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Geometrical isomerism arising from oxidative addition of an *o*-quinone monoimide to $IrCl(CO)(PPh_3)_2$

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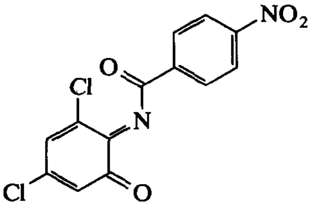
Abstract

A suspension of the *o*-quinone monoimide 1,2-N(C(O)-4-$C_6H_4NO_2$)O-2,4-$C_6H_2Cl_2$ and $IrCl(CO)(PPh_3)_2$ in CH_2Cl_2 was stirred for 3 days at room temperature. After careful chromatography two compounds were isolated, both with the empirical formula Ir(1,2-N(C(O)-4-$C_6H_4NO_2$)O-2,4-$C_6H_2Cl_2$)Cl(CO)(PPh_3)$_2$. These were shown by ^1H, ^{13}C and ^{31}P NMR and IR spectroscopy to be two of the twelve geometrical isomers possible for this complex. X-Ray crystallography confirmed these structures and showed that one isomer has *cis* and the other *trans* triphenylphosphine ligands.

Introduction

Oxidative addition of unsaturated molecules to Vaska's complex, $IrCl(CO)(PPh_3)_2$, is one of the foundation stones on which organometallic chemistry is built. For example, tetrachloro-1,2-benzoquinone adds to Vaska's complex to give the iridium(III) complex Ir(1,2-$O_2C_6Cl_4$)Cl(CO)(PPh_3)$_2$ [1]. The nitrogen analogues of *o*-quinones, *o*-benzoquinone diimines and *o*-benzoquinone diamides, will also form complexes with transition metals [2,3]. The *o*-quinone monoimide shown below exhibits similar chemistry to *o*-quinones, such as 1,4-cycloadditions with alkenes [4]. We have investigated the reaction between *o*-quinone monoimide and Vaska's complex.



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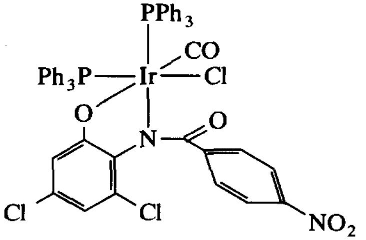
Results and discussion

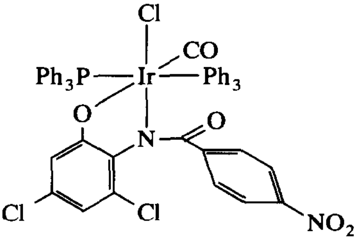
The oxidative addition reaction between the *o*-quinone imide and Vaska's complex proceeded simply upon stirring of equimolar amounts of the two reactants at room temperature in dichloromethane for 3 days. During this time the bright orange colour of the *o*-quinone imide darkened to deep orange. Careful chromatography of this solution resulted in isolation of two products, a faster moving yellow compound and, in higher yield, a slower moving orange compound.

The iridium carbonyl stretching frequency, observed in the IR spectra at 2060 and 2050 cm^{-1} for the orange and yellow compounds, respectively, confirmed that oxidative addition to give iridium(III) products had indeed taken place. Elemental analysis for the orange product was consistent with the empirical formula $Ir(1,2\text{-}N(C(O)\text{-}4\text{-}C_6H_4NO)O\text{-}2,4\text{-}C_6H_2Cl_2)Cl(CO)(PPh_3)_2$, corresponding to simple oxidative addition of the *o*-quinone imide to iridium, without either modification of the *o*-quinone imide fragment or ligand loss from iridium. The yellow product was not obtained in sufficient quantity to permit elemental analysis, but similarities in the spectral data of both products indicated that the same empirical formula was also likely for this compound.

Twelve different geometric isomers are possible for the six coordinate octahedral complex which is the product of simple oxidative addition of the *o*-quinone imide to Vaska's complex. These isomers arise from the differing arrangements of the donor atoms in the iridium coordination sphere combined with the asymmetry at the amido nitrogen centre. X-Ray crystallography of the orange and yellow products confirmed that these represent two of the possible twelve geometric isomers. The orange isomer contains the triphenylphosphine ligands in the *cis* configuration while the yellow isomer contains *trans* triphenylphosphine ligands. In both isomers the CO ligand on iridium is *trans* to the oxygen donor atom.



orange (*cis*) isomer



yellow (*trans*) isomer

The different arrangement of the triphenylphosphine ligands is clearly evident from the $^{31}P\{^1H\}$ NMR spectra of the two products. In the orange (*cis*) isomer, each PPh_3 ligand is *trans* to a different donor group and thus they are clearly chemically inequivalent. This results in a first order spectrum showing two widely separated resonances, each split into a doublet by *cis* P–P coupling ($^2J(PP) = 7.1$ Hz). In the yellow (*trans*) isomer the two PPh_3 ligands are mutually *trans* and chemical inequivalence of the two phosphorus atoms arises only from the asymmetry on the nearby amido nitrogen. This, together with the very large *trans* P–P coupling constant ($^2J(PP) = 437$ Hz) results in a second order spectrum showing an AB quartet pattern.

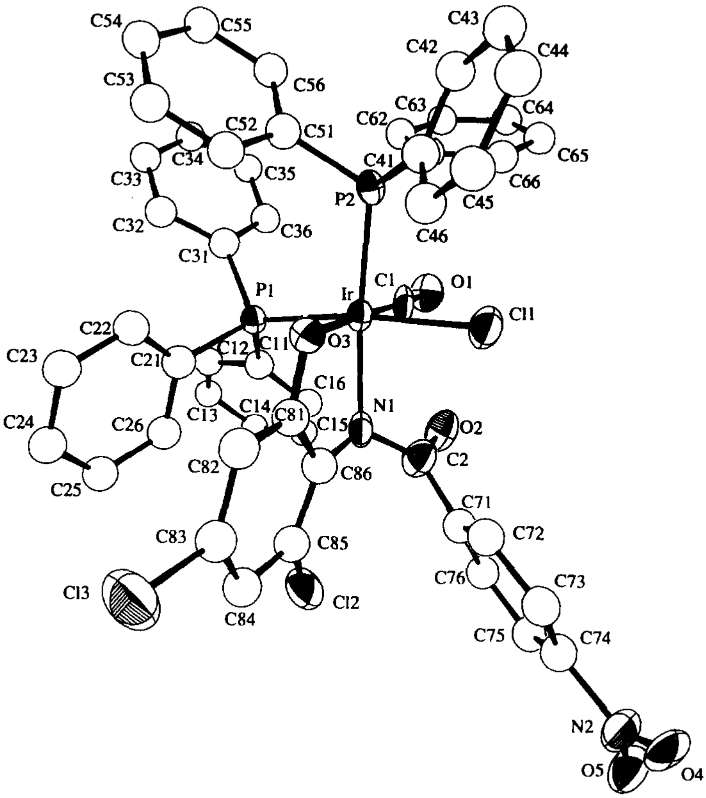


Fig. 1. Molecular geometry of orange (*cis*) isomer. Anisotropic atoms are depicted as 50% probability ellipsoids.

Both compounds contain only aromatic protons, and these are observed in the ^1H NMR spectra as a complicated set of resonances in the region 7.2–8.0 ppm, comprising the protons on the PPh_3 and chloro-substituted aryl rings. The *ortho* and *meta* protons on the *p*-nitrophenyl group appear as a pair of doublets shifted upfield to near 6 ppm.

The chemical inequivalence of the two PPh_3 ligands is again evident in the $^{13}C\{^1H\}$ NMR spectrum of the orange (*cis*) isomer, where two resonances are observed for each of the *ipso*, *ortho*, *meta* and *para* carbon atoms of the phenyl rings. Each resonance appears as a doublet as a result of P–C coupling. The resonances arising from the aromatic chelating ligand were assigned by identification of the CH and quaternary carbon atoms using the 135° DEPT spectrum editing sequence, and by comparison with assignments made for the free ligand and an olefin addition product of the ligand [4]. The $^{13}C\{^1H\}$ NMR spectrum of the yellow (*trans*) isomer was not as well resolved, with some resonances not observed. Only one set of resonances was observed for the PPh_3 phenyl carbon atoms despite the formal chemical inequivalence of these groups, although this may explain the broadening of the *ortho* and *para* carbon resonances. Some broadening is also observed for the PPh_3 resonances in the ^1H and $^{31}P\{^1H\}$ NMR spectra of the yellow (*trans*) isomer, possibly indicating that steric effects resulting

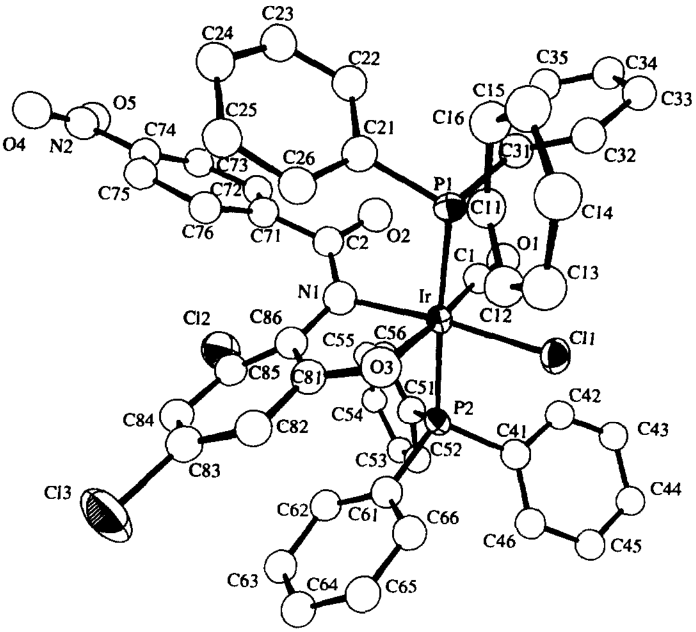


Fig. 2. Molecular geometry of yellow (*trans*) isomer. Anisotropic atoms are depicted as 50% probability ellipsoids.

from the proximity of the bulky amido substituent may be hindering rotation about the PPh_3 groups in this isomer.

The molecular geometries of both the orange (*cis*) and yellow (*trans*) isomers are depicted in Figs. 1 and 2. Selected bond lengths and angles are given in Table 1. Crystals of the orange (*cis*) isomer contain solvent ethanol molecules which are linked to each other (2.79 Å) and to the amido carbonyl oxygen (O2, 2.85 Å). In the crystals of the yellow (*trans*) isomer the water and ethanol solvent molecules are at a hydrogen bonding distance of 2.59 Å.

There appears to be no undue strain in the orange (*cis*) isomer resulting from the presence of the less common *cis* phosphine arrangement as all bond lengths and angles are considered normal for iridium(III). Any differences in bonding geometries in the coordination octahedra can be explained by small differences in structural *trans* influences of the ligands which would place them in the order P > N > Cl in the present complexes.

Further evidence for formal oxidative addition of the *o*-quinone imide to the iridium centre derives from examination of the bond lengths in the Cl_2,N,O-substituted ring. In the free *o*-quinone imide molecule or in a simple adduct of the ligand to iridium without change in formal oxidation state, this would be expected to show alternating bond lengths [2]. In the iridium complexes the ring C–C bond lengths do not vary significantly, and all are close to the expected benzenoid value of 1.39 Å, consistent with the aromaticity achieved on formal ligand reduction.

The most closely related complex to those described above is $Ir(1,2\text{-}O_2C_6Cl_4)Cl(CO)(PPh_3)_2$, prepared by oxidative addition of tetrachloro-1,2-benzoquinone to Vaska's complex [1]. This was shown by far IR and ^1H NMR spectroscopy to

Table 1

Selected bond lengths (Å) and angles (°)

	Orange (*cis*) isomer	Yellow (*trans*) isomer
Bond lengths		
Ir-C1	1.872(11)	1.86(3)
Ir-Cl1	2.415(3)	2.375(7)
Ir-P1	2.335(3)	2.402(8)
Ir-P2	2.380(3)	2.415(8)
Ir-O3	2.040(6)	2.066(19)
Ir-N1	2.115(11)	2.05(2)
C1-O1	1.131(14)	1.11(4)
O3-C81	1.380(15)	1.34(3)
N1-C86	1.400(14)	1.39(4)
C81-C82	1.376(15)	1.42(4)
C82-C83	1.41(2)	1.39(4)
C83-C84	1.37(2)	1.36(5)
C84-C85	1.379(18)	1.38(4)
C85-C86	1.40(2)	1.39(4)
C81-C86	1.396(17)	1.41(4)
N1-C2	1.394(14)	1.38(4)
C2-O2	1.215(15)	1.25(3)
C2-C71	1.520(15)	1.49(4)
P1-C(av)	1.82	1.83
P2-C(av)	1.84	1.82
Bond angles		
P1-Ir-P2	102.9(1)	174.6(3)
P1-Ir-C1	92.0(3)	92.9(9)
P1-Ir-Cl1	172.6(1)	87.6(3)
P1-Ir-O3	90.6(2)	86.0(5)
P1-Ir-N1	88.2(3)	92.5(7)
P2-Ir-C1	93.1(5)	89.9(9)
P2-Ir-Cl1	84.4(1)	87.6(3)
P2-Ir-O3	88.3(3)	91.7(5)
P2-Ir-N1	164.2(3)	91.8(7)
C1-Ir-Cl1	87.2(3)	92.0(8)
C1-Ir-O3	176.7(4)	175.2(9)
C1-Ir-N1	97.7(5)	96.5(11)
Cl1-Ir-O3	90.0(2)	92.7(5)
Cl1-Ir-N1	84.6(3)	171.5(7)
O3-Ir-N1	80.4(4)	78.9(8)
Ir-O3-C81	112.8(6)	111.8(16)
O3-C81-C86	118.9(9)	118.3(23)
C81-C86-N1	116.1(11)	113.3(21)
Ir-N1-C86	110.0(8)	110.9(16)
Ir-N1-C2	116.2(8)	121.2(18)
C2-N1-C86	124.6(9)	127.1(22)

contain *cis* PPh_3 ligands in the same plane as the chelating hydroquinone ligand. This was in direct contrast with the rhodium analogue, prepared similarly, in which the PPh_3 ligands adopt a *trans* arrangement [1]. In addition, the *cis* iridium hydroquinone complex contains a different arrangement of ligands than the orange (*cis*) isomer described above, which is possibly influenced by the bulky aryl substituent on the coordinated amido nitrogen. Overall, the differing arrangements of ligands in the orange (*cis*) isomer, the yellow (*trans*) isomer and the iridium hydroquinone complex may be the result of a balance of electronic and steric factors [5].

Experimental

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer Model 597 double-beam spectrophotometer calibrated with polystyrene film. Spectra were recorded as Nujol mulls between KBr (4000–400 cm^{-1}) plates. NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ solution. ^1H and $^{13}C\{^1H\}$ data were recorded at 400 and 100 MHz, respectively, with chemical shifts reported in ppm downfield from TMS. The atom numbering system used to report NMR data is shown in Fig. 3. $^{31}P\{^1H\}$ spectra were observed at 162 MHz with chemical shifts reported in ppm downfield from external 85% H_3PO_4. Melting points were determined on a Reichert microscope hot stage and are uncorrected. Elemental analyses for carbon, hydrogen and nitrogen were performed by Professor A.D. Campbell and associates at the University of Otago and are gratefully acknowledged. The *o*-quinone monoimide [4] and $IrCl(CO)(PPh_3)_2$ [6] were prepared by published methods.

X-Ray crystal structure determinations

X-Ray quality crystals of the orange (*cis*) isomer were grown from CH_2Cl_2/acetone/EtOH solution, while those of the yellow (*trans*) isomer were formed in CH_2Cl/MeOH/EtOH solution. X-ray intensity data were collected at room temperature on a Nonius CAD4 diffractometer. Crystallographic details are given in Table 2. The intensity sets were corrected for Lorentz and polarisation effects and for absorption by the empirical ψ scan method [7]. The structures were solved by conventional Patterson and difference Fourier techniques and refined by full matrix least-squares using SHELX-76 [8]. In both compounds, solvent molecules of crystallisation were found; the orange (*cis*) isomer contains acetone and ethanol, the yellow (*trans*) isomer contains water and methanol. The heavier atoms were assigned anisotropic thermal parameters but no attempt was made to locate hydrogen atoms. The weights used were $w = 1.0/(\sigma^2(F) + g(F)^2)$. Final atomic positions for each complex are listed in Tables 3 and 4, respectively. Supplemen-

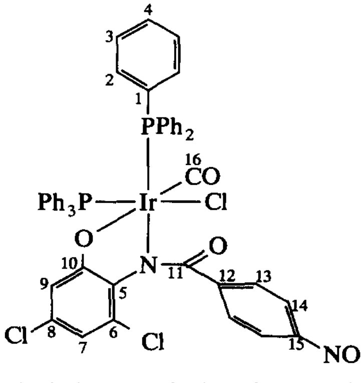


Fig. 3. Atom numbering scheme used for the reported NMR data.

Table 2

Crystal data, data collection and refinement parameters

	Orange (*cis*) isomer	Yellow (*trans*) isomer
Crystal data		
Formula	$C_{50}H_{36}Cl_3IrN_2O_5P_2$ $\cdot C_3H_6O \cdot C_2H_6O$	$C_{50}H_{36}Cl_3IrN_2O_5P_2$ $\cdot H_2O \cdot CH_4O$
Formula weight	1209.50	1155.41
Crystal system	Triclinic	Triclinic
Colour/habit	Orange/needles	Yellow/needles
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	14.148(2)	14.989(2)
b (Å)	17.605(3)	15.923(2)
c (Å)	11.618(3)	10.853(3)
α (°)	99.91(1)	97.72(2)
β (°)	111.33(1)	93.73(2)
γ (°)	75.18(1)	88.41(1)
V (Å^3)	2595.69	2560.89
Z	2	2
ρ(calc.) (g cm^{-3})	1.55	1.50
Data collection and reduction		
Temperature (K)	291 ± 1	289.5 ± 1
X-Radiation	Mo-K_α	Mo-K_α
Wavelength (Å)	0.7107	0.7107
Absorption coefficient (cm^{-1})	30.05	30.40
Crystal size (mm^3)	$0.36 \times 0.20 \times 0.08$	$0.28 \times 0.20 \times 0.03$
Scan type	$\omega-2\theta$	$\omega-2\theta$
Reflections collected	$5069[I > 3\sigma(I)]$	$1928[I > 3\sigma(I)]$
Refined parameters	356	295
Structure determination and refinement		
R	0.049	0.047
R_w [a]	0.063	0.067
g	0.0074	0.1724

[a] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w \propto 1/(\sigma^2(F) + gF^2)$.

tary data available from the authors (GRC) are atomic thermal parameters, complete lists of bond lengths and angles, and structure factor tables.

Preparations

A suspension of the bright orange *o*-quinone monoimide (30 mg, 0.092 mmol) and $IrCl(CO)(PPh_3)_2$ (72 mg, 0.092 mmol) in oxygen-free dichloromethane (10 mL) was stirred for 72 h at room temperature under N_2, during which the solids slowly dissolved to give a deep orange solution. The solvent was removed under reduced pressure, and the residue redissolved in a small amount of dichloromethane and chromatographed on silica gel. A fast moving yellow band (yellow *trans* isomer) and a slower moving orange band (orange *cis* isomer) were eluted with dichloromethane.

*Orange (*cis*) isomer*

Addition of ethanol to the dichloromethane solution obtained from chromatography followed by slow crystallisation afforded orange needles; m.p. 230°C. Anal.

Table 3

Atomic positions for orange (*cis*) isomer

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir	0.22644(4)	0.24098(3)	0.41658(4)	C43	0.0704(11)	0.0384(8)	0.6354(13)
P1	0.1499(2)	0.29158(15)	0.2229(2)	C44	0.1540(11)	−0.0213(8)	0.6319(13)
P2	0.0853(2)	0.20777(15)	0.4479(2)	C45	0.2178(11)	−0.0131(8)	0.5703(13)
Cl1	0.3259(2)	0.1929(2)	0.6176(3)	C46	0.2013(9)	0.0549(7)	0.5175(11)
Cl2	0.5451(3)	0.2355(3)	0.2923(4)	C61	0.0388(8)	0.2836(6)	0.5563(10)
Cl3	0.4864(4)	−0.0567(3)	0.1142(5)	C62	−0.0370(10)	0.3489(8)	0.5162(12)
C1	0.2060(10)	0.3416(7)	0.4995(10)	C63	−0.0599(12)	0.4090(9)	0.6051(14)
O1	0.1871(7)	0.4010(5)	0.5509(8)	C64	−0.0113(13)	0.4022(10)	0.7291(16)
N1	0.3729(7)	0.2394(6)	0.4055(8)	C65	0.0657(14)	0.3373(10)	0.7681(16)
C2	0.4386(9)	0.2782(8)	0.5055(11)	C66	0.0934(10)	0.2755(7)	0.6817(12)
O2	0.4079(7)	0.3415(5)	0.5550(8)	C71	0.5519(9)	0.2387(7)	0.5633(11)
O3	0.2569(6)	0.1298(4)	0.3340(7)	C72	0.5773(10)	0.1592(8)	0.5906(12)
N2	0.8603(11)	0.1401(13)	0.7695(13)	C73	0.6801(11)	0.1264(8)	0.6585(14)
O4	0.8775(11)	0.0725(11)	0.8038(14)	C74	0.7512(11)	0.1758(9)	0.6949(14)
O5	0.9244(10)	0.1816(11)	0.7932(14)	C75	0.7288(12)	0.2519(9)	0.6700(14)
C11	0.1859(8)	0.3819(6)	0.2110(10)	C76	0.6267(11)	0.2840(8)	0.6051(13)
C12	0.1341(9)	0.4175(7)	0.1004(11)	C81	0.3454(8)	0.1143(6)	0.3024(10)
C13	0.1629(10)	0.4809(8)	0.0789(12)	C82	0.3697(9)	0.0436(7)	0.2368(11)
C14	0.2448(12)	0.5113(9)	0.1692(14)	C83	0.4562(10)	0.0329(8)	0.1988(13)
C15	0.2953(11)	0.4781(8)	0.2806(13)	C84	0.5141(11)	0.0888(8)	0.2185(13)
C16	0.2678(10)	0.4130(7)	0.3005(12)	C85	0.4856(10)	0.1567(7)	0.2863(12)
C21	0.1852(8)	0.2237(6)	0.1007(10)	C86	0.4061(8)	0.1711(6)	0.3368(10)
C22	0.1419(9)	0.1576(7)	0.0496(11)	C51	−0.0232(8)	0.1863(6)	0.3117(10)
C23	0.1737(10)	0.1077(8)	−0.0425(12)	C52	0.0041(8)	0.1247(6)	0.2283(10)
C24	0.2481(10)	0.1208(8)	−0.0806(12)	C53	−0.0742(10)	0.1000(8)	0.1240(12)
C25	0.2924(10)	0.1833(8)	−0.0290(12)	C54	−0.1766(10)	0.1339(8)	0.1049(12)
C26	0.2628(9)	0.2364(7)	0.0631(11)	C55	−0.2054(11)	0.1934(8)	0.1863(13)
C31	0.0101(8)	0.3244(6)	0.1701(10)	C56	−0.1268(9)	0.2203(7)	0.2930(11)
C32	−0.0586(9)	0.2934(7)	0.0639(11)	O6	0.535(2)	0.271(1)	0.894(2)
C33	−0.1647(10)	0.3265(8)	0.0303(12)	C3	0.495(3)	0.352(2)	0.904(3)
C34	−0.2033(11)	0.3884(8)	0.1025(13)	C4	0.558(3)	0.387(2)	0.877(3)
C35	−0.1347(10)	0.4222(8)	0.2074(12)	C5	0.380(3)	0.376(2)	0.889(3)
C36	−0.0297(9)	0.3899(7)	0.2414(11)	O7	0.536(2)	0.509(1)	0.408(2)
C41	0.1181(8)	0.1152(6)	0.5223(10)	C6	0.567(3)	0.459(2)	0.303(3)
C42	0.0511(9)	0.1071(7)	0.5800(11)	C7	0.666(3)	0.420(2)	0.353(3)

Found: C, 54.41; H, 3.73; N, 2.40. $C_{50}H_{36}Cl_3IrN_2O_5P_2$ calc.: C, 54.33; H, 3.28; N, 2.53%. IR: ν(Ir–CO) 2060; ν(N–CO), $\nu_{as}(NO_2)$ 1585 (br); $\nu_s(NO_2)$ 1333 cm^{-1}. ^1H NMR: H_1, H_2, H_3, H_7, H_9 7.22 (m), 7.37 (m), 7.66 (m), 7.95 (m); H_{13} 5.88 (d), H_{14} 6.35 (d) (^3J(HH) = 2.2 Hz) ppm. ^{31}P NMR: −21.02 (d), −9.12 (d) (^2J(PP) = 7.1 Hz) ppm. ^{13}C NMR: C_1 127.40 (d, ^1J(PC) = 60.9 Hz), 129.93 (d, ^1J(PC) = 58.7 Hz); C_2 134.14 (d, ^2J(PC) = 14.5 Hz), 134.23 (d, ^2J(PC) = 15.0 Hz); C_3 128.19 (d, ^3J(PC) = 10.8 Hz), 128.29 (d, ^3J(PC) = 9.7 Hz); C_4 131.03 (d, ^4J(PC) = 2.6 Hz), 131.50 (d, ^4J(PC) = 2.6 Hz); C_5 125.64 (d, ^3J(PC) = 2.1 Hz); C_6, C_8 128.18, other peak obscured; C_7 117.04; C_9 115.58; C_{10} 146.38 (d, ^3J(PC) = 4.7 Hz); C_{11} 173.63; C_{12} 136.46; C_{13} 130.18; C_{14} 122.05; C_{15} 147.45; C_{16} 165.24 (d, ^2J(PC) = 5.3 Hz) ppm.

Table 4

Atomic positions for yellow (*trans*) isomer

Atom	x	y	z	Atom	x	y	z
Ir	0.22272(10)	0.16795(10)	0.16750(15)	C41	0.0990(19)	0.1295(17)	−0.126(3)
P1	0.3324(5)	0.1207(5)	0.3157(8)	C42	0.1735(19)	0.1075(17)	−0.194(3)
P2	0.1066(5)	0.2022(5)	0.0165(8)	C43	0.1717(19)	0.0586(17)	−0.311(3)
Cl1	0.2136(5)	0.0250(4)	0.0722(7)	C44	0.0902(20)	0.0214(18)	−0.359(3)
Cl2	0.1105(5)	0.4663(4)	0.2951(8)	C45	0.012(2)	0.0391(18)	−0.287(3)
Cl3	0.8831(6)	0.3032(6)	0.5358(10)	C46	0.016(2)	0.0928(18)	−0.171(3)
C1	0.309(2)	0.1916(17)	0.062(3)	C51	0.1181(19)	0.2989(17)	−0.053(3)
O1	0.3582(13)	0.1993(11)	−0.0085(19)	C52	0.057(2)	0.312(2)	−0.152(3)
N1	0.2155(16)	0.2873(14)	0.265(2)	C53	0.064(3)	0.387(3)	−0.208(4)
C2	0.2892(19)	0.3386(17)	0.285(2)	C54	0.130(3)	0.449(2)	−0.155(3)
O2	0.3534(13)	0.3206(11)	0.2169(18)	C55	0.191(3)	0.435(2)	−0.057(4)
O3	0.1301(12)	0.1510(11)	0.2944(16)	C56	0.184(2)	0.358(2)	−0.005(3)
N2	0.346(2)	0.630(2)	0.662(4)	C61	−0.0034(17)	0.2087(17)	0.080(2)
O4	0.3237(18)	0.6224(16)	0.758(3)	C62	−0.046(2)	0.2888(19)	0.107(3)
O5	0.377(2)	0.688(2)	0.614(3)	C63	−0.1331(19)	0.2920(18)	0.157(3)
C11	0.3080(18)	0.0243(16)	0.382(3)	C64	−0.168(2)	0.216(2)	0.183(3)
C12	0.2301(18)	−0.0194(17)	0.355(3)	C65	−0.1225(19)	0.1366(18)	0.164(3)
C13	0.2166(19)	−0.0945(17)	0.411(3)	C66	−0.0406(16)	0.1336(15)	0.106(2)
C14	0.285(2)	−0.1178(19)	0.497(3)	C71	0.2988(19)	0.4109(18)	0.386(3)
C15	0.3604(18)	−0.0715(17)	0.527(3)	C72	0.345(2)	0.480(2)	0.352(3)
C16	0.3734(18)	0.0007(17)	0.477(3)	C73	0.359(2)	0.555(2)	0.449(4)
C21	0.3542(19)	0.1942(17)	0.460(3)	C74	0.329(2)	0.552(2)	0.564(3)
C22	0.438(2)	0.230(2)	0.493(3)	C75	0.284(2)	0.4875(19)	0.596(3)
C23	0.446(3)	0.276(2)	0.614(4)	C76	0.2675(19)	0.4141(18)	0.506(3)
C24	0.378(3)	0.285(2)	0.697(3)	C81	0.0962(18)	0.2249(16)	0.347(2)
C25	0.298(2)	0.2499(20)	0.660(3)	C82	0.0204(17)	0.2246(15)	0.418(2)
C26	0.2823(19)	0.2027(17)	0.538(3)	C83	−0.020(2)	0.303(2)	0.453(3)
C31	0.4363(17)	0.0939(16)	0.245(2)	C84	0.0070(19)	0.3760(17)	0.417(3)
C32	0.463(2)	0.011(2)	0.219(3)	C85	0.0828(18)	0.3735(16)	0.350(3)
C33	0.548(2)	−0.010(2)	0.153(3)	C86	0.1345(17)	0.3007(15)	0.322(2)
C34	0.597(2)	0.059(2)	0.126(3)	O6	0.768	0.332	0.833
C35	0.573(2)	0.1386(20)	0.158(3)	O7	0.708	0.191	0.883
C36	0.4889(18)	0.1600(17)	0.216(3)	C3	0.621	0.224	0.852

*Yellow (*trans*) isomer*

Addition of ethanol to the dichloromethane solution obtained from chromatography followed by slow crystallisation afforded yellow needles. IR: ν(IR–CO) 2050; ν(N–CO), $\nu_{as}(NO_2)$ 1563 (br); $\nu_s(NO_2)$ 1340 cm^{-1}. ^1H NMR: H_1, H_2, H_3, H_7, H_9 7.30 (br), 7.51 (br), 7.88 (br); H_{13} 5.55 (d), H_{14} 5.65 (d) (^3J(HH) = 2.2 Hz) ppm. ^{31}P NMR: AB quartet −7.96 (d), 3.82 (d) (^2J(PP) = 437 Hz) ppm. ^{13}C NMR: C_1 130.34 (d, ^1J(PC) = 89.2 Hz); C_2 134.68 (m); C_3 128.25 (d, ^3J(PC) = 10.3 Hz); C_4 130.79; C_5 125.85; C_6, C_8 peaks not observed; C_7 116.04; C_9 115.74; C_{10} 142.26; C_{11} 167.04; C_{12} 137.48; C_{13} 130.79; C_{14} 123.80; C_{15} 147.32 ppm; C_{16} not observed.

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