Terdentate (P,N,N) Complexes of a New Pyridyl Azine Phosphine *Z,E*-$PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N$ and its Deprotonated Derivative (an Azo Phosphine) with Transition Metals

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tert-Butyl diphenylphosphinomethyl ketone hydrazone, *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ condensed with 2-acetylpyridine to give *Z,E*-$PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N$ **Ia**, which reacts with $[M(CO)_4(nbd)]$ (nbd = norbornadiene) to give highly coloured tricarbonyl complexes $[M(CO)_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]$ (M = Mo **1a**, W **1b** or Cr **1c**). Under mild conditions, **Ia** reacted with $[PtMe_2(cod)]$ (cod = cycloocta-1,5-diene) to give the dimethylplatinum(II) complex $[PtMe_2\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]$ **2** containing the bidentate azine phosphine ligand. Complex **2** reacted with MeI to give the *fac*-trimethylplatinum(IV) iodide salt $[PtMe_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]I$ **3** in which the phosphine is terdentate. Under slightly acidic conditions, **Ia** reacted with $[PtMe_2(cod)]$ to give a yellow methylplatinum(II) cation isolated as the PF_6 salt, $[PtMe\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]PF_6$ **4a**. Deprotonation of this cation with NaOMe gave the deep blue neutral methylplatinum(II) complex $[PtMe\{PPh_2CH{=}C(Bu^t){-}N{=}N{-}C(Me){=}C_5H_4N\}]$ **5a**, containing a terdentate azo phosphine ligand. Treatment of $[PtCl_2(cod)]$ with **Ia** gave the yellow chloride salt $[PtCl\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]Cl$ **4b**, which with NH_4PF_6 gives the corresponding PF_6 salt **4c**. Sodium methoxide immediately deprotonates **4b** to give the intensely deep blue neutral chloroplatinum(II) complex $[PtCl\{PPh_2CH{=}C(Bu^t){-}N{=}N{-}C(Me){=}C_5H_4N\}]$ **5b**. Treatment of $[PdCl_2(NCPh)_2]$ with **Ia** gave the yellow chloropalladium(II) chloride salt $[PdCl\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]Cl$ **4d**, which on deprotonation with NEt_3, gives the deep purple, neutral chloropalladium(II) complex **5c**. Infrared, ^{31}P-$\{^1H\}$, ^1H, some ^{13}C-$\{^1H\}$ NMR and UV/VIS data are given.

In a previous paper[1] we described the preparation of a new chelating (P,N) compound *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ from the phosphino dimethylhydrazone *Z*-$PPh_2CH_2C(Bu^t){=}NNMe_2$ by a hydrazine-exchange reaction. It condenses with aldehydes and ketones [QC(=O)R] to give mixed-azine monophosphines of type $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Q)R$.[1-6] We have studied the co-ordination chemistry[1-6] of these azine phosphines, in particular the promotion of agostic C–H interaction[3] or aryl fluoride co-ordination[4] with ruthenium(II), and cyclometallation with Ir^I,[5] W^0 (ref. 6) and Pt^{II}.[7] Recently, we reported the synthesis of an azine diphosphine *Z,Z*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$, and the ability of it, or its corresponding *E,Z*-isomer, to co-ordinate to Group 6 metal carbonyls,[8] and also to platinum and palladium,[9,10] either in a bidentate (P,P) or terdentate (P,N,P) manner. Since pyridine derivatives[11-14] have been widely used as nitrogen-donor ligands with both 'soft' and 'hard' metal centres, we incorporated the pyridine functionality into our azine–phosphine system, in order to investigate the co-ordination chemistry of a potential terdentate (P,N,N) ligand. In this paper we describe the synthesis of a new pyridyl azine phosphine *Z,E*-$PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N$ **Ia** and its complexes with Group 6 metal carbonyls and also with palladium and platinum. There are several reports on other types of pyridylphosphine ligands which are quite different from **Ia** and the co-ordination chemistry of these has been reviewed.[13] They include $R_2P(CH_2)_nR'$ (n = 1–3, R = Ph, R′ = a 2-pyridyl moiety), $R_nPR'_{3-n}$ (n = 0–2), $R'PhP(CH_2)_nPPh(R')$ (n = 1–3) $R'(CH_2)_2PR(CH_2)_nR'$ (n = 2 or 3) and $[Ph_2P(CH_2)_n]_2R''$ (n = 1 or 2, R″ = a pyridine-2,6-diyl moiety).

Results and Discussion

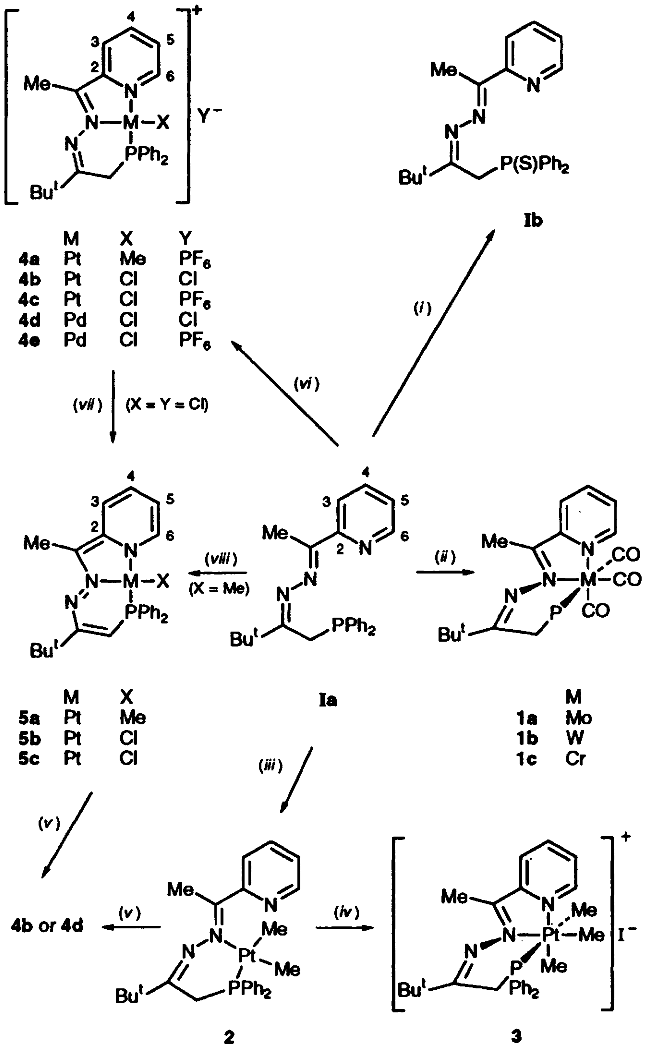
Complexes of **Ia** *with Group* 6 *Metal Carbonyls*.—The various reactions of the pyridyl azine phosphine **Ia** are summarised in Scheme 1. The compounds described were characterised by elemental analyses (Experimental section) and by IR and ^{31}P-$\{^1H\}$ (Table 1), ^1H (Table 2), ^{13}C-$\{^1H\}$ NMR (Table 3) and UV/VIS (Table 4) spectroscopies. The phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ condensed rapidly with 2-acetylpyridine in ethanol to give the crystalline pyridyl mixed-azine phosphine *Z,E*-$PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N$ **Ia** in *ca.* 70% yield. This phosphine was found to be very air sensitive and was stored under nitrogen or argon at −15 °C. The ^{31}P-$\{^1H\}$ NMR spectrum in $CDCl_3$ is a singlet at δ −12.1. Treatment of **Ia** with monoclinic sulfur in benzene solution gave the corresponding phosphine sulfide **Ib**, which has a phosphorus-31 chemical shift of δ 37.2.

Treatment of **Ia** with $[Mo(CO)_3(cht)]$[15] or $[Mo(CO)_4(nbd)]$[15] {cht = cyclohepta-1,3,5-triene, nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)} gave a deep purple solution, from which a purple compound was isolated in high yield. The infrared spectrum of this compound showed three bands for $\nu(C{\equiv}O)$ at 1900, 1810 and 1780 cm^{-1}, similar to literature values for zerovalent molybdenum *fac*-tricarbonyls.[8,16-18] In the ^{13}C-$\{^1H\}$ NMR spectrum, three

Table 1 Infrared [a] and $^{31}P-\{^1H\}$ NMR [b] data

Compound	IR/cm^{-1} ν(C=N)	ν(M–Cl)	ν(C≡O) [c]	$^{31}P-\{^1H\}$ NMR δ	^1J(MP)/Hz
Ia	1610m	—	—	−12.1	—
Ib	1615m	—	—	37.2	—
1a	1595w, 1610w	—	1900s, 1810m, 1780m	35.6 [d]	—
1b	1595w	—	1910s, 1820m, 1790m	28.4	229
1c	1590w, 1610w	—	1910s, 1820m, 1790m	56.1 [d]	—
2	1585m, 1595m	—	—	34.8	2164
3	1585s	—	—	−1.1 [d]	1121
4a	1590m	—	—	23.4 [d]	4299
4b	1595m	340w	—	19.4 [d]	3713
4c	1590m, 1605m	340w	—	20.1 [d]	3716
4d	1595m, 1610m	340w	—	48.0	—
4e	1590m, 1605m	340w	—	50.6 [d]	—
5a	—	—	—	−2.6	3790
5b	—	330w	—	−10.5	3377
5c	—	340w	—	17.4	—

[a] As KBr discs. [b] Recorded at 36.2 MHz, chemical shifts are in ppm relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated. [c] In CH_2Cl_2. [d] In CD_2Cl_2.



Scheme 1 (*i*) Sulfur; (*ii*) $[M(CO)_4(nbd)]$ (M = Mo, W or Cr); (*iii*) $[PtMe_2(cod)]$; (*iv*) MeI; (*v*) excess of HCl; (*vi*) for **4a**, $[PtMe_2(cod)]$–H^+–NH_4PF_6; for **4b**, $[PtCl_2(cod)]$; for **4c**, $[PtCl_2(cod)]$–NH_4PF_6; for **4d**, $[PdCl_2(NCPh)_2]$; for **4e**, $[PdCl_2(NCPh)_2]$–NH_4PF_6; (*vii*) base; (*viii*) $[PtMe_2(cod)]$–H^+, NaOMe

doublets were observed in the C≡O region, at δ 232.3 with ^2J(PC) = 9.2, 227.4 with ^2J(PC) = 10.7 and 213.9 with ^2J(PC) = 36.6 Hz. The first two resonances with small ^2J(PC) values are assigned to the carbonyl carbons *cis* to phosphorus and that with a large ^2J(PC) value is assigned to the carbonyl carbon *trans* to phosphorus.[6,8,19,20] Hence, this tricarbonylmolybdenum(0) complex has a *fac* geometry as shown in **1a**. The observed low δ_C value of 27.3 for the methylene carbon is consistent with the values obtained for methylene carbons in six-membered chelate rings.[2,6,9,20] In the proton NMR spectrum (Table 2) the methylene protons are non-equivalent, as expected for a *fac* geometry. The mass spectrum gave an intensity profile at *m*/*z* 583 (for molybdenum-98) for the parent molecular ion and profiles due to successive loss of one, two and three carbonyl ligands (see Experimental section). Similarly, treatment of the corresponding tungsten and chromium complexes $[M(CO)_4(nbd)]$ (M = W or Cr)[15,21] with the phosphine **Ia** gave the hoped for *fac*-tricarbonyl complexes **1b** and **1c**, respectively. Details of the preparation and characterising data are in the Experimental section and in Tables 1–4. The UV/VIS absorption spectra of **1a**–**1c** are discussed below.

Complexes of **Ia** *with Platinum and Palladium.*—Treatment of **Ia** with $[PtMe_2(cod)]$[9] (cod = cycloocta-1,5-diene) at *ca.* 20 °C in ethanol gave the bidentate dimethylplatinum(II) complex **2**, which has δ_P 34.8 with ^1J(PtP) = 2164 Hz. This small value of ^1J(PtP) is consistent with phosphorus *trans* to a methyl group.[2,22,23] The proton NMR spectrum showed two doublets with platinum-195 satellites for the two methyl groups on platinum; that at δ −0.24 with ^2J(PtH) = 69.3 Hz is assigned to the group *trans* to phosphorus[2,9,23,24] and the other, at δ 0.63 with ^2J(PtH) = 90.5 Hz, to the group *trans* to nitrogen.[2,25,26] The MeC=N proton resonance appeared as a doublet at δ 2.32 with satellites due to coupling to platinum-195, ^5J(PH) 2.2 and ^4J(PtH) 4.6 Hz. In the $^{13}C-\{^1H\}$ NMR spectrum the resonance for the methylene carbon appeared as a doublet at δ 24.9 with ^1J(PC) = 17.2 Hz, in agreement with the presence of a six-membered chelate ring.[2,6,9,20] The doublet at δ 7.5 with a large ^2J(PC) value of 109.6 Hz is assigned to the methyl carbon *trans* to phosphorus, whilst that at δ −23.6 with a small ^2J(PC) value of 4.4 Hz is assigned to the methyl carbon *cis* to phosphorus.[9,10] The pyridyl carbons (*e.g.* C^2–C^6) are coupled neither to phosphorus-31 nor to platinum-195, confirming the presence of an unco-ordinated pyridyl group.

Table 2 Proton NMR data[a] [[b] ^2J(PH), [c] ^2J(HH), [d] ^3J(PtH), [e] ^3J(PH), [f] ^4J(PtH), [g] ^5J(PH), [h] ^2J(PtH)]

Compound	δ(Bu^t)	δ(CH_2)	δ(=CMe)	Others
Ia	1.22 (s)	3.31 (2 H, d, 3.4[b])	2.21 (s)	—
Ib	1.21 (s)	4.07 (2 H, d, 14.9[b])	2.41 (s)	—
1a[i]	1.30 (s)	2.85 (1 H, dd, 9.5,[b] 17.6[c]) 3.09 (1 H, dd, 6.4,[b] 17.6[c])	2.15 (d, 4.9[g])	—
1b	1.30 (s)	2.82 (1 H, dd, 10.2,[b] 17.3[c]) 3.10 (1 H, dd, 6.6,[b] 17.3[c])	2.14 (d, 5.4[g])	—
1c[i]	1.32 (s)	2.91 (1 H, dd, 9.5,[b], 17.4[c]) 2.93 (1 H, dd, 6.9,[b] 17.4[c])	2.17 (d, 6.4[g])	—
2	0.89 (s)	2.51 (1 H, dd, 10.5,[b] 12.7,[c] 10.0[d]) 3.56 (1 H, dd, 10.0,[b] 12.7,[c] 18.0[d])	2.32 (d, 2.2,[g] 4.6[f])	−0.24 (3 H, d, 7.8,[e] 69.3,[h] PtMe *trans* to P) 0.63 (3 H, d, 7.5,[e] 90.5,[h] PtMe *trans* to N)
3[i]	1.35 (s)	2.97 (1 H, m, br, 18.0[c]) 3.40 (1 H, m, br, 18.0[c])	2.68 (d, 2.7,[g] 3.3[f])	0.53 (3 H, d, 7.7,[e] 58.3,[h] PtMe *trans* to P) 1.02 (3 H, d, 8.3,[e] 68.8,[h] PtMe *trans* to N) 1.35 (3 H, d, 6.7,[e] 68.0,[h] PtMe *trans* to N)
4a[i,j]	0.91 (s)	3.51 (2 H, d, 13.9,[b] 47.4[d])	2.62 (s, 4.4[f])	0.70 (3 H, d, 2.7,[e] 73.0,[h] PtMe) 7.93 (1 H, m, 1.2,[g] 5.6,[k] 7.6,[k], 1.5,[l] H^5) 8.28 (1 H, m, 0.7,[g] 0.7,[m] 1.5,[l] 8.0,[k] H^3) 8.40 (1 H, m, 0.4,[n] 1.7,[l] 7.6,[k] 8.0,[k] H^4) 8.89 (1 H, m, 3.5,[o] 34.5,[d] 5.6,[k] 1.7,[l] 0.7,[m] H^6)
4b[i]	0.92 (s)	3.55 (2 H, d, 14.1,[b] 39.6[d])	2.71 (s, 10.3[f])	—
4c[i]	0.89 (s)	3.95 (2 H, d, 14.5,[b] 43.0[d])	2.78 (s, 10.5[f])	—
4d	0.90 (s)	3.33 (2 H, d, 14.9[b])	2.84 (s)	—
4e[i]	0.90 (s)	4.01 (2 H, d, 15.4[b])	2.96 (s)	—
5a[j]	1.26 (s)		2.20 (s, 3.4[f])	0.67 (3 H, d, 2.2,[e] 69.8,[h] PtMe) 4.25 (1 H, d, 3.2,[b] 50.0,[d] =CHP) 6.95 (1 H, m, 1.4,[g] 1.3,[l] 5.8,[k] 7.2,[k] H^5) 7.20 (1 H, m, 1.3,[g] 2.2,[l] 8.2,[k] H^3) 8.20 (1 H, m, 33.0,[d] H^6)
5b	1.26 (s)		2.25 (s, 2.2[f])	3.99 (1 H, d, 4.6,[b] 31.2,[d] =CHP)
5c	1.28 (s)		2.44 (s)	3.82 (1 H, d, 3.6,[d] =CHP)

[a] Recorded at 100 MHz, chemical shifts are in ppm relative to $SiMe^4$, J values are in Hz, solvent $CDCl_3$ unless otherwise stated. [i] In CD_2Cl_2. [j] Recorded at 250 MHz. [k] ^3J(HH). [l] ^4J(HH). [m] ^5J(HH). [n] ^6J(PH). [o] ^4J(PH).

Treatment of complex **2** with MeI gave the *fac*-trimethylplatinum(IV) iodide salt **3**; a 1 : 1 electrolyte with a specific molar conductivity (Λ_m) of 0.104 Ω^{-1} cm^2 mol^{-1} in acetone solution.[27] The low ^1J(PtP) value of 1121 Hz is similar to other values reported for platinum(IV)–tertiary phosphine complexes.[2,9,10] The proton resonance at δ 0.53(d) with ^3J(PH) 7.7 and ^2J(PtH) 58.3 Hz is assigned to the PtMe group *trans* to phosphorus,[2,9,10,28] whilst the two doublets at δ 1.02 with ^3J(PH) 8.3 and ^2J(PtH) 68.8 Hz and 1.35 with ^3J(PH) 6.7 and ^2J(PtH) 68.0 Hz are assigned to the two PtMe groups *trans* to nitrogens,[2,9,10,25,26] as expected for a *fac* geometry. Treatment of **Ia** with [PtMe$_2$(cod)] in the presence of acetic acid followed by NH_4PF_6, or treatment of the dimethylplatinum(II) complex **2** with 1 mol equivalent of HCl at 20 °C followed by NH_4PF_6, gave the methylplatinum(II) salt $[PtMe\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]PF_6$ **4a** with a terdentate pyridyl azine phosphine ligand. The $^{31}P-\{^1H\}$ NMR spectrum showed a singlet at δ 23.4 with ^1J(PtP) = 4299 Hz. The latter value is slightly higher than most others[2,14,29–33] (*i.e.* 3000–4000 Hz) for tertiary phosphine ligands *trans* to nitrogen donors, however a value of 4220 Hz was observed for a cyclometallated alkylplatinum(II) complex, *viz.* $[(PhMe_2P)Cl\text{-}Pt(Me_2)NCH_2CHCHCH_2NMe_2)PtCl(PMe_2Ph)]$.[34] The presence of a *cis*-alkyl ligand is known to increase ^1J(PtP) relative to a *cis*-halide ligand.[10,22,34,35] In the proton NMR spectrum, the platinum–methyl protons appeared as a doublet at δ 0.70 with ^3J(PH) = 2.7 and ^2J(PtH) = 73.0 Hz. A detailed NMR study at high field (400 and 250 MHz), including [proton, ^{13}C, two-dimensional $^1H-^{13}C$ correlation spectroscopy (COSY), attached proton test and homonuclear decoupling experiments], has enabled us to assign all the pyridyl protons (H^3–H^6, see Fig. 1) and carbons (C^2–C^6); for example, the H^6 proton resonates at δ 8.89 with couplings to the H^3 (0.7), H^4 (1.7), H^5 (5.6), ^{31}P (3.5) and ^{195}Pt (34.5 Hz) nuclei. The carbon-13 resonance at δ 23.7 for the methylene carbon confirmed the presence of the six-membered chelate ring.[2,6,9,20] The pyridyl carbons C^3 and C^6 showed couplings to platinum-195 of ^3J(PtC) = 15.0 Hz and ^2J(PtC) = 38.6 Hz, respectively, indicative of co-ordination of the pyridyl nitrogen to platinum. Treatment of **Ia** with [PtCl$_2$(cod)],[9] or of **2** with an excess of HCl, gave the terdentate chloroplatinum(II) chloride salt **4b**, which has δ_P 19.4 with ^1J(PtP) = 3713 Hz, and one IR band at 340 cm^{-1} for ν(Pt–Cl). The corresponding PF_6 salt **4c** was prepared by the addition of NH_4PF_6 to a methanolic solution of **4b**. Similarly, the analogous terdentate chloropalladium(II) chloride salt **4d** and the PF_6 salt **4e** were prepared and characterised.

The methylene protons on a carbon adjacent to a C=N bond and a co-ordinated tertiary phosphine group are activated and can often be removed by a base such as NEt_3 or by NaOMe.[2,10] Treatment of the methylplatinum(II) chloride salt $[PtMe\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)C_5H_4N\}]Cl$, prepared *in situ* from [PtMe$_2$(cod)] and **Ia** in the presence of acetic acid, with 1 equivalent of NaOMe in methanol removed one of the methylene protons to give the intensely dark blue neutral methylplatinum(II) complex $[PtMe\{PPh_2CH{=}C(Bu^t){-}N{=}N{-}C(Me){=}C_5H_4N\}]$ **5a**, containing an azo phosphine ligand. Removal of a methylene proton in the six-membered chelate ring is likely to induce high conjugation and transfer (or localisation) of the negative charge on to the pyridine nitrogen, thus converting the azine (–C=N–N=C–) backbone into the more conjugated azo (=C–N=N–C=) backbone with an exocyclic carbon–carbon double bond to the pyridyl residue, as shown in **5a**–**5c**. Similar deprotonation processes resulting in stable $=C_5H_4N^-$ moieties have been observed with cationic complexes containing ligands such as 1,3-bis(2′-pyridyl)-2,3-diazaprop-1-ene, HC(R)=NNH(R) (R = 2-pyridyl), and related 2-pyridylhydrazones, *viz.* $R^1R^2C{=}$

Table 3 ^{13}C-{^{1}H} NMR data[a]

					Pyridyl carbons		PPh$_2$					
Compound	*Me*C=	C*Me*$_3$	CH$_2$P	*C*Me$_3$	C^2	C^3–C^6	C$_{ipso}$	C$_{ortho}$	C$_{meta}$	C$_{para}$	C=N	Others
Ia	13.8 (d, 2.7)	28.7 (d, 1.3)	26.2 (d, 23.0)	38.9 (s)	155.5 (s)	121.1 (s), 123.4 (s), 135.6 (s), 148.2 (s)	139.0 (d, 17.3)	132.9 (d, 20.4)	128.2 (d, 7.0)	128.5 (s)	158.8 (s), 168.6 (d, 5.5)	—
1a	14.6 (d, 1.5)	28.5 (s)	27.3 (d, 15.0)	40.4 (d, 5.0)	152.7 (s)	123.0 (s), 123.8 (s), 133.8 (s), 152.2 (s)	131.0 (d, 23.5), 134.1 (d, 32.1)	130.3 (d, 12.4), 134.2 (d, 12.4)	127.7 (d, 8.4), 128.7 (d, 9.9)	128.6 (s) 130.4 (s)	154.7 (d, 6.1), 169.6 (s)	213.9 (d, $C\equiv O$ *trans* to P, 36.6), 227.4 (d, $C\equiv O$ *trans* to N, 10.7), 232.3 (d, $C\equiv O$ *trans* to N, 9.2)
1b[b]	15.2 (d, 2.4)	28.6 (s)	27.1 (d, 18.8)	40.8 (d, 4.9)	154.2 (s)	124.2 (s), 125.1 (s), 133.9 (s), 152.4 (s)	130.0 (d, 29.9) 133.3 (d, 39.2)	130.6 (d, 12.0) 134.6 (d, 13.8)	128.3 (d, 8.8) 129.1 (d, 10.2)	129.3 (s), 131.1 (s)	156.4 (d, 7.2) 172.0 (d, 0.8)	208.6 (d, $C\equiv O$ *trans* to P, 35.3), 221.5 (d, $C\equiv O$ *trans* to N, 7.2), 227.1 (d, $C\equiv O$ *trans* to N, 6.4)
1c[b]	14.7 (d, 2.4)	28.6 (s)	27.1 (d, 16.9)	40.4 (d, 5.2)	153.8 (s)	122.3 (s), 123.8 (s), 133.4 (s), 152.8 (s)	130.3 (d, 23.3), 135.3 (d, 32.2)	130.5 (d, 10.9), 134.0 (d, 12.6)	127.9 (d, 8.4), 129.0 (d, 9.3)	128.7 (s), 130.7 (s)	154.5 (d, 8.0), 170.6 (s)	224.6 (d, $C\equiv O$, 3.1), 234.2 (d, $C\equiv O$, 17.7), 239.7 (d, $C\equiv O$, 15.3)
2	19.4 (s)	27.6 (s)	24.9 (d, 17.2)	39.3 (d, 2.0)	155.7 (s)	123.4 (s), 124.4 (s), 134.7 (s), 148.4 (s)	128.1 (d, 10.9, 132.9 (d, 10.8)	131.9 (d, 11.8), 134.9 (d, 13.8)	128.3 (d, 10.1), 128.7 (d, 9.0)	130.0 (d, 1.6) 130.8 (d, 1.9)	162.7 (d, 3.7), 170.1 (s)	−23.6 (d, PtMe *trans* to N, 4.4), 7.5 (d, PtMe *trans* to P, 109.6)
4a[b,c]	17.1 (s)	27.7 (s)	23.7 (d, 33.5)	42.4 (d, 2.3)	156.6 (s)	127.0 (d, C^3, 3.0, 15.0[d]), 129.0 (C^5),[e] 142.0 (s, C^4), 147.5 (s, C^6, 38.6[d])	126.5 (d, 64.3)	134.1 (d, 11.6, 32.0[d])	129.5 (d, 6.2)	133.0 (s)	156.7 (d, 2.7), 177.4 (s)	−11.3 (d, PtMe, 7.1)
5a[b,c]	15.1 (s)	30.6 (s)	—	41.3 (d, 12.5)	161.3 (s)	119.7 (d, C^5, 3.2, 28.0[d]) 119.8 (d, C^3, 2.4, 19.3[d]), 139.5 (s, C^4), 145.4 (s, C^6, 39.2[d])	135.1 (d, 67.2)	133.1 (d, 10.8, 31.6)[d]	128.6 (d, 10.8)	130.2 (d, 2.7)	—	−12.2 (d, PtMe, 7.6), 63.1 (d, =CHP, 77.0, 19.0[d]), 145.8 (s, NC=), 176.6 (d, NC=, 9.1)

[a] Recorded at 100.6 MHz, chemical shifts are in ppm relative to SiMe$_4$, *J*(PC) values in Hz in parentheses, solvent CDCl$_3$ unless otherwise stated. [b] In CD$_2$Cl$_2$. [c] Recorded at 62.9 MHz. [d] *J*(PtC) values. [e] Obscured by C$_{meta}$ resonance.

Table 4 UV/VIS data[a]

Complex	Colour	$\lambda_1{}^b$/nm	λ_2/nm
1a	Purple	285 (15 400)	564 (5 000)
1b	Blue	300 (11 800)	574 (7 100)
1c	Blue	400 (2 900)	600 (2 500)
5a	Blue	345 (7 700)	614 (12 600)
5b	Blue	336 (5 300)	600 (10 400)
5c	Purple	253 (22 100)	578 (3 900)

[a] Recorded in freshly prepared dichloromethane solutions using silica cells on a Perkin-Elmer 402 UV/VIS spectrometer. Absorption coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) in parentheses. Bands observed below 250 nm are not included as these are subject to solvent effects. [b] Only the most intense band is quoted.

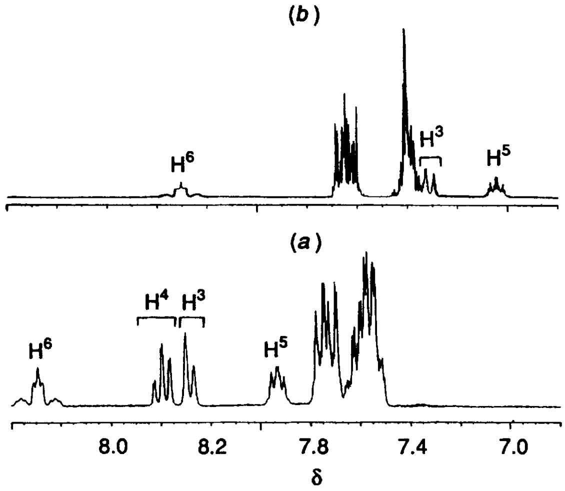


Fig. 1 Proton NMR (250 MHz) spectra in the aromatic region for (*a*) the pyridine cation **4a** and (*b*) its corresponding deprotonated (blue) complex **5a**. The effect of deprotonation on the pyridine residue is clearly shown. For **5a** the resonance for H^4 (δ *ca.* 7.4) is hidden behind the phenyl resonances as shown by the $^1H-^{13}C$ COSY experiment

NNH(R) (R^1 = 2-pyridyl, 2-quinolyl, 8-quinolyl or 1-isoquinolyl; R^2 = H, Me, Et, Pr^n or Bu^n), and di-2′-pyridylamine.[11,36,37] Deprotonation of di-2′-pyridylmethane with $LiBu^n$ gives an alkali-metal derivative, in which a lithium atom is co-ordinated to the nitrogen atom of the $=C_5H_4N^-$ moiety.[38] Furthermore, some photoinduced intramolecular hydrogen-transfer processes have been known to generate $=C_5H_4NH$ moieties.[39–41] Our neutral azo phosphine complex **5a** showed a phosphorus-31 resonance at δ −2.6 with a $^1J(PtP)$ value of 3790 Hz, consistent with a phosphorus atom *trans* to a nitrogen donor. In the proton NMR spectrum the =CHP proton appeared as a doublet at δ 4.25 with satellites, $^2J(PH)$ = 3.2 and $^3J(PtH)$ = 50.0 Hz, whilst the carbon-13 resonance for the =CHP carbon absorbed at δ 63.1 with $^1J(PC)$ = 77.0 Hz.[10] The protons (H^3, H^5 and H^6, see Fig. 1) and carbons (C^2–C^6) were assigned using a two-dimensional $^1H-^{13}C$ COSY experiment at 250 MHz; the resonances due to C^5 and C^3 appeared as doublets at δ 119.7 [$^4J(PC)$ = 3.2, $^3J(PtC)$ = 28.0] and 119.8 [$^4J(PC)$ = 2.4, $^3J(PtC)$ = 19.3], respectively. Similarly, the chloride salts **4b** (Pt) and **4d** (Pd) were deprotonated with NaOMe or NEt_3 to give the corresponding neutral azo phosphine complexes **5b** and **5c**, respectively. These neutral blue (Pt) or purple (Pd) azo phosphine complexes of type $[MCl\{PPh_2CH{=}C(Bu^t){-}N{=}N{-}C(Me){=}C_5H_4N\}]$ **5** (M = Pt or Pd) are immediately reprotonated with 1 equivalent of HCl to give the corresponding yellow chloride salt **4b** or **4d**. Treatment of **5a** with an excess of HCl gave the chloroplatinum(II) chloride salt **4b** and methane.

UV/VIS Spectroscopy of Complexes of types **1** *and* **5**.—The Group 6 metal carbonyls **1a**–**1c**, containing the *Z,E*-azine phosphine ligand, and the platinum(II) and palladium(II) complexes **5a**–**5c**, containing the azo phosphine ligand, are highly coloured. Their UV/VIS spectroscopic data are given in Table 4. In each case only one absorption band was observed in the visible region [λ_2 = 560–600 nm; absorption coefficient (ε) = 2500–13 000 $dm^3\ mol^{-1}\ cm^{-1}$) but several absorption bands (ε = 2900–22 000 $dm^3\ mol^{-1}\ cm^{-1}$) were present in the UV and far-UV region. The origins of these deep blue or purple colours are not clear since several electronic transitions are possible in these systems. For example, the azo functionality is known to induce metal to ligand charge transfer (m.l.c.t.) involving the ligand's π* (N=N) orbital,[42] whereas pyridine derivatives are known to engage in metal-to-ligand charge transfers as well as ligand-centred (l.c.) π–π* excitations,[43] and there is also evidence for strong mixing between the l.c. and m.l.c.t. transitions.[44]

Experimental

The apparatus used and general techniques were the same as in other recent papers from this laboratory.[9] *tert*-Butyl diphenylphosphinomethyl ketone hydrazone was prepared as reported previously.[1] Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer, NMR spectra using a JEOL FX-90Q (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively), a Bruker ARX-250 (operating frequencies for ^1H and ^{13}C of 250.13 and 62.9 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively); ^1H and ^{13}C shifts are relative to tetramethylsilane and ^{31}P shifts to 85% phosphoric acid. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec with 8 kV acceleration. For metal complexes *m/z* values are quoted for ^{98}Mo, ^{184}W, ^{195}Pt and ^{106}Pd.

Z,E-$PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N$ **Ia**.—A solution containing *tert*-butyl diphenylphosphinomethyl ketone hydrazone, *Z*-$PPh_2CH_2(Bu^t)C{=}NNH_2$ (2.0 g, 6.7 mmol) and 2-acetylpyridine (0.80 cm^3, 7.12 mmol) in degassed ethanol was put aside at *ca.* 20 °C for 30 min, and then cooled to −15 °C. This gave the required phosphine **Ia** as a white crystalline solid (1.86 g, 69%) (Found: C, 73.6; H, 7.15; N, 10.2. $C_{25}H_{28}N_3P{\cdot}0.4EtOH$ requires C, 73.8; H, 7.3; N, 10.0%).

Z,E-$P({=}S)Ph_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N$ **Ib**.—A mixture of compound **Ia** (80 mg, 0.20 mmol) and monoclinic sulfur (6.5 mg, 0.20 mmol) was refluxed in benzene (2.0 cm^3) for 1 h. The reaction mixture was then filtered and the solvent removed under reduced pressure. The required product **Ib** was obtained as fine white needles by recrystallising the residue from methanol. Yield 45 mg, 52% (Found: C, 68.45; H, 6.7; N, 9.55. $C_{25}H_{28}N_3PS{\cdot}0.3MeOH$ requires C, 68.5; H, 6.7; N, 9.5%).

fac-$[Mo(CO)_3\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}]$ **1a**. —(*i*) *From* $[Mo(CO)_3(\eta^6\text{-cht})]$. A solution of $[Mo(CO)_3(\eta^6\text{-cht})]$ (0.24 g, 0.87 mmol) in benzene (2.0 cm^3) was added to a solution of compound **Ia** (0.42 g, 1.05 mmol) in benzene (3.0 cm^3) and the resultant mixture put aside for 1 h. The required product **1a** crystallised as an intensely purple solid and was collected. Yield 0.48 g, 97%. A sample for microanalysis was obtained by recrystallisation from dichloromethane (Found: C, 56.5; H, 4.8; N, 7.25. $C_{28}H_{28}MoN_3O_3P{\cdot}0.2CH_2Cl_2$ requires C, 56.5; H, 4.8; N, 7.0%). *m/z* (EI): 583 (M^+), 555 (*M* − CO), 527 (*M* − 2CO) and 499 (*M* − 3CO).

(*ii*) *From* $[Mo(CO)_4(nbd)]$. Complex **1a** was prepared and isolated in 80% yield after treating $[Mo(CO)_4(nbd)]$ with 1 mol equivalent of **Ia** in a similar fashion to that described in method (*i*).

$\textit{fac}\text{-}[\mathrm{W(CO)_3\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]$ **1b**.—Compound **Ia** (100 mg, 0.25 mmol) and $[\mathrm{W(CO)_4(nbd)}]$ (95 mg, 0.25 mmol) were refluxed together in benzene solution for 15 h. The required product **1b** crystallised from the cooled solution as a deep purple solid (117 mg, 70%). A sample for microanalysis was obtained by recrystallisation from dichloromethane–methanol (Found: C, 47.75; H, 4.1; N, 5.8. $\mathrm{C_{28}H_{28}N_3O_3PW{\cdot}0.6CH_2Cl_2}$ requires C, 47.7; H, 4.1; N, 5.8%). *m*/*z* (EI): 669 (M^+), 613 (M − 2CO) and 585 (M − 3CO).

$\textit{fac}\text{-}[\mathrm{Cr(CO)_3\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]$ **1c**.—Compound **Ia** (80 mg, 0.20 mmol) and $[\mathrm{Cr(CO)_4(nbd)}]$ (50 mg, 0.20 mmol) were refluxed in benzene (2.5 $\mathrm{cm^3}$) for 7.5 h and then cooled to *ca.* 20 °C. The required product **1c** separated as a dark blue solid, and was filtered off and washed with methanol. Yield 50 mg, 48% (Found: C, 61.4; H, 5.3; N, 7.3. $\mathrm{C_{28}H_{28}CrN_3O_3P{\cdot}0.8MeOH}$ requires C, 61.0; H, 5.6; N, 7.4%).

$[\mathrm{PtMe_2\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]$ **2**.—A solution of compound **Ia** (145 mg, 0.36 mmol) in ethanol (2.0 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{PtMe_2(cod)}]$ (120 mg, 0.36 mmol) in ethanol (2.0 $\mathrm{cm^3}$) and the mixture put aside for 30 min. The required dimethylplatinum(II) complex **2** crystallised as yellow microcrystals and was collected. Yield 168 mg, 74% (Found: C, 51.65; H, 5.5; N, 6.7. $\mathrm{C_{27}H_{34}N_3PPt}$ requires C, 51.75; H, 5.45; N, 6.7%). *m*/*z*(EI): 626 (M^+), 611 (M − Me) and 595 (M − 2Me).

$\textit{fac}\text{-}[\mathrm{PtMe_3\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]\mathrm{I}$ **3**.—An excess of iodomethane (0.1 $\mathrm{cm^3}$) was added to a solution of complex **2** (50 mg, 0.80 mmol) in benzene (2.0 $\mathrm{cm^3}$) and the mixture put aside at room temperature for 20 min. The resulting dark blue solution was evaporated to dryness under reduced pressure and the residue triturated with diethyl ether; this gave the trimethylplatinum(IV) complex **3** as a blue solid, which was filtered off and washed with diethyl ether. Yield 53 mg, 86% (Found: C, 43.85; H, 4.85; N, 5.45. $\mathrm{C_{28}H_{37}IN_3PPt}$ requires C, 43.8; H, 4.85; N, 5.45%). Λ_m(acetone) = 0.104 Ω^{-1} $\mathrm{cm^2\ mol^{-1}}$.

$[\mathrm{PtMe\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]\mathrm{PF_6}$ **4a**.—A solution of $[\mathrm{PtMe_2(cod)}]$ (80 mg, 0.24 mmol) in benzene (1.0 $\mathrm{cm^3}$) was added to a solution of compound **Ia** (80 mg, 0.27 mmol) in ethanol (2.0 $\mathrm{cm^3}$) and glacial acetic acid (0.1 $\mathrm{cm^3}$) added. The solvents were then removed under reduced pressure and a saturated ammonium hexafluorophosphate(V) solution in ethanol (1 $\mathrm{cm^3}$) was added to the residue. The monomethylplatinum(II) complex **4a** crystallised as yellow needles (102 mg, 56%). An analytically pure sample was obtained by recrystallisation from dichloromethane–hexane (Found: C, 41.25; H, 4.15; N, 5.5. $\mathrm{C_{26}H_{31}F_6N_3P_2Pt}$ requires C, 41.3; H, 4.15; N, 5.5%). *m*/*z* (EI): 610 (M − $\mathrm{HPF_6}$) and 595 (M − $\mathrm{HPF_6}$ − Me).

$[\mathrm{PtCl\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]\mathrm{Cl}$ **4b**.—Acetic acid (0.1 $\mathrm{cm^3}$) and a solution of compound **Ia** (165 mg, 0.41 mmol) in dichloromethane (2.0 $\mathrm{cm^3}$) were added to a solution of $[\mathrm{PtCl_2(cod)}]$ (150 mg, 0.40 mmol) in dichloromethane (1 $\mathrm{cm^3}$). The reaction mixture was put aside to stand for 20 min at 20 °C, after which the solvent was removed under reduced pressure. Addition of diethyl ether to the residue gave the chloroplatinum(II) salt **4b** as a bright yellow solid (260 mg, 97%) (Found: C, 45.0; H, 4.45; N, 6.0. $\mathrm{C_{25}H_{28}Cl_2N_3PPt{\cdot}0.25Et_2O}$ requires C, 45.5; H, 4.50; N, 6.1%).

$[\mathrm{PtCl\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]\mathrm{PF_6}$ **4c**.—This salt was obtained in 40% yield after treating the chloroplatinum(II) chloride salt **4b** with $\mathrm{NH_4PF_6}$ in MeOH, in a similar manner to that described for **4a** (Found: C, 38.75; H, 3.65; N, 5.4. $\mathrm{C_{25}H_{28}ClF_6N_3P_2Pt}$ requires C, 38.65; H, 3.65; N, 5.4%).

$[\mathrm{PdCl\{PPh_2CH_2Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]\mathrm{Cl}$ **4d**.—A solution of $[\mathrm{PdCl_2(NCPh)_2}]$ (330 mg, 0.87 mmol) in dichloromethane (2.0 $\mathrm{cm^3}$) was added to a solution of compound **Ia** (350 mg, 0.87 mmol) in benzene (3.0 $\mathrm{cm^3}$). The chloropalladium(II) chloride salt **4d** crystallised as yellow microcrystals (300 mg, 60%) (Found: C, 49.8; H, 4.8; N, 7.0. $\mathrm{C_{25}H_{28}Cl_2N_3PPd{\cdot}0.4CH_2Cl_2}$ requires C, 49.8; H, 4.8; N, 6.9%).

$[\mathrm{PdCl\{PPh_2CH_2(Bu^t)C{=}N{-}N{=}C(Me)C_5H_4N\}}]\mathrm{PF_6}$ **4e**.—A saturated solution of $\mathrm{NH_4PF_6}$ in ethanol was added to a solution of the chloropalladium(II) chloride salt **4d** (300 mg, 0.52 mmol) in ethanol (2 $\mathrm{cm^3}$). The $\mathrm{PF_6}$ salt **4e** was obtained as a pale yellow solid (290 mg, 81%) (Found: C, 42.65; H, 4.0; N, 6.0. $\mathrm{C_{25}H_{28}ClF_6N_3P_2Pd{\cdot}0.28CH_2Cl_2}$ requires C, 42.65; H, 4.0; N, 5.9%).

$[\mathrm{PtMe\{PPh_2CH{=}C(Bu^t)N{=}N{-}C(Me){=}C_5H_4N\}}]$ **5a**.—A solution of compound **Ia** (125 mg, 0.31 mmol) in ethanol (2.0 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{PtMe_2(cod)}]$ (100 mg, 0.30 mmol) in dichloromethane. Glacial acetic acid (0.2 $\mathrm{cm^3}$) was then added. When the effervescence had subsided, sodium methoxide (0.673 mol $\mathrm{dm^{-3}}$ in methanol, 0.45 $\mathrm{cm^3}$, 0.30 mmol) was then added. The required deprotonated product **5a** precipitated as a dark blue solid. Yield 122 mg, 67% (Found: C, 49.75; H, 4.8; N, 6.5. $\mathrm{C_{26}H_{30}N_3PPt{\cdot}0.25CH_2Cl_2}$ requires C, 49.75; H, 4.85; N, 6.6%). *m*/*z* (EI): 610 (M^+) and 595 (M − Me).

$[\mathrm{PtCl\{PPh_2CH{=}C(Bu^t)N{=}N{-}C(Me){=}C_5H_4N\}}]$ **5b**.—The chloroplatinum(II) complex **4b** (200 mg, 0.30 mmol) was dissolved in methanol (2.5 $\mathrm{cm^3}$). A solution of sodium methoxide in methanol (0.673 mol $\mathrm{dm^{-3}}$, 0.45 $\mathrm{cm^3}$, 0.30 mmol) was then added. The required product **5b** precipitated as a deep blue solid which was collected. Yield 102 mg, 54%. A sample for microanalysis was recrystallised from dichloromethane–methanol (Found: C, 47.0; H, 4.3; N, 6.4. $\mathrm{C_{25}H_{27}ClN_3PPt{\cdot}0.1CH_2Cl_2}$ requires C, 47.0; H, 4.3; N, 6.5%). *m*/*z* (EI): 630 (M^+).

$[\mathrm{PdCl\{PPh_2CH{=}C(Bu^t)N{=}N{-}C(Me){=}C_5H_4N\}}]$ **5c**.—The palladium(II) complex **4d** (80 mg, 0.14 mmol) was dissolved in dichloromethane (1.5 $\mathrm{cm^3}$). Triethylamine (0.02 $\mathrm{cm^3}$, 0.14 mmol) was added. The resulting intensely purple solution was evaporated to dryness under reduced pressure and the residue triturated with methanol, to give the required product **5c** as a purple solid (68 mg, 91%) (Found: C, 54.1; H, 4.85; N, 7.65. $\mathrm{C_{25}H_{27}ClN_3PPd{\cdot}0.2CH_2Cl_2}$ requires C, 54.1; H, 4.90; N, 7.50%), *m*/*z* (EI): 541 (M^+).

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