Coupling of Arylamines with Coordinated Arylazopyrimidines in Palladium(II) Complexes

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2-(Arylazo)pyrimidine (**1**) reacts with palladium chloride and gives Pd(aapm)Cl_2 (**2**) which undergoes a palladium(II)-mediated novel carbon–nitrogen bond formation reaction of the aromatic amines to the *ortho*-C–H function of the pendant aryl ring in the coordinated 2-(arylazo)pyrimidine. The reactant, Pd(papm)Cl_2 (**2a**) and the product, Pd(papm-N-C_6H_4-OCH_3-*p*)Cl (**5a**) have been characterised by X-ray crystal structure. The coupled products exhibit low energy transitions (NIR region) unlike the parent complex, Pd(aapm)Cl_2. The cyclic voltammogram shows an oxidation couple at positive potential to SCE. The EHMO calculation suggests that the spectral feature in Pd(aapm)Cl_2 (**2**) is due to the MLCT [d(Pd)→π*(azo)] whereas in Pd(aapm-N-C_6H_4-X-*p*)Cl (**3**–**6**) the transition at the NIR region is due to the intravalence charge transfer (IVCT) transition.

Introduction

Arylazoheterocycles are light-sensitive, redox-active, and efficient colorant materials.[1−9] Presence of an arylazo group at the *ortho* position of the N-heterocycles constitute an azoimine, −N=N−C=N−, function.[7−9] They have successfully been used to stabilise the low-valent metal redox state.[7−17] The coordination of arylazoheterocycles to a metal centre alter the electrophilic character of the ligand and provides a fascinating area in the metal-assisted organic synthesis. This has been observed in the metal complexes of 2-(arylazo)pyridines.[18−25] The complexes undergo different organic transformations at the pendant aryl ring such as hydroxylation,[18−20] thiolation,[21−23] and the C−N coupling[24,25] reaction with aromatic amines. This has encouraged us to design 2-(arylazo)pyrimidines [aapm (**1**)][13,14,19] that is more π-acidic than 2-(arylazo)pyridine due to the π-acidity order, pyrimidine > pyridine. Copper(I)[13] and isomers of ruthenium(II) complexes[14] of **1** have been reported from our group. Palladium(II) forms [2-(arylazo)pyrimidine]dichloropalladium(II) [Pd(aapm)Cl_2 (**2**)] and its reaction with OH^- in air or Tollen's reagent gives (azophenolatopyrimidine)palladium(II) complex.[19] This is believed to be formed by the hydroxylation of the C−H bond *ortho* to the azo group of 2-(arylazo)pyrimidine. Heterocyclic bases (e.g., pyridine and derivatives R-Py) react with Pd(aapm)Cl_2 and substitute the ligand followed by isomerisation to *trans*-Pd(R-Py)$_2Cl_2$.[26] In continuation of our work to explore the reactivity of palladium−aapm complexes, we discuss in this article the palladium(II)-mediated C−N coupling reaction of aromatic amines to the *ortho*-C−H function of the pendant aryl ring in the coordinated 2-(arylazo)pyrimidine. The reactant and product have been characterised by X-ray crystallography. The coupled products exhibit different electronic and redox behaviour from that of the reactants and have been accounted for by EHMO calculations.

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Results and Discussion

Synthesis of Parent Complexes

The general abbreviation of 2-(arylazo)pyrimidine is aapm (**1**). 2-(Phenylazo)pyrimidine [papm (**1a**)], 2-(*p*-tolylazo)pyrimidine [tapm (**1b**)], and 2-(*p*-chloro-phenylazo)pyrimidine [Clpapm (**1c**)] are three ligands used in this work. They act as *N*,*N*′-bidentate chelators with an azoimine function, −N=N−C=N−, where N refers to N(8)(azo) and *N*′ refers to N(3)(pyrimidine). The reaction of aapm with Pd(MeCN)$_2Cl_2$ in MeCN has yielded orange-red Pd(aapm)Cl_2 (**2**) in high yield.[19,27]

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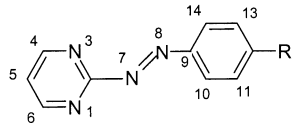


a: R = H, (papm)

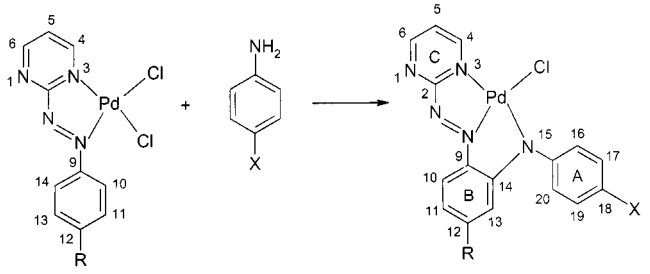
b: R = H, 12-Me (*p*-tapm)

c: R = H, 12-Cl (*p*-Clpapm)

aapm, **1**

The C−N Coupling Reaction

Addition of $ArNH_2$ (in 1:1 stoichiometry) in an MeCN suspension of Pd(aapm)Cl_2 (**2**) under refluxing conditions, changes the intense orange-red colour to greenish-brown. Chromatographic purification of the reaction mixture separates an orange-brown band. The orange-brown band has been identified as an amine product coupled to Pd(aapm)Cl_2 and is abbreviated Pd(aapm-N-C_6H_4-X-*p*)Cl [where X= H (**3**), Me (**4**), OMe (**5**), Cl (**6**)]. The reaction is shown in Equation (1). The arylamination takes place at the *ortho* position of the aryl ring (B ring) of aapm to the azo function and forms a palladium(II) complex of tridentate *N*,*N*′,*N*′′-chelating ligand [where N is N(8)(azo); *N*′ is N(3)(pyrimidine); *N*′′ is N(15)(arylamine)]. Free ligands do not couple with arylamines even if forced but they react smoothly in the palladium(II) complex.



2 Pd(aapm-N–C_6H_4–X-*p*)Cl (**3** - **6**) (1)

Spectral Studies

Infrared spectra of Pd(aapm)Cl_2 (**2**) show two distinct Pd−Cl stretches [ν(Pd−Cl) = 340, 360 cm^{-1}] in agreement with *cis*-$PdCl_2$ configuration.[19,27] A sharp single band at 1400−1415 cm^{-1} corresponding to $\nu_{N=N}$ in the ligand is shifted to 1380−1385 cm^{-1} in Pd(aapm)Cl_2. This lowering of the frequency is due to N-coordination.[18] In the coupled products, Pd(aapm-N-C_6H_4-X-*p*)Cl (**3**−**6**), $\nu_{N=N}$ appears at 1290−1300 cm^{-1}; this significant reduction in azo stretching may be due to the intramolecular charge delocalisation from the fused N-C_6H_4-X-*p* fragment to the azo function (vide infra). A single stretch at 340−350 cm^{-1} in **3**−**6** supports the presence of a Pd−Cl bond. A chloroform solution of Pd(aapm)Cl_2 exhibits a strong absorption[19] at ca. 425 nm. On comparison with the free ligand solution spectra,[13] the transition has been assigned to the MLCT band which is also supported by an EHMO calculation (vide infra). The spectral structure changes abruptly in Pd(aapm-N-C_6H_4-X-*p*)Cl (**3**−**6**) and exhibits an intense band in the NIR region (750−1100 nm) with five/six well-defined transitions (Figure 1). The spectroscopic data are collected in Table 1. The transitions have been accounted from EHMO calculation and are assigned to HOMO→LUMO transitions where the HOMO has a major share from the arylamine group and the LUMO is dominated by the azo group (vide infra). The observed trend of the band maxima (λ_{max}) for the substituent in the aryl ring follows as *p*-chloroaniline (**6**) < aniline (**3**) < *p*-toluidine (**4**) < *p*-anisidine (**5**). The electron-donating substituent in the X-C_6H_4-N- fragment increased the energy of the HOMO[27,28] and in *p*-anisidine the energy was maximised. In *p*-choloroaniline the energy of the HOMO was reduced due to the electron-withdrawing effect of the Cl group. The substituent (R) in the arylazopyrimidine [R-C_6H_4-N=N-$C_4H_3N_2$ (**1**)] fragment also shifted the band maxima in the order Pd(Clpapm-N-C_6H_4-X-*p*)Cl (**c**) > Pd(papm-N-C_6H_4-X-*p*)Cl (**a**) > Pd(tapm-N-C_6H_4-X-*p*)Cl (**b**). This is due to the lowering of the energy of the LUMOs in **c** compared to **a** due to the electron-withdrawing power of Cl. The reverse case is seen in the complexes **b** due to the +I effect of the Me group that has a destabilising effect on the LUMOs.

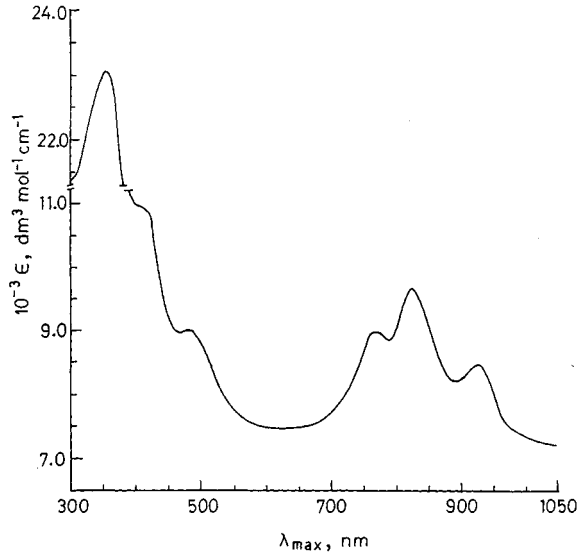


Figure 1. Electronic spectra of Pd(papm-N-OCH_3-*p*)Cl (**5a**) in $CHCl_3$

The ^{1}H NMR spectra of the complexes are compared in order to determine the bonding mode and stereochemistry. The ^{1}H NMR spectra of the ligands aapm (**1**) and Pd(aapm)Cl_2 (**2**) were reported from our group.[13,26] The signals were assigned on the basis of chemical shifts, spin-spin interaction and their effect on substitution. In Pd(aapm)Cl_2 the signals in general are downfield shifted compared to free ligand values.[26] Pd(aapm-N-C_6H_4-X-*p*)Cl show complex NMR spectra. The *N*-aryl (A-ring) and azoaryl (B-ring) proton signals appear on the upfield side. The effect of the substituent X (X-C_6H_4-N) on the signal movement of the arylamine protons (A-ring protons: 16-H to 20-H) is in accordance with the electronic property of X. It is observed that the electron-donating substituent (Me/OMe) moves the signals upfield while the electron-withdrawing group Cl moves them downfield with reference to

Table 1. Solution spectral and cyclic voltammetric data

Compound	Electronic spectroscopic data[a] λ_{max} [nm] (ε [$dm^3 \cdot mol^{-1} \cdot cm^{-1}$])	Cyclic voltammetric data[b] $E_{1/2}$ [V] (ΔE_p [mV]) Oxidation $E^1_{1/2}$	Reduction $-E^2_{1/2}$	$-E^3_{1/2}$	$-E^4_{1/2}$
Pd(papm-N-C_6H_5)Cl (**3a**)	914 (6289), 819 (7419), 760 (6353), 474 (5975)[c], 410 (10327), 340 (23019)	1.174 (107)	0.347 (88)	0.873 (140)	0.982 (167)
Pd(papm-N-C_6H_4-Me−*p*)Cl (**4a**)	921 (6518), 820 (7619), 761 (6925), 479 (6419)[c], 409 (8344), 345 (18295)	1.275 (105)	0.364 (90)	0.834 (160)	1.103 (100)
Pd(papm-N-C_6H_4-OCH_3−*p*)Cl (**5a**)	926 (8428), 821 (9648), 765 (8963), 473 (9046)[c], 416 (10919), 344 (23127)	1.021 (100)	0.627 (75)	0.958 (160)	1.109 (110)
Pd(papm-N-C_6H_4-Cl−*p*)Cl (**6a**)	901 (6531), 815 (7353), 755 (6689), 470 (6452)[c], 410 (8468), 343 (16846)	1.185 (91)	0.316 (90)	0.751 (110)	1.048[d]
Pd(tapm-N-C_6H_5)Cl (**3b**)	878 (6285), 792 (7532), 723 (6375), 470 (6014)[c], 409 (10469), 340 (22310)	1.042 (95)	0.382 (100)	0.943 (120)	1.192 (140)
Pd(tapm-N-C_6H_4-Me−*p*)Cl (**4b**)	882 (6687), 798 (7728), 733 (7081), 466 (7715)[c], 395 (11649), 340 (23337)	1.129 (100)	0.435 (110)	0.889 (90)	1.124 (120)
Pd(tapm-N-C_6H_4-OCH_3−*p*)Cl (**5b**)	894 (9323), 811 (11232), 756 (10426), 475 (11384)[c], 390 (15648), 340 (23254)	1.005 (98)	0.425 (92)	0.865 (120)	1.114 (110)
Pd(tapm-N-C_6H_4-Cl−*p*)Cl (**6b**)	865 (8736), 792 (10362), 722 (9840), 474 (10243)[c], 394 (1612 2), 341 (28015)	1.190 (105)	0.389 (94)	0.783 (100)	1.069[d]
Pd(Clpapm-N-C_6H_5)Cl (**3c**)	918 (6715), 825 (7830), 765 (7129), 476 (8117)[c], 411 (10925), 340 (22833)	1.000 (130)	0.422 (80)	0.825 (77)	1.107 (175)
Pd(Cllpapm-N-C_6H_4-Me−*p*)Cl (**4c**)	922 (8097), 828 (8995), 768 (8143), 481 (9660)[c], 405 (14475), 344 (26010)	1.115 (140)	0.436 (85)	0.832 (82)	1.120 (180)
Pd(Clpapm-N-C_6H_4-OCH_3−*p*)Cl (**5c**)	930 (1530)[c], 830 (1728), 772 (1590), 407 (3850), 309 (17822)	0.957 (160)	0.415 (75)	0.761 (70)	1.004 (200)
Pd(Clpapm-N-C_6H_4-Cl−*p*)Cl (**6c**)	905 (6792), 818 (7840), 760 (7145), 478 (7824)[c], 409 (11455), 336 (23121)	0.945 (150)	0.365 (83)	0.745 (70)	0.985 (170)

[a] Solvent $CHCl_3$. [b] Solvent MeCN, supporting electrolyte Bu_4NClO_4, Pt-disk milli working electrode, Pt-wire auxiliary electrode, reference electrode SCE, at 298 K. [c] Shoulder. [d] E_{pc}.

the unsubstituted system. A similar situation is also observed for the substituent R on the arylazopyrimidine (R-C_6H_4-N=N-$C_4H_3N_2$) protons of the B-ring (10-H to 13-H). The cross interactions i.e., the effect of substituent X at the *N*-aryl ring on the azoaryl protons or vice versa are not remarkable. Azoaryl signals (10-H to 13-H) are severely affected in Pd(aapm-N-C_6H_4-X-*p*)Cl relative to Pd(aapm)Cl_2 and are shifted upfield by 0.2−1.0 ppm. Pyrimidine protons (4-H to 6-H of C-ring) in **3**−**6** are shifted upfield by 0.1−0.5 ppm compared to the parent complex Pd(aapm)Cl_2 and are hardly affected by the substituents in the aryl rings (X or R). Coupling of arylamine with the aryl part of aapm (B-ring) has changed the electronic behaviour of the molecule. The azopyrimidine function is electron-deficient while the *N*-aryl (ring A) is a σ-donor and may cause an intramolecular charge-transfer transition. This may be the reason for the large upfield shifting of the arylazopyrimidine proton signals (4-H to 13-H). Solution electronic spectral properties also support this behaviour (vide supra).

X-ray Structure Studies

The X-ray structures of Pd(papm)Cl_2 (**2a**) and Pd(papm-N-C_6H_4-OCH_3-*p*)Cl (**5a**) have been determined. Perspective molecular views are shown in Figures 2 and 3 and the selected bond parameters are listed in Tables 2 and 3.

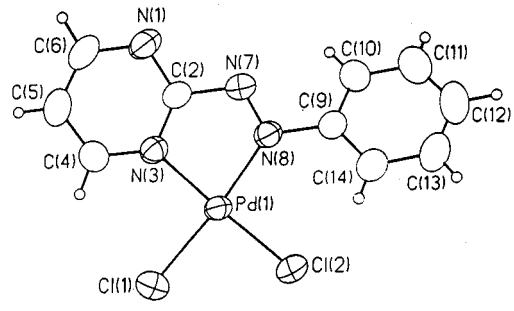


Figure 2. Drawing of Pd(papm)Cl_2 (**2a**), showing the atom numbering scheme; non-hydrogen atoms are represented by their 50% probability ellipsoids

a. Geometrical Features

The Pd(papm)Cl_2 has a *cis*-$PdCl_2$ configuration (Figure 2). The asymmetric unit of the crystal lattice consists of two molecules. These two molecules have parallel cores with a Pd···Pd separation of 3.4201(5) Å. The molecular packing diagram viewed down the *a* axis shows a Pd···Pd separation between asymmetric units of 3.9881(4) Å and the pendant phenyl rings are oriented in a parallel manner to ensure some sort of π-interaction. The packing also exhibits a benzene molecule at the special position and a weak Pd···Cl nonbonding intermolecular interaction (3.3−3.4 Å) where

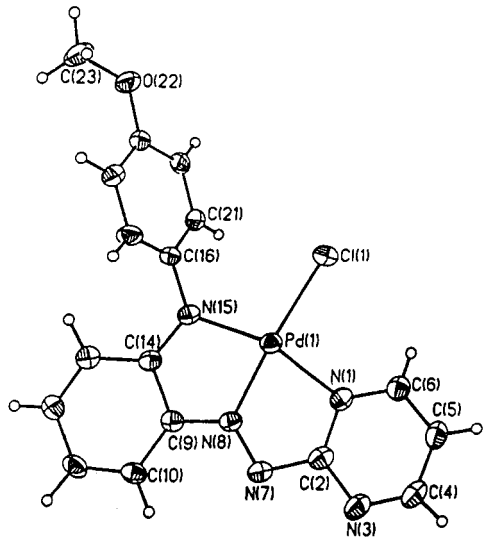


Figure 3. Drawing of Pd(papm-N-C_6H_4-OCH_3-*p*)Cl (**5a**), showing the atom numbering scheme; non-hydrogen atoms are represented by their 50% probability ellipsoids

Table 2. Selected bond lengths [Å] and angles [°] and their estimated standard deviations for **2a**

Distances			
Pd(1)−N(3)	2.014(3)	Pd(1A)−N(3A)	2.009(3)
Pd(1)−N(8)	2.041(3)	Pd(1A)−N(8a)	2.015(3)
Pd(1)−Cl(1)	2.2882(9)	Pd(1A)−Cl(1A)	2.2845(9)
Pd(1)−Cl(2)	2.2800(9)	Pd(1A)−Cl(2A)	2.2808(9)
N(7)−N(8)	1.260(3)	N(7A)−N(8a)	1.260(3)
C(2)−N(3)	1.344(4)	C(2)−N(7)	1.408(4)
C(2A)−N(3A)	1.346(4)	C(2A)−N(7A)	1.407(4)
Angles			
N(3)−Pd(1)−N(8)	77.74(10)	N(3A)−Pd(1A)−N(8A)	77.39(11)
Cl(1)−Pd(1)−Cl(2)	89.50(3)	Cl(1A)−Pd(1A)−Cl(2A)	90.93(4)
N(3)−Pd(1)−Cl(1)	93.98(8)	N(3A)−Pd(1A)−Cl(1A)	94.89(9)
N(3)−Pd(1)−Cl(2)	174.76(8)	N(3A)−Pd(1A)−Cl(2A)	171.90(8)
N(8)−Pd(1)−Cl(2)	98.82(8)	N(8A)−Pd(1A)−Cl(2A)	96.90(7)
N(8)−Pd(1)−Cl(1)	171.68(8)	N(8A)−Pd(1A)−Cl(1A)	172.15(8)

Table 3. Selected bond lengths [Å] and angles [°] and their estimated standard deviations for **5a**

Distances			
Pd(1)−N(3)	2.029(4)	C(2)−N(7)	1.379(5)
Pd(1)−N(8)	1.937(3)	Pd(1)−Cl(1)	2.302(1)
Pd(1)−N (15)	2.026(3)	C(9)−N(8)	1.336(5)
N(7)−N(8)	1.315(4)	C(14)−N(15)	1.333(5)
C(2)−N(3)	1.362(5)		
Angles			
N(3)−Pd(1)−N(8)	78.86(14)	N(8)−Pd(1)−Cl(1)	176.29(11)
N(8)−Pd(1)−N(15)	81.76(14)	N(1)−N(8)−N(7)	120.6(3)
N(3)−Pd(1)−Cl(1)	97.52(11)	Pd(1)−N(3)−C(2)	110.0(3)
N(15)−Pd(1)−Cl(1)	101.88(10)	Pd(1)−N(15)−C(14)	111.5(3)
N(3)−Pd(1)−N(15)	160.59(14)	Pd(1)−N(8)−C(9)	116.4(2)

Pd and Cl belong to two different molecules in the asymmetric unit. The two independent molecules are chemically similar. The PdN_2Cl_2 coordination sphere is planar with no atom deviating more than 0.06 Å from the mean plane. The chelate ring is planar (deviation < 0.04 Å) and the bond angle lies in the range 77.6±2°. This deviates from ideal square-planar angles. The Cl−Pd−Cl angle is ca. 90.2°. The pendant phenyl ring is no longer in plane with the chelated fragment and is twisted by ca. 42.5°.

The crystallographic asymmetry unit of Pd(papm-NC_6H_4-OCH_3-*p*)Cl contains 25 non-hydrogen atoms, of which 17 lie in a plane nearly perpendicular to the crystallographic *c* axis. These atoms comprise of two chelate rings, the aromatic groups fused to them, and the Pd and Cl atoms. The remaining atoms of the asymmetric unit comprise the methoxyphenyl group. The Pd atom lies in the square plane defined by the N_3Cl donor centres (deviation 0.02 Å). Two chelate planes Pd,N(3),C(2),N(7),N(8) (deviation < 0.01 Å) and Pd,N(15),C(14),C(9),N(8) (deviation < 0.01 Å) are coplanar and the chelate angles are 78.86(14) and 81.76(14)°, respectively. The pendant methoxyphenyl ring (A ring) is inclined at an angle of 54.99(15)° with the principal plane of 17 atoms.

b. Bond Parameters

In Pd(papm)Cl_2 the Pd−N(azo) bond length is slightly longer (ca. 2.03 Å) than that of the Pd−N(pyrimidine) (ca. 2.01 Å). This is the reverse in the case of other complexes. In copper(I) and ruthenium(II) complexes of papm, the M−N(azo) distance is significantly shorter than that of the M−N(pyrimidine) distance [Cu(papm)$_2$(ClO_4):[13] Cu−N(azo) 1.99 Å, Cu−N(pyrimidine) 2.03 Å; Ru(papm)$_2$$Cl_2$:[14] Ru−N(azo) 2.00 Å; Ru−N(pyrimidine) 2.06 Å]. This is due to π-back bonding involving metal t_2 and ligand π*(azo) orbitals.[7,13,14,29] The N=N bond length is 1.260(3) Å and is comparable with that of the copper(I)[13] complex but shorter than that of the ruthenium(II)[14] complexes. Efficient π-back bonding in (arylazopyrimidine)ruthenium(II) complexes enhances the N=N distance.[14] In Pd(papm-NC_6H_4-OMe-*p*)Cl the Pd−N(azo) [Pd−N(8)],

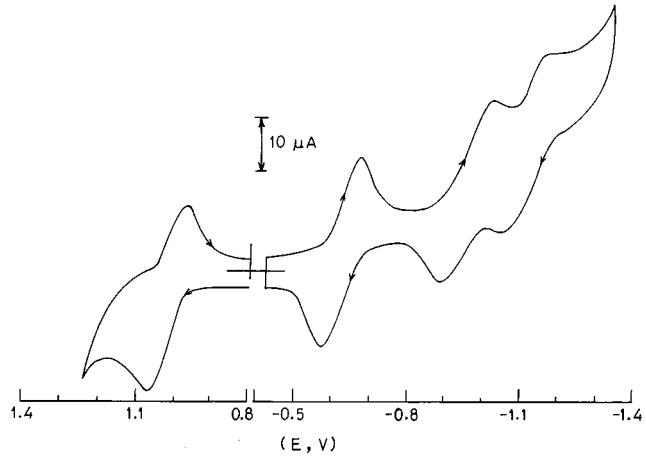


Figure 4. Cyclic voltammogram of Pd(papm-N-C_6H_4-OCH_3-*p*)Cl (**5a**) in MeCN (0.1 M Bu_4NClO_4) at 298 K

Pd−N(pyrimidine) [Pd−N(3)], and Pd−N(arylamine) [Pd−N(15)] distances are 2.028(4), 1.938(3), and 2.028(4) Å, respectively. The N=N length is 1.314(4) Å. The N=N distance is not available for the free ligand; however, the data available in some azo ligands[30−32] suggest that it is ca. 1.25 Å. In this case the N=N distance in **5a** is unusually long compared to the parent complex **2a**. This elongation may be due to intramolecular charge delocalisation from the arylamine fragment (vide supra) to the azopyrimidine.

Electrochemistry

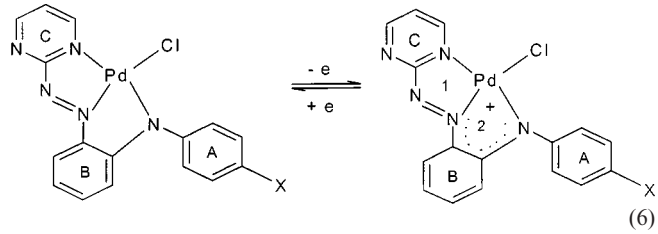
The redox behaviour of **3**−**6** in acetonitrile solution was examined by cyclic voltammetry at a Pt-disk working electrode and the potentials are reported with reference to the SCE. The results are given in Table 1, and a representative voltammogram is shown in Figure 4. Pd(aapm)Cl_2 does not exhibit any redox response positive to the SCE and on the negative side a quasireversible redox couple ($\Delta E_P > 130$ mV) followed by an irreversible response at potential > -1.0 V is observed. Pd(aapm-N-C_6H_4-X-*p*)Cl (**3**−**6**) exhibited four successive redox couples: one of them at high positive potential (1.0−1.3 V) and three at the negative side of the SCE. Arylazopyrimidines are reduced at the negative potentials, −1.0 to −1.4 V.[13,14] The reduction is regarded as the electron accommodation in the LUMO characterised by the azoimine function. There are four successive redox-accessible levels in the azoimine function [Equations (2) to (5)]. In the present examples, three negative redox couples may correspond to three reductions [Equations (2) to (4)]. However, the couple at the positive potential is difficult to assign as Pd^{II} is redox-inactive. We suggest that this couple is due to oxidation of the ligand at the easily oxidisable azoarylamine chelated centre (chelate ring 2) [Equation (6)]. The first three redox couples [Equations (2), (3), and (6)] are quasireversible (ΔE_P = 70−100 mV) and the fourth response [Equation (4)] is irreversible in nature ($\Delta E_P > 130$ mV).

(2)

(3)

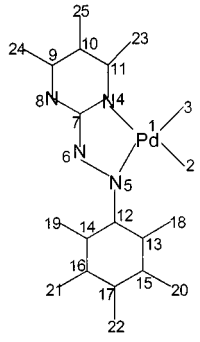
(4)

(5)

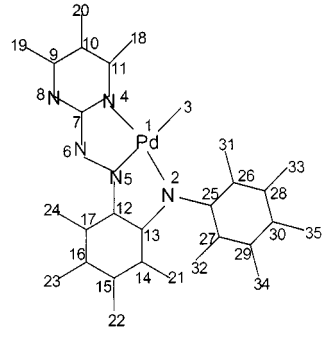


(6)

Table 4. Relative percentages of atomic contributions to the MOs of the complexes in **i** and **ii**



i



ii

% Contribution MO	Energy [eV]	Pd	N (pyrimidine)	N=N (azo)	azoaryl	arylamine
structure (**i**)						
45a (HOMO−1)	−11.781	93				
46a (HOMO)	−11.569	83	2	8		
47a (LUMO)	−10.714	9	1	67	7	
48a (LUMO+1)	−9.259		99			
structure (**ii**)						
57a (HOMO−2)	−11.623	84		6		
58a (HOMO−1)	−11.591	81	4	4		
59a (HOMO)	−11.457	37				53
60a (LUMO)	−10.724	9	9	68	13	
61a (LUMO+1)	−9.260		98			

The oxidation of coordinated *ortho*-phenylenediamine to semibenzoquinone diimine and benzoquinone diimine are known in the literature and support this observation.[34,35] The redox potential varies in the usual manner with the substituent at the *N*-aryl (A-ring) and azoaryl (B-ring) ring.[13,19]

Electronic Structure − EHMO Calculation

In order to have an insight into the difference in electronic behaviour of Pd(aapm)Cl_2 and Pd(aapm-N-C_6H_4-X-*p*)Cl towards their spectral and electrochemical properties, the MO calculations have been performed in the framework of extended Hückel formalism on a model complex as shown in structures **i** and **ii** (shown in Table 4). Crystallographic data were used as the parameters for bond lengths and bond angles. The relative percentages of the atomic contributions to the MOs are given in Table 4. In complex

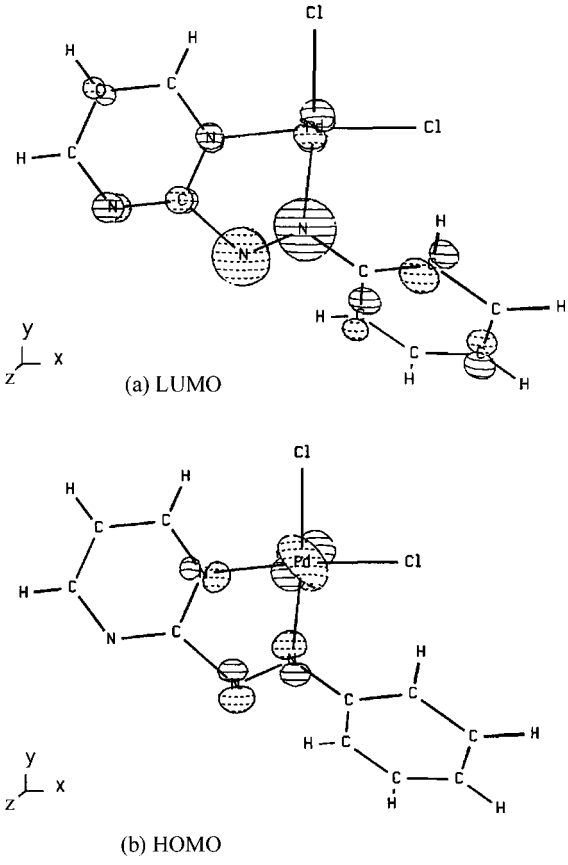


Figure 5. LUMO and HOMO of Pd(papm)Cl_2

Pd(aapm)Cl_2 the LUMO (47a) (Figure 5, a) is ligand-dominated with 67% character of azo (N=N), 5% of pyrimidine-N and a small contribution (9%) from the Pd d_{yz} orbital. The HOMO (46a) is mainly a metal orbital (83%) (Figure 5, b) and contributed from d orbitals (total 78%, of which d_z^2 41% and d_{xy} 37%) and a small part of the 4s orbital (5%). In complex Pd(aapm-N-Ar)Cl the LUMO

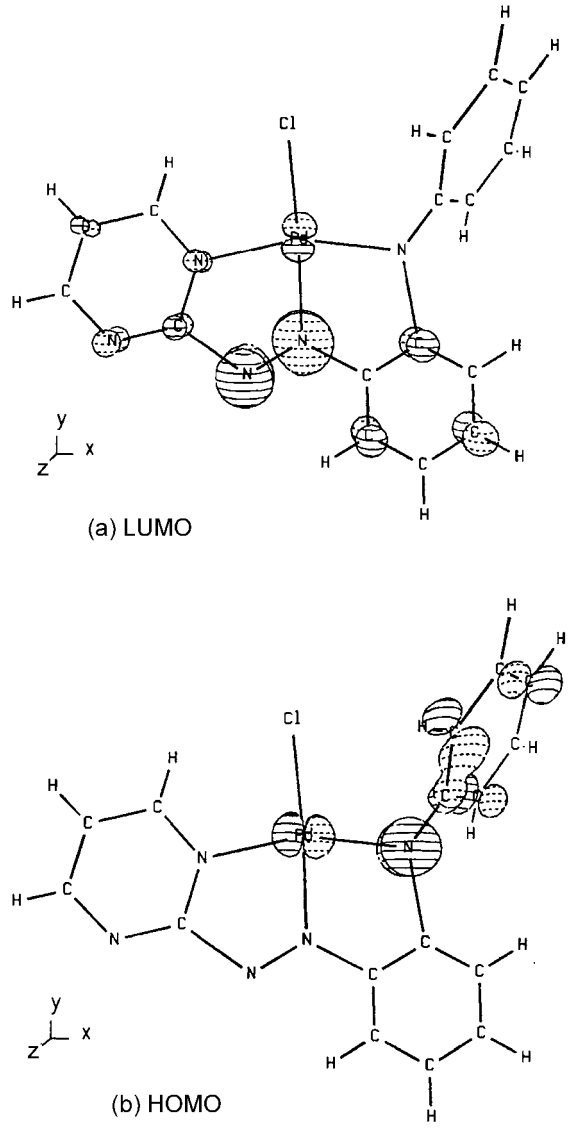


Figure 6. LUMO and HOMO of Pd(papm-N-C_6H_5)Cl

(60a) (Figure 6, a) is characterised by the azo group (68%), pyrimidine group (22%), and a small part of the metal orbital (d_{yz}, 9%). The HOMO (59a) (Figure 6, b) is computed from the admixture of the metal d_{xz} orbital (37%) and the *N*-aryl (ring A) (53%) and contributes to 90% of the character of the function.

Some experimental findings may be rationalised on the basis of EHMO results. The solution electronic spectra of complex **2** may exhibit a HOMO→LUMO (46a→47a) transition corresponding to the MLCT band. The first reduction will certainly be localised due to electron accommodation at the LUMO (47a) [π*(azo)] and the second electron will enter at the LUMO+1 (48a), which is purely pyrimidine in character (99%). Thus, the second reduction is irreversible in nature. The spectral and electrochemical behaviour of Pd(aapm-NAr)Cl is entirely different from the parent complex. The low-energy spectral band is associated with a HOMO→LUMO (59a→60a) charge transfer.[28,35,36] The HOMO is from a major portion (53%) of the N−Ar

group (ring A) and the LUMO shares 68% azo and 22% pyrimidine character. Thus, the transition is characterised as an intravalence charge-transfer transition (IVCT). Other spectral transitions may be characterised as HOMO−1 (58a)→LUMO (60a), HOMO−2 (57a)→LUMO (60a), HOMO (59a)→LUMO+1 (61a), etc. The redox behaviour at a positive potential to SCE may correspond to electron extraction from the HOMO (59a), which has a major share from the N−Ar group. The reductions correspond to sequential electron feeding at the LUMO (60a); LUMO+1 (61a) and LUMO+2 (62a).

Experimental Section

General Remarks: 2-(Arylazo)pyrimidines were prepared by the reported procedure.[13] $PdCl_2$ was purchased from Arora Matthey. Aniline, *p*-toluidine, *p*-anisidine, *p*-chloroaniline were received from the Sisco Research Lab. The purification of acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were done as before.[13] Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All other chemicals and solvents were of reagent grade and were used without further purification. Commercially available SRL silica gel (60−120 mesh) was used for column chromatography. Spectroscopic data were obtained using the following instruments: UV/Vis/NIR spectra: JASCO UV/Vis/NIR model V 570 and Hitachi U-3501. IR spectra (KBr disk, 4000−200 cm^{-1}): FTIR JASCO model 420. ^1H NMR spectra: Bruker (AC) 300 MHz FTNMR spectrometer. Electrochemical measurements were performed using a computer-controlled PAR model 270 VERSASTAT Electrochemical instruments with Pt-bead and GC-electrodes. All measurements were carried out under dinitrogen at 298 K with reference to a saturated calomel electrode (SCE) in acetonitrile. The reported potentials are uncorrected for junction potential.

Preparation of the Complexes: The dichloro[2-(arylazo)pyrimidine]-palladium(II) [Pd(aapm)Cl_2 (**2**)] complexes were prepared by a literature method[19] in the yield of 85−90%. A representative case is given in detail.

a. Dichloro[2-(phenylazo)pyrimidine]palladium(II) [Pd(papm)Cl_2 (2a)]: To an MeCN (10 mL) solution of $PdCl_2$ (0.18 g, 1.01 mmol), 2-(phenylazo)pyrimidine [papm (**1a**)] (0.2 g, 1.09 mmol) was added dropwise and the mixture was stirred for 1 h. The orange-red precipitate was filtered and washed with MeOH. The dried mass was dissolved in a minimum vol. of CH_2Cl_2 and purified by chromatography on a silica gel (60−120 mesh) column and the desired orange-red band was eluted with MeCN/benzene (30% v/v).Yield 85%. ***NOTE:*** Benzene is carcinogenic and precaution must be taken during its use!

b. Chloro[(2-(14-imidophenyl)phenylazo)pyrimidine-*N*,*N*′,*N*′′]palladium(II) [Pd(papm-N-C_6H_5)Cl (3a)]: To an acetonitrile solution (15 mL) of Pd(papm)Cl_2 (0.3 g, 0.83 mmol), an aniline (0.1 g, 1.08 mmol) solution in acetonitrile (10 mL) was slowly added. The reaction mixture was stirred and refluxed continuously for 4 h and the colour of the solution changed gradually from orange-red to greenish-brown. The solution was concentrated in air, and the residue was washed thoroughly first with water (2 × 5 mL) and then with 50% aqueous ethanol (3 × 5 mL). The residue was dissolved in dichloromethane (10 mL) and the solution was column-chromatographed on silica gel prepared in benzene. An orange-brown band was eluted with an acetonitrile/benzene (1:9) mixture. The eluted solution, on concentration in vacuo, gave a pure orange-brown compound, isolated in 45% yield. The orange-brown product is the desired coupled product, Pd(papm-N-C_6H_5)Cl. Pd(papm-N-C_6H_5)Cl (**3a**): $C_{16}H_{12}ClN_5Pd$ (416.2): calcd. C 46.16, H 2.89, N 16.83; found C 46.25, H 2.95, N 16.70. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 370, $\nu_{N=N}$ 1296, $\nu_{C=N}$ 1585. All the other compounds were prepared according to the same procedure, the yields varied between 40 and 65% for the orange-brown compound. Pd(papm-N-C_6H_4-Me-*p*)Cl (**4a**): $C_{17}H_{14}ClN_5Pd$ (430.2): calcd. C 47.45, H 3.26, N 16.28; found C 47.35, H 3.32, N 16.30. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 368, $\nu_{N=N}$ 1295, $\nu_{C=N}$ 1580. Pd(papm-N-C_6H_4-OCH_3-*p*)Cl (**5a**): $C_{17}H_{14}ClN_5OPd$ (446.2): calcd. C 45.75, H 3.14, N 15.69; found C 45.85, H 3.20, N 15.75. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 366, $\nu_{N=N}$ 1290, $\nu_{C=N}$ 1577. Pd(papm-N-C_6H_4-Cl-*p*)Cl (**6a**): $C_{16}H_{11}Cl_2N_5Pd$ (450.6): calcd. C 42.63, H 2.44, N 15.54; found C 42.50, H 2.51, N 15.63. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 365, $\nu_{N=N}$ 1298, $\nu_{C=N}$ 1580. Pd(tapm-N-C_6H_5)Cl (**3b**): $C_{17}H_{14}ClN_5Pd$ (430.2): calcd. C 47.45, H 3.26, N 16.28; found C 47.60, H 3.35, N 16.37. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 365, $\nu_{N=N}$ 1290, $\nu_{C=N}$ 1580. Pd(*p*-tapm-N-C_6H_4-Me-*p*)Cl (**4b**): $C_{18}H_{16}ClN_5Pd$ (444.2): calcd. C 48.66, H 3.60, N 15.77; found C 48.84, H 3.68, N 15.85. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 371, $\nu_{N=N}$ 1288, $\nu_{C=N}$ 1585. Pd(tapm-N-C_6H_4-OCH_3-*p*)Cl (**5b**): $C_{18}H_{16}ClN_5OPd$ (460.2): calcd. C 46.96, H 3.48, N 15.22; found C 46.89, H 3.56, N 15.30. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 370, $\nu_{N=N}$ 1285, $\nu_{C=N}$ 1578. Pd(tapm-N-C_6H_4-Cl-*p*)Cl (**6b**): $C_{17}H_{13}Cl_2N_5Pd$ (464.6): calcd. C 43.93, H 2.79, N 15.07; found C 43.75, H 2.85, N 15.15. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 367, $\nu_{N=N}$ 1280, $\nu_{C=N}$ 1585. Pd(Clpapm-N-C_6H_5)Cl (**3c**): $C_{16}H_{11}Cl_2N_5Pd$ (450.6): calcd. C 42.63, H 2.44, N 15.54; found C 42.40, H 2.50, N 15.62. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 365, $\nu_{N=N}$ 1295, $\nu_{C=N}$ 1580. Pd(Clpapm-N-C_6H_4-Me-*p*)Cl (**4c**): $C_{17}H_{13}Cl_2N_5Pd$ (464.6): calcd. C 43.93, H 2.79, N 15.07; found C 44.13, H 2.82, N 15.00. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 366, $\nu_{N=N}$ 1292, $\nu_{C=N}$ 1584. Pd(Clpapm-N-C_6H_4-OCH_3-*p*)Cl (**5c**): $C_{18}H_{15}Cl_2N_5OPd$ (494.7): calcd. C 44.96, H 3.12, N 14.57; found C 45.15, H 3.18, N 14.50. $\nu_{Pd\text{-}Cl}$ 365, $\nu_{N=N}$ 1290, $\nu_{C=N}$ 1585. Pd(Clpapm-N-C_6H_4-Cl-*p*)Cl (**6c**): $C_{16}H_{10}Cl_3N_5Pd$ (485.0): calcd. C 39.59, H 2.06, N 14.44; found C 39.40, H 2.10, N 14.38. IR (cm^{-1}): $\nu_{Pd\text{-}Cl}$ 368, $\nu_{N=N}$ 1300, $\nu_{C=N}$ 1588.

Molecular Orbital Calculations: Extended Hückel Molecular Orbital calculations[34,36] were performed using the ICON software package originally developed by Hoffmann. The orthogonal coordinate system chosen for the calculations are defined in Figures 5 and 6. The atomic parameters were taken from the crystallographic data (Table 5). For drawing figures and diagrams the graphic package CACAO was used.

X-ray Crystallography: Crystals of Pd(papm)Cl_2 suitable for X-ray work were grown by slow diffusion of benzene into a dichloromethane solution at 283 K. The crystal size was 0.26 × 0.25 × 0.23 mm. The crystals of Pd(papm-N-C_6H_4-OCH_3-*p*)Cl suitable for X-ray work were obtained from diffusion of hexane into a dichloromethane solution at 298 K. The crystal size was 0.22 × 0.19 × 0.10 mm. Crystal data and collection parameters are listed in Table 5. Data were gathered with a CAD4/PC V diffractometer with graphite monochrochromator (λ = 0.71073 Å) at 297(2) K. The crystals were mounted on glass fibres and covered with epoxy. Scan parameters were derived from ω-θ scans of 25 reflections. Three monitor reflections were measured after every 30 min of X-ray exposure as a check on experimental stability. The orientation of the crystal was checked after every 500 intensity measurements. Absorption corrections were based on ψ-scans of 12 reflections with bisecting-mode Eulerian χ values in the range of 0−86° for Pd(papm)Cl_2 and 2−83° for Pd(papm-N-C_6H_4-OCH_3-*p*)Cl. The structure was solved by direct methods and refined by full-matrix least squares. In Pd(papm)Cl_2 the asymmetric unit consists of two full molecules and a half molecule of benzene. Systematic absences are consistent

Table 5. Crystallographic data for **2a**·0.25C_6H_6 and **5a**

	2a·0.25C_6H_6	**5a**
Empirical formula	$C_{11.50}H_{9.50}Cl_2N_4Pd$	$C_{17}H_{14}ClN_5OPd$
Formula mass	381.03	446.18
Temperature [K]	299(2)	297(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_{1/n}$	$Pna2_1$
a [Å]	10.6455(7)	17.1717(19)
b [Å]	22.1264(16)	14.5001(14)
c [Å]	12.0316(10)	6.6869(5)
β [°]	109.216(6)	90
V [Å^3]	2676.1(3)	1665.0(3)
Z	8	4
$\rho_{calcd.}$ [g cm^{-3}]	1.891	1.780
2θ range [°]	4−55	5−55
Index range	$0 \le h \le 13$, $0 \le k \le 28$, $-15 \le l \le 14$	$0 \le h \le 22$, $-18 \le k \le 0$, $0 \le l \le 8$
R_1[a] [$I > 2\sigma(I)$] (%)	3.06	2.84
wR_2[b] (%)	6.57	6.17
GOF[c]	1.018	1.052
Transmission, max./min.	0.937/0.894	0.974/0.891
Largest diff. peak and hole [eÅ^{-3}]	0.416 and −0.429	0.331 and −0.383

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^{1/2}]$. [c] GOF is defined as $[w|F_o - F_c|/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variable, respectively.

with the space group of $Pna2_1$ or the centric group *Pnma* for Pd(papm-N-C_6H_4-OCH_3-*p*)Cl. The refinement in the centric group (*Pnma*) leads to residuals of $R_1 = 0.12$ and $wR2 = 0.44$. In space group $Pna2_1$ the values are $R_1 = 0.0287$ and $wR2 = 0.0630$ and thus chosen as the correct space group. All data were corrected for Lorentz polarisation and an empirical absorption correction was done on the basis of azimuthal scans. Of 6435 reflections in $Pd(papm)Cl_2$ 6117 [$I > 2\sigma(I)$] were used for the structure solution. In Pd(papm-N-C_6H_4-OCH_3)Cl the unique reflections (2068) were used for the structure solution. Data were processed with an Alpha Station 2004/166 (open VMS/Alpha V 6.2) using the program XCAD4B and the commercial package SHELXTL Rel. 505/VMS. All non-hydrogen atoms were located from subsequent difference Fourier maps. CCDC-135187 and -135188 contain the supplementary crystallographic data for [$Pd(papm)Cl_2$] (**2a**) and [Pd(papm-N-C_6H_4-OMe-*p*)Cl] (5a), respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: ^{1}H NMR spectroscopic data, a packing diagram, and Walsh diagrams are available (see footnote on the first page of this article).

Acknowledgments

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[1] A. Hilton, T. Renouard, O. Maury, H. Le Bozec, I. Ledoux, J. Zyss, *Chem. Commun.* **1999**, 2521.
[2] J. Otsuki, K. Sato, M. Tsujino, N. Okuda, K. Araki, M. Seno, *Chem. Lett.* **1996**, 847.
[3] J. S. Kang, H. T. Wong, D. H. Choi, *Mol. Cryst. Liq. Cryst.* **1999**, *327A*, 1.
[4] T. G. Deligeorgiev, D. Simov, *Dyes Pigments* **1998**, *38*, 115.
[5] F. Hlel, L. Smiri, *J. Chem. Crystallogr.* **1999**, *29*, 667.
[6] O. Cakir, E. Bicer, *Electroanalysis* **1997**, *9*, 87.
[7] B. K. Ghosh, A. Chakravorty, *Coord. Chem. Rev.* **1989**, *95*, 239.
[8] S. Goswami, R. N. Mukherjee, A. Chakravorty, *Inorg. Chem.* **1983**, *22*, 2825.
[9] P. Majumdar, S.-M. Peng, S. Goswami, *J. Chem. Soc., Dalton Trans.* **1998**, 1569.
[10] D. Dutta, A. Chakravorty, *Inorg. Chem.* **1983**, *22*, 1085.
[11] T. K. Misra, D. Das, C. Sinha, *Polyhedron* **1997**, *16*, 4163.
[12] T. K. Misra, D. Das, C. Sinha, P. K Ghosh, C. K. Pal, *Inorg. Chem.* **1998**, *37*, 1672.
[13] P. K. Santra, D. Das, T. K. Misra, R. Roy, C. Sinha, S.-M. Peng, *Polyhedron* **1999**, *18*, 1909.
[14] P. K. Santra, T. K. Misra, D. Das, C. Sinha, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* **1999**, *18*, 2869.
[15] W. Y. Wong, S. H. Cheung, S. M. Lee, S. Y. Leung, *J. Organomet. Chem.* **2000**, *596*, 36.
[16] K. Pramanik, M. Shivakumar, P. Ghosh, A. Chakravorty, *Inorg. Chem.* **2000**, *39*, 195.
[17] R. Samanta, P. Munshi, B. K. Santra, N. K. Loknath, M. A. Sridhar, J. S. Prasad, G. K. Lahiri, *J. Organomet. Chem.* **1999**, *579*, 311.
[18] C. K. Pal, S. Chattopadhyay, C. Sinha, D. Bandyopadhyay, A. Chakravorty, *Polyhedron* **1994**, *13*, 999.
[19] P. K. Santra, R. Roy, C. Sinha, *Proc. Indian Acad. Sci. (Chem. Sci.)* **2000**, *112*, 523.
[20] P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello, S. Han, *J. Am. Chem. Soc.* **1983**, *105*, 6327.
[21] A. Bharath, B. K. Santra, P. Munshi, G. K. Lahiri, *J. Chem. Soc., Dalton Trans.* **1998**, 2643.
[22] B. K. Santra, G. K. Lahiri, *J. Chem. Soc., Dalton Trans.* **1997**, 129.
[23] B. K. Santra, P. Munshi, G. Das, P. Bharadwaj, G. K. Lahiri, *Polyhedron* **1999**, *18*, 617.
[24] A. K. Ghosh, P. Majumdar, L. R. Falvello, G. Mostafa, S. Goswami, *Organometallics* **1999**, *18*, 5086.
[25] A. Saha, A. K. Ghosh, P. Majumdar, K. N. Mitra, S. Mondal, K. Rajak, L. R. Falvello, S. Goswami, *Organometallics* **1999**, *18*, 3772.
[26] R. Roy, D. Das, M. Banerjee, C. Sinha, A. Mahapatra, *Transition Met. Chem.* **2001**, *26*, 205.
[27] R. Roy, P. K. Santra, D. Das, C. Sinha, *Synth. React. Inorg. Met.-Org. Chem.* **2000**, *30*, 1975.
[28] D. J. Gordon, R. F. Fenske, *Inorg. Chem.* **1982**, *21*, 2907.
[29] I. Chakraborty, S. Bhattacharyya, S. Banerjee, B. K. Dirghangi, A. Chakravorty, *J. Chem. Soc., Dalton Trans.* **1999**, 3747.
[30] D. Das, PhD Thesis, Burdwan University, India, **1998**.
[31] M. J. Alder, W. I. Cross, K. R. Flower, R. G. Pritchard, *J. Chem. Soc., Dalton Trans.* **1999**, 2563.
[32] K. S. Y. Leung, Y. Li, *Inorg. Chem. Commun.* **1999**, *2*, 599.
[33] H.-Y. Cheng, B.-C. Tzeng, S. -M. Peng, *Bull. Inst. Chem. Acad. Sin.* **1994**, 51 and references therein.
[34] C. K. Pal, S. Chattopadhyay, C. Sinha, A. Chakravorty, *Inorg. Chem.* **1996**, *35*, 2442.
[35] M. Haga, E. S. Dodsworth, A. B. P. Lever, *Inorg. Chem.* **1986**, *25*, 447.
[36] C. K. Pal, S. Chattopadhyay, C. Sinha, A. Chakravorty, *Inorg. Chem.* **1994**, *33*, 6140.

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