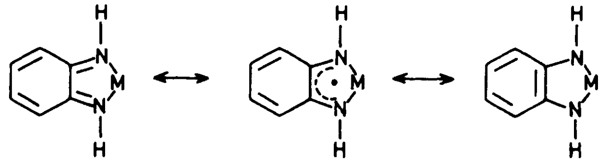
Iridium Nitrosyl Complexes of 9,10-Phenanthrenequinone Di-imine. Crystal Structure of $[Ir(NO)\{HNC_{14}H_8N(PPh_3)\}(PPh_3)][PF_6]$, a Species containing a Phosphazene–Imido-ligand [†]

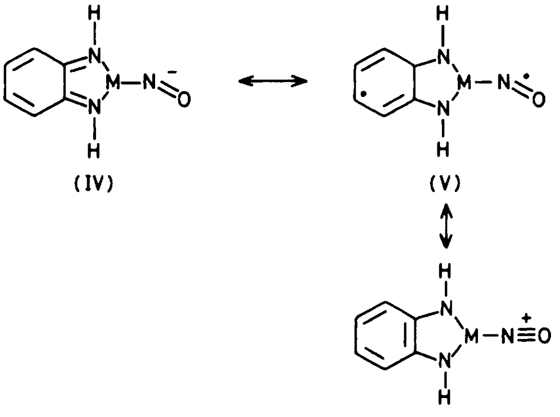
Paolo Dapporto, Gianfranco Denti, Giuliano Dolcetti, and Mauro Ghedini [*]
Dipartimento di Chimica, Universita della Calabria, 87030 Arcavacata (CS), Italy

9,10-Phenanthrenequinone di-imine (H_2pqd) reacts with $[Ir(NO)(MeCN)_3(PPh_3)_2]^{2+}$ yielding the expected five-co-ordinate $[Ir(NO)(H_2pqd)(PPh_3)_2]^{2+}$ which, by treatment with weak bases, gives the monocationic title compound, whose structure has been determined crystallographically. The compound is monoclinic, space group $P2_1$, with $a = 10.867(4)$, $b = 22.423(8)$, $c = 9.227(4)$ Å, $\beta = 101.12(4)°$, and $Z = 2$. It contains a phosphazene–imido-ligand, formed by transfer of a triphenylphosphine group from the metal to an imino-nitrogen atom, a nitrosyl group, and a triphenylphosphine molecule, in a nearly square-planar arrangement.

In spite of their interesting redox properties, α-dialdimines as ligands in transition-metal complexes are not widely reported in the literature. Like the strictly related *o*-quinones, these ligands can adopt [1] three different co-ordination modes (I)—(III), the actual electronic configuration of the system depending both on the charge density at the metal centre and on the oxidizing ability of the di-imine itself.



(I) (II) (III)



(IV) (V) (VI)

On the other hand, the capability of the co-ordinated nitrosyl group to behave as either a one- or a three-electron donor is well established.[2] Thus, when a di-imine and a nitrosyl ligand are both present in the co-ordination sphere of a transition metal, in addition to their effects on the electronic density of the metal, we can anticipate some mutual influence on their individual modes of co-ordination. As previously suggested for *o*-quinones,[3] this property depends on the interaction between the appropriate atomic orbital of the metal and the π* molecular orbitals of the ligands; a schematic picture of canonical forms (IV)—(VI) representing the system for a given oxidation state of the metal shows the relationship between the formal charges of the ligands and their bonding modes.

Having already studied iridium nitrosyl complexes containing ligands with a low-energy π* orbital, *viz.* quinones,[4] catechols,[3,5] 1,10-phenanthroline,[6,7] 2,2′-bipyridyl,[6] and 2-aminophenols,[8] we now report a study of the reaction between the dicationic nitrosyl complex $[Ir(NO)(MeCN)_3(PPh_3)_2]^{2+}$ and the 9,10-phenanthrenequinone di-imine (H_2pqd), and the reactivity of the product of this reaction toward bases. The choice of this α-di-imine ligand was based on its relatively easy synthesis and the stability of its bis(trimethylsilyl) derivative.

Experimental

Apparatus.—All the reactions were performed in an atmosphere of nitrogen purified over R 3-11 BASF deoxygenating catalyst and dried over molecular sieves. The subsequent work-up of the reaction products was carried out in air. Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer; the samples were run as KBr pellets. Phosphorus-31 n.m.r. spectra were obtained using a Varian Associates XL-100 spectrometer with 85% H_3PO_4 as external reference, downfield shifts being regarded as negative. Conductivity measurements were carried out with a Jones 0.1-cm cell and a LKB 5300B Conductolyzer conductivity bridge. Elemental analyses were performed by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

Solvents and Chemicals.—All the solvents, purified and dried as described in the literature, were deoxygenated prior to use; all transfers were carried out with a flexible needle or syringe technique. 9,10-Phenanthrenequinone di-imine (H_2pqd) was prepared as described previously,[9] as was the complex $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ (1).[10,11]

Preparations.—$[Ir(NO)(H_2pqd)(PPh_3)_2][PF_6]_2$ (2). In a typical preparation, a suspension of complex (1) (0.4 mmol) in methylene chloride (15 cm^3) was treated with a benzene solution (15 cm^3) of the stoicheiometric amount of H_2pqd, and the mixture stirred at room temperature for 4 h. The red

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[†] Nitrosyl(10-triphenylphosphazenylphenanthren-9-ylamido-*NN′*)triphenylphosphineiridium(1+).

Supplementary data available (No. SUP 23539, 17 pp.): thermal parameters, phenanthrene ring angles, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Physical data for nitrosyl complexes

Compound [a]	I.r. data (cm^{-1}) [b] ν(NO)	ν(NH)	^{31}P N.m.r. (p.p.m.) [c]	Λ [d]/Ω^{-1} cm^2 mol^{-1}
(1) $[Ir(NO)(MeCN)_3(PPh_3)_2]^{2+}$	1 540s		13.27 [e]	178.0
(2) $[Ir(NO)(H_2pqd)(PPh_3)_2]^{2+}$	1 793s	3 293m	−11.18 [f]	165.0
(3) $[Ir(NO)\{HNC_{14}H_8N(PPh_3)\}(PPh_3)]^+$	1 815s	3 396m	−15.02 [f] −34.72	81.5
(4) $[Ir(NO)(phen)(PPh_3)_2]^{2+}$	1 805s		−11.40 [g]	195.9

[a] As PF_6^- salt. [b] For KBr pellets. [c] 85% H_3PO_4 as external standard. [d] In CH_3NO_2, 10^{-3} mol dm^{-3} at 25 °C. [e] In CH_3CN. [f] In $CHCl_3$. [g] In CH_3NO_2.

precipitate which formed was filtered off and treated with methylene chloride (10 cm^3). After discarding a yellow-brown insoluble residue, the dark red solution was treated with diethyl ether (5 cm^3) and the mixture was carefully evaporated under reduced pressure. The red microcrystalline precipitate which formed was filtered off, washed with a little diethyl ether, and dried under high vacuum (60% yield) (Found: C, 47.15; H, 3.55; N, 3.00. Calc. for $C_{50}H_{40}F_{12}IrN_3OP_4$: C, 48.3; H, 3.25; N, 3.40%).

$[Ir(NO)(Hpqd{\cdot}PPh_3)(PPh_3)][PF_6]$ (3). In a typical preparation, $NaHCO_3$ (30 mg) was added to a suspension of complex (2) (0.1 mmol) in ethanol (15 cm^3). The mixture was stirred at room temperature for 2 d. The dark red product was filtered off and recrystallized from chloroform–ethanol (76% yield). From the same mixture of solvents, crystals suitable for *X*-ray investigation were grown by slow evaporation (Found: C, 55.25; H, 3.65; N, 3.75. Calc. for $C_{50}H_{39}F_6IrN_3OP_3$: C, 54.75; H, 3.60; N, 3.85%).

Crystal-structure Determination of Complex (3).—The crystal used for data collection had dimensions 0.03 × 0.22 × 0.24 mm.

Crystal data. $C_{50}H_{39}F_6IrN_3OP_3$, M = 1 097.0, Monoclinic, space group $P2_1$, a = 10.867(4), b = 22.423(8), c = 9.227(4) Å, β = 101.12(4)°, U = 2 206.14 Å^3, D_m = 1.65, Z = 2, D_c = 1.651 g cm^{-3}, $F(000)$ = 1 088, $\mu(Mo\text{-}K_\alpha)$ = 31.49 cm^{-1}, λ = 0.710 69 Å.

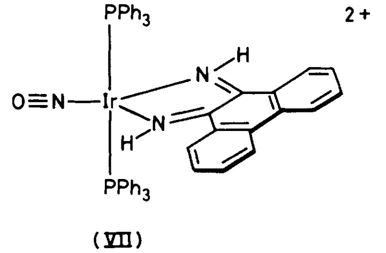
Intensity data were collected on an automatic Philips PW 1100 computer-controlled diffractometer, equipped with a graphite monochromator, using Mo-K_α radiation. All reflections with $6 \leqslant 2\theta \leqslant 40°$ were measured using an ω—2θ scan technique with a scan speed of 0.07° s^{-1} in a variable range of $(0.7 + 0.69 \tan \theta)°$ across the peak. Background times were taken as equal to half the scan time on each side of the peak. Three standard reflections were measured every 120 min during data collection, but no significant variation was noticed. The intensity data were corrected for Lorentz and polarization effects: the standard deviation $\sigma(I)$ was estimated as described elsewhere [12] with an instability factor equal to 0.03. From the total of 2 115 reflections, 1 844 were considered observed $[I \geqslant 3\sigma(I)]$. An absorption correction was applied by a numerical method; transmission factors varied between 0.53 and 0.91. Atomic scattering factors for non-hydrogen atoms were taken from ref. 13, those for hydrogen atoms from ref. 14. Corrections for anomalous dispersion effects were applied,[15] allowing the determination of the absolute structure.

Solution and refinement of the structure. The positions of the iridium and phosphorus atoms were obtained from a Patterson synthesis. The other non-hydrogen atoms were obtained from successive F_o maps. Four planar fluorine atoms of the hexafluorophosphate ion are in a disordered array, with 50% occupancies of two statistical positions. The structure was refined by use of full-matrix least squares and the SHELX program.[16] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$. The carbon atoms belonging to the phenyl groups were refined as rigid bodies, assuming a D_{6h} geometry for the rings, The hydrogen atoms were kept in calculated positions (C–H 1.08 Å) with an overall isotropic thermal parameter U of 0.05. Anisotropic thermal parameters were used for Ir, P, O, and N, isotropic thermal parameters for the other atoms. The final refinement gave an R value of 0.038, whereas $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}$ was 0.037. Despite the low final value of R, the standard deviations of the atomic parameters, and consequently those of bond distances and angles, appear to be rather high. This is probably related to the cut at 20° in ω in the data collection, caused by the low intensity of high-order reflections.

A final Fourier difference synthesis showed no remarkable features. The final positional parameters are reported in Table 2.

Results and Discussion

Synthesis and Reactivity.—The reaction (1 : 1) between the cation $[Ir(NO)(MeCN)_3(PPh_3)_2]^{2+}$ and 9,10-phenanthrenequinone di-imine (H_2pqd) in methylene chloride–benzene solution affords a red crystalline product. Spectroscopic and conductivity data (Table 1), together with analytical results, are in agreement with the formula $[Ir(NO)(H_2pqd)(PPh_3)_2][PF_6]_2$ (2). The i.r. spectrum shows a strong ν(NO) at 1 793 cm^{-1} and a medium ν(NH) at 3 293 cm^{-1}. The ^{31}P n.m.r. spectrum consists of a singlet at −11.18 p.p.m. suggesting that the two triphenylphosphine ligands occupy equivalent positions within the complex. By analogy with data for the similar complex cation $[Ir(NO)(phen)(PPh_3)_2]^{2+}$ (4; phen = 1,10-phenanthroline) (Table 1), whose structure is known,[7] we propose for complex (2) the structure (VII).



(VII)

Complex (2), suspended in ethanol in the presence of weak bases such as $NaHCO_3$ (stronger bases cause decomposition), is transformed into a brown-red crystalline product (3) whose structure cannot easily be established from analytical and spectroscopic data. The analytical data are in agreement with a formula $[Ir(NO)(Hpqd)(PPh_3)_2][PF_6]$, conductivity measurements indicate a 1 : 1 electrolyte, and the i.r. spectrum contains bands at 1 815 and 3 396 cm^{-1} related to ν(NO) and ν(NH) respectively [the shift of the last absorption with

Table 2. Positional parameters (× 10^4) for $[Ir(NO)\{HNC_{14}H_8N(PPh_3)\}(PPh_3)]^+$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ir	1 686(1)	0	1 926(1)	C(17)	4 667(14)	−1 937(5)	796(16)
P(1)	2 643(6)	−849(3)	3 049(7)	C(18)	3 698(14)	−1 702(5)	1 416(16)
P(2)	−106(6)	624(3)	−709(7)	C(19)	−1 580(13)	1 008(5)	−1 295(14)
P(3)	−3 392(7)	−2 754(4)	−2 923(9)	C(20)	−2 647(13)	842(5)	−760(14)
N(1)	458(17)	682(8)	1 069(20)	C(21)	−3 770(13)	1 150(5)	−1 215(14)
N(2)	321(20)	−178(15)	2 940(25)	C(22)	−3 827(13)	1 623(5)	−2 207(14)
N(3)	2 990(21)	214(9)	1 270(23)	C(23)	−2 760(13)	1 789(5)	−2 742(14)
O(1)	3 935(18)	348(8)	887(20)	C(24)	−1 637(13)	1 482(5)	−2 287(14)
F(1)	−4 312(17)	−2 965(8)	−4 308(21)	C(25)	1 005(12)	947(6)	−1 668(10)
F(2)	−2 447(16)	−2 559(8)	−1 492(20)	C(26)	1 991(12)	1 290(6)	−902(10)
F(3) *	−4 625(30)	−2 465(15)	−2 489(37)	C(27)	2 804(12)	1 581(6)	−1 668(10)
F(4)	−2 216(31)	−2 795(16)	−3 808(36)	C(28)	2 631(12)	1 529(6)	−3 201(10)
F(5)	−3 199(34)	−2 013(16)	−3 602(40)	C(29)	1 644(12)	1 186(6)	−3 967(10)
F(6)	−3 839(31)	−3 294(15)	−2 019(38)	C(30)	831(12)	895(6)	−3 200(10)
F(7)	−2 568(31)	−3 330(14)	−2 895(35)	C(31)	−298(11)	−157(7)	−1 323(18)
F(8)	−2 766(36)	−2 405(20)	−3 967(41)	C(32)	627(11)	−446(7)	−1 919(18)
F(9)	−4 231(34)	−2 964(17)	−1 718(41)	C(33)	462(11)	−1 039(7)	−2 369(18)
F(10)	−3 852(37)	−2 123(17)	−2 877(42)	C(34)	−627(11)	−1 344(7)	−2 223(18)
C(1)	3 402(15)	−722(5)	4 947(17)	C(35)	−1 552(11)	−1 055(7)	−1 627(18)
C(2)	4 200(15)	−1 148(5)	5 725(17)	C(36)	−1 387(11)	−462(7)	−1 177(18)
C(3)	4 725(15)	−1 056(5)	7 211(17)	C(37)	−453(17)	771(8)	1 991(20)
C(4)	4 450(15)	−537(5)	7 919(17)	C(38)	−549(17)	303(8)	2 919(20)
C(5)	3 652(15)	−110(5)	7 140(17)	C(39)	−1 596(19)	298(9)	3 726(24)
C(6)	3 128(15)	−202(5)	5 654(17)	C(40)	−1 786(21)	−213(8)	4 521(26)
C(7)	1 453(12)	−1 413(7)	3 046(13)	C(41)	−2 837(25)	−249(12)	5 237(31)
C(8)	1 367(12)	−1 737(7)	4 314(13)	C(42)	−3 546(25)	232(15)	5 183(29)
C(9)	419(12)	−2 159(7)	4 275(13)	C(43)	−3 444(22)	767(10)	4 390(26)
C(10)	−444(12)	−2 258(7)	2 968(13)	C(44)	−2 387(18)	796(9)	3 651(21)
C(11)	−358(12)	−1 935(7)	1 700(13)	C(45)	−2 105(19)	1 333(9)	2 912(23)
C(12)	591(12)	−1 512(7)	1 739(13)	C(46)	−2 785(20)	1 881(10)	2 951(25)
C(13)	3 880(14)	−1 172(5)	2 219(16)	C(47)	−2 497(22)	2 361(11)	2 200(27)
C(14)	5 029(14)	−876(5)	2 401(16)	C(48)	−1 456(20)	2 363(10)	1 450(25)
C(15)	5 998(14)	−1 111(5)	1 781(16)	C(49)	−805(23)	1 860(10)	1 391(26)
C(16)	5 816(14)	−1 641(5)	978(16)	C(50)	−1 101(20)	1 325(10)	2 107(24)

* Atoms F(3)—F(10) have been assigned population parameters of 0.5.

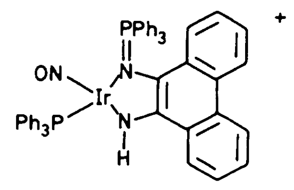
Table 3. Selected bond lengths (Å) and angles (°) of $[Ir(NO)\{HNC_{14}H_8N(PPh_3)\}(PPh_3)]^+$

Ir−P(1)	2.316(8)	N(2)−C(38)	1.43(3)	C(39)−C(44)	1.40(3)	C(45)−C(46)	1.44(3)
Ir−N(1)	2.08(2)	N(3)−O(1)	1.19(3)	C(40)−C(41)	1.43(4)	C(45)−C(50)	1.43(3)
Ir−N(2)	1.94(2)	C(37)−C(38)	1.37(3)	C(41)−C(42)	1.32(4)	C(46)−C(47)	1.35(3)
Ir−N(3)	1.71(2)	C(37)−C(50)	1.44(3)	C(42)−C(43)	1.42(4)	C(47)−C(48)	1.43(4)
P(2)−N(1)	1.64(2)	C(38)−C(39)	1.47(3)	C(43)−C(44)	1.45(3)	C(48)−C(49)	1.34(3)
N(1)−C(37)	1.44(3)	C(39)−C(40)	1.40(3)	C(44)−C(45)	1.45(3)	C(49)−C(50)	1.43(3)

P(1)−Ir−N(1)	166.7(6)	Ir−P(1)−C(1)	112.7(5)	N(1)−P(2)−C(31)	112.4(9)	Ir−N(3)−O(1)	176.1(18)
P(1)−Ir−N(2)	86.3(9)	Ir−P(1)−C(7)	108.3(5)	Ir−N(1)−P(2)	114.2(10)	N(1)−C(37)−C(38)	114.1(17)
P(1)−Ir−N(3)	93.3(7)	Ir−P(1)−C(13)	116.3(5)	Ir−N(1)−C(37)	109.9(12)	N(1)−C(37)−C(50)	124.3(18)
N(1)−Ir−N(2)	80.8(10)	N(1)−P(2)−C(19)	113.6(9)	P(2)−N(1)−C(37)	115.8(13)	N(2)−C(38)−C(37)	117.0(19)
N(1)−Ir−N(3)	99.9(9)	N(1)−P(2)−C(25)	107.8(8)	Ir−N(2)−C(38)	113.8(20)	N(2)−C(38)−C(39)	124.1(19)
N(2)−Ir−N(3)	171.3(10)						

respect to the corresponding one of complex (2) being noteworthy]. On the basis of these data one could suggest that complex (3) is simply formed by abstraction of an imino-proton from (2). On the other hand, the reaction leading to (3) from (2) is irreversible: solutions of HPF_6, even in large excess, have no effect on complex (3). Furthermore, the ^{31}P n.m.r. spectrum of complex (3), showing two different signals at −15.02 and −34.72 p.p.m., reveals very different environments for the two triphenylphosphine groups, which can hardly be attributed to stereochemical effects alone. The problem has been solved by a *X*-ray structure determination that has shown that complex (3) actually contains an unusual phosphazene-imido-ligand (VIII).

In view of the very mild conditions and the high yield of the reaction we suppose that the phosphazene formation arises from a concerted reaction in which the iridium atom assists the transfer of a triphenylphosphine to an imino-nitrogen atom previously deprotonated by the base.



(VIII)

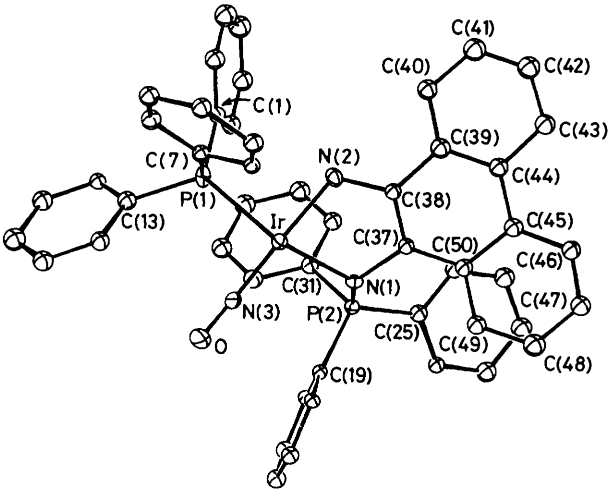


Figure. Perspective of the $[Ir(NO)\{HNC_8H_{14}N(PPh_3)\}(PPh_3)]^+$ cation

Description of the Structure of Complex (3).—The structure of complex (3) consists of $[Ir(NO)\{HNC_{14}H_8N(PPh_3)\}(PPh_3)]^+$ cations (Figure) and PF_6^- anions. Selected bond distances and angles are summarized in Table 3. The iridium atom is surrounded by the phosphorus atom of a triphenylphosphine molecule, the nitrogen atom of a nitrosyl group, and the two nitrogen atoms of the di-imine ligand, one of which has undergone substitution of a hydrogen atom by a triphenylphosphine molecule.

The co-ordination geometry about the iridium atom is square planar, all deviations from the least-squares plane being <0.1 Å. The Ir–N–O system is quite linear, with Ir–N(3) and N(3)–O lengths of 1.71(2) and 1.19(3) Å respectively and angle IrNO of 176.1(18)°. The Ir–P(1) distance [2.316(8) Å] falls in the range typical of similar square-planar iridium(I) nitrosyl complexes. The bite angle of the chelating ligand is 80.8(10)°. While not fully significant, the carbon–carbon distances of the phenanthrene frame and the C(37)–N(1) and C(38)–N(2) lengths 1.44(3) and 1.43(3) Å (very close to that expected for a carbon–nitrogen single bond) suggest that the starting di-imine may be present in its reduced form. The P(2)–N(1) distance [1.64(2) Å] is indicative of a double bond, with a strong π interaction between nitrogen and phosphorus, as found in other phosphazene compounds such as $Ph_2FP{=}NMe$,[17] $Ph_3P{=}NC_6H_5Br$,[18] $[V(CO)_6(NPPh_3)]$,[19] and $[\{Mo(CO)_3\}_2(NHPPh_3)]$.[20] The presence of a π interaction is also indicated by the bond angles around N(1) which are intermediate between tetrahedral and planar triangular values.

The Ir–N(2) distance [1.94(2) Å] is significantly shorter than that of Ir–N(1) [2.08(2) Å]. This suggests that there are two contributions to the bonding: the different electronic environments of each nitrogen atom and the influence of the appropriate *trans* group. The longer bond is formed by N(1) which shares π electrons with P(2) at the site *trans* to the phosphine molecule. The shorter bond is *trans* to the strong π-acceptor NO. Similar *trans* influences of NO and PPh_3 groups are found in the closely related iridium catecholate complex $[Ir(NO)(PPh_3)(O_2C_6Br_4)]$, in which the Ir–O bond *trans* to NO is shorter (1.905 Å) than the Ir–O *trans* to PPh_3 (2.008 Å).[3] These influences may account for the high stability of the phosphazene–imido-ligand in complex (3), especially since the free ligand is unknown.

Acknowledgements

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