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CARBON–METAL BONDED HETEROCYCLES. SYNTHESIS AND CHARACTERISATION OF [MCl{C_5H_3N(6-Cl)-C^2}$(PR_3)_2$] (M = Pd, Pt; PR_3 = PPh_3, $PMePh_2$; OR $(PR_3)_2$ = dppe)

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Summary

The complexes [Pd$(PPh_3)_4$] and [Pt$(PPh_3)_4$] react with 2,6-dichloropyridine at high temperature to give *trans*-[MCl{C_5H_3N(6-Cl)-C^2}$(PPh_3)_2$] (M = Pd, Ia; M = Pt, Ib). Ligand substitution reactions of these complexes with 1,2-bis(diphenylphosphino)ethane, dimethyldithiocarbamate, and LiBr have been carried out, and also insertion of CO into the Pd–C bond of Ia. Oxidation of Ia with H_2O_2, giving the dimeric complex [PdCl{C_5H_3N(6-Cl)-C^2}$(PPh_3)]_2$ is also reported. The complex analogous to Ia but containing $PMePh_2$ in place of PPh_3 has been obtained by oxidative addition to the Pd$(dba)_2$/$PMePh_2$ system (dba = dibenzylideneacetone).

Introduction

The recognition of heterocyclic halides as ligands for oxidative addition reactions to low-valent metal complexes has stimulated a number of recent studies [1–10]. In particular, the reaction of 2,6-dichloropyridine with [Pd$(PPh)_3]_4$ has been examined, but the characterisation of the product was not reported [1–3]. We report here the synthesis, characterisation and some reactions of [MCl{C_5H_3N(6-Cl)-C^2}$(PR_3)_2$] (M = Pd, Pt; PR_3 = PPh_3, $PMePh_2$ or dppe/2). Studies of the insertion of isocyanides into some of these complexes will be reported elsewhere [10].

Results and discussion

Synthesis and characterisation of trans-[MCl{C_5H_3N(6-Cl)-C^2}$(PPh_3)_2$] (M = Pd, Ia; M = Pt, Ib)

Oxidative addition of 2,6-dichloropyridine to [M$(PPh_3)_4$] (M = Pd or Pt) at high temperature in toluene affords σ-carbon bonded 2-pyridyl complexes in quantitative yield (eq. 1).

The spectra of complexes Ia and Ib are in accord with a *trans* configuration in the

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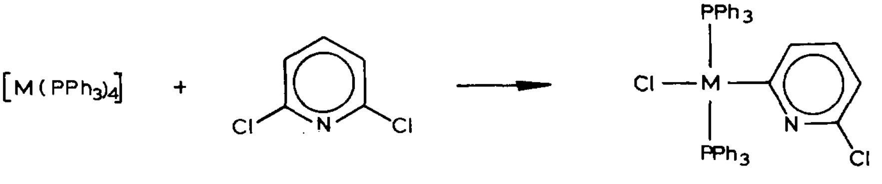
solid and in solution. The IR spectra as Nujol mulls show a single M–Cl stretching vibration at rather low frequency (ν(Pd–Cl) 293 cm^{-1}; ν(Pt–Cl) 278 cm^{-1}) indicative of the presence of a group of strong *trans* influence, such as the σ-carbon



(1)

(Ia, Ib)

bonded pyridyl species. Halogen metathesis of Ia with LiBr in acetone allows unambiguous assignment of ν(Pd–Cl) since the band at 293 cm^{-1} disappears in the bromide product and a new band is observed at 187 cm^{-1}, attributable to ν(Pd–Br). The $^{31}P\text{-}\{^1H\}$ NMR spectra in $CDCl_3$ point clearly to a *trans* configuration since only one signal at 21.65 ppm is observed for Ia, and one signal at 23.10 ppm with two satellites, due to ^{195}Pt, is observed for Ib (^1J(Pt–P) 3149 Hz). The proton NMR spectra of both compounds show a ABC pattern (see below) thus indirectly indicating that the pyridyl moiety is bonded to the metal through the carbon atom *ortho* to the nitrogen atom. Replacement of a chlorine of 2,6-dichloropyridine by a palladium species causes a marked high-field shift of the pyridine protons. Thus, whereas 2,6-dichloropyridine shows two complex multiplets at δ7.3 (2H) and at 7.6 ppm (1H), in the carbon-bonded pyridyl compound Ia the two multiplets are found at δ6.2 (2H) and 6.6 ppm (1H); in the platinum analogue Ib a still higher shielding of the pyridine protons is observed, with the multiplets centred at δ6.1 (2H) and 6.5 ppm (1H). Such up-field shifts of the pyridine protons in the Pd and Pt complexes may be the result of an increase of electronic charge in the pyridine ring, probably due to partial π-bonding between the metal center towards the aromatic ring. The ^{13}C NMR spectra of metallated pyridines have previously been shown to involve large up-field shifts for the pyridine carbon atoms compared to those in the uncoordinated pyridine rings, suggesting an increase of electron density in the pyridine ring upon coordination [1].

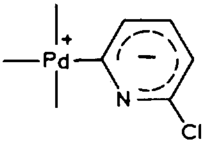
Chemical evidence for an increase of basicity of the pyridine nitrogen in these complexes was obtained by titration of compounds Ia, Ib, and 2-chloropyridine, in CH_2Cl_2/MeOH (1/2, v/v), with methanolic HCl. The following pK_a values were determined from the titration curves: Ia 3.4; Ib 4.9; 2-chloropyridine $\leqslant$ 1.2. The last value could not be determined more precisely because of the low basicity of 2-chloropyridine.

Oxidative addition of 2-haloheterocyclic ligands and structure of 2-pyridyl complexes

In the light of our observations and of earlier reports, some general comments can be made about the oxidative addition reactions and the structures of the resulting complexes.

(i) Oxidative addition. As far as organic halides are concerned, we observe the following ease of oxidative addition to [Pd(PPh_3)$_4$]: 2,6-dichloropyridine > 2-chloropyridine [2,7] > 2-chlorothiophene [8,9] ≈ 2-chlorobenzene [11,12]. This sequence, based upon the reaction temperature needed for the quantitative conversion of [Pd(PPh_3)$_4$] into products, suggests the presence of negatively charges on the

aromatic rings in the rate determining intermediates. Thus, if an S_N2 type mechanism operates for 2,6-dichloropyridine, for instance, the following zwitterion may be formed



Electron-withdrawing substituents in the aromatic ring should stabilize such intermediates and thus would account for the order given above.

The possibility of an alternative pathway involving a radical mechanism, though less probable, cannot be ruled out. In that case, electron-accepting substituents would lower the energies of the antibonding ring orbitals and thus facilitate the formation of radical anions. Once again, the reactivity of the organic halides would be enhanced by electron-withdrawing groups [11].

Interestingly, 2,6-dichloropyridine, which is potentially bifunctional in the oxidative addition reaction, reacts only with one molecule of palladium(0)- or platinum(0)-triphenylphosphine complexes even when excess of the metal(0) complex is used. One of the factors responsible for this may be the higher electron density on the metallated aromatic ring, which could inhibit the oxidative addition.

A strong influence of the metal can be observed in the oxidative addition reactions. The experimental data from this work, together with those reported elsewhere [3,5] show that the ease of addition of 2,6-dichloropyridine to $[M(PPh_3)_4]$ decreases in the following order (as indicated by the reaction temperatures, shown in parentheses):

$$\underset{(20°\mathrm{C})}{\mathrm{Ni}} \gg \underset{(90°\mathrm{C})}{\mathrm{Pd}} > \underset{(110°\mathrm{C})}{\mathrm{Pt}}$$

Several reports found in the literature confirm this trend (see for example, ref. 13). A feature which accounts for the higher reactivity of $[Ni(PPh_3)_4]$ than of the corresponding Pd and Pt complexes is its much more negative half-wave potential [14].

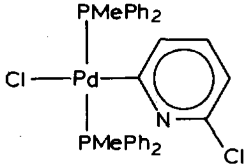
(ii)Structure of 2-pyridyl complexes. Of particular interest in this work are the changes in the structure of the 2-pyridyl complexes as the metal, the phosphine and the 2-carbon bonded pyridyl group are varied. Oxidative addition of 2,6-dichloropyridine to Pd(0)- and Pt(0)-tetrakistriphenylphosphine yields the monomeric compounds Ia and Ib, respectively. However, the reaction of 2-halopyridines with these metal complexes afforded a monomeric species with platinum [7] but a dimeric species with palladium; the X-ray structure of the dimeric complex showed it to be *trans(P,N)*-$[PdBr(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3]_2$ [4]; monomeric compounds of palladium were, however, obtained from more basic phosphines such as $PMePh_2$ [7].

The tendency of the 2-carbon bonded pyridine to coordinate another metal center through a nitrogen atom is in accord with its high basicity (see comments before). Both steric and electronic factors favour the monomeric structure of Ia, but the steric effect is likely to be less important in view of the moderate bulk of the *ortho*-chlorine atom. (In fact, a dimeric pyridyl bridged compound has been obtained from the reaction of 2-chloro-6-methylpyridine with $[Pd(PPh_3)_4]$ [15].) The electron-withdrawing power of the chlorine atom next to nitrogen must therefore account for the inability of the 2-carbon bonded pyridine to remove a PPh_3 ligand from another molecule of the palladium complex Ia.

The higher stability of platinum complexes towards dimerization is probably due to the greater ability of Pt to σ-bond PPh_3 [16], rather than to a less favourable metal–nitrogen bond strength. Indeed, the metal to nitrogen bond strength seems to follow the order Pt–N > Pd–N [17,18].

Synthesis and characterisation of trans-$[PdCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PMePh_2)_2]$ *(Ic)*

Oxidative addition of 2,6-dichloropyridine to the $Pd(dba)_2/PMePh_2$ reaction mixture (molar ratio $Pd/PMePh_2 \simeq 0.4$; dba = dibenzylideneacetone) gave a fairly good yield of Ic. Its structure, shown below, is based on spectroscopic evidence (see Table 2).

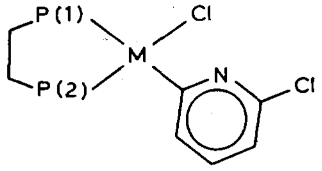


(Ic)

The ^1H NMR spectrum, of Ic shows a triplet due to "virtual" coupling at δ1.95 ppm with $|^2J(P\text{–}H)+{}^4J(P\text{–}H)|$ 6.7 Hz, characteristic of a *trans* configuration. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows only a singlet due to the equivalence of $PMePh_2$ *trans* to each other, δ(P) 7.3 ppm. The far-infrared spectrum exhibits a band at 290 cm^{-1} attributable to the ν(Pd–Cl) stretching vibration. This rather low value is in agreement with a structure in the solid in which the chlorine is *trans* to a group of strong *trans* influence, such as the carbon bonded pyridyl ligand.

Reaction of Ia and Ib with 1,2-bis(diphenylphosphino)ethane (dppe)

Complexes Ia and Ib reacted with dppe in CH_2Cl_2 (see Experimental) to yield white complexes, which are assigned the following structure:



(M= Pd, IIa ; M = Pt, IIb)

The chelating nature of the dppe ligand in IIa is clearly evident from its $^{31}P\text{-}\{^1H\}$ NMR spectrum, in which two mutually coupled phosphorus resonances at 31.23 and 49.95 ppm ($^2J(P(1)\text{–}P(2))$ 30 Hz) are observed. These are tentatively assigned to the phosphorus atoms *trans* to chlorine and carbon, respectively [19]. The magnitude of the $^2J(P,P)$coupling is consistent with a *cis* orientation for the two ^{31}P spins [20].

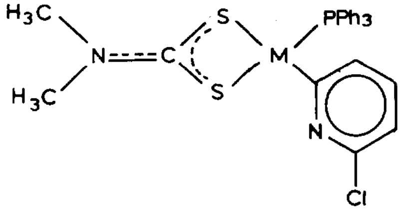
Owing to identical chemical shifts for the ^{31}P nuclei, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of IIb consists of only one single central peak together with two symmetrical sets of satellites arising from the two non-equivalent nuclei coupled to ^{195}Pt. (Accidental degeneracy has been reported for some dppe complexes of platinum [21]). Further splitting of each satellite line due to P–P coupling was also observed, supporting the structure above with the non-equivalent spins P(1) and P(2). Simulation of the spectrum gave the following parameters (Hz): ${}^1J$(Pt,P(1)) ± 1640; ${}^1J$(Pt,P(2)) ± 4210; ${}^2J$(P(1),P(2)) ∓ 3. The low value of ${}^2J$(P(1),P(2)) is consistent with a *cis* orientation of the two phosphorus spins and the values of ${}^1J({}^{195}Pt,{}^{31}P)$ are comparable with those in related compounds, such as [PtMe(Cl)(dppe) [22]. From the known dependence of ${}^1J$(Pt,P) on the nature of the *trans* ligand, P(1) is assigned *trans* to the carbon bonded pyridyl group and P(2) *trans* to the chlorine atom [20].

Only a slight support for the above structures is provided by the ${}^1H$ NMR spectra because of the complex signals from the ethane moiety (of dppe) and the pyridine ring.

The far IR spectra of IIa and IIb show two absorptions in the 280–300 cm^{-1} region, and so the metal–chlorine stretching cannot be distinguished. To assign the ν(Pd–Cl), halogen metathesis of IIa with LiBr was carried out; unexpectedly, both bands were absent in the corresponding bromide complex, preventing any assignment.

Dimethyldithiocarbamate complexes of palladium(II) and platinum(II)

Complexes *trans*-[MCl(C$_5$H$_3$N(6-Cl)-*C*^{2})(PPh$_3$)$_2$] (M = Pd or Pt) react cleanly with sodium dimethyldithiocarbamate, [Na(dmtc)], to give the mononuclear complexes:



(M = Pd, IIIa ; M = Pt, IIIb)

The dithiocarbamate ligand is coordinated to the central metal in a bidentate fashion through the sulphur atoms: ν(Pd–S) 375; ν(Pt–S) 380 cm^{-1}. The infrared spectra of the complexes also show intense bands at 1535 cm^{-1} for IIIa, and at 1545 cm^{-1} for IIIb, suggesting the presence of considerable double-bond character in the C–N bond of the coordinated dithiocarbamate. Interestingly, in the ${}^1H$ NMR spectrum the methyl protons of the dmtc group appear as two signals of equal intensity at 3.26 (3H) and 3.30 ppm (3H) for IIIa, and at δ3.20 (3H) and 3.25 ppm (3H) for IIIb. The non-equivalence of both methyl groups is in accord with the partial double bond character of the C–N bond mentioned above. The ${}^{31}P\text{-}\{{}^1H\}$ NMR spectrum of a CDCl$_3$ solution of IIIa shows only one signal at 28.38 ppm whereas the corresponding spectrum of IIIb shows a central peak at 17.02 ppm together with less intense symmetrical ${}^{195}Pt$ satellites (${}^1J$(Pt–P) 4038 Hz).

Dimerization of Ia

Compound Ia has been reported to be mononuclear, although the existence of an equilibrium between Ia and a dinuclear complex has been suggested [2]:

$$2\left[PdCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PPh_3)_2\right] \rightleftarrows \underset{\text{(IVa)}}{\left[PdCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PPh_3)\right]_2} + 2PPh_3 \qquad (1)$$

This suggestion is apparently in contrast with the ^{31}P spectrum for a $CDCl_3$ solution of Ia, which shows no signals for either free PPh_3 or IVa. However, the equilibrium may be present but lie far to the left; the equilibrium 1, is completely shifted to the right upon oxidation of the liberated phosphine with hydrogen peroxide (see Experimental).

With excess PPh_3 the mononuclear complex Ia is quantitatively regenerated. Analytical and spectroscopic data for IVa are reported in Table 1 and 2. We cannot yet say whether IVa is a chloride or a *C*,*N*-pyridyl bridged complex. Bridge-splitting by PPh_3 would suggest a chloride-bridged structure, since cleavage of the *C*,*N*-pyridyl bridges by PPh_3 proved unsuccessful for *trans*-(P,N)-$[PdBr(\mu\text{-}C_5H_3N\text{-}C^2,N)(PPh_3)]_2$ [2]. On the other hand, the presence of an *ortho*-chlorine atom in the pyridine ring of IVa by reducing the nitrogen basicity may allow its displacement by the added triphenylphosphine. Attempts to grow suitable crystals for X-ray studies are in progress.

Carbonylation studies

Our interest in the field of insertion reactions at palladium(II) and platinum(II), led us to compare the relative reactivities of $[PtClR(PPh_3)_2]$, $[PdClR(PPh_3)_2]$,

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Compound	Colour	Melting point (°C) [a]	Analyses (Found (calcd.) (%))				Mol. weight (Found (calcd.))
			C	H	N	Cl	
Ia	white	223–225	62.97	4.35	1.63	9.03	784
			(63.25)	(4.27)	(1.80)	(9.10)	(779.03)
Ib	white	255–258	57.02	3.75	1.68	8.25	885
			(56.75)	(3.83)	(1.61)	(8.17)	(867.72)
Ic	pale yellow	182–185	50.85	3.74	1.76	9.40	764
			(50.07)	(3.93)	(1.88)	(9.54)	(743.58)
IIa	white	195–198	57.47	4.11	1.99	10.26	663
			(57.03)	(4.17)	(2.15)	(10.86)	(652.87)
IIb	white	245–248	50.92	4.10	1.83	9.48	772
			(50.21)	(3.67)	(1.89)	(9.56)	(741.56)
IIIa	pale yellow	137–139	52.05	4.02	4.50	5.89	587
			(51.92)	(4.02)	(4.66)	(5.91)	(601.47)
IIIb	white	243–245	45.80	3.76	4.01	5.03	714
			(45.25)	(3.50)	(4.06)	(5.14)	(690.16)
IVa	yellow	195–198	57.34	3.96	2.73	7.49	935
			(57.28)	(3.97)	(2.90)	(7.35)	(964.53)
Va	yellow	183–185	62.60	4.02	1.64	8.91	842
			(62.51)	(4.12)	(1.74)	(8.79)	(807.39)

[a] Uncorrected values; all compounds decompose on melting.

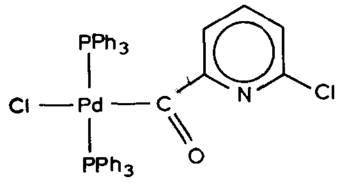
TABLE 2

SELECTED SPECTROSCOPIC DATA

Compound	IR [a] (cm^{-1})			$^{31}P-\{^1H\}$ NMR [g]		^1H NMR [g]		
	Pyridyl (1500–1600)	$\nu(M-Cl)$	Others	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	Assignment
Ia	1552m, 1527s	293m [b,c]		21.65				
Ib	1564m, 1555m, 1530s	278m		23.1	3149 [h]			
Ic	1550s, 1528s	295m		7.28		1.95(t,6)	6.7 [k]	P*Me*Ph$_2$
IIa	1550s, 1526s	298m, or 280s		31.23; 49.95	30 [i]	1.9–2.4(m,br,4)		CH_2CH_2
IIb	1562s 1526s	297s, or 280m		36.54	±1640; ±4210; ∓3 [j]	1.6–2.7(m,br,4)		CH_2CH_2
IIIa	1560s, 1527s		1535s [d] 375m [e]	28.38		3.26(s,3) 3.30(s,3)		N*Me* N*Me*
IIIb	1548w, 1529vs		1545s [d] 380m [e]	17.02	4038 [h]	3.20(s,3) 3.25(s,3)		N*Me* N*Me*
IVa	1566s, 1529s	268m [c]		28.92				
Va	1564s, 1552m	275m [c]	1664s [f], 1638m [f]	18.84				

[a] Nujol mulls. [b] $\nu(Pd-Br)$ 187 cm^{-1} in the metathetical product. [c] Assignment confirmed by their disappearance in the corresponding bromides. [d] $\nu(C=N)$ of dmtc. [e] $\nu(M-S)$. [f] $\nu(C=O)$. [g] Spectra run for $CDCl_3$ solutions. [h] $^1J(Pt,P)$. [i] $^1J(P(1),P(2))$. [j] $^1J(Pt,P(1))$, $^1J(Pt,P(2))$, $^2J(P(1),P(2)$, respectively (cf. Discussion). [k] $|^2J(P-H)+{}^4J(P-H')|$.

$[PdClR(PPh_3)]_2$ and [PdClR(dppe)] (R = 2-pyridyl-(6-Cl)) towards carbon monoxide. Attempts to insert carbon monoxide into the Pt–C σ-bond of $[PtClR(PPh_3)_2]$ and into the Pd–C σ-bond of [PdClR(dppe)] and $[PdClR(PPh_3)]_2$, by stirring CO-saturated 1,2-dichloroethane solutions of these complexes at room or higher temperature (ca. 60°C) for two days proved unsuccessful, IR spectroscopy showing that no observable reaction occurred. Stirring of a CO-saturated 1,2-dichloroethane solution of $[PdClR(PPh_3)_2]$ at room temperature, however, slowly gave the insertion product *trans*-$[PdClC(=O)R(PPh_3)_2]$ (Va):



(Va)

The reaction was monitored by IR spectroscopy on the solution, which showed two ν(C=O) bands growing up together at 1645 and 1670 cm^{-1}. The same bands are also observed in the Nujol mull IR spectrum of the isolated product Va (see Table 2). In both spectra the more intense band is at higher frequency.

The presence of two C=O vibrations is not at all unusual for α-carbon substituted carbonyl compounds. Two ν(C=O) bands were observed, for instance, for the closely related nickel derivative, *trans*-$[NiCl\overline{C(=O)C}_6H_4(3\text{-}Cl)(PEt_3)_2]$ [23], for *trans*-$[PdCl\overline{C(=O)((C_5H_3N)\text{-}C}^2)(PMePh_2)_2]$ and *trans*-$[PdCl\overline{C(=O)((C_4H_3S)\text{-}C}^2)(PPh_3)_2]$ [15]. The observed multiplicity may be due to the presence of isomers arising from rotation about the C–C bond which produce eclipsed conformers of different dipole moment. In fact, only one ν(C=O) band was reported for aroyl derivatives of Ni and Pt with unsubstituted phenyl rings [23,24], but two bands were observed for organic carbonyl compounds with substituents other than hydrogen on one α-carbon atom [26]. A *trans* structure is assigned to the acyl complex Va since only one signal is present, at 18.8 ppm, in its $^{31}P\text{-}\{^1H\}$ NMR spectrum. The IR spectrum reveals the high *trans* influence of the acyl group, in line with earlier findings [24].

Experimental

The complexes $[Pd(PPh_3)_4]$ [26], $[Pt(PPh_3)_4]$ [27] and $[Pd(dba)_2]$ (dba = dibenzylideneacetone) [28] were prepared by published methods. All other chemicals were reagent grade. Infrared spectra were recorded with Perkin–Elmer 597 (4000–200 cm^{-1}) and Beckmann IR 11 (300–120 cm^{-1}) instruments. ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded at 80 and 32 MHz, respectively, on a Varian FT-80A spectrometer operating in the FT mode. Spectra were recorded with $CDCl_3$ solutions at 30°C; ^1H chemical shifts were measured relative to internal Me_4Si, and $^{31}P\text{-}\{^1H\}$ chemical shifts were measured relative to external H_3PO_4, downfield shifts being positive. Molecular weight determinations were carried out on 1,2-dichloroethane solutions at 37°C by use of a Knauer osmometer.

Preparation of trans-$[MCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PPh_3)_2]$ ($M = Pd$, Ia; $M = Pt$, Ib)

To a solution of 2,6-dichloropyridine (0.814 g, 5.5 mmol) in oxygen-free toluene (80 ml), contained in a 250-ml two-necked flask equipped with a nitrogen supply and a reflux condenser was added $[Pd(PPh_3)_4]$ (5.78 g, 5 mmol). The mixture was stirred at 90°C for 12 h, during which off-white solid separated out. The mixture was concentrated to small volume (20 ml) and precipitation was completed by addition of diethyl ether/n-hexane (v/v = 2). The product was dissolved in CH_2Cl_2 (50 ml), a little charcoal was added, and solution was filtered, then concentrated, and diethyl ether was added to precipitate a white solid. Yield 3.5 g, 90%.

A similar procedure gave Ib, the only change being the use of a higher temperature (ca. 110°C).

Halogen metathesis of Ia

A mixture of Ia (0.5 mmol) and lithium bromide (0.22g, 2.5 mmol) was stirred in acetone at 50°C overnight. The solvent was evaporated in vacuo and the residue treated with CH_2Cl_2. After filtration, the volume was reduced and a pale-yellow crystalline solid separated. The resulting *trans*-$[PdBr\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PPh_3)_2]$ was purified by recrystallization from CH_2Cl_2/Et_2O.

Preparation of trans-$[PdCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PMePh_2)_2]$ (Ic)

To a solution of $[Pd(dba)_2]$ (0.57 g, 1 mmol) in 30 ml of nitrogen-saturated toluene in a 250 ml two-necked flask fitted with a water condenser topped by a nitrogen inlet was added methyldiphenylphosphine (0.48 g, 2.4 mmol). The solution was stirred at room temperature for ca. 0.5 h, during which time the colour turned from violet to yellow. The flask was heated on an oil bath at 90°C for 6 h. After cooling, some charcoal was added and the solution was filtered. The filtrate was evaporated to small volume (5–10 ml) and addition of diethyl ether precipitated a crude pale yellow solid. The product was purified twice by recrystallization from CH_2Cl_2/Et_2O. Yield 0.48 g, 65%.

Preparation of $[MCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(Ph_2CH_2CH_2PPh_2)]$ ($M = Pd$, IIa; $M = Pt$, IIb)

A solution of Ia (1.17 g, 1.5 mmol) in dichloromethane was stirred overnight at room temperature with 1,2-bis(diphenylphosphino)ethane (0.716 g, 1.8 mmol). The volume was reduced to 10 ml and the white complex was precipitated by adding diethyl ether. The product was recrystallized from CH_2Cl_2/Et_2O. Yield 0.88 g, 90%.

The same procedure was followed for IIb.

Preparation of $[M(dmtc)\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PPh_3)]$ ($M = Pd$, IIIa; $M = Pt$, IIIb; dmtc = dimethyldithiocarbamate)

A solution of $[Na(dmtc)]\cdot 2H_2O$ (0.10 g, 0.6 mmol) in ca. 10 ml of methanol was added to the pyridyl complex Ia (0.395 g, 0.5 mmol) in 50 ml of CH_2Cl_2. Solid NaCl immediately began to precipitate. After stirring overnight, the mixture was evaporated to dryness and the crude yellow solid treated with CH_2Cl_2 and little charcoal. Concentration of the filtered solution and addition of n-hexane caused precipitation of pale-yellow crystals of the complex IIIa (0.22 g, 73%).

The same procedure was used for preparation of the Pt analogue IIIb.

Preparation of $[PdCl\{C_5H_3N(6\text{-}Cl)\text{-}C^2\}(PPh_3)]_2$ *(IVa)*

A heterogeneous mixture of Ia (0.79 g, 1 mmol) and H_2O_2 30% (1.5 ml) in 50 ml of acetone was stirred for 12 h at room temperature. The yellow microcrystalline solid was then filtered off and washed with acetone to remove $OPPh_3$ and the excess of H_2O_2. A solution of the product in CH_2Cl_2 (30 ml) was treated with charcoal then filtered. The filtrate was concentrated and the yellow product precipitated with diethyl ether (yield 80%).

The dimeric compound IVa regenerates Ia upon addition of excess PPh_3 to its dichloromethane solution. Ca. 5 min after the addition of PPh_3, the initially yellow solution became colourless, and the course of the reaction was confirmed by monitoring of the IR spectrum in the 1500–1600 cm^{-1} region (see Table 2).

Preparation of $trans\text{-}[PdCl\{\overline{C(=O)C_5H_3N(6\text{-}Cl)\text{-}C}^2\}(PPh_3)_2]$ *(Va)*

Carbon monoxide was bubbled slowly for 20 h through a solution of Ia (0.39 g, 0.5 mmol) in 30 ml of 1,2-dichloroethane. The volume of the yellow solution was then reduced and the product was precipitated by addition of Et_2O. Recrystallization was from $1,2\text{-}Cl_2C_2H_4/Et_2O$ (yield 0.34 g, 84%).

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