# **ORGANOMETALLICS**

# Transmetalation Reactions Yield New Tetra- and Pentairidium Carbonyl Complexes Containing $\sigma$ -Bonded Phenyl Rings

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#### Supporting Information

**ABSTRACT:** The new air-stable  $\sigma$ -phenyl tetrairidium carbonyl salt  $[Et_4N][Ir_4(CO)_{11}Ph]$ , **1**, has been obtained by transmetalation reactions between  $[Et_4N][Ir_4(CO)_{11}Br]$  and SnPh<sub>3</sub>OH in 45% yield or SnPh<sub>4</sub> in 36% yield. Compound **1** reacts with PPh<sub>3</sub> to yield the complex  $[Et_4N][Ir_4(CO)_{11}(PPh_2C_6H_4)]$ , **2**, which contains an ortho-metalated bridging PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub> ligand across an edge of a tetrahedral cluster of four iridium atoms. Compound **2** reacts with Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl by halide displacement to yield the two new uncharged pentairidium complexes Ir<sub>5</sub>(CO)<sub>12</sub>(Ph)(PPh<sub>3</sub>), **3**, and Ir<sub>5</sub>(CO)<sub>11</sub>(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), **4**. Compounds **3** and **4** both contain trigonal-bipyramidal clusters of iridium atoms. Compound **3** contains a  $\sigma$ -phenyl ligand coordinated to one of the apical iridium atoms. Compound **4** contains an ortho-metalated PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub> ligand that bridges an apical-equatorial edge of the trigonal-pyramidal cluster of metal atoms. Compound **4** was also obtained from **3** by reaction with PPh<sub>3</sub>.



# INTRODUCTION

Applications of iridium in catalysis have developed slowly compared to those of other metals from the precious metals group.<sup>1</sup> Most catalytic applications are of a homogeneous type.<sup>2</sup> Today iridium is the catalyst of choice for the synthesis of acetic acid by the carbonylation of methanol.<sup>3</sup> Sinfelt showed that the addition of iridium greatly improved the activity of platinum for the catalytic reforming of petroleum.<sup>4</sup> Gates has shown that iridium carbonyl cluster complexes are precursors to catalysts that exhibit good activity for hydrogenation of aromatics.<sup>5</sup> Tin has been shown to be a valuable modifier of homogeneous transition metal catalysts.<sup>6</sup> We have recently been investigating the synthesis and reactivity of polynuclear transition metal carbonyl complexes containing organotin ligands.<sup>7,8</sup> To date, there have been very few examples of iridium carbonyl cluster complexes that contain tin ligands. Garlaschelli et al. have obtained a number of tetra- and hexairidium carbonyl complexes containing bridging  $SnX_3$  ligands, X = Cl and Br, from reaction of the complex anion  $[Ir_4(CO)_{11}Br]^-$  and  $Ir_6(CO)_{16}$  with  $SnCl_{24}$ SnBr<sub>2</sub>, and the anion  $[SnCl_3]^{-9}$  The triiridium complex Ir<sub>3</sub>- $(CO)_6(SnPh_3)_3(\mu$ -SnPh<sub>2</sub>)<sub>3</sub> was obtained from the reaction of  $Ir_4(CO)_{12}$  with an excess of HSnPh<sub>3</sub> at 125 °C, eq 1.<sup>10</sup>



We have recently obtained some new tetrairidium carbonyl complexes containing SnPh<sub>3</sub> ligands from the reactions of

 $Ir_4(CO)_{12}$  and  $Ir_4(CO)_{11}(PPh_3)$  with  $SnPh_3OH$  in the presence of  $[OH]^-$  , eq 2.  $^{11}$ 



We have now investigated the reaction of the anion  $[Ir_4(CO)_{11}Br]^-$  with SnPh<sub>3</sub>OH and SnPh<sub>4</sub>. Interestingly, the iridium-containing product from these reactions,  $[Et_4N]$ - $[Ir_4(CO)_{11}Ph]$ , **1**, does not contain a tin ligand, but instead contains a terminally coordinated  $\sigma$ -phenyl ligand. SnPh<sub>4</sub> has been shown to be useful as a source of phenyl for palladium-catalyzed Stille coupling reactions.<sup>12</sup> Tilley has reported that hafnium complexes containing the SnPh<sub>3</sub> ligand can eliminate a SnPh<sub>2</sub> group to form complexes containing a  $\sigma$ -phenyl group, e.g., eq 3.<sup>13</sup>

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### Table 1. Crystallographic Data for Compounds 1-4

	1	2	3	4
empirical formula	Ir <sub>4</sub> NC <sub>25</sub> H <sub>25</sub> O <sub>11</sub>	Ir <sub>4</sub> PNC <sub>36</sub> H <sub>34</sub> O <sub>10</sub>	Ir <sub>5</sub> PC <sub>36</sub> H <sub>20</sub> O <sub>12</sub>	Ir <sub>5</sub> P <sub>2</sub> C <sub>47</sub> H <sub>29</sub> O <sub>11</sub>
fw	1284.33	1440.49	1636.59	1792.75
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
lattice params				
a (Å)	15.6537(8)	33.565(4)	18.5348(4)	16.2096(8)
b (Å)	13.4349(7)	13.5442(18)	13.0734(3)	19.9166(10)
c (Å)	16.4958(9)	19.622(3)	15.9317(4)	16.9894(8)
$\alpha$ (deg)	90	90	90	90
$\beta$ (deg)	113.836(1)	103.262(3)	103.922(1)	108.529(1)
$\gamma$ (deg)	90	90	90	90
$V(Å^3)$	3173.3(3)	8683(2)	3747.05(15)	5200.5(4)
space group, No.	<i>P</i> 2 <sub>1</sub> / <i>n</i> , 14	C2/c, 15	<i>P</i> 2 <sub>1</sub> / <i>c</i> , 14	<i>P</i> 2 <sub>1</sub> / <i>n</i> , 14
Z value	4	8	4	4
$ ho_{ m calc} \left({ m g/cm}^3 ight)$	2.688	2.270	2.901	2.448
$\mu$ (Mo K $lpha$ ) (mm <sup>-1</sup> )	16.775	12.312	17.798	12.971
temperature (K)	294(2)	294(2)	294(2)	294(2)
$2\Theta_{\max}$ (deg)	48.88	56.68	56.58	56.78
no. obsd $(I > 2\sigma(I))$	6457	7679	6609	7459
no. params	332	474	487	529
goodness of fit (GOF)	1.085	1.059	0.999	1.097
max. shift in cycle	0.001	0.001	0.001	0.001
residuals: <sup>a</sup> R1; wR2	0.0477; 0.1266	0.0432; 0.1261	0.0453; 0.1339	0.0622; 0.2054
absorp corr, max./min.	multiscan 1.000/0.417	multiscan 1.000/0.531	multiscan 1.000/0.540	multiscan 1.000/0.426
largest peak in final diff map $(e^-/\text{\AA}^3)$	2.70	2.08	1.15	2.38
$^{a}R = \sum_{kkl} (  F_{obs}  -  F_{colo}  ) / \sum_{kkl}  F_{obs} ; I$	$R_{\rm tr} = \left[ \sum_{h \in I} w ( F_{\rm obs}  -  F_{\rm calc} )^2 \right]$	$[\Sigma_{\mu\nu} w F^2_{obs}]^{1/2}; w = 1/\sigma^2 (F_{e})$	$(F_{obs})$ : GOF = $\sum_{k \neq l} W( F_{obs}  -  $	$F_{colc}$ ] <sup>2</sup> /( $n_{dota} - n_{vari}$ )] <sup>1/2</sup>



The use of aryl tin reagents may serve a convenient and effective method for preparing polynuclear metal carbonyl complexes containing  $\sigma$ -phenyl ligands from metal carbonyl complexes containing halide ligands.

# EXPERIMENTAL SECTION

**General Data.** Reagent grade solvents were dried by the standard procedures and were freshly distilled under nitrogen prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) and electrospray ionization (ESI) were made on a VG 70S instrument. SnPh<sub>3</sub>OH and Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl were obtained from Strem and were used without further purification. SnPh<sub>4</sub> was purchased from Gelest. [Et<sub>4</sub>N][Ir<sub>4</sub>(CO)<sub>11</sub>Br] was prepared according to the published procedure.<sup>14</sup> Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å *F*<sub>254</sub> glass plates.

# Synthesis of [Et<sub>4</sub>N][Ir<sub>4</sub>(CO)<sub>11</sub>Ph], 1

(a) A 25.0 mg (0.068 mmol) amount of SnPh<sub>3</sub>OH was added to 30.0 mg (0.023 mmol) of [Et<sub>4</sub>N][Ir<sub>4</sub>(CO)<sub>11</sub>Br] in 25 mL of methanol. The reaction was stirred at room temperature for 12 h. The

solvent was then removed *in vacuo*, and the product was isolated by TLC by eluting with methylene chloride solvent to yield light yellow [Et<sub>4</sub>N][Ir<sub>4</sub>(CO)<sub>11</sub>Ph], **1**, 13.5 mg (45% yield). Spectral data for 1: IR  $\nu_{CO}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2067(m), 2028(vs), 1991(s), 1821(m), 1801(m). <sup>1</sup>H NMR (CDCl<sub>3</sub>, in ppm):  $\delta$  6.65–6.69 (m, 5H,  $\sigma$ -Ph), 0.95–0.98 (t, 12H, CH<sub>3</sub>), 1.182–1.452 (m, 8H, CH<sub>2</sub>). MS ES (negative ion) for 1: m/z = 1155 (MH). The isotope distribution pattern was consistent with the presence of four iridium atoms.

(b) A 30.0 mg (0.076 mmol) amount of SnPh<sub>4</sub> was added to 25.0 mg (0.019 mmol) of  $[Et_4N][Ir_4(CO)_{11}Br]$  in 25 mL of methanol. The reaction mixture was stirred at room temperature for 16 h. The solvent was then removed *in vacuo*. A<sup>119</sup>Sn NMR spectrum of the entire reaction mixture in CD<sub>2</sub>Cl<sub>2</sub> solvent showed only two resonances,  $\delta = -60.48$  (SnPh<sub>3</sub>Br)<sup>15</sup> and -129.79 (unreacted SnPh<sub>4</sub>, confirmed by recording a spectrum of a sample of the SnPh<sub>4</sub> from the reagent bottle). The product **1** was isolated by TLC by eluting with a 6:1 methylene chloride/hexane solvent mixture to yield 10.9 mg (yield 36.4%).

**Reaction of 1 with PPh<sub>3</sub> at 80** °C. A 2.0 mg (0.0076 mmol) amount of PPh<sub>3</sub> was added to 7.5 mg (0.0058 mmol) of 1 dissolved in 20 mL of benzene. The reaction solution was then heated to reflux for 1 h. After cooling, the solvent was removed *in vacuo*, and the product was isolated by TLC by eluting with a 3:1 hexane/methylene chloride solvent mixture to yield 5.0 mg of  $[Et_4N][Ir_4(CO)_{10}(PPh_2C_6H_4)]$ , 2 (60% yield). Spectral data for 2: IR  $\nu_{CO}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2044(s), 2012(vs), 1978(vs), 1800(m), 1761(m). <sup>1</sup>H NMR (CDCl<sub>3</sub> in ppm):  $\delta$  7.19–7.32 (m, 14H, Ph), 0.91–0.97 (t, 12H, CH<sub>3</sub>), 1.15–1.48 (m, 8H, CH<sub>2</sub>). MS ES (negative ion) for 2: m/z = 1311 (MH). The isotope distribution pattern was consistent with the presence of four iridium atoms.

**Reaction of 2 with HBF<sub>4</sub> under CO.** A 0.06 mL amount of HBF<sub>4</sub> (51% in diethyl ether) was added to 14.0 mg (0.0097 mmol) of  $[Et_4N][Ir_4(CO)_{11}(PPh_2C_6H_4)]$  dissolved in 20 mL of methanol. The reaction was stirred under an atmosphere of CO for 1 h. The solvent was removed *in vacuo*, and the product was then isolated by TLC by eluting with a 3:1 hexane/methylene chloride solvent mixture to yield 11.4 mg of the known compound  $Ir_4(CO)_{11}(PPh_3)^{16}$  (81%) and 1.0 mg of  $Ir_4(CO)_{12}$ .

Reaction of [Et<sub>4</sub>N][Ir<sub>4</sub>(CO)<sub>11</sub>Ph], 1, with Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl. A 9.20 mg (0.0118 mmol) amount of Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl was added to 14.4 mg (0.0112 mmol) of  $[Et_4N][Ir_4(CO)_{11}Ph]$  that was dissolved in 25 mL of benzene. The reaction solution was heated to reflux for 2 h. The solvent was then removed in vacuo, and the product was isolated by TLC by eluting with a 3:1 hexane/methylene chloride solvent mixture. This yielded in order of elution 1.56 mg of brown  $Ir_5(CO)_{12}Ph(PPh_3)$ , 3 (11% yield), 3.50 mg of brown Ir<sub>5</sub>(CO)<sub>11</sub>(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 4 (22% yield), 6.02 mg of yellow 2 (37% yield), and 1.21 mg of  $Ir_4(CO)_{11}$ - $(PPh_3)^{16}$  (8% yield). The yield of 4 was increased to 40% at the expense of 3 (only a trace) and 2 (17%) when the reflux period was increased to 5 h. Spectral data for 3: IR  $\nu_{CO}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2080(w), 2053(vs), 2045(vs), 2018(s), 1841(m), 1813(m). <sup>1</sup>H NMR (CDCl<sub>3</sub>, in ppm):  $\delta$ 7.19-7.41 (m, 15H, Ph), 6.67-6.72 (m, 5H, σ-Ph). MS ES (negative ion) for 3: m/z = 1635 (MH). The isotope distribution pattern was consistent with the presence of five iridium atoms. Spectral data for 4: IR  $v_{\rm CO}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2061(s), 2038(vs), 2022(s), 2007(s), 1990(m), 1850(m), 1816(m), 1787(m). <sup>1</sup>H NMR (CDCl<sub>3</sub>, in ppm):  $\delta$  7.19–7.42 (m, 29H, Ph). MS ES (positive ion) for 4: m/z = 1794 (M<sup>+</sup>), 1831(M + K<sup>+</sup>). The isotope distribution pattern was consistent with the presence of five iridium atoms.

Synthesis of 4 by the Reaction of 2 with  $Ir(CO)(PPh_3)_2CI$ . A 7.3 mg (0.0094 mmol) sample of  $Ir(CO)(PPh_3)_2CI$  was added to 13 mg (0.0090 mmol) of 4 dissolved in 25 mL of benzene. The reaction was heated to reflux for 5 h. The solvent was removed *in vacuo*, and the product was then isolated by TLC by eluting with a 3:1 hexane/ methylene chloride solvent mixture. Yield: 1.78 mg of 4 (11%).

Synthesis of 4 by the Reaction of 3 with PPh<sub>3</sub>. A 1.2 mg (0.0046 mmol) amount of PPh<sub>3</sub> was added to 5.6 mg (0.0042 mmol) of 3 dissolved in 20 mL of benzene. The reaction was heated to reflux for 1.5 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC by eluting with a 3:1 hexane/methylene chloride solvent mixture. Yield: 2.66 mg of 4 (43% yield).

Crystallographic Analyses. Single crystals of 1 (yellow), 2 (yellow), and 3 (brown) suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from hexane/methylene chloride solvent mixtures at -25 °C. Single crystals of compound 4 were grown from a benzene/methylene chloride solvent mixture by slow evaporation of solvent at room temperature. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-area detection diffractometer by using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.<sup>17</sup> Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied in each analysis by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on  $F^2$ , using the SHELXTL software package.<sup>18</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Compounds 1, 2, 3, and 4 all crystallized in the monoclinic crystal system. The space group  $P2_1/n$  was indicated by the systematic absences in the intensity data for compounds



**Figure 1.** ORTEP diagram of the molecular structure of the complex anion  $[Ir_4(CO)_{11}Ph]^-$  of 1 showing 30% thermal ellipsoid probability. The hydrogen atoms on the phenyl ring are not shown for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir1–Ir2 = 2.7494(7), Ir1–Ir3 = 2.7393(7), Ir1–Ir4 = 2.7515(7), Ir2–Ir3 = 2.7015(7), Ir2–Ir4 = 2.7235(7), Ir3–Ir4 = 2.7317(7), Ir1–C44 = 2.125(13); C44–Ir1–Ir2 = 104.4(4), Ir4–Ir1–C44 = 160.0(4).

1 and 4 and was confirmed by the successful solutions and refinements of those structures. There is one symmetry-independent molecule in the asymmetric unit in the crystal structures of 1 and of 4. The systematic absences in the intensity data for compound 2 were consistent with the space groups Cc and C2/c. The centrosymmetric space group C2/c was selected and confirmed by the successful solution and refinement of the structure. There is one symmetry-independent molecule of 2 in the asymmetric crystal unit. The crystal of 2 also contains a half-molecule of hexane from the crystallization solvent that was cocrystallized with the complex. The space group  $P2_1/c$  was identified uniquely on the basis of the systematic absences in the intensity data for compound 3. There is one molecule of methylene chloride and a half-molecule of benzene from the crystallization solvent cocrystallized with 4 in the asymmetric crystal unit. The solvent molecules were satisfactorily refined with isotropic thermal parameters.

#### RESULTS AND DISCUSSION

The new air-stable tetrairidium anion  $[Ir_4(CO)_{11}(\sigma-Ph)^-, 1]$ , was isolated as the  $[Et_4N]^+$  salt in 45% yield from the reaction of  $[Et_4N][Ir_4(CO)_{11}Br]$  with SnPh<sub>3</sub>OH.  $[Et_4N]1$  was characterized by a combination of IR, <sup>1</sup>H NMR, MS, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the tetrairidium anion 1 is shown in Figure 1. The structure of the anion 1 is similar to that of the complex anion  $[Ir_4(CO)_{11}Br]^-$  from which it was made.<sup>19</sup> The anion 1 consists of a tetrahedral Ir<sub>4</sub> cluster with 11 carbonyl ligands distributed as shown in the figure. There are three bridging carbonyl ligands. All of the other CO ligands are terminally coordinated. The Ir-Ir bond distances are similar to those found in the anion  $[Ir_4(CO)_{11}Br]^{-19}$  The anion 1 contains one  $\sigma$ -phenyl ligand that is terminally coordinated to iridium atom Ir(1). The Ir-C bond distance to the phenyl ligand, Ir(1)-C(44) = 2.125(13) Å, is slightly longer than the Ir-C distances to the  $\sigma$ -phenyl ligands in the previously reported



**Figure 2.** ORTEP diagram of the molecular structure of the complex anion  $[Ir_4(CO)_{10}(PPh_2C_6H_4)]^-$  of **2** showing 30% thermal ellipsoid probability. Hydrogen atoms are not shown for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Ir1-Ir2 = 2.7367(6), Ir1-Ir3 = 2.6633(6), Ir1-Ir4 = 2.7434(7), Ir2-Ir3 = 2.7383(7), Ir2-Ir4 = 2.7183(7), Ir3-Ir4 = 2.7728(7), Ir3-C56 = 2.096(12), Ir1-P1 = 2.286(3); P1-Ir1-Ir2 = 97.57(7), P1-Ir1-Ir3 = 90.32(8), P1-Ir1-Ir4 = 149.50(7), C56-Ir3-Ir1 = 93.3(3).

Ir<sub>3</sub>, Ir<sub>4</sub>, and Ir<sub>8</sub> complexes: Ir<sub>3</sub>(CO)<sub>9</sub>(Ph)( $\mu_3$ -PPh)( $\mu$ -dppm), 2.084(16) Å,<sup>20</sup> Ir<sub>4</sub>(CO)<sub>8</sub>( $\sigma$ -Ph)[ $\mu_4$ - $\eta^3$ -PhPC(H)CPh]( $\mu$ -PPh<sub>2</sub>), 2.09(1) Å,<sup>21</sup> and Ir<sub>8</sub>(CO)<sub>16</sub>( $\sigma$ -Ph)( $\mu$ -PPh<sub>2</sub>)( $\mu_4$ -PPh), 2.06(4) Å<sup>22</sup>

Compound 1 was also obtained in 36.4% yield from the reaction of SnPh<sub>4</sub> with  $[Et_4N][Ir_4(CO)_{11}Br]$  in methanol solvent over a 16 h period. An analysis of a reaction mixture by <sup>119</sup>Sn NMR spectroscopy revealed a resonance at  $\delta = -60.48$ , which is consistent with the formation of the tin compound SnPh<sub>3</sub>Br.<sup>15</sup> This observation confirms that the formation of 1 by the reaction with SnPh<sub>4</sub> occurs by Br for Ph transmetalation, eq 4.

$$[Ir_4(CO)_{11}Br]^- + SnPh_4 \rightarrow [Ir_4(CO)_{11}Ph]^- + SnPh_3Br$$
(4)

Transmetalation reactions between aryltin compounds and metal halide complexes of platinum<sup>23</sup> and palladium<sup>24</sup> have been known for some years. Recently, aryltin compounds have been used to transfer aryl groups to gold(I) halides.<sup>25</sup> Tin compounds also form the basis for the important transmetalation step in the well-known Stille coupling reactions.<sup>12</sup> Although SnPh<sub>3</sub>OH reacts with Ir<sub>4</sub>(CO)<sub>12</sub> in the presence of base to yield Ir<sub>4</sub>Sn complexes, eq 2, we think the reaction with the bromo complex [Ir<sub>4</sub>(CO)<sub>11</sub>Br]<sup>-</sup> reported to yield 1 here in the absence of base proceeds instead by a transmetalation process.

When compound 1 was allowed to react with PPh<sub>3</sub> in benzene solvent at reflux for 1 h, the new compound  $[Et_4N][Ir_4(CO)_{10}-(PPh_2C_6H_4)]$ , 2, was obtained and isolated in 60% yield. Compound 2, a salt, was characterized by a combination of IR, <sup>1</sup>H NMR, MS, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the tetrairidium anion of 2 is shown in Figure 2. The anion of 2 consists of a tetrahedral Ir<sub>4</sub> cluster with 10 carbonyl ligands. Three of the CO ligands are bridging ligands about the Ir(1)–Ir(2)–Ir(3) triangle. The other CO ligands are terminally



**Figure 3.** ORTEP diagram of the molecular structure of  $Ir_5(CO)_{12}Ph-(PPh_3)$ , **3**, showing 30% thermal ellipsoid probability. Hydrogen atoms are not shown for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir1-Ir2 = 2.7303(8), Ir1-Ir3 = 2.8268(8), Ir1-Ir4 = 2.7215(8), Ir2-Ir3 = 2.6848(8), Ir2-Ir4 = 2.7988(8), Ir2-Ir5 = 2.7765(8), Ir3-Ir4 = 2.7021(8), Ir3-Ir5 = 2.7629(8), Ir4-Ir5 = 2.7912(8), Ir5-C4 = 2.116(16), Ir1-P1 = 2.311(4); P1-Ir1-Ir2 = 115.81(9), P1-Ir1-Ir3 = 171.83(9), C4-Ir5-Ir2 = 102.1(4), C4-Ir5-Ir4 = 160.3(4), Ir1-Ir3-Ir5 = 108.93(2).

coordinated. The most interesting ligand is an edge-bridging PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub> group derived from the PPh<sub>3</sub> reagent that became ortho-metalated to one of the Ir atoms. The aryl group is  $\sigma$ -bonded to Ir(3). The Ir–C bond, Ir3–C56 = 2.096(12) Å, is similar in length to that of the  $\sigma$ -bonded phenyl group in anion **1**. The shortest Ir–Ir bond in the cluster is the one bridged by the PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub> ligand, Ir1–Ir3 = 2.6633(6) Å. The longest Ir–Ir bond is the one trans to the  $\sigma$ -bonded aryl group, Ir3–Ir4 = 2.7728(7) Å. This may be due to a strong trans-structural effect of the  $\sigma$ -bonded aryl group. <sup>26</sup> The fate of the phenyl group that was eliminated from **1** in the reaction and that of the hydrogen atom that was cleaved from the ortho-position of the metalated phenyl ring in **2** has not been established. It is presumed that they have been combined to form benzene.

Interestingly, when anion **2** was treated with HBF<sub>4</sub> under an atmosphere of CO for 1 h, the anion was neutralized by the addition of H<sup>+</sup>. The H<sup>+</sup> was added to the carbon atom of the metalated phenyl ring. A CO ligand was added to the complex, and the known compound  $Ir_4(CO)_{11}(PPh_3)^{16}$  was obtained in 81% yield together with a trace of  $Ir_4(CO)_{12}$ .

Compounds 2 (37% yield) and  $Ir_4(CO)_{11}(PPh_3)$  (8% yield) together with two new pentairidium compounds,  $Ir_5(CO)_{12}Ph-(PPh_3)$ , 3 (11% yield), and  $Ir_5(CO)_{11}(PPh_3)(PPh_2C_6H_4)$ , 4 (22% yield), were obtained from the reaction of 1 with  $Ir(CO)-(PPh_3)_2Cl$  in a benzene at reflux. The yield of 4 was increased to 40% at the expense of the formation of 3 by increasing the reaction time to 5 h, probably because 3 reacts with PPh\_3 to yield 4; see below. Compounds 3 and 4 were both characterized by single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of 3 is shown in Figure 3. The compound contains a trigonal-bipyramidal cluster of five iridium atoms. The apical iridium atom Ir(1) contains a PPh\_3 ligand, and apical

iridum atom Ir(5) contains a terminally coordinated  $\sigma$ -phenyl ligand. The Ir–Ir bond distances span a considerable range, 2.6848(4)–2.8269(8) Å. The two longest Ir–Ir bonds lie trans to the phosphine and  $\sigma$ -phenyl ligands, Ir(1)–Ir(3) = 2.8269(8) Å and Ir(4)–Ir(5) = 2.7912(8) Å, respectively. The Ir–C bond to the  $\sigma$ -phenyl ligand is similar in length to that found in 1,



Figure 4. ORTEP diagram of the molecular structure of  $Ir_5(CO)_{11}$ -(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 4, showing 30% thermal ellipsoid probability. Hydrogen atoms are not shown for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir1–Ir2 = 2.7555(12), Ir1–Ir3 = 2.7932(12), Ir1–Ir4 = 2.7047(13), Ir2–Ir5 = 2.6891(12), Ir3–Ir5 = 2.6948(12), Ir4–Ir5 = 2.7607(14), Ir2–C70 = 2.14(2), Ir1–P1 = 2.317(6), Ir5–P2 = 2.289(7); P1–Ir1–Ir2 = 109.66(14), P1–Ir1–Ir3 = 170.05(15), P2–Ir5–Ir2 = 93.34(16), P2–Ir5–Ir3 = 104.09(16), P2–Ir5–Ir4 = 154.95(16), Ir1–Ir2–Ir5 = 108.71(4), Ir3–Ir2–C70 = 103.8(6), Ir1–Ir2–C70 = 138.1(5), Ir5–Ir2–C70 = 90.1(5).

#### Scheme 1

Ir5-C4 = 2.116(16) Å. Compound 3 has four bridging carbonyl ligands with two bridging to each of the apical Ir atoms of the cluster.

An ORTEP diagram of the molecular structure of 4 is shown in Figure 4. This compound also consists of a trigonal-pyramidal cluster of five iridium atoms. As in 3, the apical iridium atom Ir(1) also contains a PPh<sub>3</sub> ligand. There is a bridging PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub> ligand similar to that found in 2 with the phosphorus atom coordinated to Ir(5) and the metalated phenyl ring coordinated to the equatorial Ir atom, Ir(2), Ir2–C70 = 2.14(2) Å. The PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-bridged bond Ir(2)–Ir(5) is the shortest in the molecule, 2.6891(8) Å, and the Ir(1)–Ir(3) bond that lies trans to the PPh<sub>3</sub> ligand is the longest in the molecule, 2.8269(8) Å, as found in 3. Anion 2 was found to react with Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl to give compound 4 in 11% yield, and 3 was transformed into 4 in 43% yield in a CO ligand substitution reaction with PPh<sub>3</sub> that also results in metallation of one of the PPh<sub>3</sub> rings and the elimination of benzene.

A summary of the reactions described in this report is shown in Scheme 1. The new air-stable anionic tetrairidium complex 1 containing a terminally coordinated ligand was obtained via a phenyl for Br exchange (transmetalation) reaction between  $[Ir_4(CO)_{11}Br]^-$  and the tin reagents SnPh<sub>3</sub>OH and SnPh<sub>4</sub>. Anion 1 reacts with PPh<sub>3</sub> to yield the tetrairidium anion 2 by the addition of one PPh3 ligand, loss of one CO ligand, and an ortho-metalation of one of the phenyl rings of the PPh<sub>3</sub> ligand. The original phenyl ligand in 1 and the hydrogen atom that was cleaved from the metalated phenyl ring were eliminated from the complex in this reaction; presumably they were combined to form benzene. When 2 was treated with H<sup>+</sup> in the presence of CO, the ortho-metalation was reversed presumably via protonation at one of the metal atoms followed by C-H reductive elimination of the metalated phenyl ring and the addition of CO to that site. Treatment of 1 with  $Ir(CO)(PPh_3)_2Cl$  also yielded some 2, possibly by a simple competing reaction of 1 with some PPh<sub>3</sub> released from the  $Ir(CO)(PPh_3)_2Cl$ . In addition the two new pentairidium complexes 3 and 4 were obtained from this reaction. Complex 3 was formed by an addition of one equivalent of  $Ir(CO)(PPh_3)_2Cl$  to 1 accompanied by the loss of one PPh<sub>3</sub>



ligand and Cl<sup>-</sup>. Compound 4 was formed by an addition of one equivalent of  $Ir(CO)(PPh_3)_2Cl$  to 1 accompanied by the loss of one CO ligand and Cl<sup>-</sup>. Interestingly, compound 4 was also obtained by the reaction of 2 with one equivalent of Ir(CO)- $(PPh_3)_2Cl$  that was accompanied by the loss of one PPh\_3 ligand and Cl<sup>-</sup> and also by reaction of 3 with PPh\_3 that was accompanied by a loss of CO and the elimination of the  $\sigma$ -phenyl ligand and the hydrogen atom from the metalated phenyl ring.

# CONCLUSIONS

Phenyl-substituted tin compounds are active for the synthesis of anionic stable  $\sigma$ -phenyl iridium carbonyl cluster complexes by transmetalation reactions. The anion 1 has sufficient nucleophilicity to react with the chloroiridium complex Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl by halide displacement to yield uncharged pentairidium complexes. Investigations of reactions of 1 with other metal halide complexes are in progress.

# ASSOCIATED CONTENT

**Supporting Information.** CIF files for the structural analyses are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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