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Conformation and ligand exchange reactions of *trans*-[PdCl(C₆H₄-2-N₂Ph)(PR₃)₂] and related complexes

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Abstract

Rotation about the metal–carbon bond in *trans*-[MCl(C₆H₄-2-N₂Ph)(PMe₂Ph)₂] (M = Pd, Pt) is slow at 273 K, and phosphine exchange occurs at ambient temperature. Chloride removal from *trans*-[PdCl(C₆H₄-2-N₂Ph)L₂] (L = PMe₂Ph, PMe₃, PEt₃) by silver(I) or methyl trifluoromethanesulfonate is complicated by phosphine abstraction, but reaction of [PdCl(C₆H₄-2-N₂Ph-C, N)L] with AgSO₃CF₃ in the presence of 2,6-lutidine (2,6-dimethylpyridine) or 2-fluoropyridine produces [Pd(am)(C₆H₄-2-N₂Ph-C, N)L]SO₃CF₃. Addition of phosphine yields *trans*-[Pd(am)-(C₆H₄-2-N₂Ph)L₂]SO₃CF₃. At or below ambient temperature the 2,6-lutidine complexes exhibit non-equivalent methyl signals in their ¹H NMR spectra, and the 2-fluoropyridine species exist as *syn* and *anti* isomers. These observations are consistent with slow rotation about the Pd–C and Pd–N bonds in complexes containing PMe₃ and PEt₃, as well as in those containing PMe₂Ph.

Introduction

We have previously described the formation of *trans*-[M(η¹-C₅H₅)(C₆H₄-2-N₂Ph)(PEt₃)₂] (M = Pd or Pt) from the reactions of [M(η⁵-C₅H₅)(C₆H₄-2-N₂Ph-C, N)] with PEt₃ [1]. More recently we have noted NMR spectroscopic phenomena in these and their rearranged products which are characteristic of hindered rotation of either the 2-(phenylazo)phenyl ligands and/or another group [2]. To aid the interpretation of these observations it is necessary to establish whether or not the bulky 2-(phenyl-

azo)phenyl group is able to rotate readily past the two *trans* PEt_3 ligands at ambient temperature (and if so at what temperatures this rotation becomes slow) and we address this question here.

Dimethylphenylphosphine has been extensively used as a probe for hindered rotations of this type, especially in nickel(II) complexes; in the absence of a plane of symmetry through the metal–phosphorus bond, the methyl groups are magnetically non-equivalent. Thus, the ^1H NMR spectra of *trans*- $[\text{NiXR}(\text{PMe}_2\text{Ph})_2]^{x+}$ reveal two triplets for the methyl groups when R is 2-tolyl [3], 3-tolyl [4,5], 1-naphthyl [3], trichlorovinyl [5], 3-methylpyridine [5], or alkoxy carbene [6], indicating that these planar groups lie perpendicular to the coordination plane and that rotation about their Ni–C bonds is slow. With R groups such as mesityl, C_6F_5 or C_6Cl_5 , which have an additional plane of symmetry containing the two phosphorus atoms, only one methyl triplet is observed [7]. With two asymmetric R groups, on the other hand, the presence of *syn* and *anti* isomers has been established, for example by the observation of four sets of methyl triplets when the two groups are different [5,8], as in *trans*- $[\text{Ni}(\text{C}_6\text{H}_4\text{-2-Cl})(\text{C}_6\text{H}_4\text{-2-Me})(\text{PMe}_2\text{Ph})_2]$. Separate ^{31}P NMR signals for each rotational isomer have occasionally been reported [8], and in a few cases such *syn* and *anti* isomers have been isolated [9].

Similar observations have been made for some platinum compounds, including that of the non-isochronous behaviour of the methyl groups of *cis*- $[\text{PtCl}_2\{\text{C}(\text{OR})\text{-R}'\}(\text{PMe}_2\text{Ph})]$ that established perpendicular coordination and hindered rotation of the alkoxy carbene ligands [10], and the detection of *syn* and *anti* isomers of $[\text{PtR}_2(\text{dppm-}P, P')]$ and *cis*- $[\text{PtR}_2(\text{dppm-}P)_2]$ (R = 2-tolyl or 1-naphthyl; dppm = bis(diphenylphosphino)methane) by ^{31}P NMR spectroscopy [11]. Examples of analogous phenomena involving palladium compounds are lacking, however. Although it is reasonable to expect very similar behavior, the conventional assumption that if rotation past coordinated PMe_2Ph is hindered then so will be rotation past other ligands (including PEt_3) which subtend larger cone angles [12] at the metal is more dubious. The uncertainty lies in the inherent asymmetry of PMe_2Ph , which could conceivably restrict rotations only in certain conformations. We show below that 2-(phenylazo)phenyl and some related aryl groups do not, in fact, readily undergo rapid rotation in compounds of the type *trans*- $[\text{PdXR}(\text{PMe}_2\text{Ph})_2]$ (X = halide). Replacement of X by 2,6-lutidine (2,6-dimethylpyridine) or 2-fluoropyridine has enabled us to extend these conclusions to both PEt_3 and PMe_3 derivatives.

Results and discussion

The ^1H NMR spectrum of *trans*- $[\text{PdBr}(2\text{-tolyl})(\text{PMe}_2\text{Ph})_2]$ in CDCl_3 solution at ambient temperature shows the presence of two triplets for the methyl (phosphine) signals (Table 1), establishing that the 2-tolyl group lies perpendicular to the molecular plane and rotation about the Pd–C bond is restricted. The geometrically related but more bulky 2-(phenylazo)phenyl complexes of Pd and Pt, *trans*- $[\text{MCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$, likewise show two sets of methyl triplets in their ^1H NMR spectra at 273 K, with ^{195}Pt satellites in the latter case (Table 1). We note also that the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of this palladium complexes exhibits two triplets for the methyl carbons, establishing the use of this nucleus as a probe for such asymmetry.

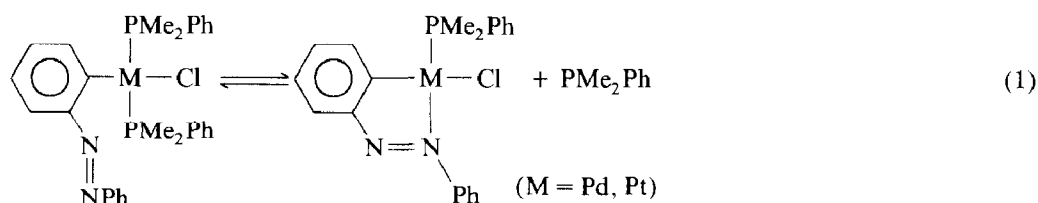
Table 1

Salient NMR data for previously unreported compounds (in CDCl₃ solution at 298 K unless otherwise stated). All bis(phosphine) compounds are of *trans* geometry.

	$\delta(P)$	$(\delta(F))$	$\delta(H)$ ($J(PH)$ in Hz)
[Pd(2-CH ₃ C ₆ H ₄)Br(PMe ₃ Ph) ₂]	-9.4		1.37 (t, 3.4), 1.50 (t, 3.4), P(CH ₃) ₂ Ph
[PdCl(C ₆ H ₄ -2-N ₂ Ph)(PMe ₃ Ph) ₂] ^b	-8.4		1.20 (br), 1.46 (br), P(CH ₃) ₂ Ph
[PtCl(C ₆ H ₄ -2-N ₂ Ph)(PMe ₂ Ph) ₂] ^c	-6.8 (J(PPt) 2813)		1.41 (t, 3.6), 1.52 (t, 3.6), P(CH ₃) ₂ Ph
[Pd(2,6-Me ₂ C ₅ H ₃ N)(C ₆ H ₄ -2-N ₂ Ph)(PMe ₂ Ph) ₂][SO ₃ CF ₃]	-10.7		2.59, 2.79, (CH ₃) ₂ C ₅ H ₃ N; 1.17 (t, 3.4), 1.29 (t, 3.4) P(CH ₃) ₂ Ph
[PdCl(C ₆ H ₄ -2-N ₂ Ph)(PMe ₃) ₂]	-17.4		1.05 (t, 3.4), P(CH ₃) ₃
[Pd(2,6-Me ₂ C ₅ H ₃ N)(C ₆ H ₄ -2-N ₂ Ph)(PMe ₃) ₂][SO ₃ CF ₃]	-19.5		2.95, 3.06, (CH ₃) ₂ C ₅ H ₃ N; 0.92 (t, 3.5), P(CH ₃) ₃
[Pd(2-FC ₃ H ₄ N)(C ₆ H ₄ -2-N ₂ Ph)(PMe ₃) ₂][SO ₃ CF ₃] ^a	(a) major -18.0 d (J(PF) 3.6 Hz)	-63.6 t (J(PF) 3.4 Hz)	0.88 (t, 3.6), P(CH ₃) ₃
	(b) minor -19.2 d (J(PF) 6.9 Hz)	-60.3 t (J(PF) 6.9 Hz)	not observed
[PdCl(C ₆ H ₄ -2-(2-C ₃ H ₄ N))(PEt ₃) ₂]	9.9 br 6.0 ^a		1.47 (q, 7.6, P(CH ₂ CH ₃) ₃ ; 0.92 (t, 7.6), P(CH ₂ CH ₃) ₃ 3.11, 3.17, (CH ₃) ₂ C ₅ H ₃ N; 1.1 (m), P(CH ₂ CH ₃) ₃ ; 0.88 (m), P(CH ₂ CH ₃) ₃
[Pd(2-FC ₃ H ₄ N)(C ₆ H ₄ -2-N ₂ Ph)(PEt ₃) ₂][SO ₃ CF ₃] ^b	(a) major 9.8 ^a	-62.2	1.1 (m), P(CH ₂ CH ₃) ₃ ; 0.93 (m), P(CH ₂ CH ₃) ₃
	(b) minor 9.6 ^a	-61.0	1.89 (d, 10.7), P(CH ₃) ₂ Ph 1.95 (d, 10.8, J(PH) 38), P(CH ₃) ₂ Ph
[PdCl(C ₆ H ₄ -2-N ₂ Ph-C,N)(PMe ₂ Ph)] ^a	12.7		2.87, (CH ₃) ₂ C ₅ H ₃ N; 1.58 (d, 10.2), P(CH ₃) ₂ Ph
[PtCl(C ₆ H ₄ -2-N ₂ Ph-C,N)(PMe ₂ Ph)] ^a	-6.5 (J(PPt) 3985)	-62.9	1.47 (d, 11.0), P(CH ₃) ₃ 2.81, (CH ₃) ₂ C ₅ H ₃ N; 1.52 (d, 10.7), P(CH ₃) ₃ 1.55 (d, 10.9), P(CH ₃) ₃ 2.08 (dq, 9.4, 7.6), P(CH ₂ CH ₃) ₃ ; 1.22 (dt, 17.0, 7.6), P(CH ₂ CH ₃) ₃ 2.84, (CH ₃) ₂ C ₅ H ₃ N; 1.79 (dq, 8.3, 7.7) P(CH ₂ CH ₃) ₃ ; 1.10 (dt, 17.4, 7.6) P(CH ₂ CH ₃) ₃ 1.90 (dq, 9.4, 7.6), P(CH ₂ CH ₃) ₃ ; 1.18 (dt, 17.8, 7.6) P(CH ₂ CH ₃) ₃
[Pd(2-FC ₃ H ₄ N)(C ₆ H ₄ -2-N ₂ Ph)(PEt ₃) ₂][SO ₃ CF ₃]	12.6 -4.8 -3.7 -2.2 30.9 27.5		
[Pd(2-FC ₃ H ₄ N)(C ₆ H ₄ -2-N ₂ Ph)(PEt ₃) ₂][SO ₃ CF ₃]	32.2	-62.4 ^c	

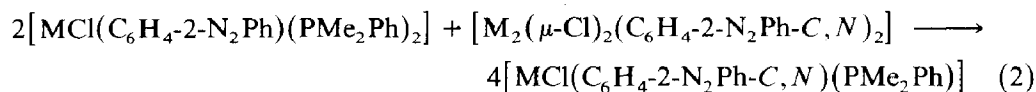
^a 233 K. ^b 273 K. ^c 244 K.

The ^1H NMR triplets of these two 2-(phenylazo)phenyl compounds collapse to broad singlets at 298 K. It seems unlikely that this could be caused by the onset of rapid rotation about the M–C bonds, leading to averaging the proton environments, since this is not observed for the complex containing the smaller 2-tolyl group. We believe instead that intermolecular phosphine exchange is responsible, and note that this effect has been observed previously for some nickel compounds [1,13]. In our case the catalyzing phosphine is released by a reversible ring closure of the 2-(phenylazo)phenyl group (eq. 1), presumably initiated by attack of the nitrogen

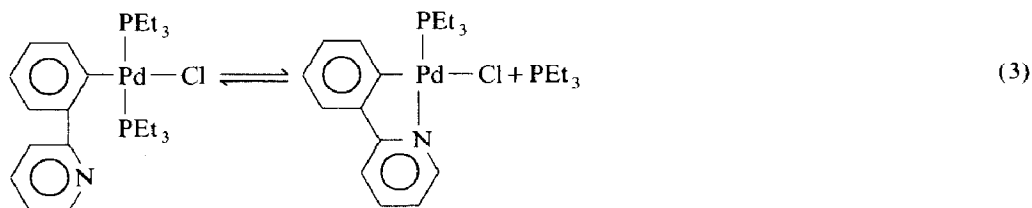


atom at the metal. This process has been observed previously in *trans*-[PtCl(C₆H₄-2-N₂Ph)(PMePh₂)₂] [14], though it does not proceed with the more nucleophilic and less easily displaced PEt₃ ligands of *trans*-[MCl(C₆H₄-2-N₂Ph)(PEt₃)₂] (M = Pd or Pt) [1].

In support of this interpretation we note that *trans*-[MCl(C₆H₄-2-N₂Ph)(PMe₂Ph)₂] and [M₂Cl₂(C₆H₄-2-N₂Ph-C,N)₂] react readily in CDCl₃ at room temperature to give [MCl(C₆H₄-2-N₂Ph-C,N)(PMe₂Ph)] (eq. 2), a reaction previously observed for the analogous PMePh₂ systems [14] but which is not observed in the use of the PEt₃ derivatives.



When the more nucleophilic 2-(2-pyridyl)phenyl ligand is employed instead of 2-(phenylazo)phenyl even PEt₃ is readily released from Pd (eq. 3), and is available to catalyze a rapid intermolecular exchange of PEt₃ at *trans*-[PdCl(C₆H₄-2-{2-C₅H₄N})](PEt₃)₂. Upon attempted isolation the latter loses PEt₃ to yield [PdCl(C₆H₄-2-{2-C₅H₄N}-C,N)(PEt₃)].



The ^1H NMR spectrum of *trans*-[PdCl(C₆H₄-2-{2-C₅H₄N})](PEt₃)₂ in CDCl₃ or acetone-*d*₆ at 213 K shows the resonances expected for two *trans*-PEt₃ ligands, though somewhat broadened. At 298 K the spectrum reveals the quartet and triplet of the ethyl protons, with no apparent coupling to ^{31}P . At higher temperatures the signals broaden again, beginning to sharpen at 333 K to doublets of quartets and triplets characteristic of ethyl groups coupled to one ^{31}P . This behavior is consistent with the occurrence of the reversible reaction shown in eq. 3, the liberated PEt₃ exchanging with the PEt₃ ligands in *trans*-[PdCl(C₆H₄-2-{2-C₅H₄N})](PEt₃)₂ [15].

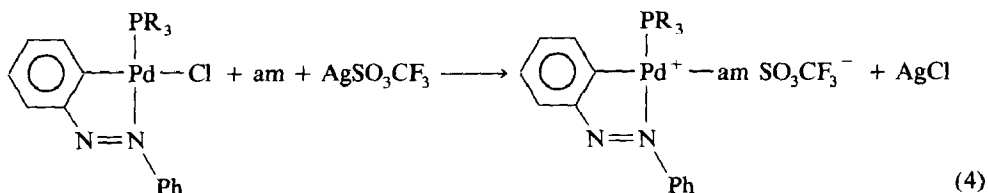
The effect of the increased exchange rate at higher temperatures is probably enhanced by a shift of equilibrium 3 to the right.

In order to determine whether rotation of the 2-(phenylazo)phenyl group occurs past the more symmetrical phosphines PEt_3 and PMe_3 , we replaced the chloride of $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PR}_3)_2]$ by 2,6-lutidine (2,6-dimethylpyridine) or 2-fluoropyridine. Hindered rotation should result in non-isochronous methyl (pyridine) signals from the former ligand, and the formation of *syn* and *anti* isomers in the case of the latter. Ligand replacements of this type are commonly performed by use of a silver salt to abstract the halide, and there is evidence that electrophilic attack of Ag^+ at the halide promotes its expulsion [16].

Treatment of $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]$ with AgSO_3CF_3 in the presence of 2- $\text{FC}_5\text{H}_4\text{N}$, however, led unexpectedly to the mono(phosphine) complex $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]\text{SO}_3\text{CF}_3$. Several small-scale reactions were performed on similar mixtures ($\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]$ and 2,6-lutidine; $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$ and 2,6-lutidine; $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-(2-C}_5\text{H}_4\text{N)})(\text{PEt}_3)_2]$ and 2,6-lutidine; $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]$ and acridine) and monitored by NMR spectroscopy. In each case, after treatment with AgSO_3CF_3 signals characteristic of mono(phosphine) palladium complexes were observed as the major products. We conclude that the second phosphine is abstracted by either the AgCl byproduct or by the AgSO_3CF_3 itself.

Two related reaction mixtures, $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]$ and 2,6-lutidine, and $\text{trans}[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$ and 2,6-lutidine, were treated with MeSO_3CF_3 as an alternative halide abstraction agent [17]. In the former case, the bis(phosphine) complex $\text{trans}[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]\text{SO}_3\text{CF}_3$ was the major product, although ^{31}P NMR signals for $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]\text{SO}_3\text{CF}_3$ and PMeEt_3^+ were also observed among the products. With the PMe_2Ph complex, however, a mixture of products was obtained, including substantial amounts of $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_2\text{Ph})]\text{SO}_3\text{CF}_3$ and PMe_2Ph^+ . It is thus apparent that neither of these chloride abstraction methods can be relied upon with complexes of this type.

Since the desired bis(phosphine) complexes may be generated by treating the mono(phosphine) derivatives with free phosphine, and these mono(phosphine) complexes in turn are more efficiently produced according to equation 4 ($\text{am} = 2,6\text{-lutidine}$ or 2-fluoropyridine), we did not examine further the halide abstraction reactions from the bis(phosphine) compounds.



The ^1H NMR spectrum of $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_2\text{Ph})]\text{SO}_3\text{CF}_3$ in CDCl_3 reveals the expected doublet for the phosphine methyls and a singlet for the lutidine methyls (Table 1). Addition of one mol equivalent of PMe_2Ph to this solution produces $\text{trans}[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]\text{SO}_3\text{CF}_3$, which reveals two triplets for the non-isochronous methyls of the *trans*- PMe_2Ph groups, and two singlets for the methyl groups of the lutidine. Thus,

the lack of fast rotation of the 2-(phenylazo)phenyl ligand shown by the phosphine methyl signals is confirmed by the observation of non-equivalent methyl groups of the coordinated 2,6-lutidine, which also lies perpendicular to the molecular plane.

Similarly the equivalent methyl groups of the lutidine in both $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_3)]\text{SO}_3\text{CF}_3$ and $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]\text{SO}_3\text{CF}_3$ are rendered non-equivalent by addition of a second phosphine to form *trans*- $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PR}_3)_2]\text{SO}_3\text{CF}_3$ (R = Me, Et), as revealed at ambient temperature by ^1H NMR spectroscopy. The 2-(phenylazo)phenyl group is thus incapable of fast rotation past not only the *trans* PEt_3 ligands, which subtend greater cone angles than PMe_2Ph , but also the *trans* PMe_3 ligands, which are smaller than PMe_2Ph [12]. The bis(phosphine)lutidine complexes tend to lose lutidine on attempted crystallization and none was isolated in pure form. In each reaction of $[\text{Pd}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PR}_3)]\text{SO}_3\text{CF}_3$ with PR_3 , NMR spectroscopic analysis revealed the presence of ~3% of $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PR}_3)_3]\text{SO}_3\text{CF}_3$ along with some unchanged mono(phosphine) complex, an observation which is compatible with ready loss of 2,6-lutidine from palladium.

The complexes $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PR}_3)]\text{SO}_3\text{CF}_3$ (R = Me, Et), prepared in a manner analogous to that used for the lutidine derivatives, readily lose the weakly nucleophilic 2-fluoropyridine ligand, and can only be isolated in the presence of excess ligand. The rapid and reversible loss of 2- $\text{FC}_5\text{H}_4\text{N}$ can be monitored by ^{19}F NMR spectroscopy in CDCl_3 . The ^{19}F resonance of $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]^+$ is at -62.4 ppm at 244 K, but moves to -64.4 ppm at 298 K. Addition of free 2- $\text{FC}_5\text{H}_4\text{N}$ to the solution does not produce a separate signal at 298 K, but moves the resonance further towards the position for the uncoordinated ligand (-67.3 ppm). At 233 K, separate, broad resonances for free and coordinated fluoropyridine can be seen at -67.9 ppm and -62.4 ppm, respectively.

The trimethylphosphine analogue, $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_3)]\text{SO}_3\text{CF}_3$, has an even greater tendency to lose fluoropyridine, and it could not be obtained analytically pure. At 233 K, separate, broad ^{19}F resonances could be seen at -62.5 and -67.4 ppm for coordinated and free ligand, even in the absence of added 2-fluoropyridine. At this temperature, a ^{31}P resonance at -3.1 ppm and a ^1H methyl (phosphine) doublet at 1.32 ppm ($J(\text{PH})$ 10.7 Hz) corresponding to $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_3)]\text{SO}_3\text{CF}_3$ (this species may contain coordinated CDCl_3 or SO_3CF_3^- : vide infra) could be seen, as well as those from the fluoropyridine complex (Table 1). As the temperature is raised, the signals for $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_3)]\text{SO}_3\text{CF}_3$ and $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_3)]\text{SO}_3\text{CF}_3$ (plus free fluoropyridine) broaden and coalesce, producing at 328 K moderately sharp resonances at $\delta(\text{F}) -66.2$ and $\delta(\text{P}) -3.8$, and $\delta(\text{H}) 1.69$ ($J(\text{PH})$ 10.9 Hz).

The addition of one molar equiv of PEt_3 to $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]\text{SO}_3\text{CF}_3$ converts it into *trans*- $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]\text{SO}_3\text{CF}_3$, which also releases a small amount of 2- $\text{FC}_5\text{H}_4\text{N}$ in CDCl_3 solution. At 220 K the ^{19}F and ^{31}P NMR spectra show the presence of two isomers (Table 1), in about 1/2 ratio, which we judge to be *syn* and *anti* rotational isomers respectively. Small amounts of the mono(phosphine) compound are also present. As the temperature is raised to 273 K the ^{19}F resonance of free 2- $\text{FC}_5\text{H}_4\text{N}$ broadens and coalesces, while those due to the two conformers of *trans*- $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})\text{-}$

$(\text{PEt}_3)_2\text{SO}_3\text{CF}_3$ retain their integrity. We assign this broadening to the rapid exchange of the free and coordinated fluoropyridine of the mono(phosphine) complex. Above 273 K, both isomers of the bis(triethylphosphine) complex lose 2- $\text{FC}_5\text{H}_4\text{N}$; a new ^{31}P resonance at 10.8 ppm grows in as those of the fluoropyridine complex diminish, while the ^{19}F resonance of free 2- $\text{FC}_5\text{H}_4\text{N}$ sharpens and grows at -67.3 ppm. By 316 K loss of 2- $\text{FC}_5\text{H}_4\text{N}$ from palladium is almost complete. All these effects of temperature variation are reversible. Addition of an excess of free 2- $\text{FC}_5\text{H}_4\text{N}$ displaces the equilibria in the expected direction. The detection of two rotational isomers of *trans*- $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})\text{-C}_6\text{H}_4\text{-2-N}_2\text{Ph}](\text{PEt}_3)_2\text{SO}_3\text{CF}_3$ at ambient temperature again provides evidence that the carbon-bonded (2-phenylazo)phenyl group is unable to rotate rapidly past *trans* PEt_3 groups.

The PMe_3 complex displays similar behavior, complicated somewhat by a more ready loss of both 2- $\text{FC}_5\text{H}_4\text{N}$ and PMe_3 in solution. Thus, addition of one PMe_3 to a CDCl_3 solution of $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PMe}_3)]\text{SO}_3\text{CF}_3$ produces a substantial amount of the tris(phosphine) complex $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_3]\text{SO}_3\text{CF}_3$ and free 2-fluoropyridine, as well as the expected *trans*- $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_2]\text{SO}_3\text{CF}_3$. The remaining mono(phosphine) complex and a substantial amount of *trans*- $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_2]\text{SO}_3\text{CF}_3$ (arising from loss of 2-fluoropyridine from the bis(phosphine) compound) are also present. Even at 233 K, loss of 2- $\text{FC}_5\text{H}_4\text{N}$ from the bis(phosphine) complex is considerable.

At 233 K, *syn* and *anti* isomers of *trans*- $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_2]\text{SO}_3\text{CF}_3$ are present in about 1/5 ratio. Fluorine-phosphorus coupling is resolved in both cases. At 263 K, the ^{19}F signal of the major isomer remains a sharp triplet, but the signal due to the minor isomer has broadened, along with that for free 2-fluoropyridine. This could be due to the onset of rapid rotation of 2- $\text{FC}_5\text{H}_4\text{N}$ interconverting the two isomers (the unequal populations resulting in the resonance due to the major isomer remaining relatively sharp) or a fast intermolecular ligand exchange affecting only the minor isomer. At 297 K, the ^{19}F NMR spectrum exhibits only broad resonances due to the major isomer of *trans*- $[\text{Pd}(2\text{-FC}_5\text{H}_4\text{N})(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_2]\text{SO}_3\text{CF}_3$ and free 2-fluoropyridine. The ^{31}P NMR signals for this complex, *trans*- $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_2]\text{SO}_3\text{CF}_3$ and the mono(phosphine) complex are also all broad, as are the relevant ^1H methyl signals. The resonances from the tris(phosphine) complex $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_3)_3]\text{SO}_3\text{CF}_3$ remain sharp. Thus it is clear that restricted rotation of the 2-(phenylazo)phenyl and 2-fluoropyridine ligands persists at least up to 263 K. Above this temperature the information is lost, either because of intermolecular exchange of 2- $\text{FC}_5\text{H}_4\text{N}$ or the onset of its rapid rotation. Addition of excess 2- $\text{FC}_5\text{H}_4\text{N}$ to this system displaces the equilibrium towards the coordinated fluoropyridine complexes.

The coordination sites vacated by 2- $\text{FC}_5\text{H}_4\text{N}$ in all of its complexes could be filled by either CDCl_3 or SO_3CF_3^- , and there is evidence that both are involved. Halocarbons such as CHCl_3 or CH_2Cl_2 can readily ligate to metal ions in this part of the Periodic Table [18]. The ^{19}F NMR signal for free CF_3SO_3^- in our complexes is sharp and appears at -78.7 ppm at temperatures below 263 K. In reaction mixtures of the 2-fluoropyridine complexes in which ligand loss is observed, however, this signal broadens slightly at about 273 K, to sharpen at -78.3 ppm at higher temperatures. Treatment of $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]$ with AgSO_3CF_3 in CDCl_3 , followed by PEt_3 addition, generates *trans*- $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]\text{SO}_3\text{CF}_3$ in the absence of pyridine ligands. At 213 K and 233 K, the dominant ^{19}F

resonance is at -78.7 ppm, consistent with ionic triflate, but a minor peak is present at -78.3 ppm. These signals coalesce to one broad signal at 263 K, and re-emerge as a sharp peak at -78.3 ppm at 298 K. We conclude that CDCl_3 is coordinated to most of these palladium molecules, but SO_3CF_3^- competes to a minor extent and enters into a fast exchange above 263 K. Treatment of these mixtures with 2,6-difluoropyridine does not alter the nature of the NMR spectra, indicating that this ligand is a weaker nucleophile than either CDCl_3 or SO_3CF_3^- .

Experimental

NMR spectra were recorded on Varian XL-300 or Bruker WP200SY instruments operating in the FT mode. Microanalyses were performed at the University of Glasgow. Preparations of $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]$ and *trans*- $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]$ have been described previously [1,14], as has the procedure for executing small scale reactions in NMR tubes [1].

Preparation of trans-[PdBr(2-MeC₆H₄)(PMe₂Ph)₂]

A solution of $[\text{PdCl}_2(\text{PMe}_2\text{Ph})_2]$ (0.45 g, 0.99 mmol) in THF was treated with 2 molar equivalents of 2-tolylmagnesium bromide, prepared from 2-bromotoluene and magnesium in THF. The mixture was stirred for 1 h at room temperature, the solvent was then removed, and the residue was crystallized from methanol to give *trans*-bromo(2-methylphenyl)bis(dimethylphenylphosphine)palladium (0.2 g, 40%). Found: C, 49.9; H, 5.2; Br, 14.4. $\text{C}_{23}\text{H}_{29}\text{BrP}_2\text{Pd}$ calcd.: C, 50.0; H, 5.3; Br, 14.45%.

Preparation of trans-[PdCl(C₆H₄-2-N₂Ph)(PMe₂Ph)₂]

To a suspension of $[\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})_2]$ (0.354 g, 0.55 mmol) in toluene (25 ml) under nitrogen was added a solution of dimethylphenylphosphine (0.302 g, 2.19 mmol) in toluene (2 ml). The solvent was removed from the resulting orange-brown solution, and the residue was crystallized from hexane to yield purple or orange crystals of *trans*-chloro(2-{phenylazo}phenyl)bis(dimethylphenylphosphine)palladium (0.73 g, 65%). Found: C, 55.7; H, 4.9; N, 4.9. $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{P}_2\text{Pd}$ calcd.: C, 56.1; H, 5.2; N, 4.7%. The purple and orange forms give identical infrared and ^1H NMR spectra. The purple form is slowly converted into the orange one, a process which is accelerated by sunlight.

Preparation of [PdCl(C₆H₄-2-N₂Ph-C,N)(PMe₂Ph)]

To a suspension of $[\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})_2]$ (0.16 g, 0.24 mmol) in toluene (25 ml) was added *trans*- $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$ (0.3 g, 0.5 mmol). The mixture was stirred at room temperature for 18 h. Removal of solvent and crystallization of the yellow residue from ether gave orange needles of chloro(2-{phenylazo}phenyl-C,N)(dimethylphenylphosphine)palladium. Found: C, 52.1; H, 4.0; N, 6.1. $\text{C}_{20}\text{H}_{20}\text{ClN}_2\text{PPd}$ calcd.: C, 52.1; H, 4.4; N, 6.1%.

Preparation of trans-[PtCl(C₆H₄-2-N₂Ph)(PMe₂Ph)₂]

Use of the procedure employed to give the palladium analogue, but starting from $[\text{Pt}_2(\mu\text{-Cl})_2(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})_2]$ (0.144 g, 0.17 mmol) gave orange crystals of chloro(2-{phenylazo}phenyl)bis(dimethylphenylphosphine)platinum (0.199 g, 83%). Found: C, 49.4; H, 4.4; N, 4.0. $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{P}_2\text{Pt}$ calcd.: C, 48.9; H, 4.5; N, 4.1%.

Preparation of [PdCl(C₆H₄-2-(2-C₅H₄N)-C,N)(PEt₃)]

To a suspension of [Pd₂(μ-Cl)₂(C₆H₄-2-(2-C₅H₄N)-C,N)₂] [19] (0.98 g, 1.66 mmol) in toluene (50 ml) under N₂, n-butylamine (0.33 ml, 3.31 mmol) was added to effect solution. After 1 h stirring triethylphosphine (0.65 ml, 4.4 mmol) was added. An initial yellow precipitate had dissolved after 14 h stirring. Removal of solvent and crystallization of the residue from a 1/1 CH₂Cl₂/Et₂O mixture yielded bright yellow crystals of chloro(2-{2-pyridyl}phenyl-C,N)(triethylphosphine)palladium (0.65 g, 48%). Found: C, 48.9; H, 5.6; N, 3.5. C₁₇H₂₃ClNPPd calcd.: C, 49.3; H, 5.6; N, 3.4%.

Preparation of [Pd(2,6-Me₂C₅H₃N)(C₆H₄-2-N₂Ph-C,N)(PMe₂Ph)]SO₃CF₃

To a solution of [PdCl(C₆H₄-2-N₂Ph-C,N)(PMe₂Ph)] (0.3 g, 0.65 mmol) in ether (50 ml) was added 2,6-lutidine (0.7 g, 0.65 mmol) followed by AgSO₃CF₃ (0.35 g, 1.36 mmol). An immediate precipitate formed in the yellow solution. After 1 h stirring the solvent was removed and the residue was extracted into hot CH₂Cl₂ (25 ml). (The precipitate was discarded.) Addition of ether and 2 drops of 2,6-lutidine to the extract gave, on standing, orange crystals of (dimethylphenylphosphine)(2,6-lutidine)(2-{2-pyridyl}phenyl-C,N)palladium trifluoromethanesulfonate. Found: C, 49.0; H, 4.0; N, 6.1. C₂₈H₂₉F₃N₃O₃PPdS calcd.: C, 49.1; H, 4.3; N, 6.2%.

Preparation of [Pd(2,6-Me₂C₅H₃N)(C₆H₄-2-N₂Ph-C,N)(PMe₃)]SO₃CF₃

To a suspension of [Pd₂(μ-Cl)₂(C₆H₄-2-N₂Ph-C,N)₂] (1.9 g, 2.9 mmol) in toluene (50 ml) under nitrogen was added n-butylamine (0.5 g). The mixture was stirred for 1 h to effect solution, then trimethylphosphine (0.5 ml, 4.9 mmol) was added by syringe. After a further 1 h stirring the solvent was evaporated to leave a deep red oil. NMR spectroscopy revealed that this was mainly [PdCl(C₆H₄-2-N₂Ph-C,N)(PMe₃)], along with a small amount of *trans*-[PdCl(C₆H₄-2-N₂Ph)(PMe₃)₂]. It was used without further purification.

Some of this red oil (0.38 g) was dissolved in ether, and 2,6-lutidine (0.11 ml) and AgSO₃CF₃ (0.37 g) were added. After 20 min stirring the solvent was evaporated and the yellow solid was extracted into hot CH₂Cl₂ (25 ml). The extract was filtered and ether was added to the filtrate along with one drop of 2,6-lutidine. The solution was left overnight to give orange crystals of (2,6-lutidine)(2-{phenylazo}phenyl-C,N)(trimethylphosphine)palladium trifluoromethanesulfonate. Found: C, 44.5; H, 4.2; N, 6.8. C₂₃H₂₇F₃N₃O₃PPdS calcd.: C, 44.6; H, 4.4; N, 6.8%.

Preparation of [Pd(2-F-C₅H₄N)(C₆H₄-2-N₂Ph-C,N)(PMe₃)]SO₃CF₃

To an ether solution (50 ml) of the unpurified [PdCl(C₆H₄-2-N₂Ph-C,N)(PMe₃)] obtained as described above (0.43 g) were added 2-fluoropyridine (0.15 g) and AgSO₃CF₃ (0.35 g). The solvent was removed after 30 min and the sticky residue was extracted into hot CH₂Cl₂ (25 ml). After filtration of the extract to remove silver salts, several attempts were made to crystallize the product from CH₂Cl₂, Et₂O or pentane, and in the presence of an excess of 2-fluoropyridine. These led only to the formation of a red oil, shown by NMR spectroscopic examination to be the desired product (Table 1).

Preparation of [Pd(2,6-Me₂C₅H₃N)(C₆H₄-2-N₂Ph-C,N)(PEt₃)]SO₃CF₃

To a solution of [PdCl(C₆H₄-2-N₂Ph-C,N)(PEt₃)] (0.60 g, 1.36 mmol) in ether (20 ml) were added 2,6-lutidine (0.2 ml) and AgSO₃CF₃ (0.7 g, 2.7 mmol). After 1 h

stirring the solvent was evaporated and the residue was extracted into hot CH_2Cl_2 . Silver salts were removed by filtration, and ether was added to the filtrate along with 2 drops of 2,6-lutidine. This afforded orange crystals of (2,6-lutidine)(2-{phenylazo}phenyl-*C,N*)-(triethylphosphine)palladium trifluoromethanesulfonate (0.7 g, 78%). Found: C, 47.2; H, 4.7; N, 5.7. $\text{C}_{26}\text{H}_{33}\text{F}_3\text{N}_3\text{O}_3\text{PPdS}$ calcd.: C, 47.2; H, 5.0; N, 6.35%.

Preparation of [Pd(2-F-C₅H₄N)(C₆H₄-2-N₂Ph-C,N)(PEt₃)]SO₃CF₃

(a) To a solution of $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph-C,N})(\text{PEt}_3)]$ (0.84 g, 1.90 mmol) in ether (20 ml) were added 2-fluoropyridine (0.3 ml) and AgSO_3CF_3 (0.98 g, 3.81 mmol). Removal of the solvent after 1 h, followed by extraction with hot CH_2Cl_2 , and filtration to remove silver salts, left an orange solution. This was evaporated to dryness and the residue was crystallized from a 1:1 mixture of CH_2Cl_2 /ether, containing a few drops of 2- $\text{FC}_5\text{H}_4\text{N}$ to yield orange-yellow needles of (2-fluoropyridine)(2-{phenylazo}phenyl-*C,N*)-(triethylphosphine)palladium trifluoromethanesulfonate (1.18 g, 94%). Found: C, 44.0; H, 4.2; N, 6.3. $\text{C}_{24}\text{H}_{28}\text{F}_4\text{N}_3\text{O}_3\text{PPdS}$ calcd.: C, 44.2; H, 4.3; N, 6.4%.

(b) To a solution of *trans*- $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-N}_2\text{Ph})(\text{PEt}_3)_2]$ (0.22 g, 0.55 mmol) in ether (50 ml) were added 2- $\text{FC}_5\text{H}_4\text{N}$ (0.07 g, 0.72 mmol) and AgSO_3CF_3 (0.3 g, 1.2 mmol). The mixture was stirred for 5 min, the solvent was evaporated, and the residue was extracted into CH_2Cl_2 and the extract filtered. Removal of solvent and crystallization from CH_2Cl_2 /Et₂O (1/1) gave yellow-brown needles of the product, shown by ¹H, ¹⁹F, and ³¹P NMR analysis to be identical to that described above.

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