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Electrophilic Attack on Dinuclear Iridium Complexes by Halogens. Structure of $[Ir_2I_2(\mu\text{-}I)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]I\cdot 2CHCl_3$

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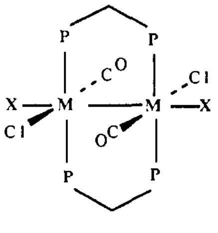
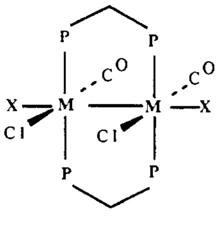
Introduction

Diphosphine-bridged dinuclear complexes show remarkably high chemical reactivity in their reactions with small molecules.[1] Among the most widely studied are the *face-to-face* M(I) dimers *trans*-$[MCl(CO)(dppm)]_2$ (M = Rh[2] (**1**), Ir[3] (**2**)), which are known to react smoothly with activated acetylenes[4–6] and H_2.[7] Addition of halogens to **1**[8] and the related *trans*-$[RhCl(CO)(dam)]_2$[9] (dam = bis(diphenylarsino)methane) was reported by Balch, and structure I was suggested for the Rh(II) dimeric products.



I



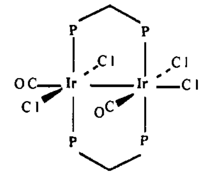
II

An indirect evidence of the two-center, two-fragment oxidative addition later came from the structural determination of $[Rh_2Cl_4(CO)_2(dmpm)_2]$[10] (dmpm = bis(dimethylphosphino)methane). The tetrachloride, which has structure I, was obtained from *trans*-$[RhCl(CO)(dmpm)]_2$ by chlorine abstraction from chlorinated solvents or direct Cl_2 addition. The alternative structural arrangement with cis CO ligands (II) was reported for the species $[Ir_2Cl_4(CO)_2(dppm)_2]$.[7] However, no details on the formation of the species were given at that time.

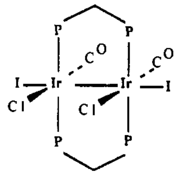
Herein we report on the oxidative addition of X_2 (X = Cl, I) to *trans*-$[IrCl(CO)(dppm)]_2$ (**2**). In addition, the reactivity of $[IrI(CO)(dppm)]_2$ (**3**) with I_2 is described.

Results and Discussion

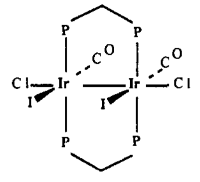
Bubbling Cl_2 through a CH_2Cl_2 suspension of the purple *trans*-$[IrCl(CO)(dppm)]_2$ rapidly produces a light yellow solution. The solid isolated, formulated as $[Ir_2Cl_4(CO)_2(dppm)_2]$ (**4**), displays two bands in the terminal carbonyl region in the infrared spectrum at 2011 and 1994 cm^{-1}. In CH_2Cl_2 solution the CO stretching peaks move up to 2033 and 2017 cm^{-1} (Table I). The somewhat analogous complex $[Ir_2Cl_2(CO)_2(CH_3O_2CC{=}CHCO_2CH_3)_2(dppm)_2]$, which has both cis Cl and CO ligands, also reveals two terminal carbonyl bands.[7] The single resonance in the $^{31}P\{^1H\}$ NMR spectrum of **4** at δ −16.47 suggests the presence in solution of a symmetric species with chemically equivalent iridium centers. On the basis of spectroscopic data, **4** is assigned structure II, with carbonyl groups in a mutually cis arrangement on adjacent iridium atoms. An unsymmetrical structure (III) would also give rise to two distinct carbonyl stretches, as observed in the case of $[Ir_2Cl_2(CO)_2(\mu\text{-}DMA)(dppm)_2]$[6] (DMA = dimethylacetylenedicarboxylate), whereas two ^{31}P NMR signals must be expected for the two inequivalent sets of P nuclei. Although non conclusive, the structural assignment is consistent with the fact that solutions of **4** are nonconducting. Compound **4** was also observed to be the major species formed in the reaction of **2** with 1 or 2 equiv of $HgCl_2$.



III



IV



V

Addition of 1 equiv of molecular iodine to a CH_2Cl_2 suspension of **2** immediately affords a dark orange solution. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of a major symmetric species (singlet at δ −25.9), whereas minor symmetric products give signals at lower field (singlets at δ −17.5 and −22.0, respectively). Over a 12-h period, the disappearance of the least intense signal at δ −17.5 is observed. The species corresponding to the major signal in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture could be obtained as the only product by reaction of **2** with 10 equiv of I_2 over a 1-h period. The orange-brown product, formulated as $[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ (**5**), is nonconducting in either CH_2Cl_2 or acetone solution. As for **4**, the IR spectrum of **5** in the solid state displays two strong absorptions in the terminal carbonyl region (at 2032 and 2008 cm^{-1}, respectively). The same pattern can be seen in CH_2Cl_2 solution (Table I). According to the findings above reported, **5** is assigned structure IV, with the iodo ligands *opposite* the Ir–Ir bond. A compound with the same stoichiometry as **5** could be obtained as one of several products in the reaction of **2** with CH_2I_2, and its solid-state structure determination revealed the same ligand arrangement as in structure IV.[11] On the other hand, structure V would bring the two bulky iodo groups too close to one another, thus destabilizing the structure.

The ^1H NMR spectrum of **5** in the methylene region shows a single resonance at δ 5.00 as a virtual quintet (due to coupling to four equivalent P nuclei). Interestingly, the ^1H NMR spectrum of **4** in the same region has a similar feature (Table I), thus suggesting a very similar structural arrangement. The simplicity of the ^1H NMR spectrum of **5** raises the question whether **5** (and therefore **4** too) have structure IV, which accounts for IR spectra, or structure I, which could explain the ^1H NMR parameters in solution. Unfortunately, we have not been able to obtain suitable crystals of **4** or **5** to substantiate structural assignments.

The diiodo species $[IrI(CO)(dppm)]_2$ (**3**) can be obtained as an orange air-stable solid by reaction of the chloro analogue **2** with a 5-fold molar excess of LiI.[12] The solid-state IR spectrum of **3** shows two carbonyl stretching at 1935 and 1728 cm^{-1}, respectively. The asymmetric nature of **3** is preserved in solution, provided oxygen is excluded. Two absorptions are indeed observed at 1946 and 1730 cm^{-1} in the CH_2Cl_2 infrared spectrum of **3**. This asymmetry is confirmed by the presence of two distinct resonances in the $^{31}P\{^1H\}$ NMR spectrum (Table I).

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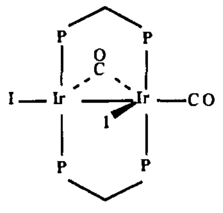
Table I. Spectroscopic Data[a]

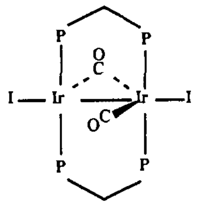
	infrared, ν(CO) (cm^{-1})		NMR	
	solid[b]	soln[c]	$\delta(^{31}P\{^1H\})$[d]	$\delta(^1H)$[e]
$[IrCl(CO)(dppm)]_2$ (**2**)	1953 (vs)[f]	1954 (vs, br)[f]	1.85 (s)	
$[IrI(CO)(dppm)]_2$ (**3**)	1935 (vs), 1728 (st)	1946 (vs), 1730 (st)	3.68 (m), −5.46 (m)	4.75 (m, 2 H, J(HH) = 13.9 Hz, J(PH) = 3.5 Hz), 4.60 (m, 2 H, J(HH) = 13.9 Hz, J(PH) = 6.0 Hz)
	1948 (vs), 1741 (st)[g]	1960 (vs), 1742 (st)[g]	4.00 (m), −4.93 (m)[h]	4.71 (m, 2 H), 4.56 (m, 2 H)[g]
$[Ir_2Cl_4(CO)_2(dppm)_2]$ (**4**)	2011 (st), 1994 (vs, br)	2033 (st), 2017 (vs)	−16.47 (s)	4.58 (q, 4 H, J(PH) = 4.5 Hz)
$[Ir_2Cl_2I_2(CO)_2(dppm)_2]$ (**5**)	2032 (vs, sh), 2008 (vs)	2029 (st, sh), 2011 (vs)	−25.9 (s)	5.00 (q, 4 H, J(PH) = 4.5 Hz)
$[Ir_2I_2(\mu\text{-}I)(CO)_2(dppm)_2]I$ (**6**)	2023 (st), 1996 (med, sh)	2029 (vs), 1991 (med, sh)	−26.14 (s)	6.16 (m, 2 H, J(HH) = 14.5 Hz, J(PH) = 3.8 Hz), 3.88 (m, 2 H, J(HH) = 14.5 Hz, J(PH) = 5.8 Hz)

[a] Abreviations used: st = strong, vs = very strong, sh = shoulder, med = medium, br = broad, s = singlet, m = multiplet, q = quintet. [b] Nujol mull. [c] CH_2Cl_2 solution. [d] In CH_2Cl_2/acetone-d_6 (20%) at 22 °C. [e] In CD_2Cl_2 at 22 °C. $J(PH) = |^2J(PH) + ^4J(PH)|$. [f] Reference 3. [g] Reference 15. [h] CD_2Cl_2 at 22 °C and 162 MHz.[11] Phenyl resonances were not reported.

A complex with identical stoichiometry was independently prepared during the course of this work by Cowie and co-workers,[13] and its reactivity with H_2 studied. The species, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$, prepared from the reaction of **2** with 10 equiv of KI, was later reported to give a stable O_2 adduct,[14] and full details of its molecular structure were given.[15] The main structural feature of Cowie's complex is the presence of a bridging carbonyl group which is accompanied by a formal metal–metal bond. The remaining carbonyl ligand is terminally bound to one iridium center on the same side of the bridging one (structure VI).



VI



VII

The structure of **3** could not be unequivocally identified. Because of the difference in the spectral parameters (Table I), one might conclude that **3** must have structure VII, that is with the iodo groups trans on adiacent metals. However the slightly different spectral data may be due only to different spectral conditions, and **3** is tentatively assigned the same structure as Cowie's species.

Compound **3** spontaneously reacts with 1 equiv of I_2 in CH_2Cl_2 to give a red solution of the oxidized product $[Ir_2I_2(\mu\text{-}I)(CO_2)(dppm)_2]I$ (**6**). Although the starting species **3** has a bridging carbonyl ligand, only CO stretches in the terminal carbonyl region are displayed in the IR spectrum of **6** (both in solution and in the solid state). The air-stable compound is found to be conducting in CH_2Cl_2 solution. The equivalent conductance at 43.04 Ω^{-1} mol^{-1} cm^2 clearly accounts for a 1:1 electrolyte.[16]

The ^1H NMR spectrum of **6** in CD_2Cl_2 has a pattern different from that observed for the neutral **4** and **5**, displaying two separate dppm methylene resonances at δ 6.16 and 3.88, with a ^2J(HH) coupling at 14.5 Hz. The solid-state structural features of **6** have been revealed by an X-ray structure determination. After several attempts fragile X-ray quality crystals were grown from $CHCl_3$. The complex crystallized along with two molecules of $CHCl_3$ of crystallization, which are readily lost when the crystals are exposed to air. Figure 1 shows a perspective view of the cation of **6**. Selected bond distances and angles are listed in Table II.

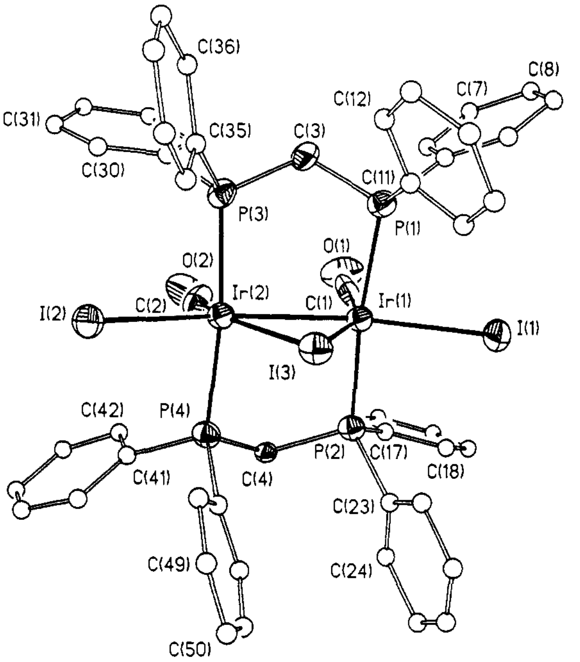


Figure 1. Perspective view of the cation in $[Ir_2I_2(\mu\text{-}I)(CO)_2(dppm)_2]I$ showing 30% thermal contours and uniform, arbitrarily sized circles for the carbon atoms of phenyl rings. Phenyl hydrogens are omitted.

Positional parameters are given in Table III. The cation has the expected structure for a dinuclear complex bridged by two mutually trans dppm ligands which occupy axial positions. The distinctive feature of the structure is the bridging iodo group in the equatorial plane of the cation (Ir(1)–I(3)–Ir(2) = 62.0 (1)°). The two iridium atoms have slightly distorted local octahedral geometries, and are separated by 2.787 (2) Å. This distance is in agreement with the presence of a single bond, and it is comparable to the corresponding distances found in $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (2.705 (1) Å),[14] $[Ir_2Cl_2(CO)_2(\mu\text{-}CO)(dppm)_2]$ (2.779 (1) Å),[3] $[Ir_2Cl_2(CO)_2(\mu\text{-}DMA)(dppm)_2]$ (2.7793 (3) Å),[6] and $[Ir_2(SnCl_3)_2(CO)_2(\mu\text{-}S)(dppm)_2]$ (2.878 (1) Å),[17] all of which have a similar overall structure. The terminal carbonyl ligands are mutually cis on adiacent iridium centers, each one being pseudotrans to the bridging iodo ligand. The coordination in the equatorial plane is completed by a terminal iodo ligand on each iridium atom. Both terminal Ir–I bonds (Ir(1)–I(1), 2.731 (3) Å; Ir(2)–I(2), 2.732 (2) Å), which occupy the site *opposite* the metal–metal bond, are slightly longer than the corresponding distance in $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (Ir(1)–I(1), 2.6811 (7) Å),[15] but shorter than the same distance in $[Ir_2Ir_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ (2.764 (1) Å). Although its trans influence is less effective than

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Table II. Selected Bond Distances (Å) and Angles (deg) for $[Ir_2I_2(\mu\text{-}I)(CO)_2(DPM)_2]I\cdot 2CHCl_3$

Bond Distances			
Ir(1)–Ir(2)	2.787 (2)	Ir(2)–I(2)	2.732 (2)
Ir(1)–I(1)	2.731 (3)	Ir(2)–I(3)	2.711 (3)
Ir(1)–I(3)	2.702 (2)	Ir(2)–P(3)	2.361 (7)
Ir(1)–P(1)	2.374 (8)	Ir(2)–P(4)	2.378 (7)
Ir(1)–P(2)	2.380 (7)	Ir(2)–C(2)	1.84 (4)
Ir(1)–C(1)	1.78 (4)	C(2)–O(2)	1.13 (4)
C(1)–O(1)	1.18 (5)		

Bond Angles			
Ir(2)–Ir(1)–I(1)	165.4 (1)	Ir(2)–Ir(1)–I(3)	59.2 (1)
I(1)–Ir(1)–I(3)	106.5 (1)	Ir(2)–Ir(1)–P(1)	94.4 (2)
I(1)–Ir(1)–P(1)	86.4 (2)	I(3)–Ir(1)–P(1)	86.2 (2)
Ir(2)–Ir(1)–P(2)	92.4 (2)	I(1)–Ir(1)–P(2)	87.1 (2)
I(3)–Ir(1)–P(2)	97.6 (2)	P(1)–Ir(1)–P(2)	173.2 (2)
Ir(2)–Ir(1)–C(1)	94.9 (12)	I(1)–Ir(1)–C(1)	99.5 (12)
I(3)–Ir(1)–C(1)	153.8 (11)	P(1)–Ir(1)–C(1)	92.4 (12)
P(2)–Ir(1)–C(1)	86.6 (11)	Ir(1)–Ir(2)–I(2)	163.2 (1)
Ir(1)–Ir(2)–I(3)	58.8 (1)	I(2)–Ir(2)–I(3)	104.4 (1)
Ir(1)–Ir(2)–P(3)	91.9 (2)	I(2)–Ir(2)–P(3)	89.2 (2)
I(3)–Ir(2)–P(3)	96.2 (2)	Ir(1)–Ir(2)–P(4)	94.1 (2)
I(2)–Ir(2)–P(4)	86.0 (2)	I(3)–Ir(2)–P(4)	89.7 (2)
P(3)–Ir(2)–P(4)	173.2 (3)	Ir(1)–Ir(2)–C(2)	96.6 (10)
I(2)–Ir(2)–C(2)	100.2 (10)	I(3)–Ir(2)–C(2)	155.0 (9)
P(3)–Ir(2)–C(2)	88.4 (10)	P(4)–Ir(2)–C(2)	87.6 (11)
Ir(1)–I(3)–Ir(2)	62.0 (1)	Ir(1)–P(1)–C(3)	106.3 (11)
Ir(1)–C(2)–P(4)	111.8 (7)	Ir(2)–P(3)–C(3)	112.7 (9)
Ir(2)–P(4)–C(4)	107.2 (8)	Ir(1)–C(1)–O(1)	176 (3)
Ir(2)–C(2)–O(2)	178 (3)	P(1)–C(3)–P(3)	117 (2)
P(2)–C(4)–P(4)	114 (1)		

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

atom^b	*x*	*y*	*z*	*U*(eq)
Ir(1)	198 (1)	2755 (1)	7784 (1)	44 (1)^a
Ir(2)	362 (1)	2061 (1)	6836 (1)	46 (1)^a
I(1)	−214 (2)	3130 (1)	8758 (1)	71 (1)^a
I(2)	121 (2)	1130 (1)	5999 (1)	77 (1)^a
I(3)	−826 (2)	1557 (1)	7490 (1)	56 (1)^a
I(4)	210 (2)	5849 (2)	6549 (1)	88 (1)^a
P(1)	−1275 (6)	3362 (4)	7402 (3)	50 (3)^a
P(2)	1666 (6)	2220 (3)	8262 (3)	46 (3)^a
P(3)	−834 (6)	2803 (4)	6324 (3)	51 (3)^a
P(4)	1650 (6)	1301 (4)	7258 (3)	48 (3)^a
O(1)	1408 (21)	3983 (13)	7599 (10)	98 (12)^a
O(2)	1903 (19)	3006 (13)	6544 (11)	95 (12)^a
C(1)	955 (27)	3479 (20)	7675 (14)	76 (15)^a
C(2)	1328 (24)	2635 (20)	6655 (11)	66 (13)^a
C(3)	−1193 (25)	3535 (16)	6714 (10)	66 (12)^a
C(4)	2395 (18)	1796 (13)	7802 (9)	36 (9)^a
C(5)	−1454 (22)	4238 (15)	7658 (11)	53 (7)
C(6)	−807 (23)	4765 (16)	7554 (12)	61 (8)
C(7)	−948 (23)	5472 (15)	7730 (11)	60 (8)
C(8)	−1669 (24)	5611 (15)	8030 (11)	60 (8)
C(9)	−2310 (29)	5085 (20)	8136 (15)	89 (11)
C(10)	−2156 (25)	4388 (17)	7948 (12)	66 (9)
C(11)	−2479 (23)	2928 (15)	7407 (11)	57 (7)
C(12)	−3232 (27)	2979 (18)	6977 (13)	74 (9)
C(13)	−4146 (32)	2739 (21)	6986 (16)	93 (12)
C(14)	−4356 (30)	2411 (19)	7428 (15)	86 (11)
C(15)	−3600 (29)	2372 (18)	7853 (14)	77 (10)
C(16)	−2652 (31)	2621 (20)	7856 (15)	87 (11)
C(17)	2560 (22)	2857 (14)	8639 (11)	54 (7)
C(18)	2508 (22)	3010 (15)	9163 (11)	55 (7)
C(19)	3134 (26)	3488 (17)	9447 (13)	71 (9)
C(20)	3847 (25)	3849 (16)	9218 (12)	65 (8)
C(21)	3831 (34)	3677 (24)	8699 (18)	112 (14)
C(22)	3281 (25)	3178 (17)	8422 (12)	67 (9)
C(23)	1594 (23)	1552 (14)	8765 (11)	52 (7)
C(24)	2432 (25)	1320 (17)	9025 (12)	67 (9)
C(25)	2369 (29)	753 (19)	9439 (14)	79 (10)
C(26)	1497 (35)	534 (22)	9483 (16)	98 (12)
C(27)	692 (29)	753 (19)	9240 (14)	82 (10)
C(28)	726 (25)	1294 (17)	8859 (12)	68 (9)
C(29)	−377 (20)	3244 (13)	5797 (10)	44 (6)
C(30)	−396 (24)	2897 (16)	5315 (12)	64 (8)
C(31)	65 (31)	3203 (21)	4905 (15)	93 (12)
C(32)	457 (33)	3877 (22)	4980 (17)	104 (13)
C(33)	524 (28)	4236 (19)	5470 (14)	81 (10)
C(34)	112 (27)	3893 (18)	5892 (13)	76 (10)
C(35)	−2011 (20)	2463 (13)	5957 (10)	42 (6)
C(36)	−2650 (25)	2902 (16)	5598 (12)	66 (9)
C(37)	−3549 (29)	2647 (19)	5293 (14)	83 (10)
C(38)	−3857 (27)	1989 (18)	5404 (14)	75 (10)
C(39)	−3272 (28)	1560 (18)	5755 (14)	80 (10)
C(40)	−2354 (26)	1779 (17)	6037 (12)	68 (9)
C(41)	2554 (22)	1039 (14)	6837 (11)	54 (7)
C(42)	3208 (25)	1540 (16)	6713 (12)	65 (8)
C(43)	3862 (28)	1306 (19)	6398 (14)	82 (10)
C(44)	3923 (28)	610 (19)	6244 (14)	81 (10)
C(45)	3264 (29)	173 (20)	6358 (14)	85 (11)
C(46)	2581 (28)	322 (19)	6678 (14)	80 (10)
C(47)	1333 (21)	472 (14)	7560 (10)	48 (7)
C(48)	532 (24)	93 (16)	7350 (12)	61 (8)
C(49)	405 (26)	−538 (17)	7593 (13)	72 (9)
C(50)	1020 (29)	−843 (19)	7995 (14)	82 (10)
C(51)	1811 (31)	−410 (22)	8169 (15)	96 (12)
C(52)	2073 (24)	228 (16)	7991 (12)	65 (8)
C(53)*	7253	465	8702	89 (11)
C(54)*	2712	5835	226	576 (159)
Cl(1)*	7283 (16)	16 (9)	9238 (6)	187 (10)^a
Cl(2)*	7970 (15)	1295 (9)	8898 (10)	205 (11)^a
Cl(3)*	8305 (15)	53 (10)	8345 (8)	203 (11)^a
Cl(4)*	1606 (28)	5686 (23)	288 (12)	383 (28)^a
Cl(5)*	3382 (26)	5209 (14)	304 (16)	354 (25)^a
Cl(6)*	3356 (27)	6420 (36)	677 (27)	663 (61)^a

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} Atoms marked with an asterisk. Starred atoms are those of the $CHCl_3$ solvent molecules.

that of CH_2[18] or H[19] ligands, the Ir–Ir bond in **6** causes a certain degree of "trans-lengthening", as normal terminal Ir–I distances are slightly shorter.[20,21] Both methylene groups of dppm ligands are bent away from the bridging iodo group. In order to minimize intraligand nonbonded contacts, the cation is twisted about the Ir–Ir bond by ca. 13°, thus affording staggered CO groups. All other bond distances and angles are normal.

The formation of **4–6** is another example of transannular halogen oxidative addition to the $M_2(dppm)_2$ framework,[22] wherein the nature of the products is sterically induced. In particular, we believe that the ionic **6** is the result of I^- loss following the electrophilic attack of I_2 to **3** and formation of a species with too great steric demands. Likewise, steric crowding was invoked to explain the formation of cationic halo-bridged species upon treatment of neutral polycarbonyl dinuclear complexes with halogens.[23]

Experimental Section

All experiments were performed under a dry nitrogen atmosphere in dried solvents. Lithium iodide (Aldrich), iodine (Aldrich), and gas chlorine (J. T. Baker) were used as received. $[IrCl(CO)(dppm)]_2$[3] was prepared according to the literature. ^1H and $^{31}P\{^1H\}$ NMR spectra were run on a Bruker AC 300 spectrometer operating at 300.13 and 121.5 MHz, respectively. Chemical shifts were referenced to internal TMS (^1H) and external 85% H_3PO_4 (^{31}P) standards. Infrared spectra were recorded with a Perkin-Elmer 1330 spectrophotometer either as Nujol

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mulls or as dichloromethane solutions. Analyses were performed by the Microanalytical Service within our department.

Preparation of Compounds. [IrI(CO)(dppm)]$_2$ (3). A solution of LiI (78.4 mg, 0.59 mmol) in dry methanol (3 mL) was added to a suspension of the red-purple *trans*-[IrCl(CO)(dppm)]$_2$ (**2**) (150 mg, 0.117 mmol) in CH_2Cl_2 (10 mL). After 30 min of stirring, diethyl ether was dropwise added to the resulting orange solution to give a dark orange microcrystalline precipitate. The solid was filtered, washed with small portions of water, methanol, and ether, and dried in vacuo. Yield 153 mg, 90%. Anal. Calcd for $C_{52}H_{44}I_2O_2P_4Ir_2$: C, 42.69; H, 3.03; I, 17.35. Found: C, 41.82; H, 2.95; I, 17.98.

[Ir$_2$Cl$_4$(CO)$_2$(dppm)$_2$]·CH$_2$Cl$_2$ (4). A stream of chlorine was passed through a suspension of **2** (50 mg, 0.039 mmol) in CH_2Cl_2 (5 mL) for 2–3 min. Immediately, the formation of a yellow solution was observed. Stirring was then continued for an additional 20 min, after which time addition of diethyl ether resulted in the precipitation of a light yellow solid. The solid was recrystallized from CH_2Cl_2–Et_2O and collected in 82% yield. Anal. Calcd for $C_{52}H_{44}Cl_4O_2P_4Ir_2{\cdot}CH_2Cl_2$: C, 44.36; H, 3.23; Cl, 14.82. Found: C, 44.36; H, 3.22; Cl, 13.75. The presence of solvent was confirmed by ^1H NMR spectroscopy.

[Ir$_2$Cl$_2$I$_2$(CO)$_2$(dppm)$_2$] (5). A solution of iodine (99.1 mg, 0.39 mmol) in CH_2Cl_2 (3 mL) was added to a suspension of **2** (50 mg, 0.039 mmol) in CH_2Cl_2 (5 mL). The resulting red-orange solution was stirred for 1 h. The orange-brown product was obtained by precipitation with diethyl ether (20 mL). Yield: 87%. Anal. Calcd for $C_{52}H_{44}Cl_2I_2O_2P_4Ir_2{\cdot}2CH_2Cl_2$: C, 38.13; H, 2.84; I, 14.90. Found: C, 38.28; H, 2.66; I, 14.47.

[Ir$_2$I$_2$(μ-I)(CO)$_2$(dppm)$_2$] I (6). An orange-brown solution of **3** (50 mg, 0.034 mmol) in CH_2Cl_2 (5 mL) turned red-brown upon addition of a solution of 1 equiv of iodine (8.7 mg, 0.034 mmol) in CH_2Cl_2 (2 mL). After 1 h of stirring, addition of diethyl ether precipitated the product as a red solid, which was recovered in 78% yield after recrystallization from $CHCl_3$. **6** was found to be conducting in CH_2Cl_2 solution (λ_M = 43.04 Ω^{-1} mol^{-1} cm^2). Anal. Calcd for $C_{52}H_{44}I_4O_2P_4Ir_2$: C, 36.38; H, 2.58. Found: C, 35.98; H, 2.51. In vacuo drying caused complete loss of cocrystallized solvent molecules, otherwise seen by X-ray crystallography.

X-ray Structure Analysis. A suitable crystal was mounted on a glass fiber and immediately coated with epoxy to minimize solvent loss. Unit cell parameters were obtained from least-squares refinement of the setting angles of 28 carefully centered reflections ($14.61 \leq 2\theta \leq 29.96$). Intensity data were collected on a Siemens R3m/V diffractometer employing the ω-scan technique in the range $3.0 \leq 2\theta \leq 50.0$ with graphite-monochromated Mo Kα radiation. Two standard reflections showed no decrease in intensity during data collection. Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on ψ scans was applied.[24]

The iridium and iodine atoms were located using the direct methods routine of the program SHELX 76.[25] Subsequent refinements and difference Fourier calculations, using the Siemens SHELXTL PLUS software package, led to the location of the remaining atoms. The structure was refined by full-matrix least-squares methods, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. All but phenyl carbon atoms were assigned anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions with fixed ($U = 0.08$ Å^2) contributions. The $CHCl_3$ molecules were found to be disordered giving rise to high thermal parameters for all solvent atoms. In attempt to resolve this disorder, C atoms [C(53), C(54)] were fixed at the located positions, and only the isotropic thermal parameters were refined. Whereas chlorine atoms were anisotropically refined, hydrogen atoms of solvent molecules were not included owing to the relatively high thermal parameters of bonded atoms. The final model converged to $R = 0.078$ and $R_w = 0.084$. On the final ΔF map the highest peaks (2.28–1.82 e Å^3) were in the vicinities of Ir(1), P(2), and C(1). The positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table III. Pertinent details of crystal data and intensity data collection are in Table IV.

Table IV. Crystallographic Data

compd	[Ir$_2$I$_2$(μ-I)(CO)$_2$(DPM)$_2$]I·2CHCl$_3$
formula	$C_{54}H_{44}Cl_6I_4Ir_2O_2P_4$
fw	1953.5
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	13.755 (3)
b, Å	18.953 (4)
c, Å	25.378 (4)
β, deg	100.75 (1)
V, Å^3	6500
Z	4
F(000)	3648
ρ_{calcd}, g cm^3	1.996
cryst size, mm	0.23 × 0.45 × 0.30
λ, Å	0.710 73
temp, °C	25
2θ range, deg	3.0–50.0
scan type	ω
scan speed, deg/min	variable between 2.00 and 15.00
μ (Mo Kα), cm^{-1}	63.38
range of transm factors	0.072–0.148
No. of unique data	11 508 (h, k, $\pm l$)
No. of data obsd	5478 [$I > 3\sigma(I)$]
No. of params refined	393
R^a	0.078
$R_w{}^a$	0.084
GOF^a	1.40

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|^2)/(N_o - N_p)]^{1/2}$.

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen positional parameters and complete listings of bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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