Selective Oxidative Addition at Single Centers in Triiridium Clusters. Crystal and Molecular Structures of One- and Two-Fragment Addition Products, $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(t\text{-}BuNC)_3(CH_3)]I$ and $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(dppm)I(OH)]\cdot CH_2Cl_2$

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Summary: Oxidative addition to the 46- and 50-electron clusters $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(dppm)]$ and $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(t\text{-}BuNC)_3]$ in both cases gives reaction at a single, formally 16-electron, iridium center. The products are $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(dppm)XY]$ (X = I, Y = I, OH; X = H, Y = Cl) and $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(t\text{-}BuNC)_3(R)]X$ (RX = MeI, BzBr, HCl, I_2, $HgCl_2$), respectively. The latter complexes contain unusual complex cations, $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(t\text{-}BuNC)_3(R)]^+$, in which R^+ has added to a formally 16-electron iridium center to give a 16-electron iridium(III) cation.

Oxidative addition to mononuclear d^8 complexes has been implicated as an elementary step in many important catalytic processes and is perhaps the best studied of all oxidative-addition processes.[1] With reference to catalysis on larger metal aggregates and surfaces, it is also important to understand the effects of adjacent metal centers.[2] Additions to dinuclear complexes are well-known, dividing roughly into those which add the oxidizing addendum across both metals with concomitant formation of a metal–metal bond and those where M–M bonding is not an option and the metals behave essentially as mononuclear centers.[3–8] In cluster systems, studies are less numerous and are rarely simple site-specific additions such as those we report here. For example, in triosmium clusters, there is a large class of compounds $Os_3H(\mu\text{-}X)(CO)_{10}$, formed by oxidative addition of HX. The anion, X^-, acts as a formal three-electron donor, is always bridging, and is often quite complex, as in additions of organic acids, amines, alcohols, thiols, etc.[9] In triplatinum clusters, bridging ability is vital, as fragmentation occurs with H_2 or HCl, and is only prevented if the addendum contains SR^- or PR_2^- to maintain the cluster after oxidative addition.[10] Overall, there is a lack of well-defined and relatively simple cluster examples amenable to systematic study.

In this context, the group of trinuclear clusters based on triangular $M_3(\mu\text{-}PPh_2)_3$ cores (M = Rh, Ir)[11–19] presents an especially interesting opportunity. When the cluster electron count is increased by the addition of extra ligands, the average metal–metal distances increase dramatically, but the integrity of the complexes is preserved by the phosphido bridges. For example, the 46-, 48-, and 50-electron clusters $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(\mu\text{-}dppm)]$ (1;[18] dppm = bis(diphenylphosphino)methane), $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(\mu\text{-}dppm)]$ (2),[19] and $[Ir_3(\mu\text{-}PPh_2)_3(CO)_5(t\text{-}BuNC)_2]$ (**4a**)[18] have respective distances of 2.80, 2.99, and 3.19 Å for the Ir–Ir bonds to apical iridium (Scheme 1). These variable electron counts and flexible metal–metal distances provide an ideal framework to examine the role of adjacent metals in oxidative-addition chemistry.

Reactions of 1 with diiodine or hydrogen chloride under mild conditions[20,21] give products whose ^{31}P NMR spectra are very similar to that of the starting material,[18,22] withdoublets due to P(1,3) and P(4,5) and a triplet of triplets due to P(2).[23] However, for example in the I_2 adduct, shielding at P(1,3) (158.7 ppm) is dramatically increased relative to 1 (241.7 ppm), indicating that reaction

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(20) A solution of diiodine (0.005 g, 0.02 mmol) in dichloromethane (2 mL) was added dropwise to a stirred solution of 1 (0.032 g, 0.02 mmol) in dichloromethane (5 mL). After 5 min, solvent was removed *in vacuo* and the residue recrystallized from dichloromethane/hexane to yield **3a** as dark red crystals (0.03 g, 0.016 mmol). IR (KBr disk; ν(CO), cm^{-1}): 2020 (m), 1948 (m, sh), 1932 (s). ^{31}P NMR (101.3 MHz, CD_2Cl_2; ppm relative to H_3PO_4): 158.7 (d, 39 Hz, P(1,3)), 138.6 (tt, 39, 191 Hz, P(2)), –24.9 (d, 191 Hz, dppm). A sample of this product (0.03 g, 0.016 mmol) in dichloromethane (5 mL) was passed through an activated 80–200 mesh alumina column (10 × 0.5 cm). Removal of solvent and recrystallization from dichloromethane/hexane gave **3b** as red crystals (0.025 g, 0.014 mmol). IR (KBr disk; ν(CO), cm^{-1}): 2015 (m), 1950 (m, sh), 1937 (s). ^{31}P NMR (101.3 MHz, CD_2Cl_2; ppm relative to H_3PO_4): 173.4 (d, 36 Hz, P(1,3)), 123.7 (tt, 36, 185 Hz, P(2)), –20.4 (d, 185 Hz, dppm). Crystal data: $C_{65}H_{55}Cl_2IO_4P_5Ir_3$, monoclinic, $P2_1/n$ (No. 14), a = 17.575(2) Å, b = 19.408(2) Å, c = 18.905(3) Å, β = 104.25(1)°, V = 6250 Å^3, Z = 4. Data were collected at ambient temperature on a Nonius CAD-4 diffractometer using Mo Kα radiation and an $\omega/2\theta$ scan in the 2θ range 0–45°. The structure was solved using direct methods and refined by least squares using 401 parameters and 5447 independent reflections to give R = 0.049 and R_w = 0.061.

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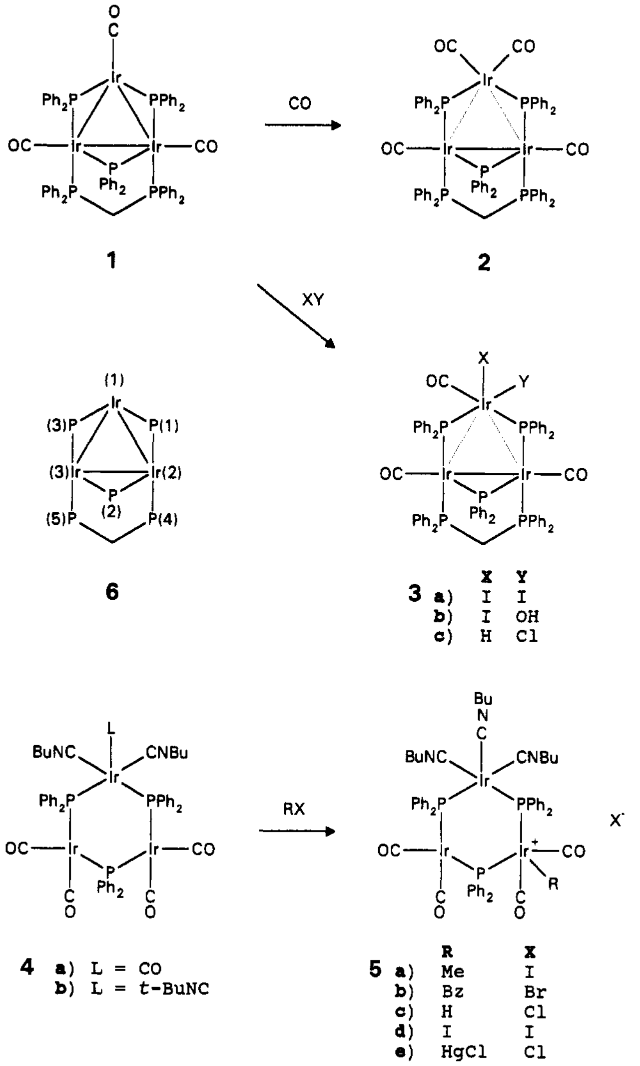
Scheme 1. Oxidative-Addition Reactions, Structures for 1–5, and Atom-Numbering Scheme (6)



occurs at the apical Ir(1) position to form **3a** (Scheme 1). This structure is confirmed by X-ray diffraction study of a sample carefully purified on an alumina column, except that, during the chromatography, hydrolysis of one Ir–I bond to Ir–OH occurred to give **3b**.[20] The geometry of this 48-electron product (Figure 1) is basically similar to that of the 46-electron starting complex **1**.[18] However, the two edges of the Ir_3 triangle bridged by in-plane PPh_2 groups (Ir(1)–Ir(2,3) = 2.960(1) and 2.886(1) Å) are significantly longer than those in **1** (2.805(2) Å). It is also interesting that these distances in **3b** are close to those in the other 48-electron complex **2** (average 2.99 Å),[19] illustrating once again the importance of valence electron count in these clusters. The third edge of **3b** is bridged by a phosphido group and the dppm ligand, both of which lie almost perpendicular to the iridium plane. The Ir(2)–Ir(3) distance on this edge is less changed, 2.713(1) Å compared with 2.744(3) and 2.703(3) Å in **1**[18] and **2**,[19] respectively. The iodide ligand is almost coplanar with the iridium atoms, and the hydroxide occupies an axial position at Ir(1), *cis* to the iodine.

The $^{31}P\{^1H\}$ nuclear magnetic resonance spectrum of **4b**[24,25] in dichloromethane consists of a triplet (–1.6 ppm) and a doublet (36.4 ppm), due respectively to the unique phosphorus bridge (P(2)) and to the equivalent pair of phosphorus bridges (P(1,3)). Oxidative-addition reactions with a series of addenda, MeI, BzBr, HCl, I_2, and $HgCl_2$,[26,27] give products (**5a–e**) whose ^{31}P NMR spectra each exhibit three distinct resonances comprising ABX spin systems, clearly demonstrating that all three phosphorus positions are chemically distinct. LSIMS mass spectra of the benzyl bromide adduct show the cation $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(t\text{-}BuNC)_3(PhCH_2)]^+$ and prominent peaks consistent with sequential loss of the four CO ligands. Spectra of the iodomethane adduct are similar, except that the first prominent peak is $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(t\text{-}BuNC)_3(CH_3)]^+$. In both cases assignment of the principal peaks is confirmed by computer simulation of the isotopic distributions. These results suggest that the complexes **5a–e** contain noncoordinated halide anions, and this is confirmed by X-ray diffraction in the case of the iodomethane adduct **5a** (Figure 2). The structure may be compared with the published structure of **4a**,[18,24] and in both cases the Ir_3P_3 cores are closely planar, the greatest distortion in **5a** being at P(2), which is 0.25 Å from the plane. The Ir–Ir distances are changed very little by the oxidative addition: Ir(1)–Ir(2) = 3.032(1) Å, Ir(1)–Ir(3) = 3.221(1) Å, and Ir(2)–Ir(3) Å 3.285(1) Å compared to 3.176(2), 3.199(2), and 3.329(2) Å in **4a**. The iodide ion is noncoordinated, >10 Å from the nearest iridium. Thus, the most interesting feature of the structure is the addition of the methyl group at Ir(2) to produce a formally 16-electron, cationic, Ir(III) center.

In **1**, the apical iridium can be assigned a local electron count of 16 and the two basal iridium 18 electrons each.[27] Thus, the oxidative additions proceed selectively at the 16e center to yield the 48e complexes **3**, with all local iridium centers at 18e. In **4** the local electron counts are reversed relative to those in **1**, with an apical 18e iridium

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[21] Acetyl chloride (0.05 mL) was added dropwise to a stirred solution of **1** (0.030 g, 0.019 mmol) in dichloromethane (5 mL) and methanol (1 mL). After 5 min, solvent was removed *in vacuo* and the residue recrystallized from dichloromethane/hexane to yield **3c**·CH_2Cl_2 as light red crystals (0.025 g, 0.015 mmol). IR (KBr disk; ν(CO) cm^{-1}): 1990 (s), 1952 (s), 1935 (s). ^1H NMR (250 MHz, CD_2Cl_2; δ): –10.76 (t, 17 Hz, 1H, Ir–H). ^{31}P NMR (101.3 MHz, CD_2Cl_2; ppm relative to H_3PO_4): 212.8 (d, 28 Hz, P(1,3)), 139.3 (tt, 28, 187 Hz, P(2)), –15.0 (d, 187 Hz, dppm).

[22] ^{31}P chemical shifts are relative to 85% H_3PO_4. Note that data in ref 14 were inadvertently referenced to trimethyl phosphite.

[23] The atom numbering is shown in Scheme 1, structure **6**.

[24] We previously reported X-ray structural characterization of **4a**[18] but subsequently find that **4b** is a more reliably prepared and convenient substrate. We assume that **4a** and **4b** are structurally very similar.

[25] A solution of $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$[18] (0.050 g, 0.029 mmol) in dichloromethane (10 mL) was saturated with carbon monoxide by bubbling the gas for 2 min. An excess of tert-butyl isocyanide (0.013 mL, 0.12 mmol) in dichloromethane (1 mL) was then added dropwise to the stirred solution of the iridium complex, causing a color change from deep red to orange. After 15 min, solvent was removed *in vacuo* and the residue recrystallized from dichloromethane/hexane to yield **4b**·CH_2Cl_2 as yellow crystals (0.035 g, 0.023 mmol). IR (KBr disk; cm^{-1}): ν(CN) 2210 (sh), 2175 (s), 2135 (s); ν(CO) 1957 (s), 1938 (s), 1900 (s, br). ^{31}P NMR (101.3 MHz, CD_2Cl_2; ppm relative to H_3PO_4): 1.6 (d, P(1,3)), 36.4 (t, P(2)), J(P–P) = 144 Hz. ^1H NMR (250 MHz, CD_2Cl_2; δ): 7.2–8.2 (m, 30H, Ph), 1.92 (s, 9H, *t*-Bu), 0.37 (s, 18H, *t*-Bu).

[26] A solution of iodomethane (0.0089 mL, 0.033 mmol) in dichloromethane (1 mL) was added dropwise to a stirred solution of **4b** (0.050 g, 0.033 mmol) in dichloromethane (10 mL). After 20 min, solvent was removed *in vacuo* and the residue recrystallized from dichloromethane/hexane to yield **5a**·CH_2Cl_2 as yellow crystals (0.035 g, 0.021 mmol). IR (KBr disk; cm^{-1}): ν(CN) 2225 (w), 2190 (s), 2090 (w); ν(CO) 2025 (s), 1973 (s), 1917 (s, br). ^{31}P NMR (101.3 MHz, CD_2Cl_2; ppm relative to H_3PO_4, ABX spin system): –6.0 (A), –8.4 (B), –57.1 (X), J(AB) = 157, J(AX) = 139, J(BX) = 130 Hz. ^1H NMR (250 MHz, CD_2Cl_2; δ): 7.3–8.1 (m, 30H, Ph), 2.2 (dd, 2 and 4 Hz, 3H, Me), 2.03 (s, 9H, *t*-Bu), 0.46 (s, 18H, *t*-Bu). Crystal data: $C_{56}H_{60}IN_3O_4P_3Ir_3$, monoclinic, $P2_1/c$ (No. 14), a = 22.280(5) Å, b = 13.875(2) Å, c = 21.123(5) Å, β = 107.13(2)°, V = 6240 $Å^3$, Z = 4. Data were collected at ambient temperature on a Picker four-circle diffractometer using Mo Kα radiation and a $\theta/2\theta$ scan in the 2θ range 0–50°. The structure was solved using direct methods and refined by least squares using 451 parameters and 7450 independent reflections to give R = 0.064 and R_w = 0.084.

[27] We recognize the dangers of assigning a local electron count in a cluster structure. However, in the present complexes it does appear to provide a reliable guide to site-specific reactivity.

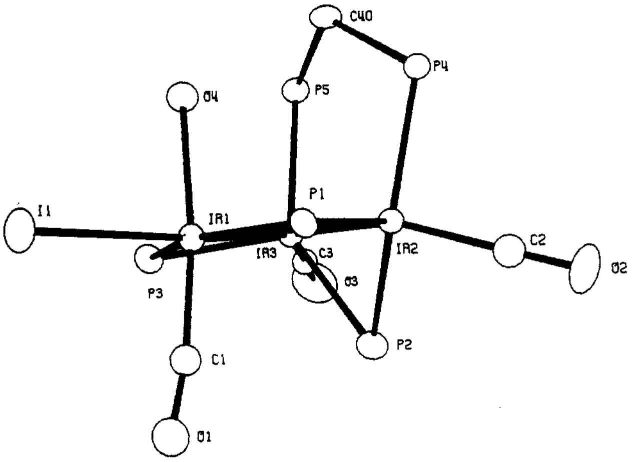
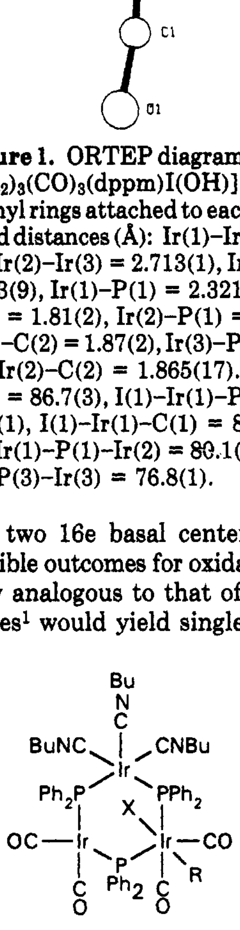


Figure 1. ORTEP diagram of a single molecule of **3b**, $[Ir_3(\mu\text{-}PPh_2)_3(CO)_3(dppm)I(OH)]\cdot CH_2Cl_2$. For clarity, the two phenyl rings attached to each phosphorus have been omitted. Bond distances (Å): Ir(1)–Ir(2) = 2.960(1), Ir(1)–Ir(3) = 2.886(1), Ir(2)–Ir(3) = 2.713(1), Ir(1)–I(1) = 2.716(2), Ir(1)–O(4) = 2.083(9), Ir(1)–P(1) = 2.321(4), Ir(1)–P(3) = 2.370(4), Ir(1)–C(1) = 1.81(2), Ir(2)–P(1) = 2.279(5), Ir(2)–P(2) = 2.317(4), Ir(2)–C(2) = 1.87(2), Ir(3)–P(2) = 2.306(4), Ir(3)–P(3) = 2.274(5), Ir(2)–C(2) = 1.865(17). Bond angles (deg): I(1)–Ir(1)–O(4) = 86.7(3), I(1)–Ir(1)–P(1) = 106.1(1), I(1)–Ir(1)–P(3) = 99.6(1), I(1)–Ir(1)–C(1) = 84.9(6), P(1)–Ir(1)–P(3) = 154.2(2), Ir(1)–P(1)–Ir(2) = 80.1(1), Ir(2)–P(2)–Ir(3) = 71.9(1), Ir(1)–P(3)–Ir(3) = 76.8(1).

and two 16e basal centers and, in consequence, more possible outcomes for oxidative-addition reactions. Chemistry analogous to that of mononuclear iridium(I) complexes[1] would yield single *trans* addition to form 7,and subsequent addition to the second iridium might also be possible. Reactions analogous to the chemistry of dinuclear iridium centers[3-8] would give two-center addition of a single addendum, with concomitant formation of an Ir–Ir bond to complete all 18-electron centers as in 8.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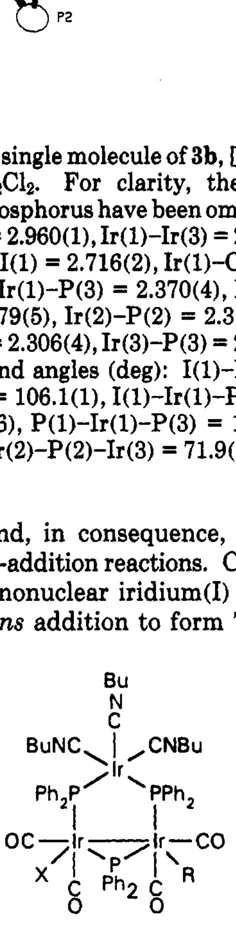
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It is therefore surprising and interesting to find that the cluster reactivity is distinct from any of these earlier models, in fact yielding formally 16-electron iridium(III) cations (5). It is also interesting in the context of the accepted mechanism for oxidative addition of alkyl halides to Ir(I): namely an S_N2 type attack on RX by the metal, with a polar transition state and ionic intermediates (RM^+X^-) which rapidly collapse to a neutral complex.[1] Observation of a stable cation in the presence of a coordinating ligand such as halide is unusual[28] and raises interesting questions as to the role of the cluster in stabilizing this intermediate. One possibility is that the other metal atoms function simply as steric blocking, but this seems relatively unlikely in view of the ability of these clusters to accommodate bulky ligands such as dppm and triphenylphosphine without undue distortion.[18] Alternatively, the other metals, although relatively distant, still have a role in satisfying the electron deficiency at the 16-electron iridium(III) center, for example by partial donation from the apical iridium, thus creating a chemistry unique to the cluster systems. Our investigations into reactions of analogous rhodium clusters and into the possibilities for double oxidative additions to these systems are continuing.

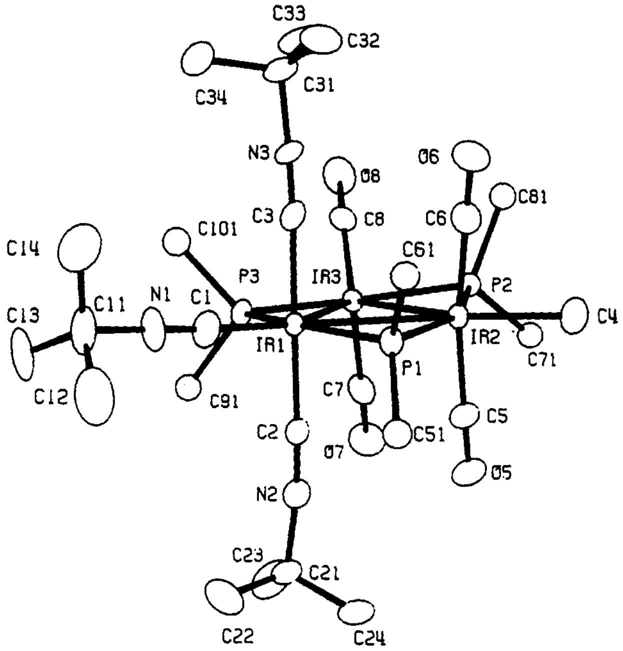

Figure 2. ORTEP diagram of a single cation of **5a**, $[Ir_3(\mu\text{-}PPh_2)_3(CO)_4(t\text{-}BuNC)_3CH_3]I$. For clarity, the two phenyl rings attached to each phosphorus are represented only by single carbon atoms. Bond distances (Å): Ir(1)–Ir(2) = 3.032(1), Ir(1)–Ir(3) = 3.221(1), Ir(2)–Ir(3) = 3.285(1), Ir(1)–P(1) = 2.347(4), Ir(1)–P(3) = 2.368(4), Ir(1)–C(1) = 1.95(2), Ir(1)–C(2) = 1.98(2), Ir(1)–C(3) = 1.98(2), Ir(2)–P(1) = 2.337(4), Ir(2)–P(2) = 2.369(4), Ir(2)–C(4) = 2.23(2), Ir(2)–C(5) = 1.91(2), Ir(2)–C(6) = 1.87(2), Ir(3)–P(2) = 2.303(4), Ir(3)–P(3) = 2.304(4), Ir(3)–C(7) = 1.87(2), Ir(3)–C(8) = 1.88(2). Bond angles (deg): P(1)–Ir(2)–P(2) = 154.9(1), P(1)–Ir(2)–C(4) = 102.9(5), P(2)–Ir(2)–C(4) = 101.9(5), C(4)–Ir(2)–C(5) = 91.9(8), C(4)–Ir(2)–C(6) = 80.0(8), Ir(1)–P(1)–Ir(2) = 80.7(1), Ir(2)–P(2)–Ir(3) = 89.3(1), Ir(1)–P(3)–Ir(3) = 87.2(1).

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Supplementary Material Available: For compounds **3b** and **5a**, unit cell, data collection and refinement parameters, fractional atomic coordinates and isotropic temperature parameters for all atoms, anisotropic temperature factors for the heavy atoms, interatomic distances, bond angles, and selected intermolecular distances and text giving analytical and spectroscopic data for **3a–c**, **4b**, and **5b–e** (Tables S1–S11) (18 pages). Ordering information is given on any current masthead page.

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[28] We do not claim special rarity for 5-coordinate, 16e Ir(III), but it usually results from addition of cationic moieties (e.g. H^+) in the presence of noncoordinating anions. Reactions of acyl chlorides to form $[MCl_2(COR)(PR'_3)_3]$ (M = Rh, Ir) provide rare examples of similarly arrested intermediates in a simple oxidative addition.[29]

[29] Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* 1981, *20*, 323–330.