

## The crystal structures of the complexes $[M(C_6H_4N=NPh)(\eta^5-C_5H_5)]$ , $M = Ni, Pd$ and $Pt$

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(Received July 8th, 1988)

### Abstract

The compounds  $[M(C_6H_4N=NPh)(\eta^5-C_5H_5)]$  ( $M = Ni$ , **1a**;  $M = Pd$ , **1b**;  $M = Pt$ , **1c**) display the unexpected reactivity pattern  $Pd > Pt > Ni$  on treatment with monotertiary phosphines. Their structures, determined by X-ray diffraction, provide no help in explaining this reactivity pattern but do illustrate the effects of differing metal size and polarisability. In particular, **1b** and **1c** display highly distorted  $M-\eta^5-C_5H_5$  geometries:  $M-C(\eta^5-C_5H_5)$  distances range from 2.167(3) to 2.408(3) Å for **1b** and 2.153(7)–2.367(8) Å for **1c**. The  $Ni-C(\eta^5-C_5H_5)$  distances in **1a** are more regular: 2.036(5)–2.148(5) Å. **1a** is monoclinic, space group  $P2_1/n$ , with  $a$  9.502(1),  $b$  16.155(2),  $c$  18.659(3) Å,  $\beta$  99.16(1)°,  $Z = 8$ ,  $R = 0.037$  for refinement of 361 parameters using 3072 unique intensities. **1b** is monoclinic, space group  $P2_1/a$ ,  $a$  7.046(1),  $b$  14.897(2),  $c$  13.709(2) Å,  $\beta$  101.66(1)°,  $Z = 4$ ,  $R = 0.022$  for refinement of 237 parameters from 3099 unique intensities. **1c** is isomorphous and isostructural with **1b**,  $a$  6.993(2),  $b$  14.846(3),  $c$  13.709(4) Å,  $\beta$  101.92(2)°.  $R = 0.027$  for refinement of 181 parameters from 2818 unique intensities.

### Introduction

The title compounds  $[M(C_6H_4N=NPh)(\eta^5-C_5H_5)]$  (**1a**,  $M = Ni$ ; **1b**,  $M = Pd$ ; **1c**,  $M = Pt$ ) show an uncommon reactivity pattern [1]. The palladium compound **1b** reacts readily and reversibly with triethyl- or tri-*n*-butyl-phosphine to produce  $[Pd(C_6H_4N=NPh)(\eta^5-C_5H_5)(PR_3)]$  (**2b**) which in turn reacts with more phosphine to yield *trans*- $[Pd(C_6H_4N=NPh)(\eta^1-C_5H_5)(PR_3)_2]$  (**3b**). An independent pathway also produces the ionic cyclopentadienide  $[Pd(C_6H_4N=NPh)(PR_3)_3]C_5H_5$  (**4b**). The platinum analogue **1c** reacts more slowly, to give the related bis- and tris-phosphine-complexes **3c** and **4c**, but no trace of the mono-phosphine species **2c** can be detected

in the solutions. The most likely explanations are either that **2c** is more reactive than **2b** or that the Pd and Pt reactions follow different paths. In either case this difference is unusual. Even more unusual, however, is the behaviour of the nickel analogue **1a**. Solutions of this compound show no tendency to react with  $\text{PBu}_3$ ,  $\text{PEt}_3$ , or pyridine [2], thus establishing the palladium complex as the most reactive of the triad.

The reactions are most likely to proceed by nucleophilic attack by phosphine at the metal atom, but this has not been established with certainty so that discussion of relative reactivity must be somewhat tentative. In any event the observed sequence is unexpected. The usual reactivity pattern for square-planar organometallic compounds of these elements is  $\text{Ni} > \text{Pd} > \text{Pt}$  [3], though for some addition reactions the sequence  $\text{Ni} > \text{Pt} > \text{Pd}$  may be more appropriate [4].

Since the observed trend is likely to be kinetic in origin, we have examined **1a**, **1b** and **1c** by X-ray diffraction to see whether structural variations provide an explanation. It was thought unlikely that the inertness of the nickel complex could be the result of steric hindrance, since cyclopentadienyl compounds with more bulky substituents than 2-(phenylazo)phenyl are known and undergo a variety of reactions. There remained the possibility of  $\eta^5$  to  $\eta^3$  ring slippage at palladium [5]. In addition, we expected that the results would permit us to compare the structures of analogous  $\text{C}_6\text{H}_4\text{N}=\text{NPh}$  complexes of nickel, palladium, and platinum. Up to now relatively few structural studies of 2-(arylo)aryl complexes of metals of the nickel triad have been described [6–8].

We also report the UV/visible spectra of the three compounds.

## Results and discussion

Crystals of the complexes **1a**, **1b** and **1c** are built up of well-separated  $[\text{M}(\text{C}_6\text{H}_4\text{N}=\text{NPh})(\eta^5\text{-C}_5\text{H}_5)]$  molecules. The structural results are summarised in Fig. 1 and 2 and Table I. In each complex the  $\text{M}^{2+}$  cation attains an 18-electron configuration by bonding to an  $\eta^5\text{-C}_5\text{H}_5$  ring and to the atoms C(1) and N(2) of a 2-(phenylazo)phenyl ligand. The M, N(2), C(1) plane is in each case nearly perpendicular to that of the  $\eta^5\text{-C}_5\text{H}_5$  ring. It is both conventional and convenient [6] to describe the resulting metal coordination as square-planar, with the  $\eta^5\text{-C}_5\text{H}_5$  ring occupying two *cis* sites.

As might be expected from the trends in metal radii and polarisabilities, the more obvious structural differences are between the nickel complex on the one hand and the palladium and platinum complexes on the other. The unit cell of the nickel complex contains two crystallographically independent molecules (A and B). These have nearly identical bond lengths and interbond angles (Table 1), and show only the slight differences in conformation which might be expected from their differing environments within the crystal. Also as expected, **1b** and **1c** are isomorphous and nearly isostructural.

### The $\text{C}_6\text{H}_4\text{N}=\text{NPh}$ ligands

In the nickel complex **1a** the phenyl ring attached to N(2) of the  $\text{C}_6\text{H}_4\text{N}=\text{NPh}$  ligand is rotated about the N(2)–C(7) bond out of the plane of the chelate ring: the |N(1)–N(2)–C(7)–C(12)| torsion angles of 50.5(4) and 42.1(4)° in molecules A and B of **1a** help to maintain the minimum intramolecular non-bonded C(8)...C( $\eta^5$ -

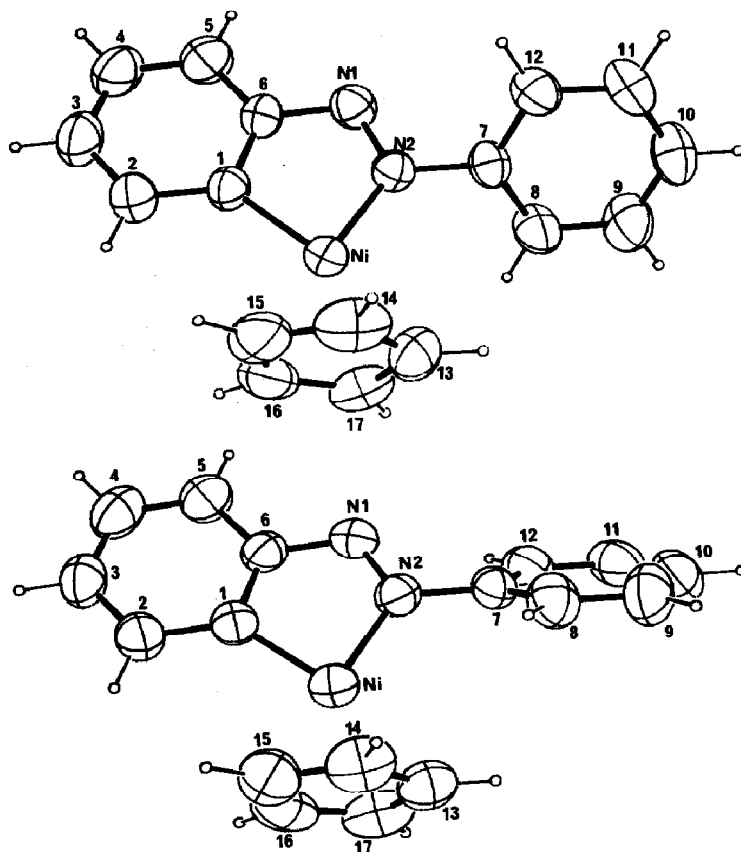


Fig. 1. Perspective views of the two crystallographically independent molecules of  $[\text{Ni}(\text{C}_6\text{H}_4\text{N}=\text{NPh})(\eta^5\text{-C}_5\text{H}_5)]$  (**1a**): (i) molecule A, (ii) molecule B. Here and in Fig. 2 H-atoms are represented by spheres of arbitrary size and non-H atoms by 50% ellipsoids. For C-atoms only the serial number is given.

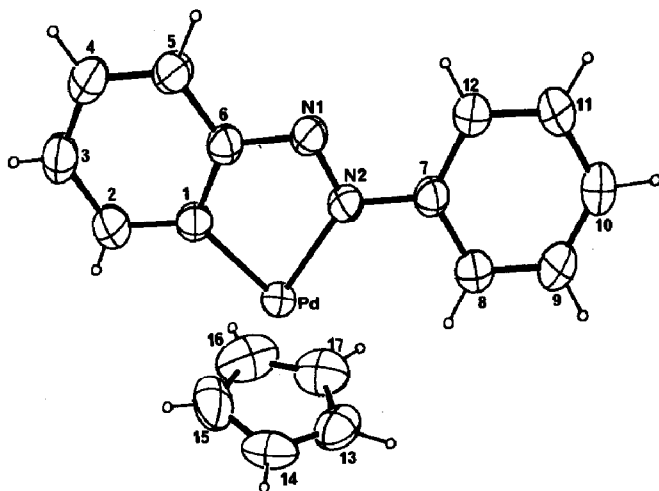


Fig. 2. Perspective view of a molecule of  $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NPh})(\eta^5\text{-C}_5\text{H}_5)]$  (**1b**). The same numbering system is used for the analogous platinum complex, **1c**, which is isostructural with **1b**.

Table 1. Selected distances (Å) and angles (deg) in  $[M(C_5H_4N=NPh)(\eta^5-C_5H_5)]$  complexes

M	Ni(A) <sup>a</sup>	Ni(B) <sup>a</sup>	Pd	Pt	Ni(A)	Ni(B)	Pd	Pt
<i>Distances</i>								
M-N(2)	1.835(4)	1.843(4)	2.033(2)	1.988(5)	1.863(4)	1.847(4)	1.960(3)	1.962(6)
M-C(13)	2.118(5)	2.148(5)	2.408(3)	2.367(8)	2.126(6)	2.138(5)	2.336(3)	2.312(7)
M-C(15)	2.041(5)	2.036(5)	2.167(3)	2.153(7)	2.064(5)	2.047(5)	2.264(3)	2.238(8)
M-C(17)	2.137(5)	2.133(6)	2.397(3)	2.355(7)	1.733	1.733	1.993	1.964
N(1)-N(2)	1.302(5)	1.298(5)	1.283(3)	1.303(6)	1.392(6)	1.377(6)	1.379(3)	1.347(7)
N(2)-C(7)	1.434(5)	1.438(5)	1.436(3)	1.434(7)	1.397(6)	1.398(6)	1.391(3)	1.406(8)
C(1)-C(6)	1.404(6)	1.413(6)	1.412(3)	1.409(8)	1.377(7)	1.376(7)	1.383(4)	1.376(9)
C(3)-C(4)	1.374(8)	1.387(8)	1.378(4)	1.384(9)	1.369(7)	1.368(7)	1.373(4)	1.382(9)
C(5)-C(6)	1.383(6)	1.395(7)	1.400(3)	1.393(8)	1.382(6)	1.380(6)	1.382(3)	1.373(8)
C(7)-C(12)	1.387(6)	1.381(6)	1.390(4)	1.388(8)	1.382(7)	1.382(7)	1.394(4)	1.409(9)
C(9)-C(10)	1.358(7)	1.364(8)	1.359(4)	1.352(10)	1.365(7)	1.372(8)	1.386(4)	1.379(9)
C(11)-C(12)	1.378(7)	1.377(8)	1.385(4)	1.374(9)	1.399(8)	1.395(7)	1.365(5)	1.332(12)
C(13)-C(17)	1.384(7)	1.399(7)	1.403(5)	1.385(12)	1.380(8)	1.381(8)	1.385(5)	1.379(14)
C(15)-C(16)	1.400(8)	1.433(8)	1.412(6)	1.416(14)	1.381(8)	1.376(8)	1.375(6)	1.374(14)
<i>Angles</i>								
N(2)-M-C(1)	83.2(2)	83.4(2)	78.7(1)	77.5(2)	144.5	144.3	147.4	146.0
C(1)-M-C(CP)	132.3	132.0	133.8	136.3	109.4(3)	109.9(4)	111.7(2)	111.2(5)
M-N(2)-N(1)	120.1(3)	119.3(3)	118.7(2)	120.3(4)	126.7(3)	126.5(3)	127.2(2)	126.6(4)
N(1)-N(2)-C(7)	113.1(3)	113.9(3)	114.0(2)	113.1(5)	132.5(4)	133.2(4)	130.6(2)	128.3(5)
M-C(1)-C(6)	110.6(3)	110.4(3)	112.2(2)	113.2(4)	116.8(4)	116.4(4)	117.2(2)	118.4(6)
C(1)-C(2)-C(3)	120.3(4)	121.1(4)	120.0(3)	118.9(6)	121.3(5)	121.2(5)	122.2(3)	122.2(6)
C(3)-C(4)-C(5)	120.2(5)	119.8(5)	119.7(3)	120.3(6)	118.9(5)	119.3(5)	118.8(3)	118.3(6)
N(1)-C(6)-C(1)	116.6(4)	116.8(4)	118.7(2)	117.7(5)	120.9(4)	121.0(4)	119.1(2)	120.4(5)
C(1)-C(6)-C(5)	122.4(4)	122.2(4)	122.2(2)	121.8(6)	119.4(4)	119.5(4)	118.7(2)	119.8(5)
N(2)-C(7)-C(12)	121.2(4)	120.5(4)	121.3(2)	120.7(5)	119.4(4)	120.0(4)	120.0(2)	119.5(6)
C(7)-C(8)-C(9)	119.5(4)	119.3(5)	119.6(3)	119.4(6)	120.7(5)	120.9(5)	120.8(3)	120.8(6)
C(9)-C(10)-C(11)	120.3(5)	119.6(5)	119.7(3)	119.4(6)	120.2(5)	120.6(5)	120.7(3)	120.9(6)
C(7)-C(12)-C(11)	119.9(4)	119.6(5)	119.2(3)	120.0(6)	108.8(5)	109.3(5)	109.4(4)	108.9(8)
C(13)-C(14)-C(15)	106.7(5)	107.4(5)	107.5(3)	108.2(8)	108.9(5)	107.8(5)	108.2(4)	108.5(8)
C(15)-C(16)-C(17)	107.6(5)	107.9(5)	107.5(4)	105.1(8)	107.9(5)	107.5(5)	107.3(4)	109.1(9)

<sup>a</sup> Ni(A) and Ni(B) refer to the two crystallographically independent molecules of the M = Ni complex. <sup>b</sup> C(CP) is the centroid of the cyclopentadienyl ring.

C<sub>5</sub>H<sub>5</sub>) separations at 3.443(6) and 3.364(6) Å. The corresponding torsion angles in **1b** and **1c**, 13.5(2) and 15.8(5)° indicate that the greater size of the Pd and Pt atoms permits the C<sub>6</sub>H<sub>4</sub>N=NPh ligands to be more nearly planar, as they are in **2b** [6], without close contacts between the C(7)–C(12) phenyl and η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> rings (the shortest C...C contacts of this type in **1b** and **1c** are 3.617(4) and 3.530(10) Å, respectively).

The N(1)–C(6) bond lengths shorten significantly as M changes from Ni, through Pd to Pt. Otherwise, corresponding bond lengths in the 2-(phenylazo)phenyl ligands of **1a**, **1b** and **1c** agree to within 0.020 Å and corresponding interbond angles to within 2.2°. Phenyl rings are coplanar to within 0.010 Å.

The N(1)–N(2), N(1)–C(6) and N(2)–C(7) bond lengths (respectively 1.292(5), 1.377(7) and 1.436(2) Å, averaged over the Ni, Pd and Pt complexes) suggest, when compared with corresponding values in the non-chelate complex **2b** (1.228(6), 1.437(6) and 1.426(6) Å), that formation of the MN<sub>2</sub>C<sub>2</sub> chelate ring in **1** involves slight delocalisation of the N=N bond. The chelate rings are nearly exactly planar: in **1b** and **1c** the maximum deviation of an atom from the MN<sub>2</sub>C<sub>2</sub> plane is 0.004(5) Å; the corresponding values in **1a** are 0.015(3) and 0.029(4) Å for molecules A and B. In all three compounds the torsion angle |C(1)–C(6)–N(1)–N(2)| is less than 2.4(4)°.

The N(2)...C(1) bite distances (Ni: 2.455(5) Å; Pd: 2.532(3) Å; Pt: 2.474(7) Å) show no systematic trend as the metal radius increases. In consequence, the N–M–C angles narrow slightly on going from Ni to Pd and Pt.

#### *The metal-cyclopentadienyl interactions*

In molecules A and B of **1a** the η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> ring is oriented so that C(13) and the midpoint of the C(15)–C(16) bond lie close to the NiN(2)C(1) plane, with C(13) *trans* to C(1). The Ni–C(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) distances fall into two groups: 2.118(5)–2.148(5) Å for atoms C(13), C(14) and C(17) [i.e. roughly *trans* to C(1)] and 2.036(5)–2.064(5) Å for C(15) and C(16) (i.e. *trans* to N(2)). The C(15)–C(16) bonds (1.400(8) and 1.433(8) Å) are longer than the remaining ring C–C distances which lie in a fairly narrow range (1.377(8)–1.399(7) Å). The higher *trans*-influence of σ-C(sp<sup>2</sup>) compared with σ-N(sp<sup>2</sup>), established for atoms C(1) and N(2) of C<sub>6</sub>H<sub>4</sub>N=NPh ligands by the lengths of *trans* Pt–Cl bonds [8], may explain the trends in the Ni–C and C–C(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) distances of **1a**. It should, however, be emphasized that more symmetrical complexes, such as [Ni(*p*-MeC<sub>6</sub>H<sub>4</sub>N<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Me-*p*)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] [9], show a similar range of Ni–C distances and that η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> rings may display evidence of greater bond localisation, even when the electronic environment of the metal is cylindrically symmetric [10]. The η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> rings in A and B are slightly, but significantly non-planar: maximum individual atomic displacements from the mean C<sub>5</sub> plane are 0.023(5) and 0.014(5) Å for A and B respectively.

Compared with **1a**, **1b** and **1c** display both a different orientation of the η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> ligand and much greater variation in their M–C(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) distances. The MN(2)C(1) plane coincides approximately with C(15) and the midpoint of the C(13)–C(17) bond, with N(2) *trans* to C(15). The M–C(15) distances (2.167(3) and 2.153(7) Å) are extremely short: they can be compared with M–C(η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>) bond lengths of 2.130(7) and 2.151(8) Å found respectively in Pd and Pt complexes [11,12]. A survey of structural data for Pd(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) complexes (Table 2) emphasizes the extreme shortness of the Pd–C(15) bond in **1b** [6,11,13–19]. It is also apparent from Table 2

Table 2

Pd–C( $\eta^5$ -Cyclopentadienyl) distances (Å)

Compound	Range	Mean	r.m.s. $\Delta^a$	Ref.
[CpPd( $\overline{C_6H_4N=NPh}$ )] <sup>b</sup>	2.167(3)–2.408(3)	2.314	0.090	this work
[CpPd(C <sub>8</sub> H <sub>13</sub> O)]	2.23(1)–2.43(1)	2.362	0.073	13
	2.25(2)–2.42(2)	2.342	0.056	
[CpPd(PPh <sub>3</sub> )(CH <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> Cl)]BF <sub>4</sub>	2.211(8)–2.399(8)	2.316	0.067	14
[CpPd(PPh <sub>3</sub> )(CH <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> OMe)]BF <sub>4</sub>	2.210(7)–2.370(7)	2.310	0.058	14
[C <sub>5</sub> Ph <sub>5</sub> Pd] <sub>2</sub> (PhC <sub>2</sub> Ph)	2.32–2.46	2.410	0.055	15
	2.27–2.37	2.312	0.041	
[CpPd( $\eta^1$ -C <sub>5</sub> H <sub>5</sub> )PPr <sub>3</sub> ] <sup>b</sup>	2.259(10)–2.390(8)	2.343	0.045	11
[CpPd(PEt <sub>3</sub> )(CH <sub>2</sub> CHPh)]BF <sub>4</sub>	2.251(7)–2.353(9)	2.292	0.039	16
[CpPd(PPh <sub>3</sub> )(CH <sub>2</sub> CHPh)]PF <sub>6</sub>	2.221(9)–2.329(8)	2.288	0.038	14
[CpPd(PPr <sub>3</sub> )(C <sub>3</sub> H <sub>4</sub> )Pd(PPr <sub>3</sub> )Br]	2.31(2)–2.39(3)	2.358	0.032	17
[CpPd(C <sub>6</sub> H <sub>4</sub> NNPh)PCy <sub>3</sub> ]	2.303(6)–2.385(6)	2.349	0.031	6
[CpPd(SbPh <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	2.23(1)–2.31(1)	2.274	0.030	18
[CpPd( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )]	2.25–2.27	2.26	0.01	19

<sup>a</sup> Root mean square deviation of Pd–C distances from their mean. <sup>b</sup> Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>.

that Pd( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) complexes show a range of asymmetry in their Pd–C bonds: in some complexes the Pd–C distances are nearly identical but in many they show pronounced variations, **1b** being particularly conspicuous in this respect. In general, the complexes in Table 2 with r.m.s.  $\Delta$  values of 0.05 Å or more for the deviations of the Pd–C distances from their mean have one Pd–C distance appreciably shorter than the remaining four, as recently predicted on the basis of EHT-MO calculations [11]. Compared with that on palladium, structural information on Pt( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) complexes is sparse and of limited accuracy [20], but **1c** seems to be unusual both in respect of the shortness of the Pt–C(15) bond and of the range of the Pt–C( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) distances (r.m.s. deviation from mean 0.080 Å).

#### Trends in metal–ligand bond lengths

It has recently been suggested that the parameter  $\Delta = r(\text{Pt-L}) - r(\text{Pd-L})$ , where the  $r(\text{M-L})$  values are corresponding bond lengths in analogous Pt and Pd

Table 3

UV/Visible bands (nm) of  $[\text{M}(\overline{C_6H_4N=N-Ph})(C_5H_5)]$  in EtOH (extinction coefficients,  $\epsilon$  (lit mol<sup>-1</sup> cm<sup>-1</sup>) in parentheses)

Ni	Pd	Pt
587 (5020)	579 (7820)	524 (7950)
500 sh	442 sh	433 (5290)
346 (10040)	414 (8140)	365 (5110)
267 (23490)	345 sh	325 (5480)
247 (25100)	330 sh	280 (9060)
201 (27310)	314 sh	234 (32350)
	264 (29970)	202 (38590)
	234 (32250)	
	229 (31920)	
	201 (35500)	

complexes, is negative if L is a soft or  $\pi$ -acid ligand and positive if L is a hard ligand. Parallel low temperature studies give  $\Delta = +0.030(4)$  Å for L = CH<sub>3</sub> and  $-0.039(1)$  Å for PMePh<sub>2</sub> [21]. For **1b** and **1c**  $\Delta = -0.029$  Å for  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> (based on the M to ring centroid distances),  $+0.002(7)$  Å for  $\sigma$ -C(*sp*<sup>2</sup>) and  $-0.055(6)$  Å for  $\sigma$ -N(*sp*<sup>2</sup>). The last result is surprising, since  $\sigma$ -N-donors are usually considered to be hard.

#### Absorption spectra

Each compound gives rise to two intense charge transfer bands in the visible region and several intense, overlapping bands in the UV (Table 3). **1c** absorbs most light up to about 600 nm, accounting for its red colour. The lowest energy absorptions of **1a** and **1b** are both near 580 nm, absorbing green but transmitting red and some blue or violet, hence accounting for their purple colours by transmitted light (**1b** is dichroic, appearing green by reflected light).

Table 4

Crystallographic details for  $[\overline{M}(\text{C}_6\text{H}_4\text{N}=\text{NPh})(\eta^5\text{-C}_5\text{H}_5)]$  (M = Ni, Pd, Pt)

Formula	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> Ni	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> Pd	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> Pt
<i>f</i> <i>w</i> , amu	305.0	352.7	441.4
Cryst. system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> -C <sub>2</sub> <sup>5</sup> <i>h</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i> -C <sub>2</sub> <sup>5</sup> <i>h</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i> -C <sub>2</sub> <sup>5</sup> <i>h</i>
<i>a</i> , Å	9.502(1)	7.046(1)	6.993(2)
<i>b</i> , Å	16.155(2)	14.897(2)	14.846(3)
<i>c</i> , Å	18.659(3)	13.709(2)	13.709(4)
$\beta$ , deg.	99.16(1)	101.66(1)	101.92(2)
<i>V</i> , Å <sup>3</sup>	2827.7(6)	1409.3(3)	1392.6(6)
<i>Z</i>	8	4	4
<i>F</i> (000), electrons	1264	704	832
<i>d</i> (calcd), g cm <sup>-3</sup>	1.433	1.662	2.105
$\mu$ (Mo- <i>K</i> $\alpha$ ), cm <sup>-2</sup>	13.7	12.9	101.7
Transmission (on <i>F</i> )	0.63–1.29	0.85–1.09	0.78–1.38
Intensity measurements			
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan width ( $\Delta\omega$ ), deg.	1.28	1.13	1.65 + 0.53 tan $\theta$
max. counting time, s	90	90	120
2 $\theta$ range, deg.	4–54	4–60	4–60
<i>q</i> <sup>a</sup>	0.03	0.03	0.03
unique reflections	6129	4084	4028
duplicate <i>I</i> estimates	1316	3193	3887
<i>R</i> (internal)	0.027	0.022	0.034
Final refinement			
reflections used [ <i>I</i> $\geq$ 3 $\sigma$ ( <i>I</i> )]( <i>n</i> )	3072	3099	2818
refined parameters ( <i>p</i> )	361	237	181
max. shift/error	0.08	0.05	0.08
<i>R</i> <sup>b</sup>	0.037	0.022	0.027
<i>R</i> <sub>w</sub> <sup>c</sup>	0.038	0.028	0.032
<i>S</i> <sup>d</sup>	1.69	1.78	2.11
weights, <i>w</i>	$\sigma^{-2}$ ( <i>F</i> )	$\sigma^{-2}$ ( <i>F</i> )	$\sigma^{-2}$ ( <i>F</i> )
$ \Delta\rho $ , electrons	0.38	0.58	1.76

<sup>a</sup> Manojlović-Muir, Lj., Muir, K.W., J. Chem. Soc., Dalton Trans., (1974) 2427. <sup>b</sup>  $R = \sum ||F_0| - |F_c|| / \sum |F_0|$ . <sup>c</sup>  $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}$ . <sup>d</sup>  $S = [\sum w(|F_0| - |F_c|)^2 / (n - p)]^{1/2}$ .

Table 5

Fractional coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) for  $[\overline{M}(\overline{C_6H_4N=NPh})(\eta^5-C_5H_5)]$  complexes

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>a</sup>
<i>(a) M = Ni</i>				
Ni(A)	-0.00418(5)	0.16553(3)	0.13026(3)	0.045
Ni(B)	-0.46802(5)	-0.47593(3)	0.13447(3)	0.049
N(A1)	-0.1192(4)	0.0107(2)	0.1109(2)	0.053
N(A2)	-0.0009(3)	0.0520(2)	0.1274(2)	0.047
N(B1)	-0.5798(4)	-0.3203(2)	0.1200(2)	0.055
N(B2)	-0.4621(3)	-0.3619(2)	0.1363(2)	0.049
C(A1)	-0.2005(4)	0.1502(2)	0.1074(2)	0.049
C(A2)	-0.3149(5)	0.2055(3)	0.0960(2)	0.063
C(A3)	-0.4527(5)	0.1765(3)	0.0813(3)	0.071
C(A4)	-0.4816(5)	0.0932(3)	0.0764(3)	0.075
C(A5)	-0.3725(5)	0.0369(3)	0.0860(2)	0.068
C(A6)	-0.2337(4)	0.0655(2)	0.1009(2)	0.049
C(A7)	0.1233(4)	0.0003(2)	0.1362(2)	0.049
C(A8)	0.2247(5)	0.0085(3)	0.1976(2)	0.066
C(A9)	0.3433(5)	-0.0423(3)	0.2067(2)	0.079
C(A10)	0.3627(5)	-0.0986(3)	0.1552(3)	0.072
C(A11)	0.2648(5)	-0.1060(3)	0.0935(3)	0.067
C(A12)	0.1441(5)	-0.0574(3)	0.0838(2)	0.058
C(A13)	0.2053(4)	0.2143(3)	0.1491(3)	0.074
C(A14)	0.1330(6)	0.2467(3)	0.0839(3)	0.080
C(A15)	0.0135(6)	0.2862(3)	0.1004(3)	0.079
C(A16)	0.0152(6)	0.2823(3)	0.1755(3)	0.079
C(A17)	0.1361(5)	0.2393(3)	0.2053(2)	0.073
C(B1)	-0.6626(4)	-0.4593(2)	0.1140(2)	0.050
C(B2)	-0.7792(5)	-0.5132(3)	0.1023(2)	0.061
C(B3)	-0.9165(5)	-0.4836(3)	0.0871(2)	0.068
C(B4)	-0.9441(5)	-0.3992(3)	0.0832(3)	0.075
C(B5)	-0.8332(5)	-0.3442(3)	0.0929(3)	0.069
C(B6)	-0.6939(4)	-0.3739(3)	0.1080(2)	0.052
C(B7)	-0.3363(4)	-0.3112(2)	0.1475(2)	0.052
C(B8)	-0.2292(5)	-0.3283(3)	0.2047(2)	0.068
C(B9)	-0.1073(5)	-0.2803(4)	0.2145(3)	0.081
C(B10)	-0.0923(6)	-0.2159(4)	0.1690(3)	0.089
C(B11)	-0.1997(6)	-0.1984(3)	0.1128(3)	0.081
C(B12)	-0.3222(5)	-0.2454(3)	0.1018(2)	0.068
C(B13)	-0.2580(5)	-0.5287(3)	0.1556(3)	0.069
C(B14)	-0.3417(5)	-0.5630(3)	0.2031(2)	0.072
C(B15)	-0.4596(5)	-0.5982(3)	0.1614(3)	0.080
C(B16)	-0.4450(6)	-0.5881(3)	0.0866(3)	0.076
C(B17)	-0.3203(6)	-0.5458(3)	0.0841(3)	0.080
<i>(b) M = Pd</i>				
Pd	-0.04383(2)	0.08619(1)	-0.23709(1)	0.034
N(1)	-0.3060(3)	0.0024(1)	-0.1287(1)	0.038
N(2)	-0.2547(2)	0.0007(1)	-0.2133(1)	0.034
C(1)	-0.0618(3)	0.1172(1)	-0.1003(1)	0.036
C(2)	0.0444(4)	0.1780(2)	-0.0338(2)	0.046
C(3)	0.0120(4)	0.1848(2)	0.0621(2)	0.049
C(4)	-0.1246(4)	0.1332(2)	0.0952(2)	0.046
C(5)	-0.2344(4)	0.0732(2)	0.0315(2)	0.043
C(6)	-0.2022(3)	0.0652(1)	-0.0656(1)	0.036



Table 5 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>a</sup>
C(7)	-0.3541(3)	-0.0656(1)	-0.2808(1)	0.036
C(8)	-0.3411(4)	-0.0611(2)	-0.3799(2)	0.051
C(9)	-0.4387(4)	-0.1241(2)	-0.4470(2)	0.057
C(10)	-0.5463(4)	-0.1899(2)	-0.4160(2)	0.051
C(11)	-0.5573(4)	-0.1952(2)	-0.3164(2)	0.051
C(12)	-0.4617(3)	-0.1335(2)	-0.2483(2)	0.045
C(13)	0.0197(5)	0.1063(2)	-0.4018(2)	0.064
C(14)	0.0192(5)	0.1879(2)	-0.3563(2)	0.066
C(15)	0.1597(6)	0.1854(3)	-0.2697(3)	0.083
C(16)	0.2588(4)	0.1027(3)	-0.2668(3)	0.083
C(17)	0.1700(5)	0.0534(2)	-0.3480(3)	0.075
H(2)	0.132(4)	0.207(2)	-0.054(2)	0.054(8)
H(3)	0.073(4)	0.220(2)	0.098(2)	0.058(8)
H(4)	-0.146(4)	0.138(2)	0.158(2)	0.061(8)
H(5)	-0.344(3)	0.040(1)	0.052(2)	0.037(6)
H(8)	-0.275(4)	-0.015(2)	-0.402(2)	0.047(7)
H(9)	-0.437(4)	-0.117(2)	-0.512(2)	0.063(8)
H(10)	-0.610(4)	-0.237(2)	-0.457(2)	0.051(7)
H(11)	-0.634(3)	-0.241(1)	-0.298(1)	0.031(5)
H(12)	-0.472(4)	-0.138(2)	-0.184(2)	0.043(6)
H(13)	-0.045(6)	0.078(2)	-0.463(3)	0.099(13)
H(14)	-0.059(4)	0.232(2)	-0.377(2)	0.064(9)
H(15)	0.195(5)	0.226(2)	-0.232(2)	0.082(11)
H(16)	0.344(6)	0.079(2)	-0.227(3)	0.084(12)
H(17)	0.196(5)	-0.010(2)	-0.366(2)	0.088(11)
(c) <i>M</i> = <i>Pt</i>				
Pt	-0.04234(3)	0.08563(1)	-0.23726(2)	0.024
N(1)	-0.3087(6)	0.0025(3)	-0.1305(3)	0.028
N(2)	-0.2509(6)	0.0019(3)	-0.2149(3)	0.024
C(1)	-0.0668(7)	0.1156(4)	-0.1010(4)	0.026
C(2)	0.0408(8)	0.1788(4)	-0.354(4)	0.036
C(3)	0.0067(9)	0.1861(4)	0.0596(5)	0.038
C(4)	-0.1315(8)	0.1339(4)	0.0923(4)	0.036
C(5)	-0.2411(8)	0.0719(4)	0.0293(4)	0.036
C(6)	-0.2089(7)	0.0636(4)	-0.672(4)	0.028
C(7)	-0.3472(7)	-0.0653(3)	-0.2829(4)	0.027
C(8)	-0.3422(9)	-0.0595(4)	-0.3823(4)	0.043
C(9)	-0.4398(11)	-0.1251(5)	-0.4488(5)	0.051
C(10)	-0.5413(9)	-0.1922(5)	-0.4162(5)	0.043
C(11)	-0.5440(9)	-0.1980(5)	-0.3161(5)	0.043
C(12)	-0.4489(8)	-0.1353(4)	-0.2497(4)	0.038
C(13)	0.0124(10)	0.1053(6)	-0.4007(5)	0.059
C(14)	0.0232(12)	0.1852(5)	-0.3558(7)	0.064
C(15)	0.1674(16)	0.1809(7)	-0.2704(7)	0.091
C(16)	0.2597(10)	0.0958(9)	-0.2672(7)	0.085
C(17)	0.1600(12)	0.0505(6)	-0.3496(6)	0.066

<sup>a</sup> For non-hydrogen atoms *U* is the mean latent root of the anisotropic displacement tensor.

The origins of the bands are unknown. The similarity between the lowest energy absorptions of **1a** and **1b**, representing as they do the opposite extremes of reactivity, means that no obvious link with chemical properties is apparent. It is, of

course possible that different transitions are involved in the two molecules, and that the similarity in energy is fortuitous.

## Conclusions

The fact that palladium and platinum have larger covalent radii than nickel is reflected in less steric congestion between the 2-(phenylazo)phenyl and cyclopentadienyl groups and, in consequence, less distortion from planarity of the  $C_6H_4N=NPh$  ligands in **1b** and **1c** than in **1a**. In addition, the greater *trans*-influence of  $\sigma-C(sp^2)$  compared with  $\sigma-N(sp^2)$  causes greater distortion of  $M-\eta^5-C_5H_5$  bonding with the more polarisable metals Pd and Pt than it does with Ni. However, we do not consider that these structural differences provide a sufficient explanation of the unusual reactivity pattern of this series of complexes.

## Experimental

Complexes **1a**, **1b** and **1c** were prepared by published procedures [22,1,23]. UV/visible spectra were recorded on an Perkin-Elmer 550SE spectrometer.

The  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra of **1a** were recorded on a Varian XL-300 spectrometer. Chemical shifts are relative to  $Me_4Si$ . The NMR spectra of **1b** and **1c** have been reported previously.

*NMR Spectra of  $[Ni(C_6H_4N=NPh)(\eta^5-C_5H_5)]$ .*  $^1H$  NMR ( $CDCl_3$ ): 7.02 ddd ( $H^3$ ), 7.18 ddd ( $H^4$ ), 7.41 m ( $H^9, H^{10}, H^{11}$ ), 7.58 m ( $H^8, H^{12}$ ), 7.84 dd ( $H^2$ ), 8.26 dd ( $H^5$ );  $J_{23}$  7.6 Hz,  $J_{24}$  1.1 Hz,  $J_{34}$  7.4 Hz,  $J_{35}$  1.3 Hz,  $J_{45}$  7.8 Hz.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ): 92.45 ( $C_5H_5$ ), 123.35 ( $C^8, C^{12}$ ), 123.97 ( $C^3$  or  $C^4$ ), 124.34 ( $C^3$  or  $C^4$ ), 128.47 ( $C^9, C^{11}$ ), 128.58 ( $C^5$  or  $C^{10}$ ), 129.18 ( $C^5$  or  $C^{10}$ ), 142.37 ( $C^2$ ), 158.00 ( $C^7$ ), 163.59 ( $C^6$ ), 177.22 ( $C^1$ ).

*X-ray diffraction study of  $[M(C_6H_4N=NPh)(\eta^5-C_5H_5)]$  ( $M = Ni, 1a; Pd, 1b; and Pt, 1c$*

All measurements were made at 22°C with Mo X-rays ( $\lambda$  0.71069 Å) using an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator. Standard computational and experimental procedures were employed [24]. Pertinent details of each analysis are summarised in Table 4. The dimensions of the dark-red specimens were: 0.72 × 0.24 × 0.28 mm (**1a**) 0.56 × 0.52 × 0.25 (**1b**) and 0.96 × 0.58 × 0.28 mm (**1c**).

The analyses were carried out in all three cases by similar procedures. The cell dimensions were determined by a least squares method from the setting angles of 20–25 reflections with  $12 < \theta(Mo-K_\alpha) < 15^\circ$ . The integrated intensities were corrected for background,  $L_p$ , and absorption effects [25]. Equivalent intensities were then averaged and the analysis proceeded with all unique reflections having  $I \geq 3\sigma(I)$ . No correction for crystal decomposition was required.

The structures were solved by Patterson and Fourier methods and were refined to convergence by full-matrix least-squares minimisation of  $\sum w(|F_o| - |F_c|)^2$ . Neutral atom scattering factors and complex anomalous dispersion corrections were taken from ref. 26. In the final calculations anisotropic displacement parameters were refined for all non-hydrogen atoms. For **1b** the H-atom positional and isotropic displacement parameters were refined whereas for **1a** and **1c** H-atom

parameters were deduced assuming that C–H 0.96 Å and that  $U(H) = 1.2 U_{iso}(C)$ . All calculations were performed on a GOULD 32/27 computer with the locally developed GX package [27]. Final atomic parameters are presented in Table 5.

### Acknowledgements

We thank Mr. R. Wat for experimental assistance, Johnson–Mathey for loans of platinum and palladium salts, N.A.T.O. for a travel grant (to G.K.A. and R.J.C.), and S.E.R.C. (U.K.) for help with the purchase of equipment.

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