Oxidative Addition of I_2, MeI, and CH_2I_2 to the Naphthalene-1,8-diamide Bridged Complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$. *X*-Ray Crystal Structure of $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]\cdot CH_2Cl_2$†

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Reaction of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**1**) with I_2, MeI, or CH_2I_2 at room temperature yields the dinuclear iridium(II) complexes $[Ir_2I_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**2**), $[Ir_2Me(I)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**3**), and $[Ir_2(CH_2I)I\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**4**) respectively. Complex (**4**) undergoes thermal oxidative isomerization to the methylene-bridged complex $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**5**). The molecular structure of (**5**) has been determined by an *X*-ray analysis. Crystals of (**5**) are monoclinic, space group $P2_1/c$, with $a = 16.253(2)$, $b = 12.214(1)$, $c = 24.919(3)$ Å, $\beta = 98.44(1)°$, and $Z = 4$. The complex is dinuclear. The two distorted octahedral environments of the metal centres share an ideal common face formed by the three donor atoms of the bridging ligands. The co-ordination spheres are analogous, the geometric arrangement of the CO and PPh_3 ligands conferring a *cis* configuration to the molecule. The intermetallic Ir · · · Ir separation is 3.0306(4) Å.

During the past several years considerable interest has been shown in the synthesis and reactivity of dinuclear transition-metal complexes.[1,2] Part of this interest has been stimulated by their potential use as models of co-operative effects between adjacent centres in heterogeneous catalytic reactions.[3,4] Of particular relevance with this regard is the reactivity of dinuclear complexes in the oxidative-addition reactions of alkyl halides.[5,6]

Our work in the area of dinuclear complexes has been focused on the synthesis and reactivity of dinuclear amido rhodium and iridium complexes $[M_2\{\mu\text{-}(NH)_2C_{10}H_6\}L_4]$ containing deprotonated diaminonaphthalene $(NH)_2C_{10}H_6{}^{2-}$ as the bridging ligand.[7–11] A distinctive feature of these complexes is their ability to undergo a variety of reactions: electrophilic addition of metal fragments,[11] electrochemical oxidation,[9] and oxidative addition.[7] To investigate further the versatility of the chemistry of these compounds we have carried out a study of the oxidative addition of I_2, MeI, and CH_2I_2 to $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$. This paper contains the results of this study that have led to the isolation of the iodo-iodomethyl $[Ir_2(CH_2I)I\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ and the di-iodo-(μ-methylene) $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ compounds formed in two different steps in the reaction of CH_2I_2 with $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$.

Results and Discussion

The Scheme summarizes the reactions described below. Reaction of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**1**) with 1 equivalent of I_2, MeI, or CH_2I_2 in dichloromethane at room temperature yields the dinuclear compounds $[Ir_2I_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**2**), $[Ir_2Me(I)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**3**), and $[Ir_2(CH_2I)I\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**4**) respectively. The complexes were obtained, after concentration of the solutions and addition of diethyl ether or hexane, as orange [(**2**)] or yellow [(**3**) and (**4**)] solids in *ca.* 70% yield, and their purity was ascertained by microanalyses. The reactions are clean; the isolated compounds were the only products detected in the i.r. spectra of the solutions during the reactions. On the basis of the spectroscopic parameters, it appears that the complexes have a geometry consistent with a two-centre oxidative addition to both iridium atoms with concurrent formation of an iridium–iridium bond.

The i.r. spectra in dichloromethane present only one ν(C≡O) band for complex (**2**) (1 980 cm^{-1}) and two ν(C≡O) bands for (**3**) (1 965, 1 985 cm^{-1}) and (**4**) (1 970, 1 995 cm^{-1}). The increases in wavenumber with respect to that of complex (**1**) (1 945 cm^{-1}) are in the range expected for an oxidation of an iridium(I) to an iridium(II) centre.[12] The phosphorus resonance of the PPh_3 ligands appears as one singlet for complex (**2**) (7.22 p.p.m.) and as two singlets for (**3**) (14.34, 13.10 p.p.m.) and (**4**) (13.53, 13.39 p.p.m.). Although the product of an oxidative addition of MeI or CH_2I_2 to only one centre would also present magnetically inequivalent PPh_3 ligands, the similarities of the chemical shift of both PPh_3 for the complexes (**3**) and (**4**) are more consistent with a two-centre oxidative addition.

We have assigned a relative *trans* disposition of the CO and PPh_3 ligands on the basis of the amido proton resonances. These resonances appear as one broad signal at δ 5.6 for complex (**2**) and at 4.13 for (**3**), and as two broad signals at 4.07 and 4.21 for complex (**4**). A large difference in these resonances would be expected for a *cis* disposition of the CO and PPh_3 ligands, similarly to that found for complex (**5**) (see below). An attempt at characterization by *X*-ray diffraction of the product of recrystallization of (**4**) from a dichloromethane–pentane solution clearly shows a dimeric molecular structure with the two iridium atoms separated by approximately 2.63 Å and with the iodine and methylene iodine groups bonded respectively to each metal centre. Unfortunately, the disordered simultaneous crystallization of small amounts of (**2**), or what we think is (**2**), in these pseudo-single crystals, and the presence of disordered solvent (CH_2Cl_2), prevented an accurate determination of the crystal structure of (**4**).

Complex (**4**) undergoes thermal oxidative isomerization to

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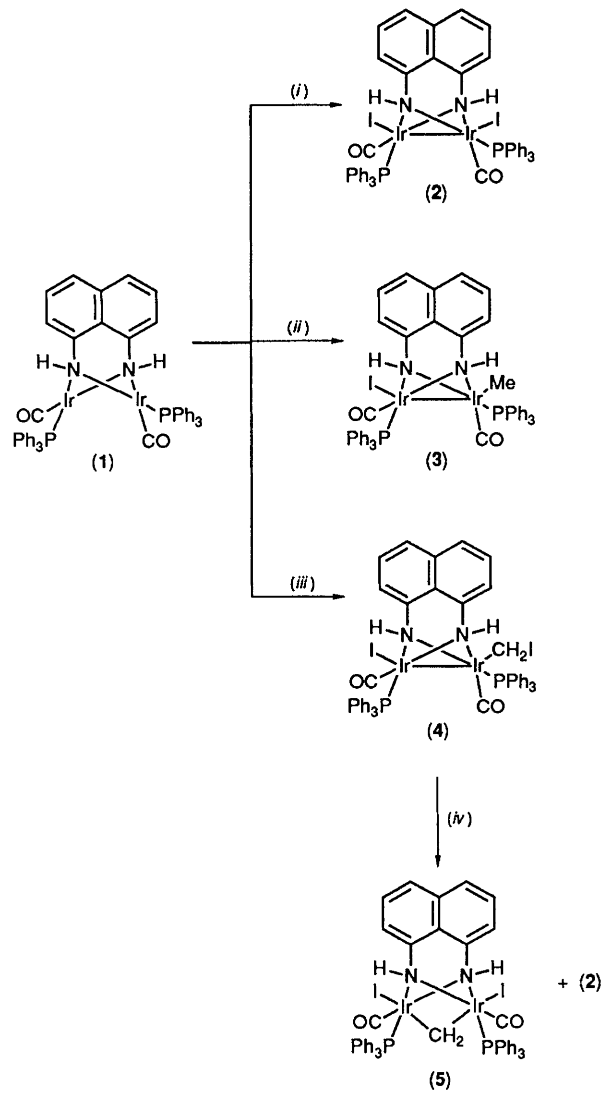
† μ-Methylene-μ-naphthalene-1,8-diamido-1κ^2*NN'*-2κ^2*NN'*-bis-[carbonyliodo(triphenylphosphine)iridium]-dichloromethane (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*i*) I_2; (*ii*) MeI; (*iii*) CH_2I_2; (*iv*) heat

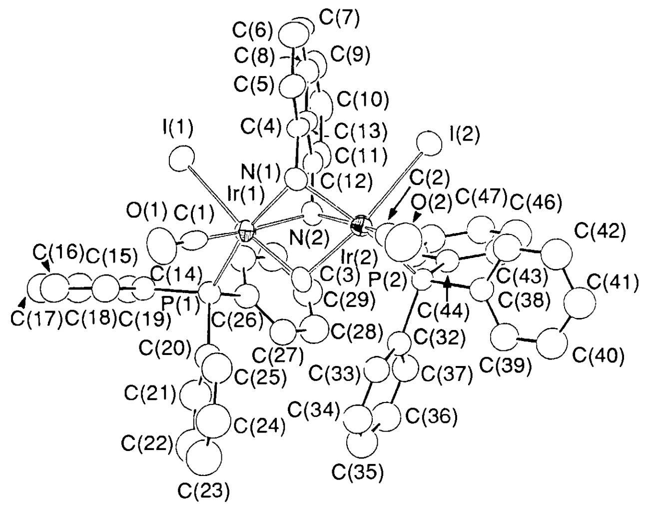


Figure. View of the molecular structure of $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**5**) with the atomic numbering scheme

the di-iodo(μ-methylene) complex $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**5**) with concomitant formation of the di-iodo compound (**2**). The reaction was carried out by refluxing a solution of (**4**) in toluene for 2 h; after cooling the solution a grey precipitate was formed. Recrystallization of the precipitate from dichloromethane–hexane gave complex (**5**) as a white air-stable powder in *ca.* 30% yield. The remaining toluene solution was evaporated to dryness; the $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. spectra of the resulting orange solid showed it to contain mostly complex (**2**). Significant amounts of di-iodo complexes $[Ir_2I_2(\mu\text{-}pz)_2L_4]$ have also been obtained in the double oxidative addition of CH_2I_2 to the pyrazolate-bridged complexes $[Ir_2(\mu\text{-}pz)_2L_4]$.[13,14]

The formulation of complex (**5**) was deduced by elemental analysis, i.r. and ^1H and ^{31}P n.m.r. spectroscopy; the crystal structure has been determined by single-crystal *X*-ray diffraction (see Figure). The spectroscopic data for (**5**) are in agreement with a relative *cis* disposition of the CO ligands (and the PPh_3 ligands). The i.r. spectrum shows a sharp band at 2 030 cm^{-1} due to $\nu(C\equiv O)$. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum exhibits only one singlet at -2.26 p.p.m. for the PPh_3 ligands. The ^1H n.m.r. spectrum shows, in addition to the aromatic resonances, the inequivalent amido protons at δ 1.95 and 4.31, and the methylene protons at 1.71(q) and 2.90(d), the spacing in both methylene signals being 5.9 Hz. The torsion angles H–C–Ir–P are around 20 and 95° (see Table 1). A small $J(^{31}P\text{–}H)$ coupling would be expected for a torsion angle of 20°.[13] We assign the doublet at δ 4.31 to the proton with torsion angles around 20°; its coupling with both phosphorus atoms would be very weak, the doublet resulting from coupling with the other methylene proton.

The results reported herein show the tendency of complex (**1**) to give di-iridium(II) compounds by oxidative addition of iodine and alkyl iodides; a similar trend has been reported for iridium complexes containing other bridging ligands in which the iridium atoms are held in relatively close proximity.[6,12,15–18] A remarkable feature of the reactivity of complex (**1**) is the double oxidative addition of CH_2I_2 in two different steps. There are few precedents[13–15,19] of the double oxidative addition of dihalogenoalkanes to dinuclear complexes; those in which the first oxidative-addition product and its subsequent oxidative-isomerization product have been isolated or detected are limited to complexes of the type $[Ir_2(\mu\text{-}pz)_2L_4]$[13,14] and $[\{Au(CH_2)_2PPh_2\}_2]$.[20,21] Also of interest is the structural change produced in the oxidative isomerization of complex (**4**) to (**5**). The relative arrangement of the CO ligands (and the PPh_3 ligands) is *trans* for complex (**4**) and *cis* for (**5**). This transformation could be explained in terms of the dissociation of the PPh_3 ligand from the iridium centre. Dissociation of phosphine from the iridium would relieve conformational rigidity at the metal centre, allowing intramolecular reorganization of (**4**) to (**5**), as has been suggested by Brost and Stobart[14] for the oxidative isomerization of $[Ir_2(CH_2I)I(\mu\text{-}pz)_2(CO)_2(PPh_3)_2]$ to $[Ir_2I_2(\mu\text{-}CH_2)(\mu\text{-}pz)_2(CO)_2(PPh_3)_2]$.

X-Ray Crystal Structure of $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]\cdot CH_2Cl_2$ (**5**).—The unit cell contains four molecules of the dinuclear complex and four dichloromethane molecules of crystallization. The Figure shows an ORTEP drawing of the molecule with the atom numbering scheme. Selected bond lengths and angles are given in Table 1. The complex presents a distorted octahedral co-ordination around the iridium atoms, both octahedra sharing the face N(1)–N(2)–C(3). The iridium co-ordination spheres are analogous, exhibiting identical relative *trans* dispositions of the terminal ligands. A formal description of each co-ordination octahedron would include the CO and PPh_3 ligands occupying relative *trans* positions to both bridging amido nitrogens. If these ligands are supposed to occupy the positions of an idealized co-ordination plane, the remaining ligands, iodine and methylene, co-ordinate almost perpendicular to this plane, and

Table 1. Selected bond lengths (Å), angles (°), and torsion angles (°) for $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]\cdot CH_2Cl_2$ (**5**), with estimated standard deviations (e.s.d.s) in parentheses

Ir(1) ··· Ir(2)	3.030 6(4)		
Ir(1)–I(1)	2.821 7(6)	Ir(2)–I(2	2.818 8(6
Ir(1)–P(1)	2.312(2)	Ir(2)–P(2)	2.337(2)
Ir(1)–N(1)	2.158(6)	Ir(2)–N(1)	2.156(5)
Ir(1)–N(2)	2.158(5)	Ir(2)–N(2)	2.160(6)
Ir(1)–C(1)	1.857(8)	Ir(2)–C(2)	1.860(9)
Ir(1)–C(3)	2.061(8)	Ir(2)–C(3)	2.068(7)
O(1)–C(1)	1.123(9)	O(2)–C(2)	1.129(11)
I(1)–Ir(1)–P(1)	90.60(5)	I(2)–Ir(2)–P(2)	88.10(5)
I(1)–Ir(1)–N(1)	98.1(1)	I(2)–Ir(2)–N(1)	95.7(1)
I(1)–Ir(1)–N(2)	96.4(1)	I(2)–Ir(2)–N(2)	96.7(1)
I(1)–Ir(1)–C(1)	86.8(2)	I(2)–Ir(2)–C(2)	91.8(3)
I(1)–Ir(1)–C(3)	172.4(2)	I(2)–Ir(2)–C(3)	171.1(2)
P(1)–Ir(1)–N(1)	166.9(1)	P(2)–Ir(2)–N(1)	172.1(2)
P(1)–Ir(1)–N(2)	99.1(2)	P(2)–Ir(2)–N(2)	102.4(2)
P(1)–Ir(1)–C(1)	90.5(3)	P(2)–Ir(2)–C(2)	89.1(3)
P(1)–Ir(1)–C(3)	93.4(2)	P(2)–Ir(2)–C(3)	98.8(2)
N(1)–Ir(1)–N(2)	70.3(2)	N(1)–Ir(2)–N(2)	70.3(2)
N(1)–Ir(1)–C(1)	99.7(3)	N(1)–Ir(2)–C(2)	97.7(3)
N(1)–Ir(1)–C(3)	76.9(3)	N(1)–Ir(2)–C(3)	76.8(3)
N(2)–Ir(1)–C(1)	169.8(3)	N(2)–Ir(2)–C(2)	165.9(3)
N(2)–Ir(1)–C(3)	76.6(2)	N(2)–Ir(2)–C(3)	76.4(3)
C(1)–Ir(1)–C(3)	99.6(3)	C(2)–Ir(2)–C(3)	93.9(3)
Ir(1)–N(1)–Ir(2)	89.3(2)	Ir(1)–N(2)–Ir(2)	89.2(2)
Ir(1)–N(1)–C(4)	115.9(5)	Ir(1)–N(2)–C(12)	114.2(4)
Ir(2)–N(1)–C(4)	114.8(4)	Ir(2)–N(2)–C(12)	115.2(5)
Ir(1)–C(3)–Ir(2)	94.4(3)		
Ir(1)–C(1)–O(1)	178.1(7)	Ir(2)–C(2)–O(2)	176.2(8)
P(1)–Ir(1)–C(3)–H(3)	17.2(7)	P(1)–Ir(1)–C(3)–H(4)	−99.5(8)
P(2)–Ir(2)–C(3)–H(3)	−21.2(7)	P(2)–Ir(2)–C(3)–H(4)	95.0(7)

the metal atoms Ir(1) and Ir(2) are slightly out of this plane towards the iodine atoms, by 0.126 0(4) and 0.085 0(4) Å respectively. The geometric arrangement of the CO and PPh_3 ligands confers a *cis* configuration to the molecule. The molecule shows a non-crystallographic mirror plane through the naphthalene ring and perpendicular to the Ir–Ir axis.

The Ir–N bond lengths [2.158(6), 2.158(5), 2.156(5), 2.160(6) Å] lie in the range observed for other iridium amido complexes.[22,23] The small N–Ir–N angles [70.3(2) and 70.3(2)°] are most likely imposed by the chelating nature of the ligand; these values compare well with those found in related rhodium compounds.[7,10,11] The Ir–C(3) bond lengths [2.061(8) and 2.068(7) Å] are slightly shorter than those for other dinuclear iridium methylene-bridged complexes.[14,15] The Ir(1)–C(3)–Ir(2) angle is 94.4(3)°; this relatively large value is in accordance with the methylene ligand bridging two formally non-bonded iridium atoms.[15,24] The Ir ··· Ir distance is 3.0306(4) Å and falls out of the range of distances attributed to Ir–Ir single bonds.[6]

Experimental

The reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ was prepared as previously reported.[10] Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. I.r. spectra were recorded on a Perkin-Elmer 783 spectrophotometer, ^{31}P and ^{1}H n.m.r. spectra in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer, chemical shifts being quoted relative to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (external, ^{31}P).

Preparations.—$[Ir_2I_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**2**). Iodine (34 mg, 0.13 mmol) was added to a solution of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (150 mg, 0.13 mmol) in dichloromethane (20 cm^3). The resulting orange solution was allowed to react at room temperature for 30 min, after which concentration of the solution and addition of diethyl ether (15 cm^3) led to an orange precipitate. The solid was filtered off, washed with diethyl ether, and dried under vacuum (134 mg, 73%) (Found: C, 41.5; H, 2.9; N, 2.2. Calc. for $C_{48}H_{38}I_2Ir_2N_2O_2P_2$: C, 41.9; H, 2.2; N, 2.0%). I.r.: ν(N–H) 3 300, 3 320 (Nujol); ν(C≡O) 1 980 cm^{-1} (CH_2Cl_2). N.m.r. ($CDCl_3$): ^{1}H, δ 5.6 (br, 2 H, NH), 6.69 [d, *J*(H–H) = 8.0, 2 H, $C_{10}H_6$], 7.09 [t, *J*(H–H) = 8.0 Hz, 2 H, $C_{10}H_6$], and 7.3—7.8 (m, 32 H, $C_{10}H_6$, C_6H_5); $^{31}P\text{-}\{^{1}H\}$, δ 7.22 (s) p.p.m.

$[Ir_2Me(I)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**3**). Methyl iodide (19 mg, 0.13 mmol) was added to a solution of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (150 mg, 0.13 mmol) in dichloromethane (20 cm^3). The solution was stirred at room temperature for 90 min, after which an orange solution was formed. The solution was concentrated and diethyl ether (15 cm^3) added to give a yellow precipitate, which was filtered off, washed with diethyl ether, and dried under vacuum (125 mg, 74%) (Found: C, 45.9; H, 3.4; N, 2.0. Calc. for $C_{49}H_{41}IIr_2N_2O_2P_2$: C, 46.6; H, 3.3; N, 2.2%). I.r.: ν(N–H) 3 320 (Nujol); ν(C≡O) 1 965, 1 985 cm^{-1} (CH_2Cl_2). N.m.r. ($CDCl_3$): ^{1}H, δ 0.15 [d, *J*(H–P) = 2.7, 3 H, CH_3], 4.13 (br, 2 H, NH), 6.33 [d, *J*(H–H) = 8.1, 1 H, $C_{10}H_6$], 6.39 [d, *J*(H–H) = 8.1, 1 H, $C_{10}H_6$], 7.04 [t, *J*(H–H) = 6.5, 1 H, $C_{10}H_6$], 7.11 [t, *J*(H–H) = 6.5 Hz, 1 H, $C_{10}H_6$], and 7.2—7.8 (m, 32 H, $C_{10}H_6$, C_6H_5); $^{31}P\text{-}\{^{1}H\}$, δ 14.34 (s) and 13.10 (s) p.p.m.

$[Ir_2(CH_2I)I\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**4**). Di-iodomethane (47 mg, 0.18 mmol) was added to a solution of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (200 mg, 0.18 mmol) in dichloromethane (20 cm^3). The resulting orange solution was allowed to react at room temperature for 60 min, after which concentration of the solution and addition of hexane (15 cm^3) led to a yellow precipitate. The solid was filtered off, washed with hexane, and dried under vacuum (170 mg, 69%) (Found: C, 42.6; H, 3.3; N, 1.7. Calc. for $C_{49}H_{40}I_2Ir_2N_2O_2P_2$: C, 42.4; H, 2.9; N, 2.0%). I.r.: ν(N–H) 3 320 (Nujol); ν(C≡O) 1 970, 1 995 cm^{-1} (CH_2Cl_2). N.m.r. ($CDCl_3$): ^{1}H, δ 1.48 [d, *J*(H–H) = 6, 1 H, CH_2I], 2.86 [t, *J*(H–H) = *J*(H–P) = 6, 1 H, CH_2I], 4.07 (br, 1 H, NH), 4.21 (br, 1 H, NH), 6.42 [d, *J*(H–H) = 7.0, 1 H, $C_{10}H_6$], 6.50 [d, *J*(H–H) = 7.0 Hz, 1 H, $C_{10}H_6$], and 7.0—7.8 (m, 34 H, $C_{10}H_6$, C_6H_5); $^{31}P\text{-}\{^{1}H\}$, δ 13.53 (s) and 13.39 (s) p.p.m.

$[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (**5**).—The complex $[Ir_2(CH_2I)I\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]$ (474 mg, 0.34 mmol) in toluene (20 cm^3) was refluxed for 2 h. After cooling the solution a grey precipitate formed, which was filtered off and washed with toluene. The solid was purified by dissolving in dichloromethane (20 cm^3), filtration, addition of hexane (15 cm^3), and partial evaporation of the solution to induce precipitation of a white solid (147 mg, 31%) (Found: C, 42.2; H, 2.9; N, 1.5. Calc. for $C_{49}H_{40}I_2Ir_2N_2O_2P_2$: C, 42.4; H, 2.9; N, 2.0%). I.r.: ν(N–H) 3 340 (Nujol); ν(C≡O) 2 030 cm^{-1} (CH_2Cl_2). N.m.r. ($CDCl_3$): ^{1}H, δ 1.71 [q, *J*(H–H) = *J*(H–P) = 5.9, 1 H, CH_2), 1.95 (br, 1 H, NH), 2.90 [d, *J*(H–H) = 5.9, 1 H, CH_2], 4.31 (br, 1 H, NH), 5.68 [d, *J*(H–H) = 7.2, 1 H, $C_{10}H_6$), 7.06 [t, *J*(H–H) = 8.3 Hz, 1 H, $C_{10}H_6$], and 7.1—7.7 (m, 34 H, $C_{10}H_6$, C_6H_5), $^{31}P\text{-}\{^{1}H\}$, δ −2.26 (s) p.p.m.

Crystal-structure Determination of $[Ir_2I_2(\mu\text{-}CH_2)\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(PPh_3)_2]\cdot CH_2Cl_2$ (**5**).—Crystals were obtained as pale yellow prismatic blocks by pentane-vapour diffusion from a dichloromethane solution.

Crystal data $C_{49}H_{40}I_2Ir_2N_2O_2P_2\cdot CH_2Cl_2$, *M* = 1 474.0, monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.253(2), *b* = 12.214(1), *c* = 24.919(3) Å, β = 98.44(1)°, *U* = 4 893.2(9) $Å^3$ (by least-squares refinement of the 28 values of 50 accurately measured reflections in the range 20—34°), $Z = 4$, $\lambda = 0.710\,69$ Å, $D_c = 2.001$ g cm^{-3}, $F(000) = 2\,784$, $\mu(\text{Mo-}K_\alpha) = 68.77$ cm^{-1}, crystal approximate dimensions 0.50 × 0.27 × 0.15 mm.

Data collection and processing. Four-circle Siemens AED diffractometer, ω—2θ scan mode, graphite-monochromated Mo-K_α radiation; 9 401 reflections measured. Of 8 141 independent reflections, 6 627 having $F \geqslant 5\sigma(F)$ were considered observed and used in the analysis. A correction for absorption effects was applied using the ψ-scan method with eight reflections[25] (maximum and minimum transmission factors 0.1208 and 0.2668).

Structure solution and refinement. Patterson and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms except carbons of phosphine ligands. The hydrogens of the methylene and amidonaphthalene ligands were found from Fourier difference maps, and refined riding on the corresponding N or C atoms, with a common isotropic thermal parameter. The remaining hydrogens were placed at their calculated positions and refined (positional and thermal parameters) riding on carbon atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)$, with the weight defined as $w = 1.465/[\sigma^2(F) + 0.000\,255F^2]$. Final R and R' values were 0.034 and 0.036. The SHELX system of computer programs was used.[26] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 27. Final atomic co-ordinates for the non hydrogen atoms of complex (**5**) are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 2. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for complex (**5**)

Atom	*x*	*y*	*z*
Ir(1)[a]	16 617(2)	20 128(2)	18 105(1)
Ir(2)[a]	25 588(2)	−27(2)	14 863(1)
I(1)[a]	16 683(4)	29 600(5)	28 439(2)
I(2)[a]	35 712(3)	−14 741(5)	21 601(2)
P(1)[a]	18 581(12)	37 146(16)	14 432(9)
P(2)[a]	35 350(12)	−912(16)	8 796(8)
O(1)	−173(3)	2 359(5)	1 651(3)
O(2)	1 578(4)	−1 807(6)	888(3)
N(1)	1 706(3)	316(5)	2 054(2)
N(2)	2 936(3)	1 459(5)	1 945(2)
C(1)	518(5)	2 227(7)	1 702(3)
C(2)	1 973(5)	−1 144(7)	1 112(4)
C(3)	1 788(4)	1 197(6)	1 103(3)
C(4)	2 029(5)	108(6)	2 604(3)
C(5)	1 615(6)	−540(7)	2 923(3)
C(6)	1 953(7)	−720(8)	3 469(4)
C(7)	2 652(7)	−235(8)	3 689(4)
C(8)	3 118(5)	422(7)	3 381(3)
C(9)	3 871(6)	897(7)	3 589(3)
C(10)	4 311(5)	1 542(7)	3 287(4)
C(11)	4 015(5)	1 721(6)	2 724(3)
C(12)	3 265(4)	1 281(6)	2 505(3)
C(13)	2 801(5)	617(6)	2 820(3)
C(14)	1 447(5)	4 946(6)	1 733(3)
C(15)	591(5)	4 995(7)	1 719(4)
C(16)	221(6)	5 913(8)	1 907(4)
C(17)	704(6)	6 801(8)	2 093(4)
C(18)	1 558(6)	6 763(8)	2 120(4)
C(19)	1 917(6)	5 846(7)	1 920(4)
C(20)	1 429(5)	3 917(7)	727(3)
C(21)	1 663(6)	4 871(8)	482(4)
C(22)	1 340(8)	5 040(11)	−69(5)
C(23)	810(7)	4 315(10)	−344(6)
C(24)	551(7)	3 477(10)	−101(5)
C(25)	864(6)	3 208(8)	452(4)
C(26)	2 970(5)	3 934(7)	1 477(3)
C(27)	3 366(5)	3 754(7)	1 030(4)
C(28)	4 252(6)	3 835(8)	1 098(4)
C(29)	4 679(6)	4 055(8)	1 599(4)
C(30)	4 298(6)	4 230(8)	2 041(4)
C(31)	3 437(5)	4 134(7)	1 983(4)
C(32)	3 338(5)	908(7)	327(3)
C(33)	2 549(5)	947(7)	23(3)
C(34)	2 361(6)	1 686(8)	−394(4)
C(35)	2 970(6)	2 389(9)	−520(4)
C(36)	3 758(6)	2 342(8)	−229(4)
C(37)	3 952(5)	1 603(7)	200(4)
C(38)	3 581(4)	−1 389(6)	504(3)
C(39)	3 707(5)	−1 374(8)	−34(4)
C(40)	3 818(6)	−2 342(9)	−298(5)
C(41)	3 824(6)	−3 332(9)	−28(4)
C(42)	3 694(6)	−3 357(9)	497(4)
C(43)	3 557(5)	−2 383(7)	773(4)
C(44)	4 596(4)	138(6)	1 176(3)
C(45)	5 223(5)	−630(7)	1 150(4)
C(46)	6 032(6)	−444(9)	1 402(4)
C(47)	6 228(6)	523(8)	1 666(4)
C(48)	5 633(6)	1 282(8)	1 713(4)
C(49)	4 821(5)	1 084(7)	1 472(4)
Cl(1)[b]	9 660(8)	−301(11)	1 230(5)
Cl(2)[b]	8 249(6)	1 235(9)	927(5)
C(50)[b]	8 743(12)	322(18)	1 359(9)
Cl(1′)[b]	9 638(10)	−254(14)	995(6)
Cl(2′)[b]	8 590(9)	1 456(11)	584(7)
C(50′)[b]	9 367(16)	565(20)	410(9)

[a] Atomic co-ordinates (× 10^5). [b] Idealized model for a disordered CH_2Cl_2 molecule. An occupancy factor 0.560(8) was refined for non-primed atoms, 0.440(8) for primed ones.

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