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Auration, Argentation, and Mercuration Reactions of an Iridaphosphirene

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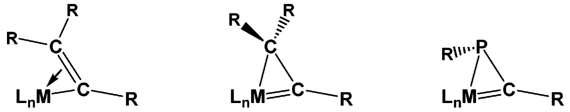
The reactions of the iridaphosphirene complex $[\mathrm{Ir}\{{=}\mathrm{C}({}^t\mathrm{Bu})\mathrm{P}(\mathrm{Cy})\}(\mathrm{CO})(\mathrm{PPh}_3)_2]$ (Cy = cyclohexyl) with either [AuCl(tht)] (tht = tetrahydrothiophene) or AgCl result in the products $[\mathrm{Ir}\{{=}\mathrm{C}({}^t\mathrm{Bu})\mathrm{P}[\mathrm{M}(\mathrm{Cl})](\mathrm{Cy})\}(\mathrm{CO})(\mathrm{PPh}_3)_2]$, M = Au or Ag. The aurated product can additionally be obtained on reaction of the iridaphosphirene with $[\mathrm{AuCl}(\mathrm{CN}{}^t\mathrm{Bu})]$, via loss of the isocyanide ligand. Treatment of $[\mathrm{Ir}\{{=}\mathrm{C}({}^t\mathrm{Bu})\mathrm{P}(\mathrm{Cy})\}(\mathrm{CO})(\mathrm{PPh}_3)_2]$ with $[\mathrm{AuCl}(\mathrm{PPh}_3)]$ in the presence of silver triflate leads to the isolation of the salt, $[\mathrm{Ir}\{{=}\mathrm{C}({}^t\mathrm{Bu})\mathrm{P}[\mathrm{Au}(\mathrm{PPh}_3)](\mathrm{Cy})\}(\mathrm{CO})(\mathrm{PPh}_3)_2][\mathrm{SO}_3\mathrm{CF}_3]$. Reaction of the iridaphosphirene with PhHgCl in the absence or presence of silver triflate affords the mercurated species $[\mathrm{Ir}\{{=}\mathrm{C}({}^t\mathrm{Bu})\mathrm{P}[\mathrm{Hg}(\mathrm{Ph})](\mathrm{Cy})\}(\mathrm{CO})(\mathrm{PPh}_3)_2]\mathrm{X}$, X = Cl or $\mathrm{CF}_3\mathrm{SO}_3$, respectively. The former exhibits a weakly mercury-coordinated chloride ion. The X-ray crystal structures of all of the complexes are described.

Introduction

The recent interest in η^2-3-electron vinyl complexes has centered on the diverse reactivity shown by these species toward nucleophiles and electrophiles and in isomerization reactions to form η^3-allyl and carbene complexes.[1] It has recently been argued on the basis of structural and spectroscopic evidence that they should be viewed, in many cases, as metallacyclopropene complexes rather than η^2-vinyl species (Chart 1).[2] In recent work, we have explored the analogy between phosphavinyl and vinyl fragments, and it has become clear that the former behave very differently than the latter within the coordination sphere of transition[3] and main-group[4] elements.

Chart 1. Generalized η^2-vinyl, Metallacyclopropene, and Metallaphosphirene Units



These studies have been aided by our high-yield synthesis of the phosphavinyl Grignard reagent, (Z)-$[\mathrm{CyP{=}C}({}^t\mathrm{Bu})\mathrm{MgCl}(\mathrm{OEt}_2)]$ (Cy = cyclohexyl),[5] which has been successfully exploited in reactions with main-group halides to yield terminal phosphavinyl–metal compounds, for example, $[\mathrm{Me}_2\mathrm{Sn}\{\mathrm{C}({}^t\mathrm{Bu}){=}\mathrm{PCy}\}_2)]$,[4a] as well as unusual heterocyclic compounds via phosphavinyl coupling reactions.[4d] This reactivity shows a marked departure from the chemistry of conventional vinyl Grignard reagents. The extension of these investigations to the formation of transition-metal–phosphavinyl complexes has been problematic because of the variable oxidation states accessible to transition metals. This often leads to an oxidative coupling of the phosphavinyl fragment to give the 2,4-diphosphabicyclo[1.1.0]butane, $\mathrm{P}_2\mathrm{C}_2{}^t\mathrm{Bu}_2$, or its 1,2-dihydro-1,2-diphosphete valence isomer.[4c] Oxidative coupling does not, however, occur in the reaction of Vaska's

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complex with (*Z*)-[CyP=C(^{t}Bu)MgCl(OEt_2)], which instead leads to the stable yet reactive iridaphosphirene complex, [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$], incorporating a three-electron phosphidocarbene ligand.[6] This complex has been found to react readily with methyl iodide, acids, and elemental chalcogens at the phosphirene P center to give a variety of λ^5-iridaphosphirene and iridaphosphirenium complexes.[7] In contrast, the reaction of [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$] with carbon monoxide leads to the initial displacement of a triphenylphosphine ligand and, ultimately, to the oxophosphaallylic complex [Ir{η^3-O=C=C(^{t}Bu)P(Cy)}(CO)(PPh_3)]$_2$ via an intramolecular phosphavinyl−CO coupling reaction.[6]

Other related work of ours dealing with metal complexes bearing unsaturated phosphorus ligands centers on the versatile ruthenium phosphavinyl compounds, [Ru{P=C(H)^{t}Bu}Cl(CA)(PPh_3)$_2$] (A = O, S).[3] These complexes display a fascinating reactivity at both the phosphavinyl phosphorus and the metal center. It has been discovered that unprecedented dimetalated phosphaalkene species are accessible through the addition of electrophilic metal fragments to these complexes. This prompted the investigations reported here on the formation of bimetallic complexes of the iridaphosphirene, [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$], with metal fragments of groups 11 and 12.

Experimental Section

General Methods. All procedures were carried out under an inert argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried and distilled using either potassium or Na/K alloy (tetrahydrofuran, toluene, diethyl ether, hexane) and calcium hydride (dichloromethane). The solvents were freeze/thaw degassed prior to use. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FTIR spectrometer with NaCl plates. NMR spectroscopy was carried out using a JEOL Eclipse 300 spectrometer. All NMR spectra were obtained at 25 °C. ^{1}H NMR spectra were run at 300.5 MHz, ^{19}F NMR spectra at 282.8 MHz, and ^{31}P{^{1}H} NMR spectra at 121.7 MHz. A pseudotriplet is denoted by pseud. t. ^{13}C NMR spectra of all of the compounds were complicated by overlapping multiplets in the aliphatic and aromatic regions, and these signals could not be confidently assigned. Electrospray (ES) and liquid secondary ion mass spectrometry (LSIMS) mass spectra and accurate mass spectra were obtained from the EPSRC Mass Spectrometry Center, University of Swansea. Microanalyses were performed by Medac Ltd., Surrey, or at University College London. Melting points were determined in sealed glass capillaries under argon and are uncorrected. The complexes [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$],[6] [AuCl(CN^{t}Bu)],[8] [AuCl(tht)] (tht = tetrahydrothiophene),[9] and [AuCl(PPh_3)][10] were prepared according to published procedures. All other reagents were used as received.

Preparation of [Ir{=C(^{t}Bu)P[Au(Cl)](Cy)}(CO)(PPh_3)$_2$] (2). (a) [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$] (100 mg, 0.11 mmol) was dissolved in tetrahydrofuran (10 mL), and a solution of [AuCl(tht)] (34 mg, 0.11 mmol) in tetrahydrofuran (5 mL) was added at −78 °C. The reaction was slowly warmed to room temperature and stirred for 20 h in the dark. Volatiles were then removed in vacuo, and the residue was taken up in a minimum volume of dichloromethane. This was layered with hexane, resulting in orange crystals of complex **2**. Yield: 85 mg (73%). **(b)** [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$] (100 mg, 0.11 mmol) was dissolved in tetrahydrofuran (10 mL), and a solution of [AuCl(CN^{t}Bu)] (34 mg, 0.11 mmol) in tetrahydrofuran (5 mL) was added at −78 °C. The solution was slowly warmed to room temperature and stirred for 18 h in the dark. The solvent was removed under vacuum and the residue dissolved in a minimum volume of dichloromethane. Layering with hexane resulted in orange crystals of **2**. Yield: 46 mg (40%). Mp: 198−200 °C. IR (Nujol): 1980 [ν(CO)] cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): δ 13.9 [pseud. t, PPh_3, 2 × $^2J_{PP}$ = 24 Hz], 9.5 [pseud. t, PPh_3, 2 × $^2J_{PP}$ = 24 Hz], −129.4 [m(br), PAuCl]. Variable-temperature ^{31}P{^{1}H} NMR studies did not lead to further resolution of the PAuCl signal. ^{1}H NMR (C_6D_6): δ 0.77−1.81 [m, 11H, Cy], 1.63 [s, 9H, ^{t}Bu], 6.79−7.87 [m, 30H, ArH]. MS (LSIMS) *m/z*: Acc. mass [M$^+$] 1160.2052, found 1160.2053; [M-Cl] 1125.2364, found 1125.2354. Anal. Calcd for $C_{48}H_{50}AuClIrOP_3$: C, 49.7; H, 4.3%. Found: C, 50.1; H, 4.5%.

Preparation of [Ir{=C(^{t}Bu)P[Au(PPh_3)](Cy)}(CO)(PPh_3)$_2$][SO_3CF_3] (3). [AuCl(PPh_3)] (53 mg, 0.11 mmol) and $AgSO_3CF_3$ (28 mg, 0.11 mmol) were suspended in tetrahydrofuran (10 mL) and stirred for 30 min at −78 °C. This solution was filtered into a solution of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh_3)$_2$] (100 mg, 0.11 mmol) in tetrahydrofuran (10 mL), also cooled to −78 °C. A color change from red to yellow was observed. The solution was allowed to warm to room temperature and was stirred for 18 h. All of the solvent was removed under a vacuum and the residue extracted with a minimum volume of toluene. Slow cooling to −30 °C yielded orange crystals of **3**. Yield: 114 mg (74%). Mp: 78−80 °C. IR (Nujol): 1974 [ν(CO)] cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): δ 41.4 [ddd, Au(PPh_3), $^2J_{PP}$ = 341 Hz, $^4J_{PP}$ = 30 Hz, $^4J_{PP}$ = 7 Hz], 11.9 [overlapping unresolved m, 2 × PPh_3], −117.2 [d of pseud. t, IrPCy, $^2J_{PP}$ = 341 Hz, 2 × $^2J_{PP}$ = 30 Hz]. ^{19}F{^{1}H} NMR (C_6D_6): δ −77.0 [s, CF_3SO_3]. ^{1}H NMR ($CDCl_3$): δ 0.50−2.05 [m, 11H, Cy], 1.62 [s, 9H, ^{t}Bu], 6.88−7.39 [m, 45H, ArH]. MS (ES) *m/z* (%): [M]$^+$ 1388 (50), [M − PPh_3]$^+$ 1125 (100). Anal. Calcd for $C_{67}H_{65}AuF_3IrO_4P_4S\cdot 2.5(C_7H_8)$: C, 57.5; H, 4.9%. Found: C, 57.4; H, 4.9%.

Preparation of [Ir{=C(^{t}Bu)P[Ag(Cl)](Cy)}(CO)(PPh_3)$_2$] (4). [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$] (80 mg, 0.09 mmol) was dissolved in tetrahydrofuran (10 mL), and a suspension of AgCl (13 mg, 0.09 mmol) in tetrahydrofuran (5 mL) was added at −78 °C. The reaction was slowly warmed to room temperature and stirred for 1 week in the dark. No discernible color change was observed. Volatiles were then removed in vacuo, and the residue was taken up in a minimum volume of toluene. Slow cooling of this solution to −30 °C yielded red crystals of **4**. Yield: 90 mg (73%). Mp: 205−207 °C. IR (Nujol): 1976 [ν(CO)] cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): δ 14.6 [m(br), PPh_3], 7.7 [m(br), PPh_3], −152.0 [doublet of m(br), PAgCl, $^1J_{PAg}$ = 702 Hz]. ^{1}H NMR (C_6D_6): δ 0.25−1.94 [m, 11H, Cy], 1.64 [s, 9H, ^{t}Bu], 6.83−7.39 [m, 30H, ArH]. MS (LSIMS) *m/z*: Acc. mass [M − Cl]$^+$ 1035.1749 (^{107}Ag, ^{193}Ir), found 1035.1762.

Preparation of [Ir{=C(^{t}Bu)P[Hg(Ph)](Cy)}(CO)(PPh_3)$_2$]Cl (5). A solution of PhHgCl (31 mg, 0.10 mmol) in tetrahydrofuran (10 mL) was added to a tetrahydrofuran solution (10 mL) of [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh_3)$_2$] (96 mg, 0.10 mmol) at −78 °C. A color change from orange to yellow was observed. The reaction

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Table 1. Crystal Data for Compounds **2**−**6**

	2	**3**·1.5C_7H_8	**4**	**5**·2.5C_7H_8	**6**·2.5C_6H_6
chemical formula	$C_{48}H_{50}AuClIrOP_3$	$C_{77.50}H_{77}AuF_3IrO_4P_4S$	$C_{48}H_{50}AgClIrOP_3$	$C_{71.5}H_{75}ClHgIrOP_3$	$C_{70}H_{70}F_3HgIrO_4P_3S$
fw	1160.41	1674.50	1071.31	1471.46	1550.02
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
crystal color	orange	orange	red	orange	red-orange
crystal size	0.15 × 0.12 × 0.12	0.20 × 0.15 × 0.10	0.15 × 0.10 × 0.10	0.15 × 0.15 × 0.10	0.10 × 0.10 × 0.10
space group	$P2_1/c$	Cc	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	13.311(3)	27.603(6)	13.390(3)	12.420(3)	17.465(4)
b/Å	15.346(3)	12.948(3)	15.254(3)	13.105(3)	15.031(3)
c/Å	22.193(4)	24.642(5)	22.148(4)	21.348(4)	26.819(5)
α/deg	90.00	90.00	90.00	96.30(3)	90.00
β/deg	105.03(3)	114.34(3)	104.21(3)	103.64(3)	102.68(3)
γ/deg	90.00	90.00	90.00	107.03(3)	90.00
V/Å^3	4378.3(15)	8025(3)	4385.5(15)	3168.3(11)	6869(2)
Z	4	4	4	2	4
calculated density (g/cm^3)	1.760	1.386	1.623	1.542	1.499
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
μ(Mo Kα)/mm^{-1}	6.589	3.639	3.683	4.678	4.321
F(000)	2256	3332	2128	1462	3068
reflns collected	27851	25680	33893	27632	38982
unique reflns (R_{int})	9606 (0.1425)	14523 (0.0592)	9842 (0.0502)	10805 (0.0559)	11957 (0.0624)
R_1 [$I > 2\sigma(I)$]	0.0584	0.0544	0.0311	0.0388	0.0596
wR'_2 (all data)	0.1392	0.1409	0.0664	0.0958	0.1608
residual e Å^{-3} (max, min)	1.826, −1.802 (both near Ir1)	1.729 (near Ir1), −0.774	0.815, −1.127	1.607 (near Hg1), −1.334 (near Ir1)	3.298 (near Ir1), −1.836 (near Hg1)

Table 2. Selected Metrical Parameters for Complexes **2**−**6** and Related Complexes

complex	Ir1−C1 (Å)	P1−C1 (Å)	Ir−P1 (Å)	Tors. (deg)[a]	P−M−X (deg)[b]
[Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh$_3$)$_2$] (**1**)[6]	1.918(14)	1.753(13)	2.442(3)	77.9	
[Ir{=C(^{t}Bu)P(Me)(Cy)}(CO)(PPh$_3$)$_2$]I[7]	1.932(4)	1.738(5)	2.3280(11)	69.1	
[Ir{=C(^{t}Bu)P[Au(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (**2**)	1.909(9)	1.753(9)	2.356(2)	80.7	177.40(9)
[Ir{=C(^{t}Bu)P[Au(PPh$_3$)](Cy)}(CO)(PPh$_3$)$_2$]OTf (**3**)	1.916(10)	1.768(10)	2.352(3)	86.5	179.12(11)
[Ir{=C(^{t}Bu)P[Ag(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (**4**)	1.916(3)	1.770(4)	2.3721(11)	82.8	172.41(4)
[Ir{=C(^{t}Bu)P[Hg(Ph)](Cy)}(CO)(PPh$_3$)$_2$]Cl (**5**)	1.923(6)	1.751(6)	2.3629(17)	73.4	168.17(18)
[Ir{=C(^{t}Bu)P[Hg(Ph)](Cy)}(CO)(PPh$_3$)$_2$]OTf· (**6**)	1.928(9)	1.755(11)	2.356(2)	73.5	169.0(3)

[a] Tors. = torsion angle between Cy and ^{t}Bu substituents. [b] P−M−X = angle of P−(Au,Ag,Hg)−(Cl,PPh$_3$,Ph).

mixture was warmed to room temperature and stirred for 3 h. Volatiles were removed in vacuo, and the residue was dissolved in dichloromethane (5 mL). Hexane was added until precipitation of the product began to occur. The solution was then cooled to −30 °C to yield orange crystals of **5**. Yield: 93 mg (77%). Mp: 114−117 °C. IR (Nujol): 1986 [ν(CO)] cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): δ 14.0 [m(br), PPh$_3$], 7.3 [m(br), PPh$_3$], −112.0 [m(br), PHgPh]. ^{1}H NMR (C_6D_6): δ 0.73−2.04 [m, 11H, Cy], 1.54 [s, 9H, ^{t}Bu], 6.80−7.61 [m, 35H, ArH]. MS (LSIMS) m/z (%): [M]$^+$ 1205 (20), [M − PPh$_3$]$^+$ 943 (100). Anal. Calcd for $C_{54}H_{55}ClHgIrOP_3$: C, 52.4; H, 4.5%. Found: C, 52.2; H, 4.0%.

Preparation of [Ir{=C(^{t}Bu)P[Hg(Ph)](Cy)}(CO)(PPh$_3$)$_2$]-[SO$_3$CF$_3$] (6). A solution of [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh$_3$)$_2$] (75 mg, 0.08 mmol) in tetrahydrofuran (10 mL) was treated with a tetrahydrofuran solution (10 mL) of [PhHg]OSO$_2$CF$_3$ prepared in situ from AgSO$_3$CF$_3$ (21 mg, 0.08 mmol) and PhHgCl (25 mg, 0.08 mmol) at −78 °C. A color change was observed from red to yellow. The reaction was warmed to room temperature and stirred for 18 h. Volatiles were removed in vacuo, and the residue was extracted with toluene (5 mL). The solution was then cooled to −30 °C to yield orange crystals of **6**. Yield: 80 mg (75%). Mp: 101−103 °C. IR (Nujol): 2000 [ν(CO)] cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): δ 12.6 [pseud. t., PPh$_3$, $2 \times {}^2J_{PP} = 30$ Hz], 7.4 [pseud. t., PPh$_3$, $2 \times {}^2J_{PP} = 30$ Hz], −109.1 [pseud. t., PHgPh, $2 \times {}^2J_{PP} = 30$ Hz]. ^{19}F{^{1}H} NMR (C_6D_6): δ −77.0 [s, CF$_3$SO$_3$]. ^{1}H NMR (C_6D_6): δ 0.29−1.75 [m, 11H, Cy], 1.43 [s, 9H, ^{t}Bu], 6.72−7.65 [m, 35H, ArH]. MS (ES) m/z (%): [M]$^+$ 1205 (100). Anal. Calcd for $C_{70}H_{70}F_3HgIrO_4P_3S$: C, 54.2; H, 4.6%. Found: C, 54.0; H, 4.3%.

X-ray Crystallography. Crystals of **2**−**6** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The data were collected at 150 K, and the structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[11] using all unique data. All non-hydrogen atoms are anisotropic with H atoms included in calculated positions (riding model). Crystal data, details of data collections, and refinement are given in Table 1. Selected metrical parameters for **2**−**6** are compiled in Table 2. The molecular structures of the complexes are depicted in Figures 1−5 and show ellipsoids at the 30% probability level.

Results and Discussion

The phosphorus center in the complex [Ir{=C(^{t}Bu)P(Cy)}-(CO)(PPh$_3$)$_2$] (**1**) has already been shown to display nucleophilic behavior in reactions with simple electrophiles such as protonating and alkylating reagents.[7] The reaction between this iridaphosphirene and [AuCl(tht)] was expected to result in displacement of the sulfur donor by the lone pair of the phosphorus. This proved to be the case with the product [Ir{=C(^{t}Bu)P[Au(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (**2**) being isolated in good yield (Scheme 1). It is noteworthy that the reaction of [AuCl(CN^{t}Bu)] with **1** also led to the isolation of complex

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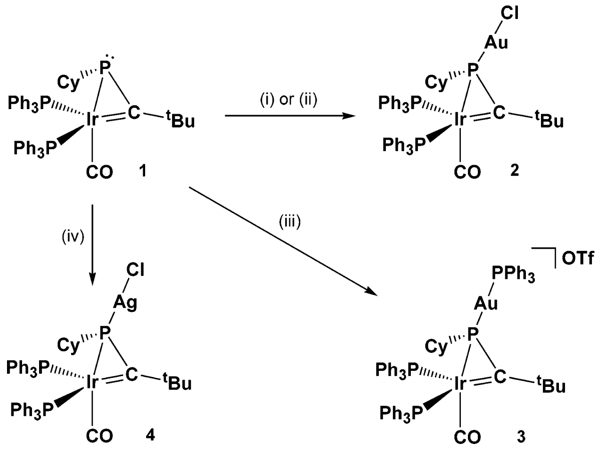
Scheme 1. (i) AuCl(tht), − tht; (ii) AuCl(CN^{t}Bu), − ^{t}BuNC; (iii) [(Ph$_3$P)Au][OTf]; (iv) AgCl



2, but in lower yield. Although it is a stronger donor to gold than tetrahydrothiophene, the isocyanide ligand can be displaced from gold(I) complexes if a more favorable donor option is available.[12] The $^{31}P\{^1H\}$ NMR spectrum of **2** suggests that the cis disposition of the triphenylphosphine ligands in the iridaphosphirene starting material is retained in the gold complex, as indicated by two overlapping doublet resonances (pseudotriplets) at 13.9 and 9.5 ppm with a mutual coupling of 24 Hz. Because of the similar coupling constants between the three phosphorus nuclei of the PPh$_3$ and iridaphosphirene ligands, pseudotriplets were observed in the spectra of all of the complexes discussed here, when sufficient resolution was obtained. The aurated phosphorus center of **2** gives rise to an unresolved multiplet resonance at −129.4 ppm in this spectrum. This represents a shift of approximately 28 ppm to lower field compared to the corresponding feature in **1**, indicating a decrease in shielding of this phosphorus center upon coordination. Moreover, the increase of the ν(CO) absorption from 1954 cm^{-1} for **1** to 1980 cm^{-1} for **2** indicates a subtle decrease in electron density at the metal center as a result of coordination to the gold fragment. The overall composition of the complex was confirmed by accurate mass spectrometry and microanalytical data.

Crystals of complex **2** suitable for X-ray analysis were grown by slow diffusion of a dichloromethane solution of the complex into hexane. The molecular structure is depicted in Figure 1. This, and the structures of the other prepared complexes, will be discussed in the structural section of this paper (see below).

On the basis of the isolobal analogy with H$^+$, the [Au(PR$_3$)]$^+$ fragment has been referred to as the "cluster chemist's proton". Given that [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh$_3$)$_2$] (**1**) is readily protonated, it was decided to explore this analogy with respect to the iridaphosphirene. Abstraction of the chloride ligand from [AuCl(PPh$_3$)] at low temperatures using silver triflate resulted in the in situ generation of [Au(PPh$_3$)]OTf (OTf$^-$ = CF$_3$SO$_3^-$), which was filtered into a tetrahydrofuran solution of complex **1**. After the reaction mixture was stirred for 18 h at room temperature, workup yielded **3** as an orange crystalline solid (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of this complex proved to be highly diagnostic because it exhibits a low field resonance at 41.4 ppm for the Au(PPh$_3$) moiety showing coupling to the phosphorus nuclei of both the iridaphosphirene ($^2J_{PP}$ = 341 Hz) and iridium-bonded triphenylphosphine ligands ($^4J_{PP}$ = 30 and 7 Hz). The iridaphosphirene phosphorus also shows a coupling to the three inequivalent PPh$_3$ ligands as a doublet of pseudotriplets at −117.2 ppm ($^2J_{PP}$ = 341 Hz, $^2J_{PP}$ = 30 Hz). The resonance for the PPh$_3$ ligands was observed as an unresolved multiplet at 11.9 ppm. In addition, the presence of the triflate counteranion was indicated by a singlet in the ^{19}F NMR spectrum of the complex at −77.0 ppm. The small shift in ν(CO) absorption in the solid-state infrared spectrum to 1974 cm^{-1} for **3** from 1980 cm^{-1} in the neutral precursor suggests that the positive charge on the complex is mainly associated with the gold(I) center.

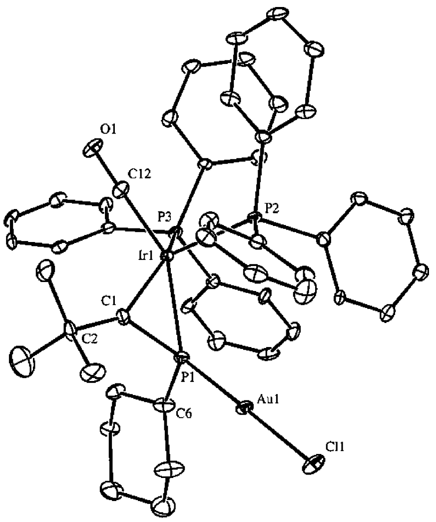


Figure 1. Molecular structure of [Ir{=C(^{t}Bu)P[Au(Cl)](Cy)}(CO)(PPh$_3$)$_2$] (**2**). Selected bond lengths (Å) and angles (deg): Au1−P1 = 2.255(2), Au1−Cl1 = 2.300(2), Ir1−C12 = 1.882(9), Ir1−C1 = 1.909(9), Ir1−P1 = 2.356(2), Ir1−P3 = 2.358(2), Ir1−P2 = 2.359(2), P1−C1 = 1.753(9), P1−C6 = 1.888(10), O1−C12 = 1.150(10), P1−Au1−Cl1 = 177.40(9), C12−Ir1−C1 = 101.7(4), C12−Ir1−P1 = 148.8(3), C1−Ir1−P1 = 47.1(3), C12−Ir1−P3 = 91.7(3), C1−Ir1−P3 = 131.1(3), P1−Ir1−P3 = 109.04(8), C12−Ir1−P2 = 96.2(3), C1−Ir1−P2 = 122.0(3), P1−Ir1−P2 = 101.47(8), P3−Ir1−P2 = 102.53(8), C1−P1−Ir1 = 52.9(3), P1−C1−Ir1 = 79.9(3).

This reactivity differs markedly from that of triaryl- or trialkylphosphines, for which a vast array of gold(I) adducts are known, in that complex **3** consists of a gold(I) center bonded to two different phosphorus environments. Many gold(I) complexes of the form [(R$_3$P)AuX] rearrange (partially or completely) to the homoleptic ion pairs [(R$_3$P)$_2$Au][AuX$_2$], such as the complexes reported recently by Schmidbaur and co-workers, (Ph$_3$P)AuS(O)$_2$R, which are in equilibrium with the homoleptic ion pair [(Ph$_3$P)$_2$Au][Au{S(O)$_2$R}$_2$].[13] Similarly, (Ph$_3$P)AuCN disproportionates to

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Chart 2. R = Alkyl, Aryl; X = Noncoordinating Anion

$$2\,[(R_3P)AuX] + 2\,PR'_3 \longrightarrow [Au(PR_3)_2]X + [Au(PR'_3)_2]X$$

yield $[(Ph_3P)_2Au][AuCN_2]$.[14] This behavior is often found in gold thiolates when 2 equiv of LAuCl react with KSR to yield $[L_2Au]^+$ and $[(RS)_2Au]^-$.[15] Attempts to make asymmetric bis(phosphine) complexes of gold(I) have foundered in the majority of cases through such rearrangements (Chart 2).[15]

This behavior is not limited to phosphines, as shown in the reaction of the 1,2,4-triphospha-3,5-ditertiarybutylcyclopentadienyl anion $K(P_3C_2{}^tBu_2)$ with $(Et_3P)AuCl$ to yield $[Au(P_3C_2{}^tBu_2)_2][Au(PEt_3)_2]$.[16] A rare example where this does not take place is the preparation of $[(CpFeC_5H_4CH_2PPh_2)Au(PPh_3)]OTf$ from the treatment of $[(CpFeC_5H_4CH_2PPh_2)AuCl]$ with $[(Ph_3P)Au]OTf$.[17] Another example is a carbaboryl phosphine complex reported by Jones and co-workers.[18]

Single crystals of complex **3** were obtained, and a structural analysis was carried out (Figure 2). This confirmed the formulation as $[Ir\{{=}C({}^tBu)P[Au(PPh_3)](Cy)\}(CO)(PPh_3)_2]OTf$ (**3**) and showed the triflate counteranion to have no interaction with the cation. The structure is discussed further below.

To broaden the investigation of the coordinating abilities of $[Ir\{{=}C({}^tBu)P(Cy)\}(CO)(PPh_3)_2]$ (**1**) to include other electrophilic metal fragments, the complex was treated with an equimolar quantity of silver chloride. Because of the well-known light sensitivity of silver compounds, the reaction was conducted in the dark. Unlike the experiments detailed here, no discernible reaction was observed after 1 day, and so, the reagents were allowed to react over an extended period (ca. 1 week). Ultimately, a good yield of the silver analogue of complex **2**, namely, $[Ir\{{=}C({}^tBu)P[Ag(Cl)](Cy)\}(CO)(PPh_3)_2]$ (**4**), was obtained (Scheme 1). The spectroscopic data for this complex are similar to those for the gold complex, **2**, with the exception of a higher-field iridaphosphirene phosphorus resonance at −152.0 ppm in its $^{31}P\{^1H\}$ NMR spectrum. Additionally, this signal displays a one-bond coupling of 702 Hz to the spin-active $^{107,109}Ag$ ($I = {}^1/_2$) nuclei. Once again, suitable single crystals were grown and a structural study was undertaken. This allowed a direct comparison to be made between the isomorphic structures of the gold and silver complexes (see Figure 3 and the structural discussion below).

In our recent work on the synthetically versatile ruthenium−phosphavinyl complexes, $[Ru\{P{=}C(H){}^tBu\}Cl(CA)(PPh_3)_2]$ (A = O, S), it was discovered that organomercury halide reagents add across the Ru−P bond to provide complexes

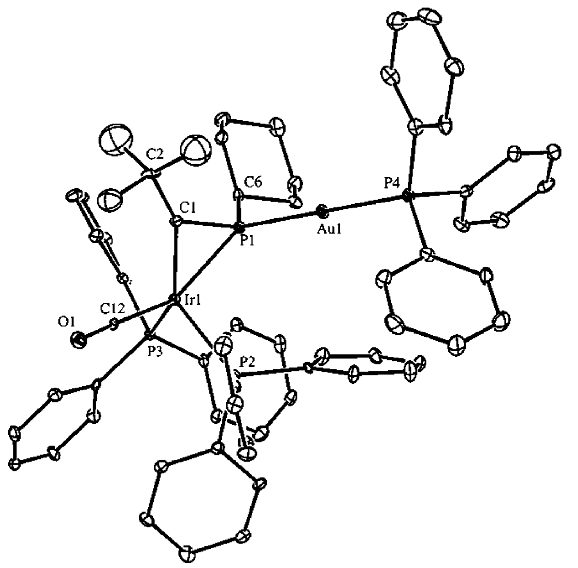

Figure 2. Structure of the cationic component of $[Ir\{{=}C({}^tBu)P[Au(PPh_3)](Cy)\}(CO)(PPh_3)_2]SO_3CF_3$ (**3**). Selected bond lengths (Å) and angles (deg): Au1−P4 = 2.299(3), Au1−P1 = 2.308(3), Ir1−C12 = 1.870(10), Ir1−C1 = 1.916(10), Ir1−P1 = 2.352(3), Ir1−P2 = 2.353(3), Ir1−P3 = 2.391(3), P1−C1 = 1.768(10), O1−C12 = 1.143(12), P4−Au1−P1 = 179.12(11), C12−Ir1−C1 = 98.7(4), C12−Ir1−P1 = 144.9(3), C1−Ir1−P1 = 47.6(3), C12−Ir1−P2 = 93.5(3), C1−Ir1−P2 = 129.7(3), P1−Ir1−P2 = 101.91(9), C12−Ir1−P3 = 102.5(3), C1−Ir1−P3 = 126.6(3), P1−Ir1−P3 = 106.53(10), P2−Ir1−P3 = 97.35(10), C1−P1−Ir1 = 53.1(3), P1−C1−Ir1 = 79.3(4).

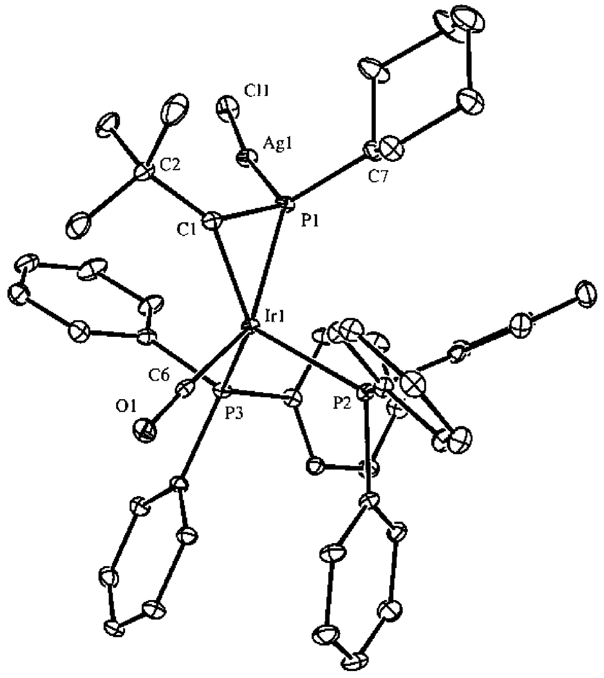

Figure 3. Molecular structure of $[Ir\{{=}C({}^tBu)P[Ag(Cl)](Cy)\}(CO)(PPh_3)_2]$ (**4**). Selected bond lengths (Å) and angles (deg): Ir1−C6 = 1.884(4), Ir1−C1 = 1.916(3), Ir1−P3 = 2.3572(10), Ir1−P2 = 2.3574(10), Ir1−P1 = 2.3721(11), Ag1−Cl1 = 2.3242(13), Ag1−P1 = 2.3522(13), P1−C1 = 1.770(4), P1−C7 = 1.868(4), O1−C6 = 1.148(4), C6−Ir1−C1 = 102.94(15), C6−Ir1−P3 = 96.76(11), C1−Ir1−P3 = 120.35(10), C6−Ir1−P2 = 91.19(11), C1−Ir1−P2 = 131.93(10), P3−Ir1−P2 = 102.77(4), C6−Ir1−P1 = 150.20(11), C1−Ir1−P1 = 47.29(11), P3−Ir1−P1 = 98.77(4), P2−Ir1−P1 = 109.82(4), Cl1−Ag1−P1 = 172.41(4), C1−P1−Ir1 = 52.71(12), P1−C1−Ir1 = 80.00(14).

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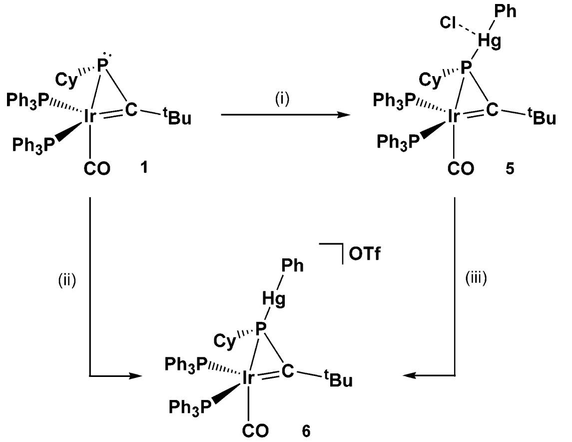
Scheme 2. (i) PhHgCl; (ii) [PhHg]OTf; (iii) AgOTf



of the form $[Ru\{P(HgR){=}C(H)^tBu\}Cl(X)(CA)(PPh_3)_2]$ (R = Me, Ph, ferrocenyl, Cl; X = Cl, I).[3b,c] This prompted us to investigate the reactivity of $[Ir\{{=}C(^tBu)P(Cy)\}(CO)(PPh_3)_2]$ (**1**) toward phenylmercury chloride. Stirring a solution containing a 1:1 mixture of the reagents, initially at −78 °C and then at room temperature, for a period of 3 h led to the formation of $[Ir\{{=}C(^tBu)P[Hg(Ph)](Cy)\}(CO)(PPh_3)_2]Cl$ (**5**) in 77% yield (Scheme 2). In this case, the $^{31}P\{^1H\}$ NMR spectrum of the complex was found to be less diagnostic than those of **2**−**4** because the resonances at 14.0, 7.3, and −112.0 ppm all appeared as broadened multiplets. Variable-temperature $^{31}P\{^1H\}$ NMR studies did not lead to greater resolution of any of these signals. The ^1H NMR data for the complex support its proposed formulation, as does its elemental analysis and mass spectrum (LSIMS), which displays a molecular ion at $m/z = 1205$. In a C_6D_6 solution, the compound gradually decomposes, leading to the crystallization of $[IrCl(CO)(PPh_3)_2]$ and the deposition of elemental mercury. A singlet observed at 255.0 ppm in the $^{31}P\{^1H\}$ spectrum of the decomposition mixture was tentatively assigned to the phosphaalkene, $(Cy)P{=}C(Ph)^tBu$. A mass spectrum was also obtained for this compound and showed a correlation between the observed isotopic abundances and their simulated values for the molecular ion. It is worth mentioning that the related iridaphosphirenium cation, $[Ir\{{=}C(^tBu)P(H)(Cy)\}(CO)(PPh_3)_2]^+$, has previously been shown to decompose via a 1,2 shift of the phosphorus-bound hydrogen to give the phosphaalkene, $(Cy)P{=}C(H)^tBu$ (^{31}P NMR δ 257).[7]

A structural investigation of complex **5** revealed the chloride to have a weak "T-shaped" interaction with the mercury center. This is depicted in the molecular structure of the complex in Figure 4. Although the synthesis of complexes of the form $[(R_3P)HgMe]X$ was reported by Coates and Lauder in 1964,[19] mercurated phosphorus complexes have been scarcely investigated, and only two phosphine compounds, $[(dpb)HgMe]_2$ (dpb = *ortho*-diphenylphosphinobenzoate)[20] and $[(Ph_3P)HgMe]NO_3$,[21] have been structurally characterized. This is mainly due to their propensity to undergo symmetrization reactions in solution[19,22] in an interesting parallel to the gold−phosphine complexes. The mercurated iridaphosphirene complexes reported here show no tendency toward symmetrization behavior in solution.

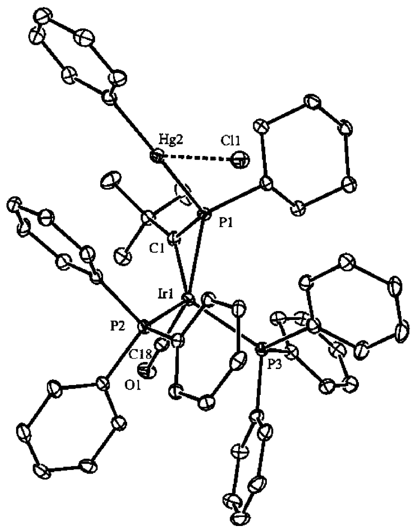


Figure 4. Molecular structure of $[Ir\{{=}C(^tBu)P[Hg(Ph)](Cy)\}(CO)(PPh_3)_2]Cl$ (**5**). Selected bond lengths (Å) and angles (deg): Hg2−C12 = 2.083(6), Hg2−P1 = 2.4037(18), Hg2−Cl1 = 2.7959(17), Ir1−C18 = 1.875(6), Ir1−C1 = 1.923(6), Ir1−P2 = 2.3576(16), Ir1−P1 = 2.3629(17), Ir1−P3 = 2.3805(19), P1−C1 = 1.751(6), O1−C18 = 1.167(7), C12−Hg2−P1 = 168.17(18), C12−Hg2−Cl1 = 100.81(18), P1−Hg2−Cl1 = 89.67(6), C18−Ir1−C1 = 99.8(2), C18−Ir1−P2 = 99.11(19), C1−Ir1−P2 = 123.87(19), C18−Ir1−P1 = 146.69(18), C1−Ir1−P1 = 46.84(18), P2−Ir1−P1 = 101.49(6), C18−Ir1−P3 = 90.81(19), C1−Ir1−P3 = 133.20(18), P2−Ir1−P3 = 98.63(6), P1−Ir1−P3 = 111.45(6), C1−P1−Ir1 = 53.3(2), P1−C1−Ir1 = 79.9(2).

It was found that the chloride of **5** could be abstracted by treatment of the complex with AgOTf to give $[Ir\{{=}C(^tBu)P[Hg(Ph)](Cy)\}(CO)(PPh_3)_2]OTf$ (**6**) (Scheme 2). The same complex could be prepared by a more direct route using the in situ preparation of [HgPh]OTf and its subsequent reaction with $[Ir\{{=}C(^tBu)P(Cy)\}(CO)(PPh_3)_2]$ (**1**). The $^{31}P\{^1H\}$ NMR spectrum of **6** is better resolved than that of **5** and shows resonances of the expected multiplicity at 12.6, 7.4, and −109.1 ppm. The ν(CO) absorption in the solid-state infrared spectrum is at 2000 cm^{-1}, a small (14 cm^{-1}) increase in frequency compared to that of $[Ir\{{=}C(^tBu)P[Hg(Ph)](Cy)\}(CO)(PPh_3)_2]Cl$ (**5**). This may suggest that the positive charge is not solely resident on the mercury but may be shared with the iridium center. Single crystals of complex **6** were obtained by cooling a toluene solution of the complex. A structural study was carried out, and the structure of its cation is shown in Figure 5.

The isolation and structural characterization of **5** and **6** is interesting because this reactivity does not simply mirror reactions of other species with phosphorus lone pairs (e.g., trialkyl- or triarylphosphines) with organomercury halides and it provides two new and unusual examples to add to the very small number of structurally investigated Hg−P bonds.

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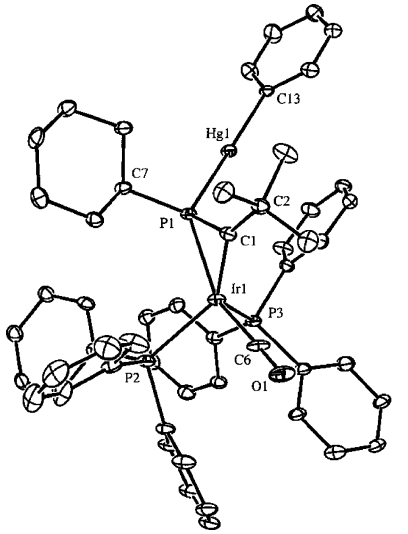

Figure 5. Structure of the cationic component of $[Ir\{=C(^tBu)P[Hg(Ph)](Cy)\}(CO)(PPh_3)_2][SO_3CF_3]$ (**6**). Selected bond lengths (Å) and angles (deg): Hg1−C13 = 2.105(9), Hg1−P1 = 2.405(3), Ir1−C6 = 1.901(12), Ir1−C1 = 1.928(9), Ir1−P3 = 2.355(3), Ir1−P1 = 2.356(2), Ir1−P2 = 2.393(3), P1−C1 = 1.755(11), O1−C6 = 1.112(13), C13−Hg1−P1 = 169.0(3), C6−Ir1−C1 = 99.1(5), C6−Ir1−P3 = 97.3(4), C1−Ir1−P3 = 125.0(3), C6−Ir1−P1 = 146.2(3), C1−Ir1−P1 = 47.1(3), P3−Ir1−P1 = 102.38(9), C6−Ir1−P2 = 91.9(4), C1−Ir1−P2 = 133.5(3), P3−Ir1−P2 = 97.64(9), P1−Ir1−P2 = 112.17(10), C1−P1−Ir1 = 53.5(3), P1−C1−Ir1 = 79.4(4).

Structural Discussion

Complexes **2**−**6** can all be described as having heavily distorted trigonal bipyramidal iridium geometries with the carbonyl ligands and P1 in axial positions, whereas the two phosphines and C1 occupy the equatorial positions. The P1−C1 bond lengths for the complexes (Table 2) are very close to that found for their precursor $[Ir\{=C(^tBu)P(Cy)\}(CO)(PPh_3)_2]$ (**1**) [1.753(13) Å][6] and the related complex $[Cp(CO)_2W=C(Ph)-P(Ph)\{\eta^1\text{-}W(CO)_5\}]$ [1.775(8) Å].[23] The Ir−C1 distances do not vary significantly in the complexes discussed here and are similar to the value found in the precursor **1**, that is, 1.918(14) Å, which is close to the mean value (1.918 Å) for all crystallographically determined Ir−C double bonds.[24] Similarly, the iridaphosphirene phosphorus center of each complex retains the pyramidal geometry found in complex **1**, and the torsion angles between the cyclohexyl and *tert*-butyl substituents (73.4−86.5°) clearly indicate that the P−C ligands within the iridaphosphirene rings of **2**−**6** are better described as phosphido carbenes than η^2-phosphavinyls. The greatest torsion angle is found in the structure of $[Ir\{=C(^tBu)P[Au(PPh_3)](Cy)\}(CO)(PPh_3)_2][SO_3CF_3]$ (**3**), probably as a result of the bulky triphenylphosphine ligand attached to the gold center. The Ir−P1 bond lengths seen in complexes **2**−**6** are all shorter than that in the precursor **1** [2.442(3) Å] because of a decreased electron density at P1, which results from its coordination to a secondary metal fragment. Interestingly, however, the Ir−P1 distances are all greater than those in the methylated complex $[Ir\{=C(^tBu)P(Me)(Cy)\}(CO)(PPh_3)_2]I$.[7] It is also worth noting that the angles of the Ir1−C1−P1 triangular unit do not change significantly (with respect to that in **1**) upon coordination of the secondary metal fragments.

The relative sizes of gold and silver atoms have been the subject of an interesting study by Schmidbaur and co-workers,[25] using a pair of isomorphous complexes, $[M(PMes_3)_2]BF_4$ (M = Au, Ag; Mes = mesityl). In contrast to the values usually quoted for the ionic or covalent radii of Au(I) and Ag(I), where silver is smaller or equal in size to gold,[26] the data from the structures of this pair indicated that the M−P distance is smaller for M = Au by 0.09(1) Å. Similarly, the lengths of Au1−P1 for **2** and Ag1−P1 for **4** also indicate that the bond length in the gold complex (**2**) is shorter by around 0.1 Å. However, it should be noted that the M−Cl distances show a much smaller difference, with Au1−Cl1 being approximately 0.02 Å shorter than Ag1−Cl1. This may be attributable to the difference in covalency between the M−P and M−Cl bonds, a factor not present in a pair of homoleptic gold and silver complexes.

Crystallographically investigated mercury−phosphorus bonds are rare, and it was only in 1988 that the first structurally characterized complex of mercury(II) containing a phosphorus ligand was reported, namely, $[Ph_3PHgPh]NO_3$.[21] The P−Hg bond length in this complex is 2.431(2) Å, which is slightly longer than in the structures of **5** [2.4037(18) Å] and **6** [2.405(3) Å]. However, the Hg−C bond lengths for the compounds $[Ph_3PHgPh]NO_3$ [2.090(5) Å], **5** [2.083(6) Å], and **6** [2.105(9) Å] are all in the same range and are very similar to that for PhHgCl itself [2.044(9) Å].[27] The Hg2−Cl1 distance of 2.7959(17) Å in **5** is greater than the sum of the atomic radii of the elements (2.5 Å)[19a] but less than the sum of the van der Waals radii (3.3 Å),[28b] and so, it is best described as a counteranion interaction. The "T-shape" motif [P1−Hg2−Cl1 = 89.67(6)°, C12−Hg2−Cl1 = 100.81(18)°] is not uncommon for mercury compounds and has been observed, for example, in the structure of $[Ph_3PHgPh]NO_3$, in which the NO_3^- counteranion has a similar interaction with the cation. Unlike PhHgCl, which has been reported as being exactly linear,[27] compounds **5** and **6** both show significant deviations from linearity at mercury, P−Hg−C = 168.17(18)° and 169.0(3)°, respectively, which is presumably due to steric reasons in both complexes. In addition, the Hg···Cl interaction in **5** could add to the deviation seen in that compound.

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Conclusions

This paper details the reactivity of the iridaphosphirene complex, [Ir{=C(^{t}Bu)P(Cy)}(CO)(PPh$_3$)$_2$] (**1**), toward electrophilic fragments of gold, silver, and mercury. This leads to a range of unprecedented aurated, argentated, and mercurated iridaphosphirene complexes. The reactions reported here, particularly with gold(I) compounds, indicate that the reactivity of the iridaphosphirene phosphorus differs from that of simple phosphines. The comprehensive structural characterization of these species reveals that only the Ir−P bond length within the Ir−C−P triangular unit of these complexes changes significantly on binding to secondary metal fragments. The structural determinations of the complex pairs **2**/**4** and **5**/**6** have also allowed the differences between gold and silver, and the effect of coordinated and noncoordinated counteranions on the geometries of the complexes, to be explored. The crystal structures of the mercurated species double the number of crystallographically determined Hg−P bonds in the literature.

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Supporting Information Available: Crystallographic data as CIF files for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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