

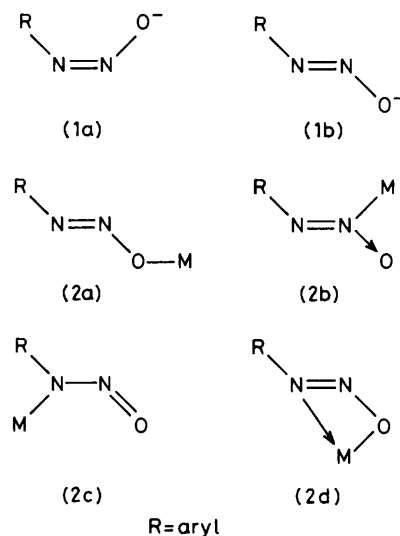
Co-ordination Chemistry of Arenediazoate Anions: Synthesis and X-Ray Crystallographic Characterisation of η -Cyclopentadienyl-(*anti-p*-nitrobenzenediazoato-*N*¹)(triphenylphosphine)nickel(II), $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)]^\dagger$

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Sodium *anti-p*-nitrobenzenediazoate reacts with $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Cl}]$ to give an 83% yield of the title complex $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)]$ (3), the first authenticated example of an arenediazoato-complex. Crystals of complex (3) are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 7.822(1)$, $b = 9.618(1)$, $c = 19.011(2)$ Å, $\alpha = 79.57(1)$, $\beta = 80.96(1)$, $\gamma = 109.04(1)^\circ$, and $Z = 2$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations. All hydrogen atoms were located from difference syntheses. Final $R = 0.043$ for 2 763 reflections with $I > 2\sigma(I)$. The arenediazoato-ligand has an *anti* configuration and co-ordinates to nickel *via* N(1) in a *monohapto*-fashion. The atoms of the $\text{NiONNC}_6\text{H}_4$ moiety are close to being coplanar. Principal dimensions include Ni-N(1) 1.901(4), Ni-P 2.166(1), Ni-C(cyclopentadienyl) 2.103(6)—2.187(7), and Ni \cdots O(1) 2.784(4) Å. The structural data are interpreted in terms of significant contributions from both diazoate and *N*-nitrosoamine anion resonance structures to the ground state of the co-ordinated arenediazoato-ligand.

The reaction between arenediazonium cations and aqueous hydroxide was first studied by Griess¹ over a century ago. There has since been considerable (and, as yet, incompletely resolved) controversy over the nature and structure of the products and the mechanisms of their formation.² Of the various species thought to be produced, the alkali-metal salts of the isomeric *syn*- and *anti*-diazooate anions (1a) and (1b) have been most completely characterised. It is now generally agreed that the chemically reactive isomer formed under conditions of kinetic control has the *syn* configuration while the less reactive thermodynamically favoured isomer has an *anti* geometry.²

Both *syn*- and *anti*-diazooate are formally related to nitrite in the same way that arenediazonium cations are related to the nitrosonium cation, *i.e.* by replacement of an oxygen atom by an arylimino-group, RN. The latter analogy sparked off the initial investigation³ into the now extensive⁴ area of transition-metal complexes of arenediazonium cations. Extending the analogy to include the diazoate anion suggests that like nitrite, diazoate should be capable of ligating main-group and transition-metal cations in both inorganic and organometallic environments. For the *anti*-diazooate anion, four non-bridging co-ordination modes (2a)—(2d) may be envisaged. In (2a)—(2c) the anion is a unidentate two-electron ligand while in (2d) it behaves as a bidentate (2 + 2)-electron chelating ligand. [Co-ordination modes analogous to (2a)—(2c) are possible for the *syn*-diazooate anion but the *syn* geometry precludes a chelate form analogous to (2d).] We are also interested in the possibility that arenediazoate might act as a precursor for the co-ordinated arenediazo-ligand *via* atom-transfer redox reactions of the kind known to generate the nitrosyl ligand from co-ordinated nitrate or nitrite.⁵ The literature, however, contains no unequivocal example of a



ligating diazoato-moiety. Early workers^{1,6} in this field isolated stable silver, mercury, and lead diazoates and it is possible that there is some degree of covalent bonding between anion and cation in these compounds. Later, Ciusa and Oreste⁷ described an extensive series of diazoate 'salts' of bivalent iron, cobalt, nickel, and copper as well as derivatives of cadmium, aluminium, and the uranyl cation. These compounds were characterised solely on the basis of their percentage metal content and their structure remains uncertain. Cobalt ammine complexes such as $[\text{Co}(\text{NH}_3)_6][\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]_2$ have also been reported⁸ but in these compounds diazoate may function simply as a counter ion. In this paper we report the synthesis and X-ray crystallographic characterisation of the first definite example of a complex containing a co-ordinated arenediazoate anion, η -cyclopentadienyl(*anti-p*-nitrobenzenediazoato-*N*¹)(triphenylphosphine)nickel(II) (3).

Supplementary data available (No. SUP 23367; 22 pp.): observed and calculated structure factors, thermal parameters, hydrogen atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Final fractional co-ordinates ($\times 10^5$ for Ni, $\times 10^4$ for others) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ni	6 846(9)	1 621(7)	80 636(4)	C(26)	171(7)	667(6)	6 152(3)
P	2 727(2)	907(1)	7 029(1)	C(31)	3 563(7)	-532(5)	6 754(3)
O(1)	-819(6)	-2 308(4)	7 488(2)	C(32)	4 504(7)	-1 144(6)	7 208(3)
O(2)	3 621(7)	4 680(7)	10 713(2)	C(33)	5 164(8)	-2 241(7)	7 050(4)
O(3)	5 262(8)	-2 961(7)	10 699(3)	C(34)	4 875(10)	-2 762(8)	6 431(4)
N(1)	710(6)	-1 835(4)	8 318(2)	C(35)	3 944(11)	-2 162(8)	5 974(4)
N(2)	-125(6)	-2 841(5)	7 969(2)	C(36)	3 274(8)	-1 055(7)	6 133(3)
N(3)	4 090(8)	-3 941(8)	10 479(3)	C(41)	1 539(7)	-2 420(5)	8 854(3)
C(11)	4 936(7)	2 411(5)	6 982(3)	C(42)	2 449(8)	-1 445(6)	9 242(3)
C(12)	6 474(7)	2 741(6)	6 411(3)	C(43)	3 282(8)	-1 945(7)	9 777(3)
C(13)	8 157(7)	3 877(6)	6 388(3)	C(44)	3 185(8)	-3 417(7)	9 910(3)
C(14)	8 300(7)	4 664(6)	6 928(3)	C(45)	2 280(9)	-4 420(7)	9 532(3)
C(15)	6 783(8)	4 323(6)	7 497(3)	C(46)	1 467(8)	-3 911(6)	8 996(3)
C(16)	5 098(7)	3 192(5)	7 529(3)	C(51)	-2 189(8)	-187(7)	8 543(3)
C(21)	1 864(6)	1 599(6)	6 247(3)	C(52)	-1 003(9)	108(8)	9 053(3)
C(22)	2 832(7)	3 003(6)	5 746(3)	C(53)	353(9)	1 557(7)	8 789(3)
C(23)	2 133(8)	3 424(7)	5 147(3)	C(54)	127(8)	2 117(7)	8 077(3)
C(24)	487(8)	2 468(7)	5 043(3)	C(55)	-1 506(8)	1 074(7)	7 948(3)
C(25)	-491(8)	1 108(6)	5 550(3)				

Experimental

The sodium salt of the *anti-p*-nitrobenzenediazoate anion was prepared by the method of Schraube and Schmidt.⁹ $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Cl}]$ was prepared as described by Moberg and Nilsson.¹⁰ I.r. spectra were determined using a Perkin-Elmer 457 grating spectrometer (calibrated with polystyrene film) and ^1H n.m.r. spectra were recorded on a Hitachi-Perkin-Elmer R20A instrument. Microanalysis was carried out by the staff of the Microanalytical Laboratory of University College, Cork.

Preparation of $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)]$ (3).—Chloro(η -cyclopentadienyl)(triphenylphosphine)nickel(II) (4.21 g, 10.0 mmol) was dissolved in *ca.* 30 cm³ of dry tetrahydrofuran (thf). Solid sodium *anti-p*-nitrobenzenediazoate (1.89 g, 10 mmol) was added portionwise to the stirred solution under a nitrogen atmosphere. The deep purple reaction mixture rapidly took on a wine-red colour. After *ca.* 30 min the solution was filtered through Celite and concentrated to dryness *in vacuo*. The brown residue was washed with diethyl ether and dissolved in dichloromethane. The filtered solution (Celite) was diluted with hexane and concentrated slowly without heat on the rotary evaporator to give the rust-coloured microcrystalline complex (3) (4.57 g, 83%). An analytically pure sample (m.p. 138.5–139.5 °C), was obtained after two further recrystallisations from CH_2Cl_2 -hexane (Found: C, 62.8; H, 4.6; N, 7.9; Ni, 10.5; P, 5.2. $\text{C}_{29}\text{H}_{24}\text{N}_3\text{NiO}_3\text{P}$ requires C, 63.1; H, 4.3; N, 7.6; Ni, 10.6; P, 5.6%). ^1H N.m.r. (CDCl_3 , SiMe_4 reference): δ 7.3–8.2 (complex multiplet, 19 H), 5.3 (s, 5 H). I.r. (KBr disc): 3 075vw, 3 055w, 1 600w (sh), 1 589s, 1 573w (sh), 1 509m (sh), 1 503s, 1 484m (sh), 1 480m, 1 478m (sh), 1 438m (sh), 1 433s, 1 425w (sh), 1 401w, 1 380m, 1 375m (sh), 1 351m (sh), 1 338s, 1 313m, 1 297m, 1 268s, 1 261s (sh), 1 183m, 1 175m (sh), 1 148s, 1 112s, 1 096s, 1 071w, 1 059w, 1 048w, 1 019w, 1 000w, 991vw, 979vw, 949m, 929vw, 908vw, 900vw, 854m, 849m (sh), 836m, 792m, 770w, 759m (sh), 752m, 744m, 723w (sh), 705m (sh), 696s, and 639w cm⁻¹. Crystals of (3) suitable for X-ray studies were obtained on slow evaporation of a concentrated solution in dichloromethane-hexane.

Crystal Data for $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)]$ (3).— $\text{C}_{29}\text{H}_{24}\text{N}_3\text{NiO}_3\text{P}$, $M = 551.6$, Triclinic, $a = 7.822(1)$, $b = 9.618(1)$, $c = 19.011(2)$ Å, $\alpha = 79.57(1)$, $\beta = 80.96(1)$, $\gamma =$

$109.04(1)^\circ$, $U = 1 293.2 \text{ \AA}^3$, $Z = 2$, $D_c = 1.42 \text{ g cm}^{-3}$, $F(000) = 572$, $\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 8.5 \text{ cm}^{-1}$, space group $P1$ or $P\bar{1}$; $P\bar{1}$ assumed and confirmed by the analysis.

Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections (with θ in the range 10–20°) measured on a Hilger and Watts Y290 four-circle diffractometer. Intensity data were collected as described previously¹¹ with a small ($0.05 \times 0.14 \times 0.30 \text{ mm}$) crystal to a maximum θ of 25° and 4 553 unique data were obtained. After corrections for Lorentz and polarisation effects and absorption, the data with $I > 2\sigma(I)$ (2 763) were labelled observed and used in structure solution and refinement. All calculations were carried out on the Amdahl V5 computer with our programs for data reduction; the SHELX¹² program system was used in subsequent calculations.

Structure Solution and Refinement.—The co-ordinates for the Ni and P atoms were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic vibration parameters. A difference map computed at an intermediate stage in the refinement revealed maxima in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealised positions (C–H 1.08 Å) and included in the final rounds of calculations. Only an overall isotropic thermal parameter was refined for the H atoms. In the final three refinement cycles a weighting scheme of the form $w = 1/[\sigma^2 F]$ was employed. Scattering factors used in the structure factor calculations were taken from refs. 13 and 14 and allowance was made for anomalous dispersion.¹⁵ Refinement converged with $R = 0.043$ and $R' = [\sum w\Delta^2 / \sum wF_o^2]^{1/2} = 0.043$ for the 2 763 reflections with $I > 2\sigma(I)$. A final difference map was devoid of any significant features. Table 1 contains the final fractional co-ordinates and Table 2 has details of interatomic distances and angles. A view of a molecule of (3) is illustrated in the Figure.

Results and Discussion

We have investigated the reactions of sodium *anti-p*-nitrobenzenediazoate with a variety of transition-metal organometallic substrates, *e.g.* $[\text{Fe}(\text{RN}_2)(\text{PPh}_3)_2(\text{CO})_2]^+$ ($\text{R} = \text{aryl}$),

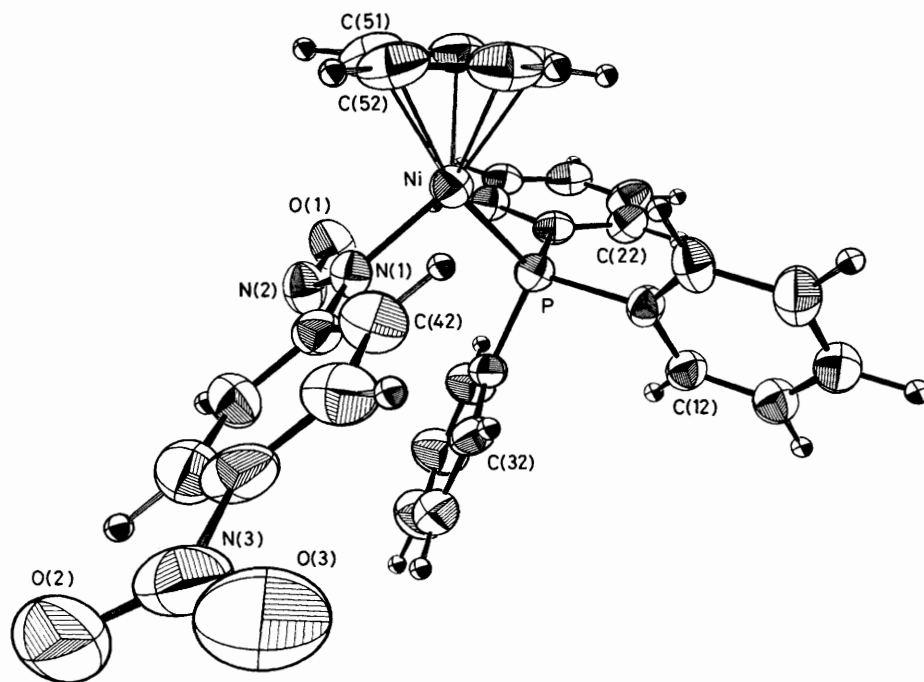


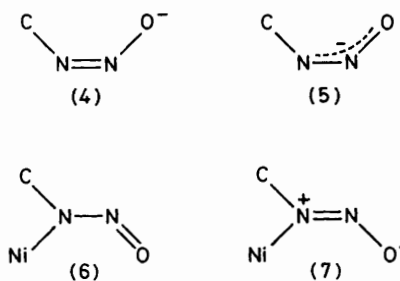
Figure. View of the molecule $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)]$ (3) with the crystallographic numbering scheme

$[\text{Fe}(\text{NO})(\text{PPh}_3)_2(\text{CO})_3]^+$, $[\text{Co}(\text{PPh}_3)_2(\text{CO})_3]^+$, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$, and $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Cl}]$. Reaction took place in all cases but the iron and cobalt complexes yielded carbonyl-free products which are currently under investigation. The reaction appears to involve at least some scission of the bond between the arene ring and diazoate nitrogen since the characteristic odour of nitrobenzene is detectable from the crude reaction products. In contrast, the nickel complex reacted smoothly with the diazoate anion in thf at room temperature and rust-coloured microcrystals of the product analysing as $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)]$ (3) were isolated from the reaction mixture in excellent yield. Pure complex (3) appears to be indefinitely air-stable in the solid state and is also stable for limited periods in chlorinated solvents even under aerobic conditions. The ^1H n.m.r. spectrum of complex (3) agreed with the formulation suggested by the microanalytical data. The i.r. spectrum of complex (3) (KBr disc) contains six strong bands in the region $1\ 100\text{--}1\ 600\ \text{cm}^{-1}$ which do not appear in the spectrum of $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Cl}]$. Bands at $1\ 589$ and $1\ 338\ \text{cm}^{-1}$ are tentatively assigned to the antisymmetric and symmetric vibrations of the ligand $p\text{-NO}_2$ group.¹⁶ Some or all of the remaining four strong i.r. bands ($1\ 503$, $1\ 268$, $1\ 148$, and $1\ 112\ \text{cm}^{-1}$) are likely to be associated with the co-ordinated NNO fragment of the diazoate ligand but a more definite assignment is not possible at this stage.

The results described above are compatible with the formulation of (3) as an 18-electron Ni^{II} complex in which the arenediazoate moiety is bound to nickel in a *monohapto*-fashion. Our X-ray analysis confirms this and establishes the mode of bonding of the arenediazoate ligand. The crystal structure contains discrete, well separated molecules with only van der Waals interactions between them. The co-ordination about nickel (Figure) is very similar to that found¹⁷ in the xanthate complex $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\sigma\text{-C}_2\text{H}_5\text{OCS}_2)]$, with Ni, P, N(1) of the arenediazoate ligand, and the midpoint of the cyclopentadienyl ring close to coplanar (Table 2) and with a P-Ni-N(1) angle of $96.1(1)^\circ$. The arenediazoate-ligand clearly has the *anti* configuration with N(2)-N(1)-C(41)

$113.6(4)^\circ$ and N(1)-N(2)-O(1) $113.1(4)^\circ$. This is the first structural characterisation of an *anti*-diazoate anion, albeit in a covalent complexed form. The structures of the anion $\text{CH}_3\text{-N=N-O}^-$ in potassium *syn*-methanediazoate¹⁸ and of $^-\text{O}_3\text{S-C}_6\text{H}_4\text{-N=N-O}^-$ in disodium *syn*-4-sulphobenzenediazoate¹⁹ have been determined crystallographically. Both structures are ionic with no metal-diazoate covalent bonding.

The *anti*- p -nitrobenzenediazoato-ligand in (3) is bound to nickel through N(1), *i.e.* co-ordination mode (2c). The NNO moiety and the arene ring are essentially coplanar and the nickel atom deviates by only $0.012\ \text{\AA}$ from the C_6NNO plane. The $p\text{-NO}_2$ group, however, is rotated slightly about the exocyclic C-N(NO_2) bond so that it makes an angle at 18.5° with the C_6NNO plane. This rotation presumably arises from crystal packing effects.



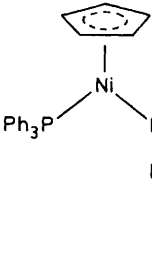
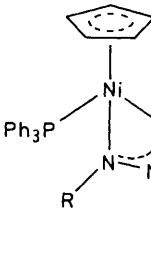
The bond lengths within the NNO fragment of the arenediazoato-ligand [N-N $1.327(6)$ and N-O $1.249(7)$ Å] may be usefully compared with those in the *syn*-methanediazoate anion¹⁸ [N-N $1.246(8)$, N-O $1.306(7)$ Å] and in the *syn*-4-sulphonatobenzenediazoate anion¹⁹ [N-N $1.296(13)$, N-O $1.318(11)$ Å]. In the *syn*-methanediazoate case the bond lengths have been interpreted in favour of a major contribution from structure (4)¹⁸ whereas in *syn*-4-sulphonatobenzenediazoate the slightly longer N-N distance led to formulation (5) being favoured.¹⁹ In the present molecule (3) the N-O

Table 2. Interatomic distances (Å) and angles (°) in $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5\text{-}(\text{PPh}_3)(\text{ON}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p))]$, with estimated standard deviations in parentheses

(a) Interatomic distances			
Ni-P	2.166(1)	N(2)-O(1)	1.249(7)
Ni-N(1)	1.901(4)	P-C(11)	1.833(5)
Ni...N(2)	2.795(4)	P-C(21)	1.832(5)
Ni...O(1)	2.784(4)	P-C(31)	1.834(6)
Ni-C(51)	2.179(6)	C(44)-N(3)	1.484(9)
Ni-C(52)	2.103(6)	N(3)-O(2)	1.229(9)
Ni-C(53)	2.133(8)	N(3)-O(3)	1.233(9)
Ni-C(54)	2.168(7)	C(51)-C(52)	1.445(9)
Ni-C(55)	2.187(7)	C(51)-C(55)	1.388(8)
N(1)-N(2)	1.327(6)	C(52)-C(53)	1.390(8)
N(1)-C(41)	1.420(7)	C(53)-C(54)	1.424(9)
		C(54)-C(55)	1.431(8)
Mean C-C (cyclopentadienyl)		1.420(8)	
Mean C-C (aromatic)		1.385(8)	
Ni-(midpoint of C ₅ H ₅ ring)		1.763(7)	
(b) Bond angles			
P-Ni-N(1)	96.1(1)	Ni-P-C(31)	116.0(1)
P-Ni...O(1)	81.6(1)	C(11)-P-C(21)	105.9(2)
P-Ni-	133.8	C(11)-P-C(31)	100.6(2)
(midpoint of C ₅ H ₅)		C(21)-P-C(31)	104.1(3)
N(1)-Ni-	129.2	C(44)-N(3)-O(2)	116.8(6)
(midpoint of C ₅ H ₅)		C(44)-N(3)-O(3)	117.5(6)
O(1)...Ni-	118.0	O(2)-N(3)-O(3)	125.7(7)
(midpoint of C ₅ H ₅)		C(5)-C(1)-C(2)	107.4(5)
Ni-N(1)-N(2)	118.9(4)	C(51)-C(52)-C(53)	109.8(5)
Ni-N(1)-C(41)	127.5(3)	C(52)-C(53)-C(54)	105.7(6)
N(2)-N(1)-C(41)	113.6(4)	C(53)-C(54)-C(55)	109.6(5)
N(1)-N(2)-O(1)	113.1(4)	C(54)-C(55)-C(51)	107.1(6)
N(2)-O(1)...Ni	77.5		
Ni-P-C(11)	115.8(2)		
Ni-P-C(21)	112.8(2)		
Mean C-C-C (C ₅ H ₅)		107.92	
Mean C-C-C (aromatic)		120.0	

distance is shorter and the N-N distance longer than those in the *syn*-diazotes mentioned above, arguing for a more significant contribution from the *N*-nitrosoamine resonance form (6) to the ground state structure of (3). The N-N bond length in (3) is significantly longer than the corresponding bond in a range of substituted azobenzenes (1.23–1.25 Å)²⁰ for which an N-N bond order of 1.9 has been suggested.²¹ It falls instead within the range found for N=N bonds in aromatic aza-heterocycles [*e.g.* 1.342(2) Å in pyrazole²² and 1.334(4) Å in pyridazine hydrochloride²³] and is noticeably shorter than typical N-N single bonds [*e.g.* 1.387(2) Å in diformylhydrazine²⁴]. The N-N bond in (3) must therefore have significant residual double-bond character and we conclude that the diazoato resonance structure (7) must, together with (6), make an important contribution to the ground state of the ligand.

The orientation of the NNO fragment of the arenediazoato-ligand relative to the nickel atom in complex (3) invites comparison with the closely related diaryltriazenido-complexes $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{RN}_2\text{R})]$ (8). It has been shown²⁵ that the 18-electron σ -diaryltriazenido-complex (8a) exists in equilibrium in solution with a paramagnetic 20-electron species (8b) in which the diaryltriazenido-ligand (isoelectronic with the arenediazoato-ligand) is bound to nickel in a chelate fashion. The geometry of complex (8b) might be expected to be similar to that of complex (3). However in the latter case the Ni...O(1) distance [2.784(4) Å] is clearly non-bonding and the diazoato-ligand is unambiguously unidentate. The Ni...O(1) distance in complex (3) may be compared with the distance of 2.811(5) Å found for the non-bonding Ni...O-(perchlorate) contacts in the orange form of 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene-nickel(II) diperchlorate, whereas a nickel-oxygen distance of *ca.* 2.2 Å would be expected for an Ni-O bonding interaction.²⁶ Further evidence for the absence of any significant interaction in (3) is provided by the absence of paramagnetic shifts in the ¹H n.m.r. spectrum.²⁵

(8a)  (8b) 

R = aryl

The Ni-P bond length in complex (3) [2.166(1) Å] is intermediate between the value found for the rather long Ni-P bond [2.184(2) Å] in $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\sigma\text{-C}_2\text{H}_5\text{OCS}_2)]$ ¹⁷ and the average value of 2.14 Å found for other $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{R}']$ (R' = CF₃, C₆F₅, or C₆H₅) complexes.^{27–29} The PPh₃ moiety has normal bond lengths and angles and an irregular 'propeller' conformation. The geometry of the Ni(η⁵-C₅H₅) group is as expected with Ni-C distances of 2.10–2.19 Å and Ni-(midpoint of C₅H₅ ring) 1.763(7) Å.

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