

Chemistry of the azine phosphine ligand Z,E -PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4): crystal structure of [Mo(CO)₄{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] ¹

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Abstract

Condensation of Z -PPh₂CH₂C(Bu^t)=NNH₂ with 4-nitroacetophenone gave the azine phosphine Z,E -PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4) (**1**). The corresponding phosphine oxide **II** was prepared by treatment of **1** with H₂O₂. The phosphine **1** with [Mo(CO)₄(nbd)] (nbd = norbornadiene) gave [Mo(CO)₄{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] (**1a**); the corresponding tungsten **1b** and chromium **1c** complexes were made similarly. The crystal structure of **1a** was determined by X-ray diffraction and showed the presence of a six-membered chelate ring with the bulky 4-nitrophenyl group held close to the metal. Oxidation of **1a** with bromine gave the seven-coordinate molybdenum(II) complex **2**. Treatment of [PtMe₂(cod)] (cod = cycloocta-1,5-diene) with **1** at 20°C gave the dimethylplatinum(II) complex [PtMe₂{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] (**3a**) which with MeI gave the iodotrimethylplatinum(IV) complex **4**. Treatment of **3a** with C=O opened the chelate ring to give the dimethyl(carbonyl)platinum(II) complex **5** containing a monodentate phosphine ligand. When **3a** was heated in toluene solution at 110°C it gave the cyclometallated methylplatinum(II) complex [PtMe{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] (**6**). Treatment of **6** with MeI gave the platinum(IV) complex **7**. The dichloropalladium(II) complex [PdCl₂{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] (**3b**) was prepared by treatment of [PdCl₂(NPh)₂] with **1** in CH₂Cl₂. Treatment of [PtCl₂(NMe)₂] with 2 equiv. of **1** gave the *trans*-bis(phosphine) complex **8**. When 2 equiv. of **1** were treated with [PtCl₂(cod)] followed by NH₄PF₆ this gave the salt **9a** containing two six-membered chelate rings; the analogous palladium(II) **9b** salt was also prepared. Treatment of 2 equiv. of **1** with [PtCl₂(cod)] followed by NH₄PF₆ gave the PF₆ salt **10** containing a six-membered chelate ring and a monodentate ligand. When **10** was treated with AgNO₃ followed by NH₄PF₆ this gave the bis-chelate complex **11** containing five- and six-membered chelate rings. Treatment of [IrCl(CO)₂(*p*-toluidine)] with **1** gave the cyclometallated iridium(III) hydride complex [IrHClCO{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] (**12**). [RuCl₂(PPh₃)₃] with the phosphine **1** resulted in the Ru(II) complex **13** in which the *ortho* hydrogens of the 4-nitrophenyl group are agostically interacting with ruthenium. Proton, phosphorus-31, some carbon-13 NMR and IR data have been obtained. Crystals of **1a** are orthorhombic, space group *Pna*2₁, with *a* = 1819.3(2), *b* = 1050.0(1), *c* = 1614.8(2) pm and *Z* = 4; final *R* = 0.0191 for 2616 observed reflections. © 1998 Elsevier Science S.A.

Keywords: Crystal structures; Molybdenum complexes; Azine phosphine complexes

1. Introduction

In a previous paper [1] we described the phosphino-hydrazone Z -PPh₂CH₂C(Bu^t)=NNH₂, prepared by treating

the phosphino-dimethylhydrazone Z -PPh₂CH₂C(Bu^t)=N–NMe₂ with hydrazine. We showed that Z -PPh₂CH₂C(Bu^t)=NNH₂ condensed readily with benzaldehyde to give the azine phosphine Z,E -PPh₂CH₂C(Bu^t)=N–N=CH(Ph) and the coordination chemistry of this azine phosphine with Group 6 metal carbonyls was studied [1] and also with palladium and platinum [2]. More recently, we have reported the condensation of Z -PPh₂CH₂C(Bu^t)=NNH₂ with aldehydes and sterically less demanding ketones {QC(=O)R} to give mixed-azine monophosphines of type Z,E -PPh₂CH₂C(Bu^t)=N–N=C(Q)R [3–9] where Q = H or Me and R is sterically more demanding than Q and of higher

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¹ I first met Jack Halpern in 1949/1950 at the University of Manchester, when I was an undergraduate, and he was a visiting Fellow from Canada working with M.G. Evans. I remember taking part in the undergraduates' tour of the research laboratories and finding what he was doing very interesting indeed, so that I stayed behind to talk to him when the rest of the group moved on. By the time I started research, in organic chemistry, he had left but our paths have crossed since then such as with mechanistic studies of oxidative addition reactions. I was extremely pleased to be asked to make this contribution and wish him the very best. Bernard Shaw.

priority, giving the *E*-configuration around the C=N bond. We have studied the coordination chemistry of these azine phosphines in particular, the promotion of agostic C–H interaction [3] or aryl fluoride coordination [4] with ruthenium(II), and cyclometallation with Ir(I) [5–7], W(0) [8] and Pt(II) [9].

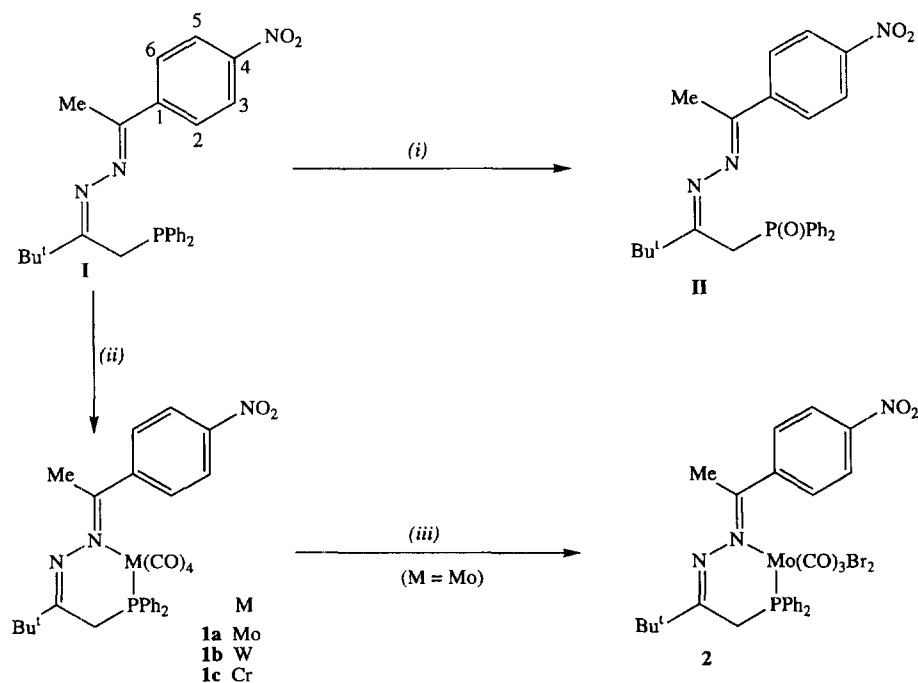
In this paper we have studied the ligating properties and reactions of the mixed azine formed by condensing 4-nitroacetophenone ($\text{CH}_3\text{COC}_6\text{H}_4\text{NO}_2$ -4) with $Z\text{-PPh}_2\text{CH}_2\text{-(Bu}^t\text{)=NNH}_2$. As described below, this mixed azine **I** was prepared in high yield as a simple geometrical isomer, which, from its subsequent chemistry, has the expected *Z,E*-configuration shown.

We have chosen to study this mixed azine phosphine containing the 4-nitro substituent as a ligand for a number of reasons. The starting material 4-nitroacetophenone was expected to condense readily to give a crystalline ligand which would be easy to isolate and characterise, with the 4-nitrophenyl and methyl protons giving distinct resonances in the NMR spectrum. The presence of the 4-nitro substituent in the phenyl ring would give a large difference in chemical shift between the pairs of *ortho* and *meta* hydrogens; larger than with other simple substituents [10], i.e. at 400 MHz the four hydrogens would approximate to an AA'XX' spin system, well removed from the phenyl hydrogens of the PPh_2 moieties [10]. Thus any interaction or metallation of the $\text{C}_6\text{H}_4\text{-NO}_2$ -4 system would be easy to detect and also to assign by proton and carbon NMR spectroscopy. One would expect of course that the 4-nitro substituent would increase the rate or tendency for nucleophilic attack on a $\text{C}_6\text{H}_4\text{NO}_2$ carbon, but reduce the rate or tendency for electrophilic attack. Thus it has been shown that the rates of palladation

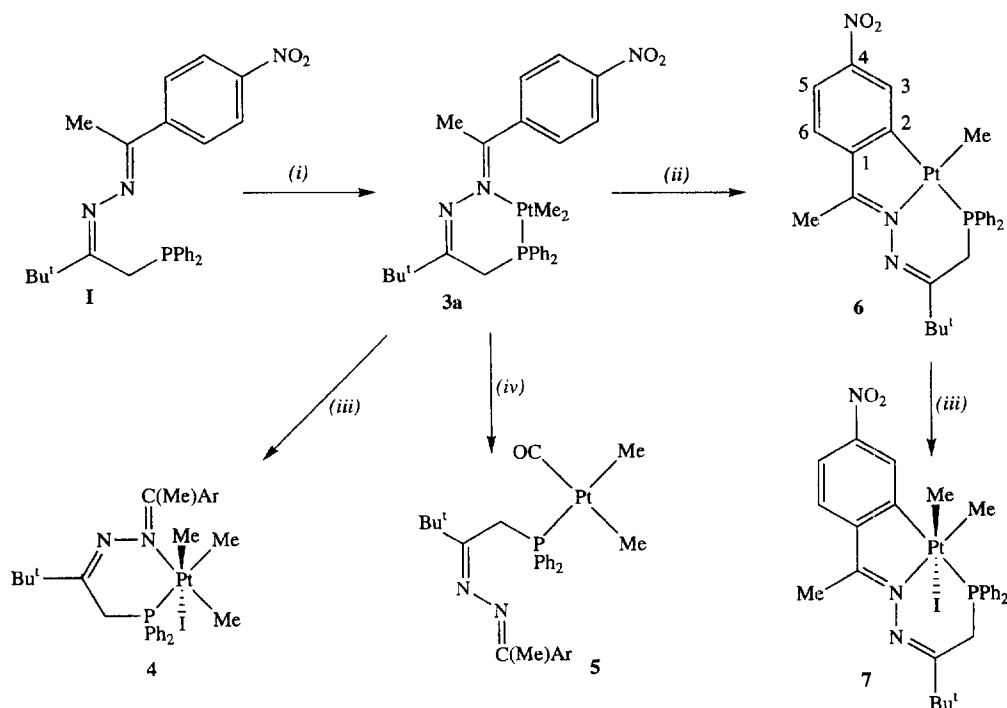
(electrophilic attack) are slowed by a nitro group, e.g. with substituted azo-benzenes [11], benzyl amines [12] or benzyl sulfides [13]. However, we found previously that cycloplatination of the mixed azine $Z\text{-PPh}_2\text{CH}_2\text{C(Bu}^t\text{)=N-N=CH(C}_6\text{H}_4\text{Y-4)}$ with Y=NO_2 was faster (~ 3 times) than with Y=H [9]. One would therefore expect platination of the 4-nitroacetophenone derivative to be just as favourable but there was also the possibility of isomerisation around the MeC=N moiety at higher temperatures leading to cyclometallation of the methyl group and not the 4-nitrophenyl group.

2. Results and discussion

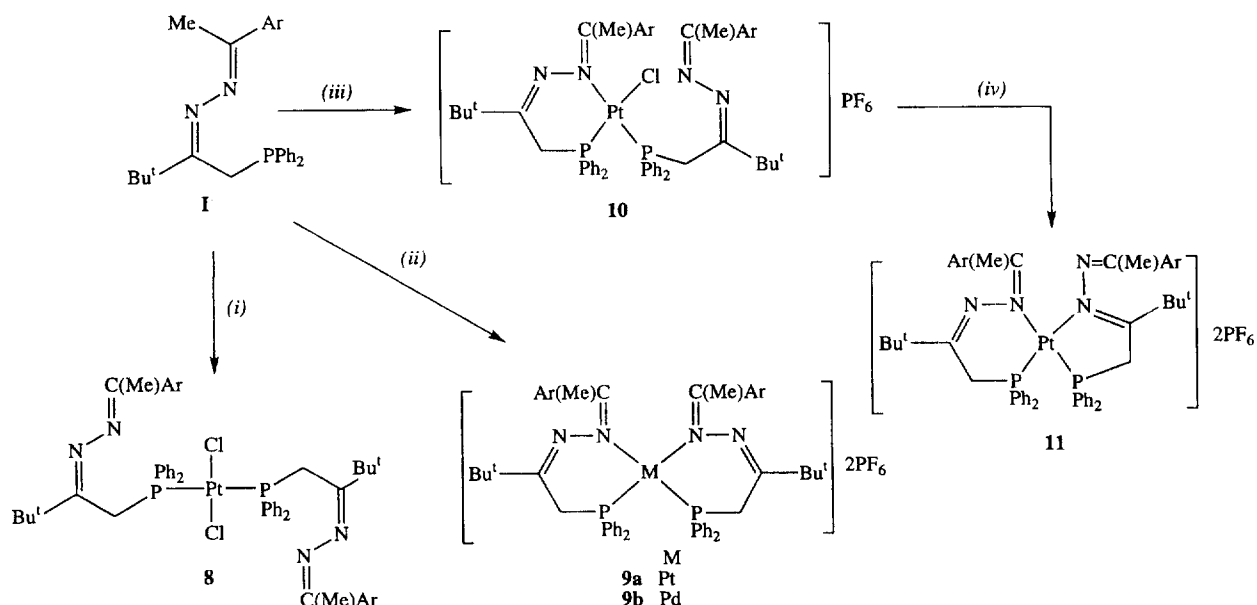
The various reactions of the new unsymmetrical azine phosphine **I** are summarised in Schemes 1–3 and 4. The compounds described in this paper were characterised by elemental analysis, mass spectroscopy, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Section 3), IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Table 1), and proton NMR spectroscopy (Table 2). The phosphino-hydrazone $Z\text{-PPh}_2\text{CH}_2\text{C(Bu}^t\text{)=NNH}_2$ condensed rapidly with 4-nitroacetophenone in ethanol solution to give the mixed azine phosphine $Z,E\text{-PPh}_2\text{CH}_2\text{C(Bu}^t\text{)=N-N=CMe(C}_6\text{H}_4\text{NO}_2\text{-4)}$ (**I**) as yellow needles, in 70% yield. In previous papers [1–9] we have formulated the configuration of analogous unsymmetrical azine phosphines as *Z,E*. The tetracarbonyl complex **1a**, which was prepared under mild conditions, where isomerisation around the C=N bonds would be minimal, was shown to have the *Z,E*-configuration by X-ray crystallography (see below); it is of course important to maintain the *Z,E*-configuration and to have a six-membered chelate ring if one is to promote cyclometallation of the 4-nitrophenyl group.



Scheme 1. (i) H_2O_2 ; (ii) for **1a**: $[\text{Mo(CO)}_4(\text{nbd})]$; for **1b**: $[\text{W(CO)}_4(\text{nbd})]$; for **1c**: $[\text{Cr(CO)}_4(\text{nbd})]$; (iii) Br_2 .



Scheme 2. Ar = (C₅H₄NO₂-4); (i) [PtMe₂(cod)]; (ii) heat, 110°C; (iii) MeI; (iv) CO.



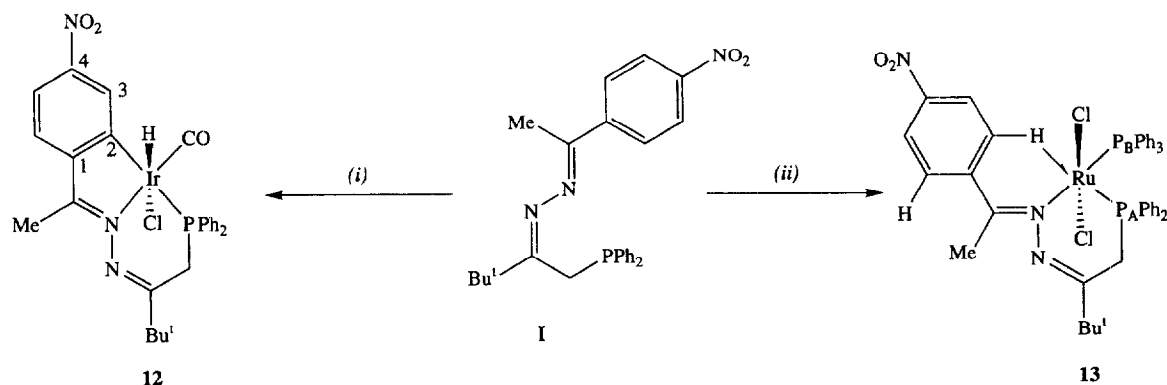
Scheme 3. Ar = (C₆H₄NO₂-4); (i) 0.5 [PtCl₂(NMe)₂]; (ii) for **9a**: 0.5 [PtCl₂(cod)], EtOH, reflux/NH₄PF₆; for **9b**: 0.5 [Na₂PdCl₄·4H₂O], EtOH, reflux/NH₄PF₆; (iii) 0.5 [PtCl₂(cod)], r.t./NH₄PF₆; (iv) AgNO₃/NH₄PF₆.

The ³¹P{¹H} NMR spectrum of **I** showed a singlet at δ_p -11.6 ppm. In the proton NMR spectrum the equivalent methylene protons gave a doublet at δ_H 3.32 ppm with a ²J(PH) value of 3.4 Hz. The *ortho* and *meta* aryl protons of the 4-nitrophenyl group gave an apparent AB pattern (a deceptively simple AA'BB' pattern) at δ_H 7.72 and 8.10 ppm (³J(HH) = 9.1 Hz). Such a pattern was observed for most of the compounds described in this paper. **I** was converted into the corresponding phosphine oxide **II** by treatment with

hydrogen peroxide. This showed a phosphorus resonance at δ_p 22.8 ppm. The methylene protons of **II** gave a doublet at δ_H 3.73 ppm with a larger ²J(PH) value (14.4 Hz) than did **I**, typical of phosphorus in oxidation state V.

2.1. Complexes of **I** with Group 6 metal carbonyls

Treatment of **I** with [Mo(CO)₄(nbd)] in C₆H₆ at ~20°C gave [Mo(CO)₄{PPh₂CH₂C(Bu')=N-N=CMe(C₆H₄NO₂-

Scheme 4. (i) $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$, C_6H_6 ; (ii) $[\text{RuCl}_2(\text{PPh}_3)_3]$, C_6H_6 .Table 1
IR and $^{31}\text{P}\{^1\text{H}\}$ NMR data ^a

	$\nu(\text{C}\equiv\text{N})$ ^b	$\nu(\text{NO}_2)$ ^b	$\nu(\text{C}\equiv\text{O})$ ^c	δP (ppm)	$^1J(\text{MP})$ (Hz)
I	1600s	1525s, 1350s		–11.6	
II	1600s	1525s, 1355s		22.8	
1a	1595w	1525m, 1340m	2010m, 1890s, 1840w	48.8	
1b	1615w	1535w, 1350m	2020w, 1895m, 1845w	42.4	257
1c	1605w	1530w, 1350w	2015m, 1905s, 1860w	66.3 ^g	
2	1600w	1540w, 1340w	2055m, 1990m, 1915m,br	61.8	
3a	1600m	1530m, 1350m		34.2 ^h	2149
3b ^d	1600m	1530s, 1350s		52.2 ^g	
3c	1595m	1530m, 1350s		49.7 ^g	
4	1600m	1525m, 1345m		6.4 ^g	1266
5	1600w	1525m, 1350m	2045s	19.0 ^j	1668
6	1615m	1535m, 1350m		34.4 ^j	2313
7	1600m	1525m, 1345m		–8.0 ^h	1538
8 ^e	1600m	1525m, 1350m		10.6	2582
9a	1600m	1530m, 1350m		27.3 ^g	3534
9b	1600m	1540m, 1350s		55.8 ⁱ	
10 ^f	1600m	1535m, 1350s		–7.3 (18)	3535
				35.3	3905
11	1600m	1540m, 1355m		14.6 (13) ^{1j}	3255
				24.2	3620
12 ^k	1615m	1515m, 1340m	2040s	16.9 ^j	
13	1620w	1525m, 1345m		47.1 (37.6) ^{g,j}	
				79.8	

^a IR data in cm^{-1} . Recorded at 36.2 MHz, chemical shifts are in ppm relative to 85% H_3PO_4 , solvent CDCl_3 unless otherwise indicated. ² $J(\text{PP})$ values (Hz) in parenthesis.

^b As compressed KBr disc.

^c In CH_2Cl_2 .

^d $\nu(\text{Pd-Cl}) = 300\text{w}$ and 340w cm^{-1} .

^e $\nu(\text{Pt-Cl}) = 350\text{w cm}^{-1}$.

^f $\nu(\text{Pt-Cl}) = 250\text{w cm}^{-1}$.

^g In CD_2Cl_2 .

^h In C_6D_6 .

ⁱ In acetone- d_6 .

^j Recorded at 101.3 MHz.

^k $\nu(\text{Ir-H}) = 2170\text{w cm}^{-1}$.

4)]] (**1a**), containing a six-membered chelate ring, as an orange crystalline solid in 91% yield (Scheme 1). The IR spectrum of this compound showed three bands for $\nu(\text{C}\equiv\text{O})$, at 2010, 1890 and 1840 cm^{-1} , similar to other values for zero-valent (P–N)-coordinated molybdenum(0) tetracarbonyls [1]. The phosphorus resonance was a singlet at 48.8 ppm and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed the presence

of four carbonyl ligands in a (2:1:1) ratio. The two mutually equivalent carbonyl groups gave a broad resonance at 207.0 ppm, the broadness probably being due to a fluxional process within the six-membered chelate ring. The two, non-equivalent carbonyl ligands gave doublets at 219.8 and 215.5 ppm, with $^2J(\text{PC})$ values of 7.2 and 36.0 Hz, respectively. One would expect the larger coupling to be due to the carbonyl

ligand *trans* to phosphorus. The low δ_c value of 25.5 ppm for the methylene carbon is typical of a methylene carbon in a six-membered chelate ring [2,14–18]. The crystal structure of complex **1a** was determined and is shown in Fig. 1, with selected bond lengths and angles in Table 3. The structure shows that the chelate ring is six-membered and that the 4-nitrophenyl group is held close to the metal and the configuration of the azine is *Z,E*, i.e. unchanged from the free ligand

I. We have found, for a series of mixed azines of type $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CQ}(\text{R})$, with R more sterically demanding than Q, that the configuration is *Z,E* [1,4–9]. It was necessary to determine the structure of the complex $[\text{Mo}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]$ and to show that the azine phosphine **I** has the *Z,E*-configuration since it was possible that isomerization around a $\text{N}=\text{C}$ might have occurred and the complex ligand might have been

Table 2
Proton NMR data ^a

	$\delta(\text{Bu}^t)$	$\delta(\text{MeC}=\text{N})$	$\delta(\text{CH}_2)$	Others
I	1.22(9H, s)	2.14(3H, s)	3.32(2H, d, 3.4 ^b)	7.72(2H, d, 9.1 ^f , ArH) 8.10(2H, d, 9.1 ^f , ArH)
II	1.20(9H, s)	2.20(3H, s)	3.73(2H, d, 14.4 ^b)	7.56(2H, d, 9.0 ^f , ArH) 7.97(2H, d, 9.0 ^f , ArH)
1a ^{p,r}	0.92(9H, s)	2.20(3H, d, 2.4 ⁱ)	2.53(1H, dd, 9.4 ^b , 12.7 ^c) 3.40(1H, dd, 10.3 ^b , 12.7 ^c)	7.49(2H, d, 9.0 ^f , ArH) 8.26(2H, d, 9.0 ^f , ArH)
1b	0.93(9H, s)	2.20(3H, d, 2.9 ⁱ)	2.65(1H, s, br) 3.39(1H, s, br)	7.47(2H, d, 8.9 ^f , ArH) 8.26(2H, d, 8.9 ^f , ArH)
1c ^{m,q}	0.85(9H, s)	2.08(3H, d, 3.2 ⁱ)	2.62(1H, s, br) 3.42(1H, s, br)	8.18(2H, d, 9.3 ^f , ArH)
2	0.93(9H, s)	2.37(3H, s)	3.74(1H, t, 15.1 ^b , 15.1 ^c) 5.12(1H, dd, 10.3 ^b , 15.1 ^c)	8.11(2H, d, 9.0 ^f , ArH) 8.33(2H, d, 9.0 ^f , ArH)
3a ^{n,q}	0.78(9H, s)	1.59(3H, d, 2.1 ⁱ , 4.6 ^h)	2.06(1H, dd, 10.5 ^b , 12.9 ^c , 9.3 ^g) 3.21(1H, dd, 10.4 ^b , 12.9 ^c , 18.0 ^g)	0.77(3H, d, 7.8 ^e , 69.8 ^d , PtMe) 1.33(3H, d, 7.8 ^e , 91.0 ^d , PtMe)
3b ^m	0.98(9H, s)	2.48(3H, d, 1.0 ⁱ)	2.56(1H, dd, 11.5 ^b , 13.2 ^c) 3.30(1H, dd, 12.9 ^b , 13.2 ^c)	7.67(2H, d, 9.1 ^f , ArH) 8.15(2H, d, 9.1 ^f , ArH)
3c ^m	1.00(9H, s)	2.51(3H, d, 1.5 ⁱ)	2.56(1H, dd, 12.7 ^b , 12.8 ^c) 3.28(1H, dd, 15.4 ^b , 12.8 ^c)	7.89(2H, d, 8.9 ^f , ArH) 8.23(2H, d, 8.9 ^f , ArH)
4 ^{m,r}	1.34(9H, s)	2.55(3H, s)	4.25(1H, dd, 9.4 ^b , 16.5 ^c) 4.46(1H, dd, 12.7 ^b , 16.5 ^c)	0.81(3H, d, 7.3 ^e , 72.7 ^d , PtMe) 1.02(3H, d, 7.6 ^e , 56.1 ^d , PtMe) 1.62(3H, d, 6.8 ^e , 76.2 ^d , PtMe) 8.05(2H, d, 8.9 ^f , ArH) 8.28(2H, d, 8.9 ^f , ArH)
5 ^s	1.21(9H, s)	2.34(3H, s)	4.00(2H, d, 12.0 ^b , 17.1 ^g)	0.12(3H, d, 13.9 ^e , 69.5 ^d , PtMe) 0.77(3H, d, 7.3 ^e , 74.7 ^d , PtMe) 7.87(2H, d, 9.0 ^f , ArH) 8.23(2H, d, 9.0 ^f , ArH)
6 ^s	0.89(9H, s)	2.55(3H, s)	3.31(2H, d, 11.5 ^b , 21.6 ^g)	1.01(3H, d, 6.7 ^e , 84.4 ^d , PtMe) 7.73(1H, dd, 8.6 ^f , 1.6 ⁱ , 6.4 ^h , H ⁶) 8.00(1H, dd, 8.6 ^f , 2.3 ^k , H ⁵) 8.64(1H, dd, 2.3 ^k , 6.8 ⁱ , 57.3 ^g , H ³)
7 ⁿ	0.78(9H, s)	2.32(3H, s, 3.7 ^h)	3.57(1H, t, 13.1 ^b , 13.1 ^c) 4.75(1H, t, 13.1 ^b , 13.1 ^c)	0.97(3H, d, 6.4 ^e , 69.1 ^d , PtMe) 1.80(3H, d, 6.4 ^e , 69.1 ^d , PtMe) 8.33(2H, d, 9.0 ^f , H ⁶) 8.98(1H, dd, 2.2 ^k , 7.9 ⁱ , 38.1 ^g , H ³)
8	1.20(18H, s)	1.97(6H, s)	4.31(4H, vt, 9.8 ^j , 24.6 ^g)	7.59(4H, d, 8.8 ^f , ArH) 8.11(4H, d, 8.8 ^f , ArH)
9a ^m	0.36(18H, s)	2.46(6H, s)	3.17(2H, t, 14.5 ^b , 14.5 ^c) 3.64(2H, t, 14.5 ^b , 14.5 ^c)	8.11(4H, d, 8.7 ^f , ArH) 8.51(4H, d, 8.7 ^f , ArH)
9b ^o	0.44(18H, s)	2.57(6H, s)	3.74(2H, dd, 16.2 ^b , 13.7 ^c) 3.91(2H, dd, 13.6 ^b , 13.7 ^c)	8.47(4H, d, 8.9 ^f , ArH) 8.72(4H, d, 8.9 ^f , ArH)
10 ^s	0.81(9H, s) 1.15(9H, s)	1.62(3H, s) 2.61(3H, s)	2.92(1H, dd, 11.1 ^b , 17.7 ^c) 4.18(1H, dd, 10.8 ^b , 17.7 ^c) 3.11(1H, t, 14.0 ^b , 14.0 ^c) 3.49(1H, t, 14.0 ^b , 14.0 ^c)	7.70(2H, d, 8.8 ^f , ArH) 8.26(2H, d, 8.8 ^f , ArH) 8.19(2H, d, 9.0 ^f , ArH) 8.38(2H, d, 9.0 ^f , ArH)
11 ^{o,s}	0.98(9H, s) 1.30(9H, s)	2.17(3H, s) 3.05(3H, s)	4.11(1H, t, 13.8 ^b , 14.0 ^c) 4.22(1H, t, 13.9 ^b , 13.9 ^c) 4.37(1H, dd, 9.4 ^b , 19.7 ^c) 4.83(1H, dd, 12.1 ^b , 19.7 ^c)	8.32(2H, d, 9.0 ^f , ArH) 8.44(4H, d, 7.0 ^f , ArH) 8.54(2H, d, 9.0 ^f , ArH)

(continued)

Table 2 (continued)

	$\delta(\text{Bu}^1)$	$\delta(\text{MeC}=\text{N})$	$\delta(\text{CH}_2)$	Others
12 ^a	0.73(9H, s)	2.76(3H, s)	3.64(1H, dd, 14.0 ^b , 12.5 ^c) 4.20(1H, t, 12.5 ^b , 12.5 ^c)	– 16.8(1H, d, 10.0 ^b , IrH) 7.90(1H, dd, 8.6 ^f , 1.4 ⁱ , H ^g) 8.06(1H, dd, 8.6 ^f , 2.2 ^k , H ^g) 8.77(1H, dd, 2.2 ^k , 6.8 ^j , H ^g)
13 ^{m,s}	0.70(9H, s)	2.66(3H, s)	3.22(2H, d, 14.9 ^b) ^t	17.47(2H, d, 8.6 ^f , ArH) 7.53(2H, dd, 8.6 ^f , 1.6 ^b , agostic-H)

^a Recorded at 100 MHz, chemical shifts (δ) are in ppm relative to SiMe₄, J in Hz, solvent CDCl₃ unless otherwise stated (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br = broad).

^b ² $J(\text{PH})$.

^c ² $J(\text{HH})$.

^d ² $J(\text{PtH})$.

^e ³ $J(\text{PH})$.

^f ³ $J(\text{HH})$.

^g ³ $J(\text{PtH})$.

^h ⁴ $J(\text{PtH})$.

ⁱ ⁵ $J(\text{PH})$.

^j $N = |^2J(\text{PH}) + ^4J(\text{PH})|$.

^k ⁴ $J(\text{HH})$.

^l ⁴ $J(\text{PH})$.

^m In CD₂Cl₂.

ⁿ In C₆D₆.

^o In acetone-d₆.

^p Recorded at –20°C.

^q Aryl protons obscured in aromatic region.

^r Recorded at 400 MHz.

^s Recorded at 250 MHz.

^t At –50°C the resonances of the methylene protons were observed at 3.24 (1H, t, 11.4^b, 11.4^c) and 3.31(1H, t, 11.4^b, 11.4^c).

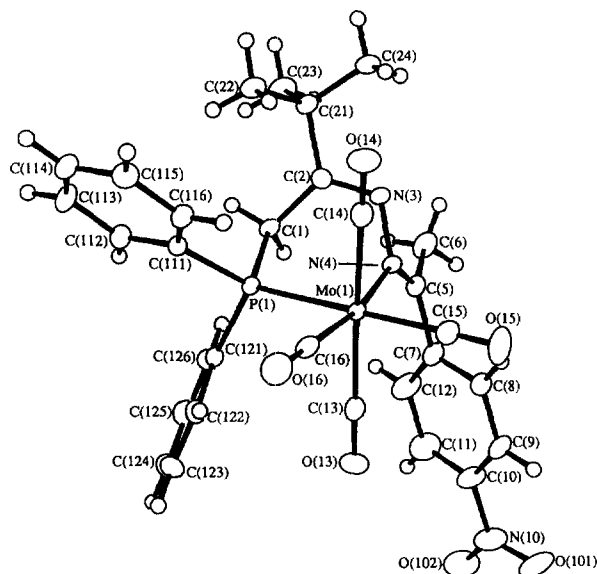


Fig. 1. Molecular structure of [Mo(CO)₄(PPh₂CH₂CBu¹)=N–N=CMe–(C₆H₄NO₂-4)] (1a).

Z,Z with the sterically demanding C₆H₄NO₂-4 group pointing away from the metal. There is nothing unusual about the bond angles and bond lengths that we determined for complex 1a.

The resonance(s) of the methylene protons of 1a were not observed in the proton NMR spectrum at 20°C. The ¹H and ¹H{³¹P} NMR spectra of 1a have therefore been studied at various temperatures. Below 253 K the two methylene pro-

tons are non-equivalent; e.g. in the ¹H{³¹P} NMR spectrum an AB pattern is observed. At this temperature it is possible that the conformation of the six-membered ring complex 1a is that found in the crystal structure (Fig. 1). As the temperature is raised the resonances of the CH₂ protons broaden until at 301 K they are too broad to be observed. At 327 K they have coalesced to a broad singlet and above this temperature the methylene protons are equivalent, reaching a fast exchange limit. Presumably, the process which causes this equivalence involves a six-membered ring inversion that effectively generates a plane of symmetry through the molecule. A medium exchange limit at 327 and 301 K causes the methylene protons to be too broad to be observed, and at 285 K and below a slow exchange limit comes into effect.

The analogous tungsten (1b) and chromium (1c) complexes were also prepared. The characterising data for these compounds can be found in Tables 1 and 2, and in Section 3. The oxidation of the tetracarbonylmolybdenum(0) complex, 1a, with bromine gave the hoped for tricarbonylmolybdenum(II) complex [MoBr₂(CO)₃(PPh₂CH₂C(Bu¹)=N–N=CMe(C₆H₄NO₂-4))] (2) as a yellow solid. The strong carbonyl absorptions, $\nu(\text{C}=\text{O})$, at 2055, 1990 and 1915 cm^{–1}, are in the expected range for a tricarbonyl derivative of seven-coordinate molybdenum(II) [19–22].

2.2. Complexes of I with platinum and palladium

We hoped to induce cyclometallation of the 4-nitrophenyl group and for this purpose we made a methylplatinum(II)

Table 3

Selected bond lengths (pm) and angles (°) for compound **1a** with e.s.d.s in parentheses

P(1)–Mo(1)	250.5(4)	N(4)–Mo(1)	231.2(4)
C(13)–Mo(1)	204.8(5)	C(14)–Mo(1)	205.1(5)
C(15)–Mo(1)	198.7(5)	C(16)–Mo(1)	196.1(5)
C(111)–P(1)	183.1(3)	C(121)–P(1)	183.9(3)
C(1)–P(1)	186.1(5)		
C(2)–C(1)	152.3(6)	C(21)–C(2)	153.5(6)
N(3)–C(2)	127.9(5)	C(22)–C(21)	153.0(7)
C(23)–C(21)	154.1(6)	C(24)–C(21)	153.3(6)
N(4)–N(3)	141.7(4)	C(5)–N(4)	129.3(5)
C(6)–C(5)	150.0(6)	C(7)–C(5)	148.5(4)
N(10)–C(10)	144.5(4)	O(101)–N(10)	122.8(5)
O(102)–N(10)	122.3(5)		
O(13)–C(13)	113.6(5)	O(14)–C(14)	113.9(5)
O(15)–C(15)	115.3(4)	O(16)–C(16)	115.6(5)
N(4)–Mo(1)–P(1)	77.1(2)	C(13)–Mo(1)–P(1)	90.7(2)
C(13)–Mo(1)–N(4)	95.8(2)	C(14)–Mo(1)–P(1)	93.8(2)
C(14)–Mo(1)–N(4)	89.7(2)	C(14)–Mo(1)–C(13)	173.6(1)
C(15)–Mo(1)–P(1)	177.8(1)	C(15)–Mo(1)–N(4)	100.8(2)
C(15)–Mo(1)–C(13)	88.9(2)	C(15)–Mo(1)–C(14)	86.8(2)
C(16)–Mo(1)–P(1)	93.3(2)	C(16)–Mo(1)–N(4)	169.9(1)
C(16)–Mo(1)–C(13)	87.4(2)	C(16)–Mo(1)–C(14)	87.8(2)
C(16)–Mo(1)–C(15)	88.9(2)		
C(111)–P(1)–Mo(1)	121.2(2)	C(121)–P(1)–Mo(1)	115.2(2)
C(121)–P(1)–C(111)	102.5(2)	C(1)–P(1)–Mo(1)	109.8(2)
C(1)–P(1)–C(111)	102.1(2)	C(1)–P(1)–C(121)	104.1(2)
C(112)–C(111)–P(1)	120.1(2)	C(116)–C(111)–P(1)	119.4(2)
C(122)–C(121)–P(1)	115.6(2)	C(126)–C(121)–P(1)	124.3(2)
H(1a)–C(1)–P(1)	109.0(2)	H(1b)–C(1)–P(1)	108.8(2)
C(2)–C(1)–P(1)	111.5(3)		
C(2)–C(1)–H(1a)	108.9(2)	C(2)–C(1)–H(1b)	109.0(3)
C(21)–C(2)–C(1)	120.4(3)	N(3)–C(2)–C(1)	122.4(3)
N(3)–C(2)–C(21)	117.2(4)	C(22)–C(21)–C(2)	108.9(3)
C(23)–C(21)–C(2)	109.0(3)	C(23)–C(21)–C(22)	109.5(4)
C(24)–C(21)–C(2)	110.6(3)	C(24)–C(21)–C(22)	109.7(3)
C(24)–C(21)–C(23)	109.1(4)	H(22a)–C(22)–C(21)	108.4(3)
H(22b)–C(22)–C(21)	107.2(3)	H(22c)–C(22)–C(21)	112.7(3)
H(23a)–C(23)–C(21)	111.6(3)	H(23b)–C(23)–C(21)	110.6(3)
H(23c)–C(23)–C(21)	106.1(3)	H(24a)–C(24)–C(21)	110.4(3)
H(24b)–C(24)–C(21)	108.6(3)	H(24c)–C(24)–C(21)	109.4(3)
N(4)–N(3)–C(2)	116.4(3)	N(3)–N(4)–Mo(1)	109.8(3)
C(5)–N(4)–Mo(1)	136.2(2)	C(5)–N(4)–N(3)	113.9(3)
C(6)–C(5)–N(4)	123.4(4)	C(7)–C(5)–N(4)	119.8(4)
C(7)–C(5)–C(6)	116.8(3)	H(6a)–C(6)–C(5)	108.7(3)
H(6b)–C(6)–C(5)	106.9(3)	H(6c)–C(6)–C(5)	112.7(3)
C(8)–C(7)–C(5)	122.0(2)	C(12)–C(7)–C(5)	117.7(2)
N(10)–C(10)–C(9)	120.6(2)	N(10)–C(10)–C(11)	119.4(2)
O(101)–N(10)–C(10)	117.8(4)	O(102)–N(10)–C(10)	118.3(4)
O(102)–N(10)–O(101)	123.9(4)		
O(13)–C(13)–Mo(1)	174.6(3)	O(14)–C(14)–Mo(1)	175.5(3)
O(15)–C(15)–Mo(1)	175.2(3)	O(16)–C(16)–Mo(1)	179.4(3)

complex by treating the azine phosphine **I** with [PtMe₂(cod)] (cod=cycloocta-1,5-diene) at ~20°C in benzene solution. This gave the hoped for bidentate dimethylplatinum(II) complex **3a** (Scheme 2), which has a δ_p value of 34.2 ppm with $^1J(\text{PtP}) = 2149$ Hz. This small $^1J(\text{PtP})$ value is consistent with phosphorus *trans* to a methyl group [2,9,14,18,23,24]. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonance for the methylene carbon was a doublet at 25.0 ppm, with $^1J(\text{PC}) = 17.3$ Hz. The methyl carbon *cis* to phos-

phorus gave a doublet at –23.2 ppm with a small $^2J(\text{PC})$ value of 4.1 Hz, whilst the methyl carbon *trans* to phosphorus gave a doublet at 7.7 ppm with a large $^2J(\text{PC})$ value of 109.4 Hz. The proton NMR spectrum showed two doublets with platinum-195 satellites for the two methyl groups on platinum; the signal at 0.77 ppm with $^2J(\text{PtH}) = 69.8$ Hz is due to the protons of the methyl group *trans* to phosphorus [2,9,14,18,24,25] and the other, at 1.33 ppm with $^2J(\text{PtH}) = 91.0$ Hz, is assigned to the protons of the methyl

group *trans* to nitrogen [2,9,14,18,26,27]. The MeC=N proton gave a doublet at 1.59 ppm with satellites ($^5J(\text{PH}) = 2.1$ Hz and $^4J(\text{PtH}) = 4.6$ Hz).

We anticipated that complex **3a** would undergo oxidative addition and treatment with an excess of MeI gave the trimethylplatinum(IV) adduct **4**. The small $^1J(\text{PtP})$ value of 1266 Hz is typical for platinum(IV) [2,18,23,28,29]. There were three chemically inequivalent platinum methyls, one *trans* to nitrogen, one *trans* to iodine ($^2J(\text{PtH}) = 72.7$ or 76.2 Hz) [30] and one *trans* to phosphorus ($^2J(\text{PtH}) = 56.1$ Hz) [31]. The proton NMR spectrum indicated a *fac*-PtMe₃ arrangement. We hoped that the six-membered chelate ring in **3a** might be sufficiently weak to open up at the N–Pt bond and when carbon monoxide was bubbled through a solution of **3a** in CDCl₃ at 20°C chelate ring opening occurred to give complex **5**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** consisted of a singlet at 19.0 ppm with platinum-195 satellites ($^1J(\text{PtP}) = 1668$ Hz). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the doublet at –1.6 ppm with a large $^2J(\text{PC})$ value of 93.3 Hz was assigned to the methyl carbon *trans* to phosphorus, whilst the doublet at 5.9 ppm with a small $^2J(\text{PC})$ value of 7.6 Hz was assigned to the methyl carbon *cis* to phosphorus. A low field doublet at 182.0 ppm with a $^2J(\text{PC})$ value of 4.6 Hz was assigned to the carbonyl ligand, which also showed a strong absorption at 2045 cm^{–1} in the IR spectrum [32].

We have recently shown that azine phosphines of type **I** form metal complexes in which the more sterically demanding aryl or alkyl group is compressed against the metal and is therefore susceptible to C–H bond activation [5,7,9]. The stereochemistry of the ligand being *Z,E* with a six-membered chelate ring when coordinated under mild conditions was shown here by the X-ray crystal structure of **1a**. It was therefore anticipated that an *ortho* hydrogen on the 4-nitrophenyl group in **3a** would be activated and might be substituted by platinum to give a cyclometallated complex, with loss of methane. We therefore heated **3a** in toluene at ~110°C and monitored the progress of the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. We found that as the resonances due to **3a** decreased in intensity a new set of resonances due to the hoped for complex **6** formed, $\delta_{\text{P}} 34.4$ ppm ($^1J(\text{PtP}) = 2313$ Hz). The cyclometallation was essentially complete after 18 h and **6** was isolated. **6** was studied by ^1H , ^{13}C , DEPT and C–H COSY NMR spectroscopy and resonances due to carbons (C¹–C⁶) and protons (H³, H⁵ and H⁶) of the 4-nitrophenyl group have been fully assigned. The platinum methyl group gave a doublet with satellites at $\delta_{\text{H}} 1.01$ ppm, $^2J(\text{PtH})$ value of 84.4 Hz, typical of a methyl group *trans* to nitrogen [2,9,14,26,27]. The two methylene protons were equivalent and gave a doublet at 3.31 ppm with satellites ($^2J(\text{PH}) = 11.5$ Hz and $^3J(\text{PtH}) = 21.6$ Hz). The resonances of the three protons attached to the *ortho*-metallated 4-nitrophenyl group were clearly observed; a doublet of doublets at 7.73 ppm, with $^3J(\text{HH}) = 8.6$ Hz, $^5J(\text{PH}) = 1.6$ Hz and $^4J(\text{PtH}) = 6.4$ Hz is due to the proton attached to C⁶ and a doublet of doublets at 8.00 ppm with coupling to hydrogen only ($^3J(\text{HH}) = 8.6$ Hz and $^4J(\text{HH}) = 2.3$ Hz) to the proton attached to C⁵. Another

doublet of doublets at 8.64 ppm with coupling to hydrogen, phosphorus and platinum ($^4J(\text{HH}) = 2.3$ Hz, $^4J(\text{PH}) = 6.8$ Hz and $^3J(\text{PtH}) = 57.3$ Hz) was assigned to the proton attached to C³. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonance for the methylene carbon was a doublet at $\delta_{\text{C}} 22.8$ ppm, with $^1J(\text{PC}) 22.9$ Hz, consistent with it being in a six-membered chelate ring [2,14–18]. The platinum methyl group gave a doublet at –15.9 ppm, the small $^2J(\text{PC})$ value of 4.7 Hz being indicative of a *cis* stereochemistry with respect to phosphorus. The metallated C² carbon of the 4-nitrophenyl group gave a doublet at 170.7 ppm, with a $^2J(\text{PC})$ value of 125.6 Hz and a $^1J(\text{PtC})$ value of 942 Hz; these coupling constants are typical of a metallated aryl carbon [23]. The C³ and C⁶ carbons gave doublets at 125.5 ppm ($^3J(\text{PC}) = 1.8$ Hz and $^2J(\text{PtC}) = 96.2$ Hz) and 127.4 ppm ($^4J(\text{PC}) = 5.9$ Hz and $^3J(\text{PtC}) = 35.8$ Hz), respectively. The quaternary carbon C¹ gave a doublet at 149.2 ppm ($^3J(\text{PC}) = 9.4$ Hz and $^2J(\text{PtC}) = 76.3$ Hz), and the C⁴ and C⁵ carbons singlets at 153.4 and 119.5 ppm, respectively.

Treatment of the *ortho*-metallated platinum(II) complex **6** with an excess of methyl iodide at ~20°C gave the platinum(IV) adduct **7**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** was a singlet at $\delta_{\text{P}} -8.0$ ppm with a $^1J(\text{PtP})$ value of 1538 Hz, typical of a platinum(IV) adduct. In the proton NMR spectrum the methyls gave doublets at $\delta_{\text{H}} 0.97$ and 1.80 ppm; both methyls gave the same coupling to platinum-195 ($^2J(\text{PtH}) = 69.1$ Hz) and to phosphorus ($^3J(\text{PH}) = 6.4$ Hz), indicating that the methyl groups are *trans* to either nitrogen or iodine and not to carbon or phosphorus. As expected the methylene protons appeared as an AB pattern in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum; at 3.57 and 4.75 ppm with $^2J(\text{HH}) = 13.1$ Hz and in the ^1H NMR spectrum $^3J(\text{PH}) \sim 13$ Hz.

We also studied the coordination chemistry of **I** with chlorides of palladium(II) and platinum(II). Treatment of *trans*-[PdCl₂(NCPh)₂] with **I** gave the expected complex [PdCl₂{PPh₂CH₂C(Bu^t)=N–N=CMe(C₆H₄NO₂-4)}] (**3b**) in good yields. The IR spectrum of complex **3b** showed bands at 300 and 340 cm^{–1} due to $\nu(\text{Pd–Cl})$, typical of a *cis*-PdCl₂ moiety, and the proton NMR spectrum showed coupling between phosphorus and methyl protons with $^5J(\text{PH}) = 1.0$ Hz. We tentatively suggest that **3b** has a six-membered chelate ring. Treatment of **3b** with NaI in acetone gave the corresponding diiodo complex **3c** in 95% yield, the characterising data for which are in Tables 1 and 2 and Section 3. When *trans*-[PtCl₂(NCMe)₂] was treated with 2 equiv. of **I** in dichloromethane at 20°C the platinum dichloride complex **8**, with *trans* monodentate phosphines was obtained. The phosphorus-31 NMR spectrum showed a singlet resonance at $\delta_{\text{P}} 10.6$ ppm with $^1J(\text{PtP}) = 2582$ Hz, this value of platinum-195 phosphorus coupling is typical of mutually *trans* phosphines coordinated to platinum(II) [23]. The proton NMR spectrum showed a well-defined ‘virtual triplet’ pattern for the CH₂ protons with $N = ^2J(\text{PH}) + ^4J(\text{PH}) = 9.8$ Hz, with satellites due to platinum-195 coupling ($^3J(\text{PtH}) = 24.6$ Hz), typical of mutually *trans* phosphines [23,28,33].

We have previously described the *cis*-bis(chelate) Pt(II) dicationic salts of the azine phosphine $[\text{PPh}_2\text{CH}_2\text{-C}(\text{Bu}^i)=\text{NN}=\text{C}(\text{H})\text{Ph}]$ [2]. It was considered that these salts were five-membered chelate ring complexes because the methylene protons could be easily deprotonated by sodium methoxide [2]. When $[\text{PtCl}_2(\text{cod})]$ was heated with 2 equiv. of **I** in ethanol for 40 min the bis(chelate) dication was formed and was isolated as the bis(hexafluorophosphate) salt **9a**. The $^1J(\text{PtP})$ value of 3534 Hz in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is in agreement with phosphorus being *trans* to nitrogen [23,34], i.e. the cation had *cis* stereochemistry. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum suggested that complex **9a** contained a six-membered chelate ring, the methylene carbon resonance consisting of a 'filled in' doublet at δ_{C} 27.1 ppm ($N = ^1J(\text{PC}) + ^3J(\text{PC}) = 40.0$ Hz), this explaining the reluctance of the methylene protons to undergo deprotonation reactions with bases such as sodium methoxide or triethylamine. In the proton NMR spectrum the methylene protons gave a doublet of doublets at δ_{H} 3.17 and 3.64 ppm and the methyl protons a singlet at 2.46 ppm. The analogous bis(chelate) palladium(II) salt **9b** was also prepared, by treating $\text{Na}_2\text{PdCl}_4 \cdot 4\text{H}_2\text{O}$ with 2 equiv. of the phosphine **I** and heating the mixture for 1 h in ethanol. The hexafluorophosphate salt **9b** was isolated and characterised in a similar manner to **9a**.

Treatment of $[\text{PtCl}_2(\text{cod})]$ with 2 equiv. of **I** at $\sim 20^\circ\text{C}$ in dichloromethane gave the monocationic salt **10**, after treatment with 1 equiv. of NH_4PF_6 in methanol. A band at 250 cm^{-1} in the IR spectrum of **10** was indicative of $\nu(\text{Pt-Cl})$ and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed an AB pattern with satellites ($\delta(\text{P}_\text{A}) - 7.3$ ppm, $^1J(\text{PtP}_\text{A}) = 3535$ Hz and $\delta(\text{P}_\text{B}) 35.3$ ppm, $^1J(\text{PtP}_\text{B}) = 3905$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 18$ Hz). This is consistent with two inequivalent mutually *cis*-phosphorus atoms, one *trans* to nitrogen ($^1J(\text{PtP}_\text{A}) = 3535$ Hz) [23,34] and the other *trans* to chlorine ($^1J(\text{PtP}_\text{B}) = 3905$ Hz) [23,35], respectively. The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum showed two AB patterns for the two sets of methylene protons. One set at δ_{H} 3.11 and 3.49 ppm (similar chemical shifts to those in **9a**) arise from the methylene protons in a six-membered chelate ring. The other two doublets, at δ_{H} 2.92 and 4.18 ppm, are assigned to the monodentate ligand coordinating through phosphorus with restricted rotation, therefore causing the inequivalent protons. The fast bombardment (FAB) mass spectrum showed a molecular ion at $m/z = 1121$, in agreement with $M - \text{PF}_6$. We therefore formulate complex **10** with the structure shown.

AgNO_3 is a well known chloride abstractor and it was anticipated that treatment of complex **10** with silver nitrate would result in the formation of a vacant site on platinum giving the nitrate analogue or, by coordination of nitrogen on the monodentate ligand, the bis-chelate complex. In fact, treatment of **10** with silver nitrate gave complex **11**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **10** at $\delta(\text{P}_\text{A}) 14.6$ ppm and $\delta(\text{P}_\text{B}) 24.2$ ppm with $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 13$ Hz, $^1J(\text{PtP}_\text{A}) = 3255$ Hz and $^1J(\text{PtP}_\text{B}) = 3620$ Hz indicated that the nitrate group had now replaced the chloride ($^1J(\text{PtP})$ for phosphorus *trans* to nitrate

ligand is larger than 4000 Hz [23,24,36]) and furthermore the chelate effect is clearly observed where $\delta(\text{P}_\text{A})$ in complex **10** has shifted from -7.3 to 14.6 ppm in complex **11**. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the two methylene carbons gave doublets, at 26.6 and 45.7 ppm with $^1J(\text{PC}) = 33.1$ and 40.8 Hz, respectively. The resonance at 26.6 ppm is assigned to the methylene carbon in the six-membered chelate ring and the resonance at 45.7 ppm to the methylene carbon in the five-membered chelate ring [14–18]. The proton NMR spectrum showed two AB patterns for the methylene protons, at 4.11 and 4.22 ppm ($^2J(\text{PH}) = 13.9$ Hz and $^2J(\text{HH}) = 13.9$ Hz) and at 4.37 ppm ($^2J(\text{PH}) = 9.4$ Hz and $^2J(\text{HH}) = 19.7$ Hz) and 4.83 ppm ($^2J(\text{PH}) = 12.1$ Hz and $^2J(\text{HH}) = 19.7$ Hz), but we have been unable to assign these resonances to the five- or six-membered chelate rings.

2.3. Complexes of **I** with iridium and ruthenium

We have recently shown that mixed azine phosphines $\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{N}-\text{N}=\text{CQ}(\text{R})\}$, where R is sterically more demanding than Q, are susceptible to C–H bond activation (fission) with Ir(I) [5,7] and also agostic interactions with Ru(II) [3]. The promotion of such reactions is probably to be due to the bulky group being forced against the metal centre, which to some extent has been confirmed by X-ray crystallography (Fig. 1). Treatment of $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ with 1 equiv. of **I** at room temperature gave the cyclometallated iridium(III) hydride **12** in 86% yield, where the 4-nitrophenyl group has undergone C–H bond fission at an *ortho* position. The phosphorus resonance of complex **12** was a singlet at 16.9 ppm and in the IR spectrum $\nu(\text{Ir-H})$ and $\nu(\text{C}\equiv\text{O})$ occurred at 2170 and 2040 cm^{-1} , respectively, these values are typical for iridium(III) hydrides of this type [5,7,37]. As with the *ortho* metallated platinum(II) complex **6**, we have used ^1H , ^{13}C , DEPT and C–H COSY NMR experiments to assign the resonances of carbons ($\text{C}^1\text{--}\text{C}^6$) and protons (H^3 , H^5 and H^6) of the 4-nitrophenyl group. The proton NMR spectrum of **12** showed the hydride resonance as a doublet at $\delta_{\text{H}} - 16.8$ ppm, typical of a hydride *trans* to chlorine [5,7,37–39]. The two methylene protons were inequivalent and gave a doublet of doublets at 3.64 ppm ($^2J(\text{PH}) = 14.0$ Hz and $^2J(\text{HH}) = 12.5$ Hz) and a triplet at 4.20 ppm ($^2J(\text{PH}) = ^2J(\text{HH}) = 12.5$ Hz). The resonance of the three protons attached to the *ortho*-metallated 4-nitrophenyl group were clearly observed, with chemical shift and coupling values similar to those of complex **6** (see Table 2). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonance for the methylene carbon was a doublet at δ_{C} 22.2 ppm, with $^1J(\text{PC}) = 25.2$ Hz, in agreement with the presence of a six-membered chelate ring [2,14–18]. The metallated C^2 carbon of the 4-nitrophenyl group gave a doublet at 164.5 ppm, $^2J(\text{PC}) = 92.1$ Hz; this coupling constant is typical of a metallated aryl carbon [5–8]. The C^3 and C^6 carbons gave doublets at 131.3 ppm ($^3J(\text{PC}) = 1.6$ Hz) and 129.1 ppm ($^4J(\text{PC}) = 6.0$ Hz), respectively. The quaternary carbon C^1 gave a

doublet at 149.2 ppm ($^3J(\text{PC}) = 8.2$ Hz) and the C⁴ and C⁵ carbons singlets at 148.9 and 118.8 ppm.

An attempt was also made to promote an agostic interaction between the *ortho*-hydrogens of the 4-nitrophenyl group and Ru(II). Treatment of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with 1 equiv. of the azine phosphine **I** at 50°C for ~1 min in benzene solution caused displacement of two PPh_3 ligands to give complex **13**, essentially in quantitative yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **13** was an AB pattern with $\delta(\text{P}_\text{A})$ 79.8 ppm and $\delta(\text{P}_\text{B})$ 47.1 ppm, $^2J(\text{PP}) = 37.6$ Hz [3]. In the proton NMR spectrum both *ortho* hydrogens of the 4-nitrophenyl group were agostically interacting, in turn, with the metal centre in a dynamic system. At ~20°C they gave doublets of doublets, at 7.53 ppm, $^2J(\text{P}_\text{A}\text{H}_\text{ortho}) = 1.6$ Hz; we have shown previously that mixed azine monophosphines analogous to **I** show agostic interaction with ruthenium(II) [3]. The methylene protons gave a doublet at 3.22 ppm, $^2J(\text{PH}) = 14.9$ Hz, but at –50°C two triplets were observed at 3.24 and 3.31 ppm with $^2J(\text{PH}) = ^2J(\text{HH}) = \sim 11$ Hz. At –50°C and below (to –80°C) the agostically interacting *ortho* hydrogen resonance gave a broad singlet. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the resonances in the aryl region were broad and complicated, with no resolved coupling between the *ortho* carbons and phosphorus.

3. Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. IR spectra were recorded using a Perkin-Elmer model 457 grating spectrometer. NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz, respectively), a JEOL FX-100 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz, respectively), a Bruker ARX-250 spectrometer (operating frequencies for ^1H , ^{31}P and ^{13}C of 250.6, 101.3 and 62.9 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^1H , ^{31}P and ^{13}C of 400.1, 161.9 and 100.6 MHz, respectively). ^1H and ^{13}C chemical shifts are relative to tetramethylsilane and ^{31}P shifts are relative to 85% phosphoric acid. Mass spectra were recorded on a VG Autospec mass spectrometer using 8 kV acceleration. For metal complexes m/z values are quoted for ^{58}Cr , ^{98}Mo , ^{184}W , ^{195}Pt and ^{106}Pd .

3.1. Syntheses

$\text{Z-PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{NNH}_2$ was prepared according to our published procedure [1].

3.1.1. $\text{Z,E-PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}=\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)$ (**I**)

p-Nitroacetophenone (0.81 g, 4.9 mmol) was added to a warm solution of the phosphino hydrazone $\text{Z-PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{NNH}_2$ (1.20 g, 4.8 mmol) in ethanol (15 cm³). The required product **I** gradually precipitated as yellow nee-

dles. These were filtered off, washed with cold methanol, and dried in vacuo. Yield: 1.51 g, 70%. *Anal.* Found: C, 70.15; H, 6.5; N, 9.25. *Calc.* for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_2\text{P}$: C, 70.1; H, 6.35; N, 9.45%. Mass spectrum (FAB): m/z 446 ($M+1$) and 388 ($M-\text{Bu}'$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ_c 15.1 (1C, d, $^6J(\text{PC}) = 3.3$ Hz, $\text{MeC}=\text{N}$), 28.7 (3C, d, $^4J(\text{PC}) = 1.6$ Hz, CMe_3), 29.2 (1C, d, $^1J(\text{PC}) = 22.8$ Hz, CH_2), 39.0 (1C, s, CMe_3), 123.1 (2C, s, C³ or C⁵), 127.2 (2C, s, C² or C⁶), 128.3, (4C, d, $^3J(\text{PC}) = 7.0$ Hz, C_meta), 128.8 (2C, s, C_para), 132.8 (4C, d, $^2J(\text{PC}) = 20.5$ Hz, C_ortho), 138.8 (2C, d, $^1J(\text{PC}) = 17.0$ Hz, C_ipso), 143.9 (1C, s, C¹ or C⁴), 147.9 (1C, s, C¹ or C⁴), 155.9 (1C, d, $^5J(\text{PC}) = 1.8$ Hz, $\text{MeC}=\text{N}$) and 170.0 (1C, d, $^2J(\text{PC}) = 5.5$ Hz, $\text{Bu}'\text{C}=\text{N}$).

3.1.2. $\text{Z,E-P(=O)Ph}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}=\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)$ (**II**)

An excess of hydrogen peroxide (5 cm³) was added to a solution of the azine phosphine **I** (100 mg, 0.22 mmol) in acetone and the resultant yellow solution put aside for 2 h. The addition of a few drops of water to the reaction mixture gave the required product **II** as yellow microcrystals. These were filtered off, washed with water and dried over P_2O_5 in vacuo. Yield: 93 mg, 93%. *Anal.* Found: C, 67.6; H, 6.25; N, 9.1. *Calc.* for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_3\text{P}$: C, 67.65; H, 6.1; N, 9.1%. Mass spectrum (FAB): m/z 461 (M^+) and 404 ($M-\text{Bu}'$).

3.1.3. $[\text{Mo}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}=\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]$ (**Ia**)

A solution of $[\text{Mo}(\text{CO})_4(\text{nbd})]$ (201 mg, 0.67 mmol) and the azine phosphine **I** (300 mg, 0.67 mmol) in benzene (3 cm³) was put aside for 1.5 h. The required product **1a** crystallised out as an orange solid. This was filtered off, washed with cold methanol and dried in vacuo. Yield: 400 mg, 91%. *Anal.* Found: C, 55.05; H, 4.35; N, 6.65. *Calc.* for $\text{C}_{30}\text{H}_{28}\text{MoN}_3\text{O}_6\text{P}$: C, 51.15; H, 4.3; N, 6.45%. Mass spectrum (FAB): m/z 655 (M^+), 627 ($M-\text{CO}$), 599 ($M-2\text{CO}$), 571 ($M-3\text{CO}$) and 543 ($M-4\text{CO}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ_c 21.8 (1C, s, $\text{MeC}=\text{N}$), 25.5 (1C, d, $^1J(\text{PC}) = 6.4$ Hz, CH_2), 27.2 (3C, s, CMe_3), 39.1 (1C, d, $^3J(\text{PC}) = 1.8$ Hz, CMe_3), 166.4 (1C, d, $^2J(\text{PC}) = 4.6$ Hz, $\text{Bu}'\text{C}=\text{N}$), 170.3 (1C, s, $\text{MeC}=\text{N}$), 207.0 (2C, s, br, $\text{C}\equiv\text{O}$ axial), 215.5 (1C, d, $^2J(\text{PC}) = 36.0$ Hz, $\text{C}\equiv\text{O}$ *trans* to P) and 219.8 (1C, d, $^2J(\text{PC}) = 7.2$ Hz, $\text{C}\equiv\text{O}$ *trans* to N).

3.1.4. $[\text{W}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}=\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]$ (**Ib**)

$[\text{W}(\text{CO})_4(\text{nbd})]$ (56.4 mg, 0.22 mmol) was added to a solution of the azine phosphine **I** (100 mg, 0.22 mmol) in benzene (2 cm³) and the mixture heated at 75°C for 8 h. When the mixture was cooled to room temperature the required product **1b** precipitated as an orange crystalline solid. This was filtered off, washed with cold methanol and dried in vacuo. Yield: 90 mg, 43%. *Anal.* Found: C, 50.6; H, 4.0; N, 5.7. *Calc.* for $\text{C}_{30}\text{H}_{28}\text{N}_3\text{O}_6\text{WP} \cdot 0.5\text{C}_6\text{H}_6$: C, 50.8; H, 4.0; N, 5.4%. Mass spectrum (FAB): m/z 741 (M^+), 713

($M-\text{CO}$), 685 ($M-2\text{CO}$), 657 ($M-3\text{CO}$) and 629 ($M-4\text{CO}$).

3.1.5. $[\text{Cr}(\text{CO})_4\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]\text{(1c)}$

The tetracarbonylchromium(0) derivative **1c** was prepared similarly from $[\text{Cr}(\text{CO})_4(\text{nbd})]$ and **1** heating together at 75°C for 2 h. Yield: 40%. Anal. Found: C, 62.85; H, 4.8; N, 6.65. Calc. for $\text{C}_{30}\text{H}_{28}\text{CrN}_3\text{O}_6\text{P}\cdot\text{C}_6\text{H}_6$: C, 62.9; H, 5.0; N, 6.1%. Mass spectrum (FAB): m/z 609 (M^+), 525 ($M-3\text{CO}$) and 497 ($M-4\text{CO}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ_c 23.2 (1C, s, $\text{MeC}=\text{N}$), 25.5 (1C, d, $^1J(\text{PC})=5.4$ Hz, CH_2), 27.2 (3C, s, CMe_3), 39.3 (1C, d, $^3J(\text{PC})=2.0$ Hz, CMe_3), 168.8 (1C, d, $^2J(\text{PC})=5.3$ Hz, $\text{Bu}'\text{C}=\text{N}$), 170.3 (1C, s, $\text{MeC}=\text{N}$), 217.6 (2C, s, br, $\text{C}\equiv\text{O}$ axial), 226.5 (1C, d, $^2J(\text{PC})$ 4.1, $\text{C}\equiv\text{O}$ trans to N) and 227.3 (1C, d, $^2J(\text{PC})$ 11.6, $\text{C}\equiv\text{O}$ trans to P).

3.1.6. $[\text{Mo}(\text{CO})_3\text{Br}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]\text{(2)}$

A solution of bromine in carbon tetrachloride (0.56 M, 0.66 cm^3 , 0.37 mmol) was added to a solution containing the tetracarbonylmolybdenum(0) complex **1a** (150 mg, 0.23 mmol) in dichloromethane (2 cm^3) at 0°C. The reaction mixture was put aside for 5 h, filtered and the mother liquor evaporated to a low volume under reduced pressure. The residue was then triturated with methanol to give the dibromide **2** as yellow microcrystals. These were filtered off, washed with cold methanol and dried in vacuo. Yield: 100 mg, 55%. Anal. Found: C, 44.55; H, 3.4; N, 5.6. Calc. for $\text{C}_{29}\text{H}_{28}\text{Br}_2\text{MoN}_3\text{O}_5\text{P}$: C, 44.25; H, 3.6; N, 5.35%. Mass spectrum (FAB): m/z 701 ($M-3\text{CO}$).

3.1.7. $[\text{PtMe}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]\text{(3a)}$

$[\text{PtMe}_2(\text{cod})]$ (80 mg, 0.24 mmol) was added to a solution of the azine phosphine **1** (107 mg, 0.24 mmol) in benzene (2 cm^3). After 0.5 h orange needles began to crystallise out from the orange solution. When precipitation was complete the dimethylplatinum(II) complex **3a** was filtered off, washed with cold methanol and dried in vacuo. Yield: 78 mg, 50%. A second crop of **3a** was obtained from the mother liquor. Yield: 30 mg, 20%. Anal. Found: C, 49.95; H, 4.9; N, 6.05. Calc. for $\text{C}_{28}\text{H}_{34}\text{N}_3\text{O}_2\text{PtP}$: C, 50.15; H, 5.1; N, 6.25%. Mass spectrum (FAB): m/z 640 ($M-\text{C}_2\text{H}_6$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ_c -23.2 (1C, d, $^2J(\text{PC})=4.1$ Hz, $^1J(\text{PtC})=761.2$ Hz, PtMe *cis* to P), 7.7 (1C, d, $^2J(\text{PC})=109.4$ Hz, $^1J(\text{PtC})=671.1$ Hz, PtMe *trans* to P), 21.3 (1C, s, $\text{MeC}=\text{N}$), 25.0 (1C, d, $^1J(\text{PC})=17.3$ Hz, CH_2), 27.5 (3C, s, CMe_3), 39.4 (1C, d, $^3J(\text{PC})=1.6$ Hz, CMe_3), 122.4 (2C, s, $\text{C}^{3,5}$ or $\text{C}^{2,6}$), 128.4 (2C, d, $^3J(\text{PC})=10.2$ Hz, C_{meta}), 128.8 (2C, s, $\text{C}^{3,5}$ or $\text{C}^{2,6}$), 128.8 (2C, d, $^3J(\text{PC})=8.3$ Hz, C_{meta}), 130.4 (1C, s, C_{para}), 130.8 (1C, s, C_{para}), 131.3 (1C, d, $^1J(\text{PC})=35.6$ Hz, C_{ipso}), 132.1 (2C, d, $^2J(\text{PC})=12.1$ Hz, $^3J(\text{PtC})=15.8$ Hz, C_{ortho}), 133.1 (1C, d, $^1J(\text{PC})=36.3$ Hz, $^2J(\text{PtC})=24.3$ Hz, C_{ipso}), 134.6 (2C, d,

$^2J(\text{PC})=13.8$ Hz, $^3J(\text{PtC})=25.7$ Hz, C_{ortho}), 144.7 (1C, s, $^3J(\text{PtC})=12.1$ Hz, C^1), 147.9 (1C, s, C^4), 160.7 (1C, d, $^2J(\text{PC})=3.6$ Hz, $\text{Bu}'\text{C}=\text{N}$) and 171.2 (1C, s, $^2J(\text{PtC})=18.3$ Hz, $\text{MeC}=\text{N}$).

3.1.8. $[\text{PdCl}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]\text{(3b)}$

$[\text{PdCl}_2(\text{NCPH})_2]$ (155 mg, 0.40 mmol) was added to a solution of the azine phosphine **1** (180 mg, 0.44 mmol) in dichloromethane (5 cm^3). The dichloropalladium(II) complex **3b** crystallised out after 2 h as yellow microcrystals. These were filtered off, washed with cold methanol and dried in vacuo. Yield: 240 mg, 96%. Anal. Found: C, 46.45; H, 4.45; Cl, 18.5; N, 6.4. Calc. for $\text{C}_{26}\text{H}_{28}\text{Cl}_2\text{N}_3\text{O}_2\text{PdP}\cdot 0.8\text{CH}_2\text{Cl}_2$: C, 46.65; H, 4.3; Cl, 18.5; N, 6.1%. Mass spectrum (FAB): m/z 587 ($M-\text{Cl}$).

3.1.9. $[\text{PdI}_2\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]\text{(3c)}$

An excess of NaI (180 mg, 1.2 mmol) was added to a solution of the palladium(II) dichloride complex **3b** (150 mg, 0.24 mmol) in hot acetone (20 cm^3). The mixture was heated under reflux for 45 min., after which the red solution was cooled to room temperature and then evaporated to low volume under reduced pressure giving the diiodopalladium(II) complex **3c** as a red solid. This was filtered off, washed with cold methanol and dried in vacuo. Yield: 175 mg, 95%. Mass spectrum (FAB): m/z 679 ($M-\text{I}$).

3.1.10. *fac*- $[\text{PtMe}_3\text{I}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_3\text{NO}_2-4)\}]\text{(4)}$

An excess of methyl iodide (0.1 cm^3) was added to a suspension of the dimethylplatinum(II) complex **3a** (40.0 mg, 0.06 mmol) in benzene (1.5 cm^3) and the resultant yellow solution was put aside for 2.5 h. The reaction mixture was then evaporated to a low volume under reduced pressure and the residue triturated with methanol to give **4** as yellow microcrystals. These were filtered off, washed with cold methanol and dried in vacuo. Yield: 43 mg, 90%. Anal. Found: C, 42.95; H, 4.65; N, 5.1. Calc. for $\text{C}_{29}\text{H}_{37}\text{IN}_3\text{O}_2\text{PtP}$: C, 42.85; H, 4.6; N, 5.15%. Mass spectrum (FAB): m/z 766 ($M-\text{C}_2\text{H}_6-\text{CH}_4$) and 640 ($M-\text{C}_2\text{H}_6-\text{MeI}$).

3.1.11. *cis*- $[\text{PtMe}_2(\text{CO})\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}')=\text{N}-\text{N}=\text{CMe}(\text{C}_6\text{H}_4\text{NO}_2-4)\}]\text{(5)}$

Carbon monoxide was passed through a solution of the dimethylplatinum(II) complex **3a** (40 mg, 0.06 mmol) in CDCl_3 (0.5 cm^3) for 1.5 h. The solvent was evaporated under reduced pressure to dryness to give the required product as a yellow crystalline solid. Yield: 39 mg, 93%. Anal. Found: C, 50.55; H, 5.4; N, 5.95. Calc. for $\text{C}_{29}\text{H}_{34}\text{N}_3\text{O}_3\text{PtP}$: C, 49.85; H, 4.9; N, 6.0%. Mass spectrum (FAB): m/z 698 (M^+), 682 ($M-\text{CH}_4$) and 640 ($M-\text{C}_2\text{H}_6-\text{CO}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3): δ_c -1.6 (1C, d, $^2J(\text{PC})=93.3$ Hz, $^1J(\text{PtC})=564$ Hz, PtMe *trans* to P), 5.9 (1C, d, $^2J(\text{PC})=7.6$ Hz, $^1J(\text{PtC})=612$ Hz, PtMe *cis* to P), 15.9 (1C, s, $\text{MeC}=\text{N}$),

28.5 (3C, s, CMe_3), 29.4 (1C, d, $^1J(PC) = 7.6$ Hz, CH_2), 39.4 (1C, d, $^3J(PC) = 1.6$ Hz, CMe_3), 123.2 (2C, s, $C^{3,5}$ or $C^{2,6}$), 127.7 (2C, s, $C^{3,5}$ or $C^{2,6}$), 128.3 (4C, d, $^3J(PC) = 10.0$ Hz, C_{meta}), 130.5 (2C, d, $^4J(PC) = 2.4$ Hz, C_{para}), 133.3 (4C, d, $^2J(PC) = 11.7$ Hz, $^3J(PtC) = 14.7$ Hz, C_{ortho}), 134.2 (2C, d, $^1J(PC) = 42.8$ Hz, $^2J(PtC) = 16.4$ Hz, C_{ipso}), 144.3 (1C, s, C^1), 148.2 (1C, s, C^4), 160.4 (1C, d, $^5J(PC) = 1.9$ Hz, $MeC=N$), 171.1 (1C, d, $^2J(PC) = 5.3$ Hz, $Bu^1C=N$) and 182.0 (1C, d, $^2J(PC) = 4.6$ Hz, $C\equiv O$).

3.1.12. $[PtMe\{PPh_2CH_2C(Bu^1)=N-N=CMe(C_6H_3NO_2-4)\}](6)$

A suspension of the dimethylplatinum(II) complex **3a** (70.0 mg, 0.10 mmol) in toluene was heated at 105°C for 17.5 h. The resultant red solution was evaporated to low volume under reduced pressure and the residue triturated with methanol to give brick red crystals of **6**. These were filtered off, washed with cold methanol and dried in vacuo. Yield: 43 mg, 66%. *Anal.* Found: C, 51.70; H, 4.75; N, 5.9. *Calc.* for $C_{27}H_{30}N_3O_2Pt \cdot 0.4C_6H_5CH_3$: C, 51.8; H, 4.85; N, 6.1%. *Mass spectrum* (FAB): m/z 654 (M^+) and 638 ($M-CH_4$). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ_c -15.9 (1C, d, $^2J(PC) = 4.7$ Hz, $^1J(PtC) = 729$ Hz, $MePt$), 16.5 (1C, s, $^3J(PtC) = 12.3$ Hz, $MeC=N$), 22.8 (1C, d, $^1J(PC) = 22.9$ Hz, CH_2), 27.8 (3C, s, CMe_3), 41.5 (1C, d, $^3J(PC) = 2.4$ Hz, CMe_3), 119.5 (1C, s, C^5), 125.5 (1C, d, $^3J(PC) = 1.8$ Hz, $^2J(PtC) = 96.2$ Hz, C^3), 127.4 (1C, d, $^4J(PC) = 5.9$ Hz, $^3J(PtC) = 35.8$ Hz, C^6), 128.6 (4C, d, $^3J(PC) = 10.0$ Hz, C_{meta}), 130.6 (2C, d, $^1J(PC) = 43.4$ Hz, $^2J(PtC) = 29.4$ Hz, C_{ipso}), 131.1 (2C, s, C_{para}), 133.6 (4C, d, $^2J(PC) = 11.7$ Hz, $^3J(PtC) = 17.6$ Hz, C_{ortho}), 149.2 (1C, d, $^3J(PC) = 9.4$ Hz, $^2J(PtC) = 76.3$ Hz, C^1), 153.4 (1C, s, C^4), 170.7 (1C, d, $^2J(PC) = 125.6$ Hz, $^1J(PtC) = 942$ Hz, C^2), 172.3 (1C, s, $^3J(PtC) = 8.8$ Hz, $(Bu^1)C=N$) and 180.6 (1C, d, $^3J(PC) = 4.7$ Hz, $^2J(PtC) = 72.2$ Hz, $(Me)C=N$).

3.1.13. $fac-[PtMe_2\{PPh_2CH_2C(Bu^1)=N-N=CMe(C_6H_3NO_2-4)\}](7)$

An excess of methyl iodide (0.1 cm^3) was added to a solution of the *ortho*-metallated platinum(II) complex **6** (24.0 mg, 0.04 mmol) in toluene (0.5 cm^3) and the resultant red solution left to stand at $\sim 20^\circ C$ for 2 h. The reaction mixture was then evaporated to low volume under reduced pressure and the residue triturated with methanol to give the required product **7** as an orange solid. This was filtered off, washed with cold methanol and dried in vacuo. Yield: 17.4 mg, 53%. *Anal.* Found: C, 42.9; H, 4.15; N, 5.15. *Calc.* for $C_{28}H_{33}IN_3O_2Pt \cdot 0.1C_7H_8$: C, 42.8; H, 4.25; N, 5.2%. *Mass spectrum* (FAB): m/z 796 (M^+), 766 ($M-C_2H_6$) and 639 ($M-C_2H_6-I$).

3.1.14. $trans-[PtCl_2\{PPh_2CH_2C(Bu^1)=N-N=CMe(C_6H_4NO_2-4)\}_2](8)$

$[PtCl_2(NCMe)_2]$ (38.3 mg, 0.11 mmol) was added to a solution of the azine phosphine **I** (100 mg, 0.22 mmol) in dichloromethane (2 cm^3) and the yellow solution left to stand

at room temperature for 15 min. The reaction mixture was then evaporated to a low volume under reduced pressure, diethyl ether added to the residue and the yellow solid **8** filtered off, washed with cold methanol and dried in vacuo. Yield: 65 mg, 51%. *Anal.* Found: C, 53.8; H, 5.0; Cl, 6.25; N, 6.95. *Calc.* for $C_{52}H_{56}Cl_2N_6O_4P_2Pt$: C, 54.0; H, 4.9; Cl, 6.15; N, 7.25%. *Mass spectrum* (FAB): m/z 1120 ($M-Cl$) and 1085 ($M-2Cl$).

3.1.15. $cis-[Pt\{PPh_2CH_2C(Bu^1)=N-N=CMe(C_6H_4NO_2-4)\}_2][PF_6]_2(9a)$

$[PtCl_2(cod)]$ (84.2 mg, 0.23 mmol) was added to a solution of the azine phosphine **I** (200 mg, 0.45 mmol) in EtOH (2 cm^3) and the mixture heated to reflux for 40 min. The resultant yellow solution was allowed to cool to room temperature, filtered and a solution of NH_4PF_6 (76.6 mg, 0.47 mmol) in MeOH (2 cm^3) added. Complex **9a** immediately precipitated as a cream solid which was filtered off, washed with cold methanol and dried in vacuo. Yield: 280 mg, 90%. *Anal.* Found: C, 45.3; H, 3.9; N, 6.4. *Calc.* for $C_{52}H_{56}F_{12}N_6O_4P_4Pt$: C, 45.4; H, 4.1; N, 6.1%. *Mass spectrum* (FAB): m/z 1230 ($M-PF_6$) and 1085 ($M-2PF_6$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2CO$): δ_c 24.9 (2C, s, $MeC=N$), 26.4 (6C, s, CMe_3), 27.1 (2C, t, $^1J(PC) + ^3J(PC) = 40.0$ Hz, CH_2), 40.8 (2C, s, CMe_3), 151.1 (2C, s, $MeC=N$) and 176.8 (2C, d, $^2J(PC) = 8.4$ Hz, $Bu^1C=N$).

3.1.16. $[Pd\{PPh_2CH_2C(Bu^1)=N-N=CMe(C_6H_4NO_2-4)\}_2][PF_6]_2(9b)$

The azine phosphine **I** (250 mg, 0.56 mmol) was added to a solution of $[Na_2PdCl_4 \cdot 4H_2O]$ (103 mg, 0.28 mmol Pd) in EtOH (6 cm^3) and the mixture heated under reflux for 1 h. The resultant yellow solution was allowed to cool to room temperature, filtered and a solution of NH_4PF_6 (101 mg, 0.62 mmol) in MeOH (4 cm^3) added. Complex **9b** immediately precipitated as a white solid which was filtered off, washed with cold methanol and dried in vacuo. Yield: 295 mg, 80%. *Anal.* Found: C, 48.4; H, 4.4; N, 6.5. *Calc.* for $C_{52}H_{56}F_{12}N_6O_4P_4Pd$: C, 48.5; H, 4.40; N, 6.55%. *Mass spectrum* (FAB): m/z 995 ($M-HPF_6-PF_6$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2CO$): δ_c 24.0 (1C, s, $MeC=N$), 26.3 (3C, s, CMe_3), 26.6 (1C, t, $^1J(PC) + ^3J(PC) = 26.0$ Hz, CH_2), 40.6 (1C, s, CMe_3), 151.2 (1C, s, $MeC=N$) and 175.6 (1C, d, $^2J(PC) = 37.8$ Hz, $Bu^1C=N$).

3.1.17. $[PtCl\{PPh_2CH_2C(Bu^1)=N-N=CMe(C_6H_4NO_2-4)\}_2]PF_6(10)$

$[PtCl_2(cod)]$ (41.2 mg, 0.11 mmol) was added to a solution of the azine phosphine **I** (100 mg, 0.22 mmol) in dichloromethane (2 cm^3) and the yellow solution put aside at room temperature for 1 h. The reaction mixture was then evaporated to dryness under reduced pressure, the yellow residue was dissolved in methanol (1 cm^3) and a solution of NH_4PF_6 (20 mg, 0.12 mmol) in MeOH (1 cm^3) added. Complex **10** slowly crystallised as yellow rosettes. These were filtered off, washed with cold methanol and dried in

vacuo. Yield: 95 mg, 70%. *Anal.* Found: C, 49.15; H, 4.4; Cl, 2.8; N, 6.4. *Calc.* for $C_{52}H_{56}ClF_6N_6O_4P_3Pt$: C, 49.3; H, 4.45; Cl, 2.8; N, 6.65%. Mass spectrum (FAB): m/z 1230 ($M-Cl$) and 1085 ($M-PF_6-Cl$).

3.1.18. $[Pt\{PPh_2CH_2C(Bu')=N-N=CMe(C_6H_4NO_2-4)\}_2][PF_6]_2$ (**11**)

$AgNO_3$ (12.1 mg, 0.07 mmol) in H_2O (3 drops) was added to a solution of the platinum(II) salt **10** (90 mg, 0.07 mmol) in acetone (2 cm^3) and the mixture left to stand for 1.5 h. The resultant $AgCl$ was filtered off through Celite and the mother liquor evaporated under reduced pressure to dryness. The remaining oil was dissolved in methanol (1 cm^3), a solution of NH_4PF_6 (11.6 mg, 0.07 mmol) in MeOH (2 cm^3) added and a white precipitate slowly began to form. Complex **11** was filtered off, washed with cold methanol and dried in vacuo. Yield: 65 mg, 65%. *Anal.* Found: C, 45.25; H, 3.65; N, 6.1. *Calc.* for $C_{52}H_{56}F_{12}N_6O_4P_4Pt$: C, 45.4; H, 4.1; N, 6.1%. Mass spectrum (FAB): m/z 1230 ($M-PF_6$) and 1085 ($M-2PF_6$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2CO$): δ_c 18.9 (1C, s, $MeC=N$), 22.9 (1C, d, $^4J(PC)=2.2$ Hz, $MeC=N$), 26.6 (1C, d, $^1J(PC)=33.1$ Hz, CH_2), 27.2 (3C, s, CMe_3), 27.7 (3C, s, CMe_3), 41.4 (1C, dd, $^3J(PC)=6.0$ Hz, $^4J(PC)=2.7$ Hz, CMe_3), 41.5 (1C, d, $^3J(PC)=2.2$ Hz, CMe_3), 45.7 (1C, d, $^1J(PC)=40.8$ Hz, CH_2), 151.1 (1C, d, $^2J(PC)=8.7$ Hz, $C=N$), 169.0 (1C, s, $C=N$), 177.0 (1C, s, $C=N$) and 186.5 (1C, s, $C=N$).

3.1.19. $[IrClHCO\{PPh_2CH_2C(Bu')=N-N=CMe(C_6H_3NO_2-4)\}]$ (**12**)

$[IrCl(CO)_2(p\text{-toluidine})]$ (98 mg, 0.25 mmol) was added to a solution of the azine phosphine **I** (100 mg, 0.22 mmol) in benzene (2 cm^3). Vigorous effervescence occurred and after ~5 min a yellow precipitate began to form. The hydrido-iridium(III) complex **12** was filtered off, washed with cold methanol and dried in vacuo. Yield: 133 mg, 86%. *Anal.* Found: C, 48.65; H, 4.2; N, 5.5; Cl, 4.9. *Calc.* for $C_{27}H_{28}ClN_3O_3PIr \cdot 0.5C_6H_6$: C, 48.65; H, 4.2; N, 5.7; Cl, 4.8%. Mass spectrum (FAB): m/z 701 (M^+), 665 ($M-HCl$) and 637 ($M-HCl-CO$). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ_c 17.4 (1C, s, $MeC=N$), 22.2 (1C, d, $^1J(PC)=25.2$ Hz, CH_2), 27.3 (3C, s, CMe_3), 41.9 (1C, d, $^3J(PC)=2.5$ Hz, CMe_3), 118.8 (1C, s, C^5), 128.8 (2C, d, $^3J(PC)=10.4$ Hz, C_{meta}), 128.9 (2C, d, $^3J(PC)=10.4$ Hz, C_{meta}), 129.1 (1C, d, $^4J(PC)=6.0$ Hz, C^6), 130.0 (1C, d, $^1J(PC)=56.7$ Hz, C_{ipso}), 130.1 (1C, d, $^1J(PC)=53.9$ Hz, C_{ipso}), 131.2 (1C, d, $^4J(PC)=2.2$ Hz, C_{para}), 131.3 (1C, d, $^3J(PC)=1.6$ Hz, C^3), 131.8 (2C, d, $^2J(PC)=9.8$ Hz, C_{ortho}), 132.3 (1C, d, $^4J(PC)=2.7$ Hz, C_{para}), 134.7 (2C, d, $^2J(PC)=12.5$ Hz, C_{ortho}), 148.9 (1C, s, C^4), 149.2 (1C, d, $^3J(PC)=8.2$ Hz, C^1), 164.5 (1C, d, $^2J(PC)=92.1$ Hz, C^2), 167.3 (1C, d, $^2J(PC)=5.5$ Hz, $C\equiv O$), 172.1 (1C, s, $MeC=N$) and 185.9 (1C, d, $^2J(PC)=4.9$ Hz, $Bu'C=N$).

3.1.20. $[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu')=N-N=CMe(C_6H_4NO_2-4)\}]$ (**13**)

$[RuCl_2(PPh_3)_3]$ (211 mg, 0.22 mmol) was added to a solution of the azine phosphine **I** (100 mg, 0.22 mmol) in benzene (2 cm^3). The black mixture was warmed to dissolve the starting material and after ~5 min a black precipitate began to form. The ruthenium(II) complex **13** was filtered off, washed with cold methanol and dried in vacuo. Yield: 140 mg, 72%. *Anal.* Found: C, 63.25; H, 4.8; N, 3.8. *Calc.* for $C_{44}H_{43}Cl_2N_3O_2P_2Ru \cdot 1.25C_6H_6$: C, 63.3; H, 5.2; N, 4.3%. Mass spectrum (FAB): m/z 879 (M^+), 843 ($M-HCl$) and 808 ($M-HCl-Cl$). $^{13}C\{^1H\}$ NMR (62.9 MHz, CD_2Cl_2): δ_c 22.9 (1C, d, $^4J(PC)=2.2$ Hz, $MeC=N$), 27.3 (3C, s, CMe_3), 32.3 (1C, d, $^1J(PC)=25.1$ Hz, CH_2), 40.4 (1C, d, $^3J(PC)=2.2$ Hz, CMe_3), 148.9 (1C, s, C^1 or C^4), 149.2 (1C, s, C^1 or C^4), 170.6 (1C, s, $C=N$) and 185.9 (1C, s, $Bu'C=N$).

3.2. Single crystal X-ray diffraction analysis of **1a**

Crystallographic measurements were carried out at 140 K on a Stoe STADI4 diffractometer operating in the ω - θ scan mode using graphite monochromated Mo $K\alpha$ X-radiation ($\lambda=71.069$ pm). The data-set was corrected for absorption using azimuthal ψ -scans (maximum and minimum transmission factors 0.744 and 0.692, respectively).

The structure was determined by heavy atom methods using SHELXS-86 [40] and was refined by full-matrix least-squares (based on F) using SHELX76 [41]. Non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms were constrained to calculated positions ($C-H=97$ pm) with an overall isotropic thermal parameter. The weighting scheme $w=[\sigma^2(F_o)+0.0008(F_o)^2]^{-1}$ was used. The final Fourier difference synthesis was flat and showed no features of chemical significance (maximum and minimum residual densities 0.35 and -0.70 e \AA^{-3}). An ORTEP [42] diagram of **1a** is given in Fig. 1.

3.2.1. Crystal data

$C_{30}H_{28}MoN_3O_6P$, $0.55 \times 0.25 \times 0.20$ mm, $M=653.48$, orthorhombic, space group $Pna2_1$, $a=1819.3(2)$, $b=1050.0(1)$, $c=1614.8(2)$ pm, $U=2.9526(12)$ nm³, $Z=4$, $D_x=1.47$ Mg m⁻³, $\mu=4.74$ cm⁻¹, $F(000)=1336$.

3.2.2. Data collection

$4.0 < 2\theta < 50.0^\circ$; scan widths $1.05^\circ + \alpha$ -doublet splitting, scan speeds 1.0 – 8.0° min⁻¹ (subject to a fast pre-scan). Number of unique data, $n=2967$; number with $F_o > 4.0\sigma(F_o)=2616$.

3.2.3. Structure refinement

Number of parameters = 346; $R=0.0191$; $R_w=0.0222$; max. $\Delta/\sigma=0.066$.

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