} NMR (C₆D₆, 121.7 MHz) δ [ppm] = 3.51 (s, ¹J_{PP} = 2888 Hz, PPh₂).

Crystallography

Crystals of complex **1** were obtained by layering pentane over a DCM solution of the complex and leaving to stand. Crystals of **2** were obtained by layering hexane over a CDCl₃ solution of the complex. The structure contained one molecule of chloroform within the unit cell. Crystals of **3** and **4** were obtained upon addition of hexane to concentrated chloroform solutions. Crystals of **5** were obtained from a saturated diethyl ether solution. X-ray diffraction experiments on Complexes **1**, **3**, **4** and **5** were carried out at University of Bristol on a Bruker APEX II diffractometer using graphite monochromised Mo-K_α radiation (λ = 0.71073 Å) (**1**, **3** and **4**) and Bruker Microstar diffractometer (**5**). Single-crystal X-ray diffraction data

collection on complex **2** was carried out at the UK National Crystallography Service at the University of Southampton^[33] and later solved at Bristol. Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. The structures were solved by direct methods in ShelXS-1997^[34] and refined by least squares minimisation against F^2 in ShelXL-2015^[35] using Olex2.^[36] Crystal Data for **1**: $C_{42}H_{36}Cl_2N_2P_2Pd$ ($M = 807.97$ g/mol): triclinic, space group $P\bar{1}$ (no. 2), $a = 10.3397(2)$ Å, $b = 12.8936(3)$ Å, $c = 15.3117(3)$ Å, $\alpha = 66.068(1)^\circ$, $\beta = 85.432(1)^\circ$, $\gamma = 77.257(1)^\circ$, $V = 1819.73(7)$ Å³, $Z = 2$, $T = 100(2)$ K, $\mu(\text{MoK}\alpha) = 0.778$ mm⁻¹, $D_{\text{calc}} = 1.475$ g/cm³, 36721 reflections measured ($5.89^\circ \leq 2\theta \leq 55.13^\circ$), 8356 unique ($R_{\text{int}} = 0.0291$, $R_{\text{sigma}} = 0.0254$) which were used in all calculations. The final R_1 was 0.0235 ($I > 2\sigma(I)$) and wR_2 was 0.0576 (all data). Crystal Data for **2**: $C_{43}H_{37}Cl_5N_2P_2Pt$ ($M = 1016.02$ g/mol): triclinic, space group $P\bar{1}$ (no. 2), $a = 11.2682(3)$ Å, $b = 11.6011(5)$ Å, $c = 16.2072(6)$ Å, $\alpha = 90.045(2)^\circ$, $\beta = 100.361(2)^\circ$, $\gamma = 104.799(2)^\circ$, $V = 2012.55(13)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{MoK}\alpha) = 3.932$ mm⁻¹, $D_{\text{calc}} = 1.677$ g/cm³, 37784 reflections measured ($5.908^\circ \leq 2\theta \leq 51.362^\circ$), 7612 unique ($R_{\text{int}} = 0.0690$, $R_{\text{sigma}} = 0.0547$) which were used in all calculations. The final R_1 was 0.0375 ($I > 2\sigma(I)$) and wR_2 was 0.0915 (all data). Crystal Data for **3**: $C_{43}H_{39}ClN_2P_2Pd$ ($M = 787.55$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 19.3177(3)$ Å, $b = 12.1127(2)$ Å, $c = 17.6845(2)$ Å, $\beta = 115.752(1)^\circ$, $V = 3727.01(10)$ Å³, $Z = 4$, $T = 100(2)$ K, $\mu(\text{MoK}\alpha) = 0.689$ mm⁻¹, $D_{\text{calc}} = 1.404$ g/cm³, 33852 reflections measured ($2.34^\circ \leq 2\theta \leq 55.084^\circ$), 8575 unique ($R_{\text{int}} = 0.0255$, $R_{\text{sigma}} = 0.0225$) which were used in all calculations. The final R_1 was 0.0245 ($I > 2\sigma(I)$) and wR_2 was 0.0639 (all data). Crystal Data for **4**: $C_{43}H_{39}ClN_2P_2Pt$ ($M = 876.24$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 11.9397(6)$ Å, $b = 26.2897(14)$ Å, $c = 12.3814(7)$ Å, $\beta = 110.885(3)^\circ$, $V = 3631.1(3)$ Å³, $Z = 4$, $T = 100(2)$ K, $\mu(\text{MoK}\alpha) = 4.060$ mm⁻¹, $D_{\text{calc}} = 1.603$ g/cm³, 33040 reflections measured ($3.098^\circ \leq 2\theta \leq 54.97^\circ$), 8314 unique ($R_{\text{int}} = 0.0535$, $R_{\text{sigma}} = 0.0572$) which were used in all calculations. The final R_1 was 0.0326 ($I > 2\sigma(I)$) and wR_2 was 0.0647 (all data). Crystal Data for **5**: $C_{58}H_{42}F_{12}N_2P_2Pt$ ($M = 1251.96$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 9.1022(15)$ Å, $b = 20.840(3)$ Å, $c = 13.098(2)$ Å, $\beta = 96.272(6)^\circ$, $V = 2469.7(7)$ Å³, $Z = 2$, $T = 100(2)$ K, $\mu(\text{CuK}\alpha) = 6.699$ mm⁻¹, $D_{\text{calc}} = 1.684$ g/cm³, 4556 reflections measured ($8.006^\circ \leq 2\theta \leq 132.756^\circ$), 4556 unique ($R_{\text{sigma}} = 0.0440$) which were used in all calculations. The final R_1 was 0.0396 ($I > 2\sigma(I)$) and wR_2 was 0.1134 (all data). The structure for **5** was refined as a two component twin against and hklf5 file, the twin scale fraction of the second component refined to 0.419(2). Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the cif files which can be found in 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. The corresponding CCDC codes are [2018543](https://doi.org/10.1107/2018543) - [2018547](https://doi.org/10.1107/2018547).

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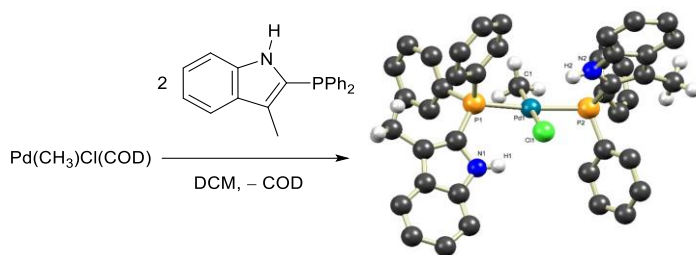
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Keywords: Phosphine • Hydrogen Bonding • Platinum • Palladium • Coordination Chemistry

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Entry for the Table of Contents



Diphenyl-2-(3-methyl)indolylphosphine: Palladium and platinum complexes containing diphenyl-2-(3-methyl)indolylphosphine were prepared and characterised. Their crystal structures revealed interactions of the indolyl units with the metal–chloride bonds directed at various positions along this bond. The complex $[\text{PtMeCl}(\text{L}_2)]$ was shown to cleave B–C bonds in the $[\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ anion.